CO2 laser interaction with germanium

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CO₂ LASER INTERACTION WITH GERMANIUM

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Supervisor: Dr. D. C. Emmony

Submitted for Ph.D. degree of
Loughborough University of Technology

Date of submission 1982
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Frontispiece:

The inspiration for much of this project.

The picture shows damage caused by a beam of infra-red laser 'light' on the surface of a germanium mirror. The spacing of the pattern bars is 10.6μm ---- the same as the free space wavelength of the laser radiation.

(To be placed following the title page).
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A study of the design and development of transversely excited atmospheric pressure carbon dioxide lasers has been carried out. Three lasers were constructed with output energies ranging from a few millijoules to several joules.

Damage in transmitting output mirrors is one of the limiting factors in the development of high energy density carbon dioxide lasers. One form of damage in uncoated germanium components is characterised by regular patterns.

A detailed examination of these damage patterns on several mirrors has been carried out using both optical and electron microscopy.

A semi-quantitative physical model describing the damage structure formation is proposed, and good agreement with experimental observation is found.

The thesis goes on to examine in depth particular aspects of the model with the object of making the analysis fully quantitative.

The thesis concludes by preparing the necessary data base for quantitative computer modelling. A full description is prepared of the behaviour of all the relevant physical parameters characterising germanium from room temperature to melting point temperature (300K - 1210K).
The technique adopted is to use a theoretical (or sometimes empirical) framework within which to extrapolate from available published data into parameter ranges not hitherto available.

For germanium, numerical values have been assigned to all relevant physical parameters (thermal, electrical and optical) over the full temperature range.

The way is now open for computer simulation of the interaction between laser radiation and germanium under a wide variety of circumstances.

A significant refinement of the model describing damage structure has already occurred.

When the magnitudes and temperature variation of $\varepsilon'$ and $\varepsilon''$ for germanium were established, the particular model behaviour of germanium suggested a generalised view of the behaviour of other materials. At the time of writing, the model is being adapted to account for the observations of other workers on a wide variety of other materials.
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1.1 Scope of project.

The project was set up to provide experience of laser design, construction and operation. Lasers were in a ferment of development at the time. One branch of gas laser evolution just emerging was operation at atmospheric pressure. The immediate objective was to design and construct a CO₂ T.E.A. laser which would deliver a substantial pulse energy.

The future course of development of the project beyond achieving a successful laser design was at the outset left entirely open; it was thought that examination of the interaction between laser radiation and thin films might be fruitful. This would bear a relationship to interests already established.

Work was being done by others in the section on I.R. Modulators based on the principle of plasma edge shift. The thin film materials were (to have the required electron concentration $\sim 10^{25} - 10^{26} \text{ m}^{-3}$) semiconducting. The expertise required for growing thin films was therefore available.

Thus the project was undertaken with a clear definition of first objective, and an approximate idea of the direction of development.

Producing a first class laser design took two years and three completed prototypes. The output pulse energy increased by
orders of magnitude from one design to the next. As is usual, a major constraint was finance. Ingenuity often had to circumvent the need for cash; the early high voltage (50kV) low inductance storage capacitors, for instance, were constructed from cooking foil.

Toward the end of the laser design stage of the project, when the most powerful model was brought into service, a number of germanium output mirrors were damaged in succession. Microscope examination revealed a very surprising feature—the damage in certain areas was very highly structured. The pattern had two recognisable periodicities, mutually perpendicular to each other. One interval in the damage over the surface was about one free space wavelength.

An extensive examination of the damage on several etalons was done using both electron and optical microscopy.

Naturally various hypotheses were proffered by various individuals. With a pattern spacing of $\lambda_0$, some form of interference pattern was a favourite candidate. But none of the more usual interference mechanisms could be worked into a scenario which would produce the observed effects—well not to complete satisfaction anyway.

The initial observations were published in Applied Physics Letters (publication attached). There was a strong initial interest amongst the scientific community; germanium windows were widely used at the time.
Germanium as a window material turned out to be relatively easily damaged as the achievable pulse powers increased. Gallium Arsenide windows were used to replace them, and the scientific community's interest in germanium waned.

But there were features about the mechanism of damage pattern formation still unresolved. Principal amongst them was the question of the exact nature and exact source of the radiation interfering with the main laser beam. The more the questions were raised, the more frustrating and the more baffling it became to explain the observations in detail. The challenge became increasingly powerful until it was irresistible. The patterns were there, and repeatable. A causal sequence of events must exist. To improve the level of analysis became a primary objective of the work.

The project moved from the essentially practical phase of laser development into a predominantly analytical stage.

Now the number of specialist areas of knowledge upon which it became necessary to draw began to proliferate. The situation under study was one of intense electromagnetic radiation producing a very particular form of damage upon a semiconductor. Thus a knowledge of the generation and propagation of electromagnetic fields, especially along interfaces was required; as also was the electrical and optical behaviour of a semiconductor throughout a very wide temperature range. These two areas may again be broken down into a large number of topics. Most of the
useful development of the subject areas of interest had taken place since circa 1960. The author, with a first degree dated 1959, was effectively taking on this problem with a clean sheet.

Perhaps it was this naivety which made possible the suggestion that the searched for secondary source of radiation which was "needed" to produce an interference pattern was the "linear melt" seen in the electron micrographs; and that these were produced by avalanche breakdown within the germanium under intense electric field. Eyebrows were raised! Avalanche breakdown at $10^{14}$ Hz?

Nevertheless, for the first time, the radiation that might be expected from such a "current filament" would interfere to produce the observed effects.

The results of the photographic examination, and the proposition describing the source and nature of the secondary radiation were published in "Laser and Optics Technology".

To consolidate this ground, the likely nature of an avalanche breakdown was thoroughly investigated. Sources describing breakdown, including breakdown at zero frequency (d.c.) were consulted. The findings of this search are recorded as section 5 of this thesis. Even the "lucky electron" turned up in a publication from Bass and Barratt.

The "avalanche breakdown" approach might be thought of as a "microscopic" view, in which the time history of individual
electrons (and holes) is considered in terms of fields, collisions, and energies. At the end of section 5, the "avalanche breakdown" proposition was still considered plausible, but lacked the power of total conviction.

To advance the search for the most complete description of damage pattern formation available, the formation of "linear melts" was reviewed once again from first principles. Only this time the adopted perspective was macroscopic; that is, the description is in terms of radiation heating the material bulk, which in turn alters the optical properties of the material as its temperature rises.

An inherent instability produces localised melting, a secondary radiation source and an interference pattern. To model this, it was decided to assemble all the necessary physical data relating to germanium; this was in preparation for eventual use in computer simulations. These aspects are covered in sections 6, 7 and 8 of this thesis. Work following this project is required to produce the necessary software to run the simulations of a laser beam interacting with a germanium window.

The macroscopic approach and the microscopic approach are not considered incompatible. They are different perspectives on the same phenomena. The author regards the macroscopic approach as an indirect attack on the problem of the pattern formation. The investi-
gation does not start with the interference damage, but rather with the fundamental physical properties of the material (e.g. thermal, electrical and optical).

As a result of this thorough but oblique approach, it has, at the time of writing, become possible to put forward a proposal to explain on a theoretical basis some results obtained by other workers which were, in the terms of the Laser and Optics Technology article, anomalous.

The requirement to meet a deadline with this piece of work has prevented a full and detailed account of this latest development being included here; a graph (Fig. 9.1) placed in the conclusion (section 9) contains the kernel of the hypothesis, but time does not allow the required accompanying exposition.

It is intended to submit an account of this latest development for publication at a future date.
The Principles of Lasers.

2.1 Introduction.

The possibility of a laser oscillator depends ultimately upon the phenomenon of stimulated emission. Einstein (1) showed (in 1917) "that molecules distributed in temperature equilibrium over states in a way which is compatible with quantum theory are in dynamic equilibrium with the Planck radiation." This led him to propose stimulated emission as a natural phenomenon. Further, by considering not only the energy implications but also the momentum implications of this he deduced that a consistent theory was only achieved if it be assumed that each elementary process (of absorption and emission of radiation) be completely directional. In contrast to the intuitively more natural supposition that spontaneous emission of a photon would be isotropic (by spherical waves for example) this result of his deductive reasoning must have been shattering, but he considered the point to be "rather certainly proved"; he adds "I have complete confidence in the reliability of the method used here."

Einstein postulated that the energy exchange processes between radiation of density $\rho$ and molecules having 'proper' states $Z_n$ and $Z_m$ with energies $E_n$ and $E_m$ ($E_m > E_n$) may be described by:

\[
\begin{align*}
\text{d}W &= A_n \text{d}t \quad \text{(spontaneous)} \\
\text{d}W &= B_n^m \rho \text{d}t \quad \text{induced by radiation} \\
\text{d}W &= B_m^m \rho \text{d}t
\end{align*}
\]
where $dW$ is the probability of the emission or absorption event taking place in the time $dt$, and the constants $A$ and $B$ which have become known as the Einstein coefficients, are characteristic of the molecule and the states $m$ and $n$ under consideration.

The possibility of equilibrium requires

\[ p_n \exp \left(-\frac{E_n}{kT}\right) B_n^m \rho = p_m \exp \left(-\frac{E_m}{kT}\right) \left(B_m^n \rho + A_m^n\right) \]  

(\(p_m\) and \(p_n\) represent the statistical weight of the states \(Z_m\) and \(Z_n\) and are independent of \(T\).)

which leads, if \(\rho \to \infty\) as \(T \to \infty\), to

\[ p_n B_n^m = p_m B_m^n \]  

and from the condition for dynamic equilibrium, Planck's law and Wien's law, it follows that

\[ \frac{A_m^n}{B_m^n} = \alpha \nu^3 \]  

(\(\nu\) is the radiation frequency, \(\alpha\) is a constant).

Since Einstein, we have

\[ \alpha = \frac{8\pi\hbar}{c^3} \]  

and the statistical weight $p$ is now usually written $g$, the degeneracy (5).

2.2 ASER.

Amplification by Stimulated Emission of Radiation found its first practical application at microwave frequencies with the Maser (2,3). Schawlow and Townes (4) proposed (1958) that the principles be extended to infrared and optical frequencies.
Laser Energy Level Schemes

(a) Three level
(b) & (c) Four level
frequencies by constructing resonant cavities many times larger than a wavelength. The function of the cavity is to provide a suitably excited atomic or molecular species with a high radiation density environment at the frequency required to induce emission.

2.3 **LASER.**

The principle features of a Laser will be outlined. Only the four level system is described, which is in the order of 100 x more efficient than a three level system. Level 4 is pumped from the ground state by one of the generally available means. These are excitation by optical illumination, electric discharge, electron beam, chemical reaction. A rapid rate spontaneous radiationless transfer to level 3, which is metastable, follows. The lasing levels 2 and 3 can thus be fairly economically raised to the necessary population inversion, when level 2 is several kT above ground level 1. Energy at a frequency $\nu_{32}$ will be enhanced by stimulated emission on passing through the conditioned laser medium. Multiple transits of photons are achieved using mirrors at each end of a cavity containing the medium. Energy is coupled out via a partially transmitting cavity mirror.

2.4 **Threshold condition.**

(ref. 5 pages 29-31).

Gain occurs if

$$\frac{N_m}{g_m} > \frac{N_n}{g_n}$$
The intensity grows as
\[ I = I_0 \exp(-k_\gamma x) \]  
---2.
where \( k_\gamma \) is the absorption coefficient which is a rapid function of frequency. \( k_\gamma \) is negative in the presence of population inversion for frequencies close to \( V_0 \)
, where
\[ V_0 = (\epsilon_m - \epsilon_n) / h \]  
---3.
Oscillation will occur if the fractional increase of beam intensity \( \exp(-k_\gamma 2L) \) during a cavity round trip (distance \( 2L \)) exceeds the losses incurred. The main losses are due to the mirrors, absorption and scattering by the medium, and diffraction. The mirror losses are usually dominant. If the reflection coefficients are \( R_1 \) and \( R_2 \) then the round trip fractional energy gain is
\[ F = R_1 R_2 \exp(-2k_\gamma L) \]  
---4.
Introducing the gain coefficient of the medium \( \alpha = -k_\gamma \), and a loss coefficient \( \gamma = - \ln R_1 R_2 = -2 \ln R \), where \( R \) is the geometric mean of the mirror reflectivities (which includes the loss due to the output coupling at one mirror), the fractional energy gain per round trip becomes
\[ F = \exp(2(\alpha L - \gamma)) \]  
---5
If \( F > 1 \), oscillation amplitude will rapidly build up until a limiting mechanism operates, usually \( N_m \) becoming depleted causing \( \alpha \) to reduce.

Note the available trade-off between \( \alpha L \) and \( \gamma \). Greater mirror losses (or percentage output energy pick-off) imply increased cavity length, and/or higher threshold level for \( N_m \).
The time at which $\alpha L \gg \gamma$ may be controlled by operating on $\gamma$ (mechanically, electrically, or chemically). Short duration giant pulses are obtained by $Q-$switching.

For steady state operation, the maximum gain coefficient for the medium, $\alpha_m$, must satisfy:

$$\alpha_m = \frac{\gamma}{L}$$

---6.

This equation is the threshold condition.

An alternative expression for the threshold condition is

$$\left( N_2 - N_1 \frac{g_2}{g_1} \right) \geq \frac{8\pi t_{spont} \nu_o^2}{c^3 g(\nu_o) t_{photon}}$$

--- 7.

where $g(\nu_o)$ is the normalised probability of a photon being stimulated in the frequency range $\nu_o$ and $\nu_o + d\nu$, $t_{spont}$ is the spontaneous emission lifetime of the transition under consideration, and $t_{photon}$ is photon lifetime in the cavity. (ref.10 pages 38-41).

2.5 The Cavity.

The cavity serves to increase the radiation density environment of the excited laser medium, for the purpose of increasing the probability of a stimulated emission. At a cavity resonance, standing waves build up when energy gain exceeds losses. The essential features are a pair of high quality mirrors used to ensure for suitable photons a large number of transits through the active laser medium. One mirror at least is partially transmitting to allow an output coupling from the cavity.
Fig. 2.5.1 - 1 Characteristics of Fabry-Perot étalon

The diagram shows the transmission as a function of the effective spacing for different values of \( S^2 \), that is, of the reflectance of each plane. To get a sharp well-defined filter, one needs a high reflectance.

Note that the condition of maximum transmission is

\[
\psi/2 = \pi/2 + q\pi
\]

or

\[
4b/\lambda = 2q + 1
\]

where \( q \) is an integer.
2.3 Stability of Laser Resonators

A laser resonator with spherical mirrors of unequal curvature is a typical example of a periodic sequence that can be either stable or unstable [6]. In Fig. 3 such a resonator is shown together with its dual, which is a sequence of lenses. The ray paths through the two structures are the same, except that the ray pattern is folded in the resonator and unfolded in the lens sequence. The focal lengths $f_1$ and $f_2$ of the lenses are the same as the focal lengths of the mirrors, i.e., they are determined by the radii of curvature $R_1$ and $R_2$ of the mirrors ($f_1=R_1/2$, $f_2=R_2/2$). The lens spacings are the same as the mirror spacing $d$. One can choose, as an element of the periodic sequence, a spacing followed by one lens plus another spacing followed by the second lens. The $ABCD$ matrix of such an element is given in No. 4 of Table I. From this one can obtain the trace, and write the stability condition (7) in the form

$$0 < \left(1 - \frac{d}{R_1}\right) \left(1 - \frac{d}{R_2}\right) < 1.$$  (8)

To show graphically which type of resonator is stable and which is unstable, it is useful to plot a stability diagram on which each resonator type is represented by a point. This is shown in Fig. 4 where the parameters $d/R_1$ and $d/R_2$ are drawn as the coordinate axes; unstable systems are represented by points in the shaded areas. Various resonator types, as characterized by the relative positions of the centers of curvature of the mirrors, are indicated in the appropriate regions of the diagram. Also entered as alternate coordinate axes are the parameters $g_1$ and $g_2$ which play an important role in the diffraction theory of resonators (see Section 4).
There are several standard cavity configurations. Most laser systems (though not all) use a stable cavity. This implies that the spatial amplitude and phase distribution over one mirror is, after one transit of the cavity, reproduced at the other. Consequently the distribution is (other parameters remaining constant) stable with time (e.g. following multiple transits). Kogelnik and Li (6) publish a stability diagram in a useful theory/tutorial paper.

The cavity is typically some $10^5$ to $10^6$ wavelengths long. Consequently the resonant frequencies (modes) are closely spaced in terms of the laser transition linewidth (Fig.2.5-1). Oscillation may occur simultaneously at several frequencies, when the output is said to be multimode. Generally, to ensure single mode operation, some care has to be exercised in the design and operation of the laser. Single mode is considered desirable for many applications, and essential for some.

2.5.1. Standard cavity configurations.

**Plane-parallel.**

The plane-parallel cavity is the most basic in concept (ref.8) Fig.2.5.1.1), and consists essentially of a Fabry-Perot etalon (11,13 page 21). The transmission as a function of wavelength is given by:

$$I_t = \frac{(1 - R)^2 I_i}{(1 - R)^2 + 4 R \cos^2 \varphi/2}$$

where $I_t$ is transmitted intensity

$I_i$ is incident intensity
R is the intensity reflectivity

\[ \Upsilon = \frac{4 \pi L \cos \Theta}{\lambda} \]

\( \Theta \) is the angle between the ray and the optic axis.

For a laser, if \( \Theta \) may be taken as zero (\( \text{TEM}_{\infty} \)), \( \Upsilon / 2 \) will change by \( \pi \) for every \( \Delta L = \frac{\lambda}{2} \). The condition for maximum transmission is also that required for use of the etalon as a resonator (12, page 40). The equation is valid for a passive volume between the mirrors, and an external source of radiation.

For a volume providing gain \( G(\nu) \) over a single transit, the required expression is (12, page 68):

\[
\frac{I_t}{I_1} = \frac{G(1 - R)^2 / (1 - RG)^2}{1 + \frac{4RG}{(1 - RG)^2} \cos^2 \frac{\Upsilon}{2}}
\]

If, as in the laser, the radiation source of intensity \( S \) is contained between the mirrors, and has an output frequency distribution \( S(\nu) \),

\[
I_t = S \frac{G(1 - R) / (1 - RG)^2}{1 + \frac{4RG}{(1 - RG)^2} \cos^2 \frac{\Upsilon}{2}}
\]

Since \( I_1 \) is now zero, and a factor \( (1 - R) \) has been dropped accordingly. Note that \( G(\nu) \) and \( S(\nu) \) will usually have the same frequency profile. \( S(\nu) \) is now the spontaneous emission.

Spontaneous emission provides "noise" in the output, while the coherent output represents amplified noise of narrow bandwidth. The coherent output will appear when \( RG = 1 \), when the expression mathematically goes to infinity. Physically the gain saturates as a dynamic equilibrium between population inversion level and power output (which depletes the inversion) so that \( RG \) is maintained about unity for the time duration of a steady output.
Fig. 2.5.1 - 1 Laser mirror configurations.

- **Plane parallel**
  \[ r_1 = \infty \]
  \[ r_2 = \infty \]

- **Large radius**
  \[ r_1 = L \]
  \[ r_2 = L \]

- **Confocal**
  \[ r_1 + r_2 = 2L \]

- **Concentric**
  \[ r_1 + r_2 = L \]

- **Hemispherical**
  \[ r_1 = L \]
  \[ r_2 = \infty \]
Practical aspects of the plane-parallel resonator (10, page 57) include the requirement of high precision of alignment (to about 1 second of arc) to avoid "walk off". Diffraction losses due to "spill over" are higher than alternative configurations. Boundary requirements of continuity of field at the mirror edge effectively place curvature on the output wavefront, so that a plane wave does not in fact represent a normal mode of the resonator. Discrimination for TEM\(_{00}\) mode against higher order modes (by diffraction loss) is only about 2:1 (c.f. confocal \~\sim\ 25:1). The precision alignment renders the plane-parallel configuration susceptible to vibration and thermal effects; the dominant mode may well be determined by a speck of dirt and/or optical inhomogeneities. The sole merit of the resonator is the high utilisation of the laser medium. Its interest (as far as gas lasers are concerned) is mainly historical.

Large radius.
For a gaussian profile TEM\(_{00}\) beam, the uniphase wavefront radius (\(R_w\)) is (10, page 59):

\[
R_w = x \left( 1 + \frac{\pi^2 r_{bo}^2}{\lambda^2 x^2} \right)
\]

where \(r_{bo}\) is the beam waist radius
\(x\) is the distance from the beam waist measured along the optic axis.

For many gas lasers \(R_w \sim 300 \, \text{m}\) at the mirror position. Thus for the mirror surface to co-incide with the wavefront would demand mirrors too difficult to make economically. In practice
mirrors of radius of curvature \( \lesssim 20 \text{m} \) are used. They make good use of the available laser active medium. This configuration is used for high power output.

The beam waist radius \( r_{bo} \) for a uniphase output obtained by using a laser with mirrors of radii \( r_1 \) and \( r_2 \) is (10, page 59):

\[
(r_{bo})^4 = \frac{\lambda^2}{\pi^2} \cdot \frac{L(r_1 - L)(r_2 - L)(r_1 + r_2 - L)}{(r_1 + r_2 - 2L)^2} \tag{5}
\]

The beam radius at the mirror \( r_{bm} \) is

\[
(r_{bm1})^4 = \frac{\lambda^2}{\pi^2} \cdot \frac{r_1^2 L(r_2 - L)}{(r_1 - L)(r_1 + r_2 - L)} \tag{6}
\]

and

\[
(r_{bm2})^4 = \frac{\lambda^2}{\pi^2} \cdot \frac{r_2^2 L(r_1 - L)}{(r_2 - L)(r_1 + r_2 - L)} \tag{7}
\]

For mirrors of identical radius:-

\[
(r_{bo})^4 = \frac{\lambda^2}{\pi^2} \cdot \frac{L (2r - L)}{4} \tag{8}
\]

\[
(r_{bm})^4 = \frac{\lambda^2 r^2}{\pi^2} \cdot \frac{L}{(2r - L)} \tag{9}
\]

Change in laser length \( L \) only "slowly" changes \( r_b \).

Mode selection of \( \text{TEM}_{\infty} \) by increasing beam radius is not very effective in the large radius resonator. Sensitivity for alignment is \( \sim 10 \) seconds of arc.
Confocal.
(ref. 7)
\[ r_1 = r_2 = L = r \]
---10.

For uniphase output, the mode volume is reduced:
\[ r_b^2 = \frac{r \lambda}{\pi} \quad r_{bo}^2 = \frac{r \lambda}{2 \pi} \]
---11.

This cavity is on the boundary between high loss and low-loss operation. Thus \( L \) is set fractionally less than \( r \) to ensure low loss conditions and stability of operation. Low sensitivity to alignment (\( \sim 1 \frac{1}{2} \) minutes of arc) makes the confocal cavity the easiest to align. It also has the best discrimination against higher order (transverse) modes (\( \sim 25:1 \))

Concentric.
\[ r_1 + r_2 = L \]
If \( r + r = L \), known as spherical.

On border between high loss - low loss operation.
As difficult to align as plane parallel.
Seldom used for gas lasers. Some merit in solid state lasers.

Hemispherical.
\[ r_1 \text{ slightly less than } L \quad r_2 = \infty \]
Has a "conical" mode volume, with diffraction limited "zero" \( r_b \) at the plane mirror.
Beams radius \( r_{bm} \) is very sensitive to \( L \) for given \( r_1 \).
Mode selection by control of beam radius is thus effective.
Only about 1/3 of cavity volume is effective - lower power output. Alignment is straightforward.
2.5.2. Laser modes.

A laser may oscillate at several frequencies simultaneously. Each frequency corresponds to a resonance mode of the optical cavity. Sometimes more than one mode gives rise to the same output frequency, when they are said to be degenerate. Simultaneously oscillating modes degrade coherence (temporal and spatial) and amplitude stability (beats) of the laser output. Many applications thus require single mode operation (TEM$_{00}$).

Two varieties of mode may be distinguished.

**Longitudinal or axial modes.**

Cavity resonance occurs when stationary waves are favoured, i.e. (for plane mirrors) when:-

$$\frac{n}{2} \lambda = L \quad \text{or} \quad \nu = \frac{nc}{2L} \quad \text{---1}$$

Differentiating yields the mode frequency spacing

$$\Delta \nu = \frac{c}{2L} \quad \text{---2}$$

For spherical mirrors supporting higher order modes TEM$_{pqn}$ the resonance condition is (10 page 66, 14)

$$\left[ n + \frac{1}{\pi} (1 + p + q) \cos^{-1} \left( 1 - \frac{L}{r} \right) \right] \frac{\lambda}{2} = L \quad \text{---3}$$

**Transverse modes.**

Any intensity distribution at one mirror capable of reproducing itself after a transit to the other mirror represents a stable transverse mode. Any linear combination of a number of such modes may also occur. Transverse Electro-Magnetic (TEM$_{pq}$)
Theory of Oscillation and Radiation Modes

Square mirrors  
Circular mirrors

Fig. 2.5.2 - la Electric field configurations for interferometers with plane mirrors.

Fig. 2.5.2 - lb Mode patterns of a gas laser oscillator (rectangular symmetry).
The pattern of several modes is shown in Fig. 2.5. It will be understood that the amplitude of the electric or magnetic vector is shown in the vertical direction, the polarization always being in the $(r, \phi)$ plane, i.e. in the plane of a reflector. A change of sign of the amplitude indicates a reversal of polarization.
A distinction may be noted in the behaviour assumed for the Fabry-Perot system, consisting of two plane end-reflectors in free space, and the closed resonant cavity such as is used in microwave work. In the latter case, application of the usual boundary conditions indicates that a cavity will be resonant only for certain wavelengths, for radiation travelling only in certain directions. Thus in a cubical cavity, the possible resonant wavelengths are given by

$$\lambda = \frac{2L}{\sqrt{A^2 + B^2 + C^2}}$$

where \(L\) is the length of the cube edge and \(A\), \(B\) and \(C\) are integers representing the number of half wavelengths in the projection of the resonant mode on the three axis directions.

For the open-sided Fabry-Perot system, and with the assumption of infinite plates, a continuous range of wavelengths from \(\lambda = L/2\) upwards is possible, resonances occurring at angles satisfying the relation \(2L \sin \theta = \text{integer} \times \lambda\). In the case of the microwave cavity the boundary conditions are well-defined in that the assumption is made of perfectly reflecting walls, so that the amplitude of the electric field falls to zero on the containing walls. In the Fabry-Perot case, with no side-walls, the boundary conditions to be imposed are less obviously defined. The radiation pattern in the cavity needs to match the surrounding free-space. In travelling from one of the end plates of the Fabry-Perot system to the other, a wave will spread beyond the limits of the second plate and some energy will be lost by diffraction. An estimate of this diffraction loss is essential for the assessment of the Fabry-Perot system as a maser resonator. Schawlow and Townes assume that the open-sided Fabry-Perot system may be treated in a similar way to a closed cavity, with the assumption that the field distribution across one end-plate may be represented as a sinusoidal function \(\sin \pi x/L\), where \(L\) is an integer. It is also assumed that the phase of the wave in the resonant system is constant across the end-plate. Fox and Li have used a Huygens treatment to determine the field distribution in such a system in the following way. As a starting point it is assumed that a plane wave of uniform amplitude is launched from one of the plates of the interferometer. Perfectly reflecting plates are assumed, a restriction of no consequence since any uniform reflec-
modes are designated in terms of the number of nodes in the
mode pattern (Fig. 2.5.2 - 1). Note the phase difference
between adjacent lobes of the pattern.
For any TEM\textsubscript{pq} mode, there will be a corresponding range of
axial modes TEM\textsubscript{pqn} separated by $c/2L$ Hz, for all values of $p, q$.
if
\[ \cos^{-1} \left( \frac{1 - L}{r} \right) = \frac{\pi}{2} \]
i.e. confocal $r = L$ then
\[ \left[ n + \frac{1 + p + q}{2} \right] \frac{\lambda}{2} = L \quad \text{(ref.7)} \]
Observe that if $p + q$ is odd, the frequency will correspond
to that of a TEM\textsubscript{oo} mode of a different $n$ value --- the modes
are degenerate.
If $p + q$ is even, the higher order mode will fall half way
between two TEM\textsubscript{oo} modes, giving a frequency separation of
c/4L Hz.
If a field distribution $F(r', \phi')$ exists over a plane
(Fig. 2.5.2 - 2), then the field distribution $H(r'', \phi'')$
over a second plane may be calculated point by point using the
Kirchoff integral (12, page 42, 15). A stable cavity pattern
demands that $H = (a + ib)F$ where $a$ and $b$ are constants. The
loss per transit is $(1 - a)$.
If in Fig. 2.5.2 - 2, $d \gg (r' \text{ or } r'')$, then the obliquity
factor may be omitted, and $L$ substituted for $d$ in the denominator
of the Kirchoff integral:
\[ H = \frac{i k}{2\pi L} \int \int F \exp(-ik(d - L)) r' \, d\phi' \, dr' \quad \text{(ref.7)} \]
where $k = \frac{2\pi}{\lambda}$
Now \[ d^2 = L^2 + (r')^2 + (r'')^2 - 2r'r'' \cos (\phi' - \phi'') \] ---6
so that approximately

\[ d - L = \frac{(r')^2}{2L} + \frac{(r'')^2}{2L} - \frac{r'r'' \cos (\phi' - \phi'')}{L} \] ---7

The terms in \((r')^2\) and \((r'')^2\) in the expression for \((d - L)\) preclude an analytical solution of 2.5.2-5 in which \((a + ib)F = H\).
Fox and Li (8) produced a computer solution by an iterative technique. Assuming a uniform distribution for \(F\) to start with (spontaneous emission illumination), it was found that after about 300 "transits", a stable pattern emerged. They interpreted this as the dominant resonant mode of the cavity. Fluctuations of amplitude at a field point over transits 100 to 300 were interpreted as beats with the next higher mode as it died away.

By "curving" the planes into a confocal arrangement the terms \(r'^2\) and \(r''^2\) vanish. A solution may then be found by using integral transform tables (16) (17),

\[ (sr_{bm})^n \exp \left( -\frac{1}{2} s^2 r_{bm}^2 \right) La^n(s^2 r_{bm}^2) \cos n\phi \] ---8

where \[ s^2 = k/L \]
and \[ La^n \] is the Laguerre polynomial (18)

\( \text{TEM}_{oo} \) mode.

The dominant mode emerges as one with a gaussian distribution of amplitude:

\[ \exp(-\frac{1}{2} s^2 r_{bm}^2) \] ---9
defining a beam concentrated mainly within a radius given
by $sr_{bm} = 3$, say.

Expressed in terms of the intensity $I_o$ on the beam axis
(10, page 52 (with error corrected)):—

$$I = I_o \exp \left[ -\frac{2r_{bm}^2}{r_m^2} \right]$$  

---10

where

$$r_m = \frac{\lambda L}{\sqrt{2\pi}}$$  

---11

(N.B. $r_m$, $r_{be}$ are defined as the beam radius at which the
intensity has fallen to $\frac{I_o}{\exp^2}$)

In regions other than at the mirrors,

$$I = I_o \exp \left[ -\frac{2r^2}{r_{be}^2} \right]$$  

---12

The semi-angular divergence of the beam is given by

$$\alpha_{TEM_{oo}} = \frac{\lambda}{\pi r_{bo}}$$  

---13

and 86.5% of the energy is contained within the radius $r_{be}$.

The beam continues to propagate as a gaussian distribution.

The beam width $r_{be}$ as a function of the distance $x$ from
the beam waist $r_{bo}$ is

$$r_{be} = r_{bo} \left[ 1 + \frac{x^2 \lambda^2}{\pi^2 r_{bo}^2} \right]$$  

---14

The beam is approximately constant in radius for some distance
after which it increases its angle of divergence until this
reaches a constant value.
c.f. a disc of uniform illumination produces a far field circular fringe system with a central bright region (Airy disc) containing 84% of the energy. The semi angular divergence is:

\[ \theta_{\text{uniform}} = 1.22 \frac{\lambda}{r_{\text{bo}}} \]

where \( r_{\text{bo}} \) is the uniformly illuminated area radius.

**Some general points.**

When several modes oscillate at once, the situation may often be treated as the sum of independent oscillators. This is because in many practical cases, (e.g. laser gas at low pressure), the oscillators are sustained by different populations of excited medium within the bandwidth of the transition ("hole burning" ref. 19). The situation may well be modified for laser gases operating at atmospheric pressure, which should bring a greater sample of the excited gas molecules into a favourable orientation for emission, thus broadening the 'burned hole'.

To obtain single mode operation, transverse modes may be selected out by use of stops, and axial modes may be selected out using a further short etalon in series with the long cavity. The simple theory suggests that the fundamental transverse mode, having the lowest diffraction loss, should always be dominant. This is not always the case. It has been proposed (13, page 219) that the greater diffraction losses of the higher order modes may be offset by a better volume utilisation of the laser medium, ensuring that the larger diameter beams...
Fig. 2.5.2-3 Hole burning in the gain curve of an oscillator above threshold

Power-frequency curves of an oscillator below threshold
\( (R = 0.01) \)

\[ R = 0.01 \]
\[ \text{all curves} \]
\[ \text{Relative excitation} \]
\[ = 4.5 \]

\[ R = 0.9 \]
\[ \text{all curves} \]
\[ \text{Relative excitation} \]
\[ = 105 \]

Power-frequency curves of an oscillator below threshold
\( (R = 0.90) \)
usually oscillate in a higher order mode.

Information concerning the active modes of a laser may be gained by examination of the beat frequencies (~ 100 MHz) between the modes. These may be sensed in the output of a suitable non-linear photodetector such as a photomultiplier tube or p-i-n photodiode (given that the source wavelength is within the spectral response of the detector). Some apparent anomalies are likely to be observed due to "pulling" which will affect different modes in differing degrees.

2.5.3. Cavity Q Factor.

The Q factor of a cavity gives a measure of the resonance bandwidth. The cavity may be described in terms of its 'passive' Q; on introducing an active medium into the cavity, its Q will be raised, and the effective bandwidth narrowed. The situation is analogous to an electrical frequency selective amplifier (with a characteristic Q) to which positive feedback is applied effectively raising the Q.

Passive cavity.

\[ Q = \frac{\sqrt{\Delta \nu}}{\Lambda \nu} \]  
---1

\[ Q = \frac{\text{Angular frequency}}{\text{Fraction of energy lost per second}} \]  
---2

\[ Q = 2\pi \sqrt{\frac{\text{energy stored}}{\text{energy lost per second}}} \]  
---3

it may be shown:-

\[ Q = \frac{2\kappa L}{(1-R)\lambda} \]  
---4

(\(\kappa L\ll L\); (1-R) is total power loss per reflection, sum of diffraction + reflection losses).
Considering equation 3 applied to one photon in a cavity where the mirrors are of reflectivity $R_1$ and 100% respectively, and the losses due to diffraction and absorption are negligible in comparison to reflection losses, then:

On average a photon will make $\frac{1}{1-R_1}$ passes before escaping. The time taken is $(\text{distance travelled})/\text{speed}$, i.e.,

$$\text{time in cavity} = \frac{2L}{c(1-R_1)}$$

---5

Rate of loss of energy

$$= \frac{h\nu c(1-R_1)}{2L}$$

---6

The energy stored in the cavity by one photon $= h\nu$

Substituting into eqn. 3:

$$Q = 2\pi \frac{\nu}{c(1-R_1)} 2L$$

$$Q = \frac{4\pi L}{\lambda (1-R_1)}$$

---7

(ref.10, page70)

If instead, each mirror has reflectivity $R$, the expression is

$$Q = \frac{2\pi}{\lambda} \frac{L}{(1-R)}$$

---4

(ref.7; ref.12, page41)

Boyd and Gordon (7) point out that if losses are very small ($R \approx 1$), then the optical resolving power (20)

$$\text{resolving power} = \frac{2\pi L \sqrt{R}}{\lambda (1-R)}$$

---8

is approximately equal to the cavity $Q$. 
It will be noted that $Q$ increases with resonator length $L$. This holds true until the diffraction and absorption losses become comparable with reflection losses, when further increase of length reduces $Q$.

**Active cavity.**

With gain between the reflectors, the denominator of eqn. 2 may in principle become zero, with a corresponding infinitely large $Q$ (narrow linewidth). In practice, spontaneous emission and thermal noise give rise to a finite linewidth, due to the random phase so introduced.

If the dominant factor is spontaneous emission ($h\nu \gg kT$), then Schawlow and Townes\(^\text{4}\) give the oscillator bandwidth $\Delta \nu_{osc}$ (assuming a single mode may be isolated) as:

$$\Delta \nu_{osc} = \frac{4\pi h \dfrac{\nu}{a}}{p} (\Delta \nu_a)^2 \quad --9$$

O.S. Heavens quotes the alternate form (21; page 31).

$$\Delta \omega_{osc} = \frac{2\hbar}{p} \dfrac{\omega}{a} (\Delta \nu_a)^2 \quad --9a$$

where subscript $a$ indicates transition (atomic or molecular) quantities, and $P$ is the power level of the oscillation.

Conversely, if $h \ll kT$ (microwave maser, (3, 4)), and the energy of stimulated emission is much larger than the background thermal radiation, then

$$\Delta \nu_{osc} = \frac{4\pi kT(\Delta \nu_a)^2}{p} \quad --10$$
A noise temperature may be defined by $h\nu/k$, which at microwave frequencies is $\sim 1K$.

In summary, the greater the power level at which the laser is operating (single mode), the greater is the stimulated emission compared to background thermal radiation and spontaneous emission. Thus the more distinctly will the coherent radiation stand out against the "broadband" background with a narrow bandwidth.

Finally note that from

$$P = \frac{\omega \mathcal{E}}{Q}$$  \hspace{1cm} \text{---2a}$$

comes the useful form

$$P = 2\pi \Delta \nu \mathcal{E}$$  \hspace{1cm} \text{---2b}$$

Mode "pulling".

(ref.13, page 81)

Consider a cavity with one (say) available resonant mode of frequency $\nu_c$ and linewidth $\Delta \nu_c$. The active medium line is at $\nu_a$ of linewidth $\Delta \nu_a$, where $\Delta \nu_a \gg \Delta \nu_c$.

The actual frequency of oscillation $\nu_{osc}$ will be determined mainly by the higher $Q$ component, and is given by the theory covering coupled oscillations as:

$$\nu_{osc} = \nu_c + (\nu_a - \nu_c) \frac{\Delta \nu_c}{\Delta \nu_a}$$  \hspace{1cm} \text{---11}$$
or:

$$\nu_{osc} = \nu_c + (\nu_a - \nu_c) \frac{Q_c}{Q_a}$$  \hspace{1cm} \text{---11a}$$
Fig. 2.5.3 (a–c). Pulling of cavity modes.

Fig. 2.6. Gaussian and Lorentz lines of common linewidth. \((G_p\) and \(L_p\) denote the peak intensities.)
When the oscillation of cavity modes is being studied by inference from extracted beat frequencies, mode pulling will give rise to sets of frequencies differing slightly from those expected from a simple analysis. Mode pulling may remove degeneracies.

Section 2.6 Linewidth.

The linewidth of a laser oscillator is determined by the interaction of several factors – mainly the cavity $Q$, and the transition linewidth $\Delta \nu_a$. We have discussed the factors influencing the cavity $Q_c$. Now the factors contributing to $\Delta \nu_a$ will be examined.

The three main factors are: intrinsic linewidth; Doppler broadening; Collision or pressure broadening. (22, 23).

2.6.1. Intrinsic Linewidth.

Linewidth of transition in single isolated atomic or molecular systems, derived from uncertainty principle

$$\Delta E \Delta t \sim h$$

If the lifetime of a given transition can be measured, $\Delta E$ may be estimated:

$$\Delta (h \nu) \gamma_{\text{spont}} \sim h$$

or

$$\Delta \nu = \frac{1}{\gamma_{\text{spont}}}$$

This is the intrinsic linewidth of the transition.

One implication of this interpretation is that only the ground state energy is sharply defined among the stationary states.

A discussion of Natural linewidth is given in ref. 24 (22 pt.2).
2.6.2 Doppler width.
Due to the random thermal motion of the radiation sources (atoms, molecules), the observed radiation will be subject to a Doppler shift in frequency. A distribution of velocities among the sources will give rise to a particular corresponding frequency distribution profile. A thermal (Maxwell) distribution of velocities gives rise to a Gaussian frequency profile. The broadening is said to be inhomogeneous, because each particular atom (or molecule) makes a unique contribution to the overall radiation output.

The frequency profile is described by:

\[ g(\nu) = \frac{2(\pi \ln 2)^{\frac{1}{3}}}{\nu} \exp \left[ -\frac{(\nu - \nu_0)^2}{\left(\frac{1}{2} \Delta \nu\right)^2} \right] \]

The peak:

\[ g(\nu_0) = \frac{2(\pi \ln 2)^{\frac{1}{3}}}{\nu} \]

The half width:

\[ \Delta \nu = \frac{2V_o}{c} \left( \frac{2kT \ln 2}{m_a} \right)^{\frac{1}{2}} \]

(10. page 41; 13, page 44).

2.6.3 Pressure or collision broadening.
When a atom (or molecule) is radiating during an energy state transition, if it is subject to a collision or near miss, it is to be expected that the radiation process will be disturbed. A change of phase at this time contributes extra Fourier components to the radiated frequency spectrum. The line broadening produced is said to be homogenous, because it results from the interaction of the fundamental particles with each other.
The corresponding frequency distribution profile is described by the Lorentz expression:

\[ g(\nu) = \frac{\Delta \nu}{2 \pi \left[ \nu - \nu_0 \right]^2 + \left( \frac{\Delta \nu}{2} \right)^2} \]  

(The factor \( \frac{\Delta \nu}{2 \pi} \) ensures normalisation: \( \int_{-\infty}^{+\infty} g(\nu) \, d\nu = 1 \))

The peak:

\[ g(\nu_0) = \frac{2}{\pi \Delta \nu} \]

The half width:

\[ \Delta \nu = \frac{1}{\pi \tau} \]

(10, page 42; 13, page 45).

2.6.4 General remarks.

A comprehensive discussion is to be found in ref. 25.

Any practical frequency profile will be a resultant derived from the broadening mechanisms. The combined effect of natural and Doppler broadening may be combined by taking an integral, since the two effects are independent. The result is the "Voigt profile". (23, page 391).

In many practical cases one effect predominates, e.g. Doppler broadening predominates in a light gas (hydrogen, say) at low pressure and at 300 K.

Other mechanisms for broadening have been discussed in the literature (e.g. resonance broadening, ref. 22, page 93).
Section 2.6 has dealt with the linewidth of the fundamental transition giving rise to the radiation. It has already been pointed out in section 2.5 that an oscillator output frequency (Laser light) and linewidth is primarily determined by the relevant frequency determining element of highest Q. This is usually a mode of the active cavity, for which the linewidth is narrow compared to the transition linewidth.
References.

Section 2 Principles of Lasers.

1. A. Einstein Physikalische Zeitschrift 18, 121 (1917)


15. R.S. Longhurst: Geometrical and Physical Optics Longmans, Green & Co. Ltd.


References section 2 cont.


Development of a CO₂ TEA laser

3.1 Introduction.

The objective was to build a laser which would produce radiation of sufficient intensity to damage materials irradiated by it. Some experience with C₂H₂ CO₂ lasers operating at 70 W was available within the group. The characteristics of CO₂ lasers were suitable for the application, and appeared the optimum choice in terms of available resources and expertise.

3.2 Principles of the CO₂ laser.

The relevant energy levels are vibrational and rotational levels of the ground electronic states of CO₂ and N₂ molecules. The laser transition is from the asymmetric 000₁ to the symmetric 1000 vibration of the CO₂ molecule. The energy difference is \( \sim 0.11 \text{eV} (\lambda = 10.6 \mu \text{m}) \). A near resonant (with CO₂* 000₁) rotational level of nitrogen (N₂* V = 1) is metastable, and serves to store excitation energy in a form readily available to the upper laser level of the CO₂. The lower laser level (\( \sim 0.16 \text{eV above ground} \)) is relaxed by collision, primarily with He atoms.

Briefly, the sequence of events pertinent to high pressure CO₂ laser is:-

a) Energy is stored in a capacitor at high voltage.
b) Discharge through the laser gas is initiated, and the stored energy "dumped" into the laser medium in a time (\( \sim 250 \text{ns} \)) too short to allow arc formation.
Fig. 3.2 - 1

(a) Modes of oscillation of CO₂ molecule:
- Bending mode
- Symmetric mode
- Asymmetric mode

(b) Carbon dioxide laser energy levels.

Variation of radiated pulse shape with increasing N₂ content:

(a) CO₂:N₂ = 5:1
(b) CO₂:N₂ = 3:1
(c) CO₂:N₂ = 1:1.5
The mechanism of laser action is as follows: direct electronic excitation of the nitrogen molecule into its 1 state by a collision of the first kind. This process is represented as follows:

$$e_t + N_2 = N_2^* + e_s$$  (7.6)

A collision of the second kind with a carbon dioxide molecule in the ground state with excitation to the 001 state follows:

$$N_2^* + CO_2 = N_2 + CO_2^* (001)$$  (7.7)

This takes place because, as can be seen from the energy level diagram, the two energy values almost coincide. The 100 vibrational state is of much lower energy and so cannot be populated by this process.

The population of the 001 levels now exceeds the population of the 100 levels and so the population inversion condition for laser action to take place between these levels has been achieved. However, two points must be born in mind. First, a transition from the 001 level to the 100 level must obey a selection rule which states that $J$ can only change by ±1. Thus if $J = 10$ for a particular level then only the transitions from $J = 9$ to $J = 10$ and $J = 11$ to $J = 10$ are permitted. If $J$ changes by +1 the transition is called a $P$-branch transition and if $J$ changes by −1 it is called an $R$-branch transition. A transition from $J = 9$ to $J = 10$ is called $P10$ and a transition from $J = 11$ to $J = 10$ is called $R10$. Second, the population of the rotational levels of the 001 state will have a Boltzmann distribution, so, after taking degeneracy into account the effective population of a $J = 11$ level, for instance, will be less than the $J = 9$ level. The result of this is that $P$-branch transitions dominate because it so happens that a particular $P$-branch level will fill up (in order to restore equilibrium) by depletion of the population of the $R$-branch above it quicker than the $R$-branch level population decays by spontaneous emission to the lower laser level. The wavelengths associated with the most powerful transitions of the carbon dioxide laser at normal operating temperatures are: $P18 - 10.57 \mu m$, $P20 - 10.59 \mu m$, $P22 - 10.61 \mu m$ and the separation between each transition is about 53 GHz.

Each gain curve corresponding to a $P$-branch transition has a line-width of about 50 MHz. In comparison with other gas lasers this is a narrow Doppler width and comes about because the wavelength is some twenty times as long and the mass of the molecule is greater than that of most atoms. Reference to equation 3.43 will immediately show that these factors will reduce the Doppler width considerably. The sum of the areas under each gain curve in fig. 7.11 is proportional to the population inversion between the 001 and the 100 levels and hence proportional to the intensity of the output. These areas are not in fact equal and it so happens that because of the relative $J$-level populations the area under the $P20$ gain curve is largest. The axial mode separation for a 100 cm long cavity is by equation 4.21 about 150 MHz. Figure 7.11 shows the $P18$ and $P20$ gain curves and the axial mode spacing.

It is apparent from fig. 7.11 that where a tube one metre in length is used, only one axial mode can oscillate under a gain curve at any given time. If a much longer cavity were to be used the modes would be closer together and so several would oscillate. The mode which experiences the greatest gain will tend to grow in intensity at the expense of the others. This happens because the mode which starts to oscillate initially depletes the population of the appropriate 001 level and, as explained above, it so happens that the relaxation rate into such a depleted level from other $J$ levels associated with the same vibrational level (in order to restore a Boltzmann distribution) is much faster than the spontaneous decay rate from any $J$ level to a lower vibrational level. Hence the inversion between other levels tends to feed into the first. The gain profiles will uniformly decrease together and it follows therefore that the $P$-branch transitions are effectively homogeneously broadened. For a short cavity where only one mode oscillates, the change in cavity length due to instabilities will cause the output power to fluctuate. If the laser is tuned so that the axial mode frequency is at the centre, for example, of the $P20$ gain curve, then a gradual reduction in power will be observed as the axial mode frequency drifts. If the next mode peaks up at $P18$ or $P22$ it will take over, so not only does the power fluctuate, but a frequency fluctuation is also obtained. On the other hand for the case of a 10 m cavity with a corresponding mode separation of 15 MHz, several modes will be present under each gain curve, and so the $P$-branch with a maximum gain always oscillates because one axial mode will always be present under the Doppler gain curve.
Vibrational modes of molecules important in $\text{CO}_2$ laser mixtures. Energy transfer times are illustrated for the partial pressures given below each molecular species. Total pressure is 300 Torr and a 400 K temperature is assumed.

**Fig. 3.2 -2b**

<table>
<thead>
<tr>
<th>Material</th>
<th>Power Tolerance</th>
<th>Absorption (per cm thickness)</th>
<th>Reflectivity from one surface</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>&gt; 200 W cm$^{-2}$ (edge cooled)</td>
<td>≈ 3% (at &lt; 40°C)</td>
<td>36%</td>
<td>Good chemical stability. Insoluble in water.</td>
</tr>
<tr>
<td>Gallium Arsenide</td>
<td>&gt; 1 kW cm$^{-2}$</td>
<td>2%</td>
<td>27%</td>
<td>Good chemical stability. Insoluble in water. Expensive.</td>
</tr>
<tr>
<td>Alkali Halides (eg. potassium bromide, sodium chloride)</td>
<td>&gt; 1 kW cm$^{-2}$</td>
<td>&lt; 0.01%</td>
<td>4%</td>
<td>Hygroscopic. Cheap. Difficult to cost. Easily polished.</td>
</tr>
<tr>
<td>Intran (eg. magnesium fluoride, zinc sulphide)</td>
<td>≈ 20 W cm$^{-2}$</td>
<td>10%</td>
<td>17%</td>
<td>Insoluble in water. Rugged. Easily polished.</td>
</tr>
</tbody>
</table>

Carbon dioxide laser output mirror materials.

**Fig. 3.2 - 3**
c) The cavity gain builds up, with laser oscillation occurring ~1μs after cessation of the discharge.

d) The laser radiation pulse consists typically of a peak ~0.1μs wide and a tail lasting up to several μs at a lower intensity (Fig.3.2.1).

Some insight into the temporal features of this sequence may be gained from the work of Denes & Weaver (19) whose analysis is in part based upon the work of Taylor & Bitterman (22) and Cheo (23). Reference to Fig.3.2.2 shows energy transfer times in a 1:3:1 CO₂:N₂:He mix at a total pressure of 300 Torr at T = 400K. The 10^00, 02^20, 02^00 and 01^0 levels in CO₂ interchange energy in less than 30ns, and constitute the effective lower laser level. Relaxation to the ground state, mainly by collision with He, is in ~1.3μs. The CO₂(00^31) and N₂(v = 1) levels interchange energy in less than 1μs and act as the upper laser level. Since relaxation to the N₂ ground state occurs in ~10ms, the upper laser level is depleted primarily by relaxation to the 03^10 and 03^30 levels of CO₂ in ~22μs.

Because the gain in the cavity occurs after cessation of the current pulse and electron excitation process, the population inversion is apparently due to afterglow vibrational relaxation processes. Thus the cavity gain increases immediately following discharge due to the preferential relaxation of the lower laser level at a 2μs rate. In the absence of oscillation, the cavity gain will peak after ~2μs and decay at a 20μs rate. When oscillation occurs, an initial peak of stimulated emission diminishes the
Atmospheric pressure, pulsed excitation techniques—described by Beaulieu

**Fig. 3.3 - 1** Pin-bar structure

**Fig. 3.3 - 2** Double Rogowski system

Double Rogowski electrode structure for large volume excitation at atmospheric pressure (Lamberton and Pearson).
population inversion, after which stimulated emission continues at a rate predominantly determined by the rate at which the lower laser level can be depleted, and until the energy stored in the $N_2(v = 1)$ level is depleted.

Pearson & Lamberton (7) point out that the pulse tail only occurs when operation is multimode, and probably represents the slower build up of higher order transverse modes.

3.3 Atmospheric pressure operation.

Pulsed lasers provide high peak radiation power, particularly when operated at high gas pressure.

At about this time workers were making significant advances with high pressure operation (2,3). The enticement is a $(\text{pressure})^2$ dependence of power/unit active volume, and a total pulse energy proportional to pressure. Beaulieu (3) achieved pulsed atmospheric pressure operation with his transverse excitation using a pin and bar structure.

Beaulieu's design suffered from a poor aspect ratio discharge cross-section together with large ratio of dead to active volume. The possibility of a uniform discharge at atmospheric pressure throughout the laser cavity volume was to be realised by several workers using various designs (4,5,6). The essential features are preionisation followed by a very short duration discharge. This combination permits the excitation energy to be deposited whilst avoiding the formation of arcs. Pearson & Lamberton's design (7) was additionally robust, using electrodes proof against damage from an accidental arc.
population inversion, after which stimulated emission continues at a rate predominantly determined by the rate at which the lower laser level can be depleted, and until the energy stored in the \textit{N}_2(v = 1) level is depleted. Pearson & Lamberton (7) point out that the pulse tail only occurs when operation is multimode, and probably represents the slower build up of higher order transverse modes.

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Fig. 3.4.2-1
Laser Mk.2. viewed toward the germanium output mirror.
The line of sight is almost coincident with the line
of the output beam. Note the storage capacitor.

Fig. 3.4.2-2
The low inductance storage capacitor was constructed
using aluminium foil. The working voltage was 25kV.
3.4 The three lasers constructed.
At the outset of this project, there was not enough experience or cash available to enable a complete design to be drawn up prior to building. The approach had to accept the constraint of using available materials wherever feasible. The development was therefore an iterative process of step by step refinement in the light of experience as it was gained, and improved components as funds became available.

3.4.1 Laser Mk.1.
Our first model Mk.1 was based on Beaulieu's design. It was successful in producing laser radiation.
To illustrate the value of practical experience, "current hogging" among the multiple discharges was prevented by IKO resistors of moulded carbon 1W rating. At a pulse rate of 1p.p.s., 1W was more than adequate. Nevertheless, from time to time a resistor would shatter explosively. Thus it was we were forced to take account of the maximum voltage rating (750V) which had hitherto been overlooked!
Our pin and bar model was never put into service. Pearson & Lamberton published their designs (6,7). Lamberton demonstrated his Rogowski electrode(3) machine to us at S.E.R.L., and we decided to immediately commence work on Mk.2.

3.4.2. Laser Mk.2.
A Rogowski electrode design was derived based on materials available to us. Some square section brass bar dictated the dimensions of the Rogowski profile, (1cm plane width) whilst the milling machine dictated the length at 70cm. The perspex case was designed to match.
3.4 V

Fig. 3.4.2-3
Laser Mk.2, showing the double Rogowski electrode system and the trigger gap.

Fig. 3.4.2-4
Laser Mk.2. Rogowski electrodes.

Fig. 3.4.3-1
Oscilloscope trace of the output pulse of Laser Mk.3.
The peak output corresponds to an intensity of $\sim 5\text{MW/cm}^2$.
The time scale is 100ns/division.
There were of course many problems of detail involving mechanical structure, optimum use of machine shop expertise, available machine processes, gas handling technology, cavity adjustment methods etc., etc. These problems were overcome by means of the group expertise.

The most interesting technical difficulty concerned the discharge capacitor. The self-inductance of available units (redundant from another project) was measured \(^9\) and found excessive (\(~200\text{nH, 0.25\mu F, 30kV}\)). Commercial units were beyond our financial reach at the time. We constructed several capacitors to our own design, using aluminium foil (cooking) and polypropylene film dielectric, all immersed in liquid paraffin and contained in a perspex case. The problems arising from the high voltage operation (e.g. internal corona associated with trapped air bubbles etc.,) were considerable. The capacitors were serviceable, and in use till we became more wealthy. The principles of low inductance capacitor structures are given by Gabriel et al \(^{10}\).

Our Mk. 2 laser gave valuable experience. But it was smaller in active volume than we would have liked.

### 3.4.3. Laser Mk.3.

The basic features of the Mk.2 design were considered satisfactory. The aim behind Mk.3 was to scale up the key features of Mk.2 to achieve greater pulse energy. The main modification was therefore an increase in active volume. This meant in practice an increase in the width of the Rogowski electrode profile. Large electrode structures presented us with major problems of manufacture, especially if an accurately formed non-standard (to the machine shop) profile were specified.
Various techniques were being tried by other workers (pressing, explosive forming, numerical control milling), but orthodox milling was the only real alternative for us. It was therefore decided to use mild steel electrodes with a 1/4 circle profile bounding the plane section, as a reasonable practical approximation to the Rogowski shape. The electrodes were nickel plated. The choice of plating material was thought to be important, as it was supposed that photoemission from the cathode provided the initiating ions for the main discharge. With these features it was possible to obtain an effective electrode width of 2 cm, giving an excited gas volume $2 \times 1.7 \times 70(=240) \text{cm}^3$.

Additionally, a good deal of attention was given to minimising the inductance of the discharge circuit. A commercial low inductance capacitor ($L \approx 30 \text{nH}$) was used. A pressurised trigger spark gap enabled the filamentary (high inductance) arc length to be minimised.

One final general point worth recording; the ease with which a volume discharge was obtained was much increased by passing the helium (most of which had been used in experiments elsewhere, and had been pumped back into the storage cylinder) through a copper tube spiral immersed in liquid nitrogen. Residual impurities would be frozen out.

3.5 Main features of laser Mk.3.

3.5.1 General.

The laser enclosure was made of 1/4" perspex, with a total length of about 1 m, and 10 cm square cross-section.
One side could be removed for access. Mk.2 had revealed the necessity for a gas-tight main frame to combat "breathing" over the discharge cycle. The gas mixture was introduced into the chamber over its whole length, to ensure uniformity of composition. Exhaust was by a similar structure on the other side of the chamber. Regulation and mixing of the gases was achieved with a triple needle valve flow-meter device fed directly from the gas bottles. The laser structure was mounted on a bench in a total enclosure for safety. Access was through a perspex (infra-red opaque) sliding door.

3.5.2 Optical features.
As has been noted, a cavity suitable for high power output is the "large radius" type. Mk.3 used a 10m radius total reflector, and a plane partial reflector, seperated by 0.34m. Gas was excited within a volume of about 60cm x 2cm x 2cm (\(\sim \frac{1}{4}l\)).

Total reflector: gold coated zirconium-copper, radius of curvature 10m.
Partial reflector: single crystal germanium etalon; diameter 3.7cm, thickness 0.6cm; flat to within \(\frac{1}{4}\) wavelength Hg green; planes parallel to within 5 seconds of arc.
Applying the equations (section 2.5.1) 6 & 7 to find the uniphase mode beam radius at the reflectors yields: - etalon, \(r_1 = \) , beam radius = 3.1mm; mirror, \(r_2 = 10m\), beam radius = 9.7mm.
3.5.5 Electrical features.

Power supply: Mains derived fully variable 0-100kV 50Hz rectified; delivered to laser via chain of resistors limiting peak charging current.

Storage capacitor: 0.05μF, 60kV commercial low inductance (measured as ~15nH with self-resonant frequency of ~6kHz) by Nivertron Ltd.

Electrodes: Quasi-Rogowski profile: 70cm length; central plane 2 cm wide, bounded by cylindrical sections of radius 2cm. Bounding curve at either end determined "by eye". Separation of electrodes 1.7cm. Electrical feed via multiple connection to copper sheet to minimise inductance.

Trigger gap: "top hat" design for minimum inductance. Short arc path by nitrogen pressurisation. "Firing" by car ignition coil with electronic timing and count.

Trigger wire: 10μm diameter tungsten wire fed by 100 μF capacitor.

Discharge circuit: compact geometry, designed for minimum current loop enclosed area for minimal inductance. Robust, to withstand peak current > 500A, and accompanying electromagnetic forces.
3.6 Principle operating parameters of Mk.3.

3.6.1 General.

Economy of gas use was always a high priority. Despite the acknowledged desirability of effecting a complete change of gas between each output pulse as did S.E.R.L. and others, Mk.3 was operated with a complete change of gas in the chamber once in about 15 minutes. No evidence was obtained to indicate that any substantial disadvantage obtained from this practise. Indeed, S.E.R.L. have since developed a sealed laser unit.

Increased frequency of an arc discharge is the main indication of gas problem. This may be due to an accumulation of products generated in the discharge, or change of composition due to "breathing". It is probable that the latter factor was dominant in Mk.3, and determined the minimum useful gas flow rate.

The frequency of arc discharge was nearly always higher following switch-on, and diminishing progressively with use. This experience was common to other users. One suggestion circulated at the time was that the electrode tarnish might be performing a useful role. Firstly if the tarnish was in fact oxide, the electron emission produced at the electrode surface during pre-ionisation would be enhanced (11,12,13,14), thus aiding the diffuse discharge. Additionally the formation of tarnish would remove O₂ (deriving from the dissociation of CO₂) from the gas mix as it was formed, a gas thought to promote the formation of arcs. In any case, Mk3 performance improved with use, sufficient circumstance to ensure that such questions were pursued no further, decision being in favour of using the laser output to investigate damage mechanisms.
The overall laser performance is a function of a number of interdependent parameters, chiefly capacitor value, discharge volume, operating voltage and gas ratios. These parameters are rendered interdependent by the requirement for a diffuse discharge. A number of parametric studies (7,15,16,17,13) have been performed on particular laser structures, demonstrating boundaries outside which a diffuse discharge was unobtainable. Energy conversion efficiency is dependent on the operating regime.

3.6.2 Performance details.

Gas flow. A CO$_2$:N$_2$:He ratio of 1:1:4 was adopted. Following a period of experimentation, experience showed that flow rates of 40:40:160cm$^3$/min worked well, with a minimum of arc formation. Starting was not always straightforward. Normal running could usually be achieved by flushing with He, and lowering the voltage until diffuse discharge was obtained. Then the flow rates of CO$_2$ and N$_2$ were gradually raised, together with voltage until the usual values were reached. Following this procedure, performance was usually good and reasonably consistent.

Operating voltage seemed most satisfactory around 34kV (input energy 30J), but values between 22kV and 40kV produced a diffuse discharge.

Pulse rate about 1 pulse per second.
Pulse energy was in the region of 4J, but depending on the operating voltage at the time. Measurement was by a cone calorimeter and thermistor bridge.

Temporal profile was a well defined peak (~30ns FWHM), with a tail lasting ~600ns. The pulse was observed by a photon-drag detector made available by Dr. H.F. Kimmitt (University of Essex) (20, 21, 22) together with calibration data. A photon-drag device operates at room temperature, and gives absolute values for instantaneous power (temporal profile), peak power and (on integration) total energy. A typical value for peak power of ~5mW/cm$^2$ averaged over the beam X-section of ~4cm$^2$ was obtained. The temporal profile was also examined with a Pb-Sn-Te detector. These are sensitive, give only relative values of incident intensity without special calibration, and must be used at liquid nitrogen temperatures. The resolution of our system was ~50ns.

Spatial profile was of a multimode output covering an approximate rectangular aperture 2cm x 2cm. Many of the patterns showed a broadly striated structure (~5 bands). There was no single characteristic pattern, nor a recognisably predominant one. The laser alignment, when adjusted, was usually for maximum total pulse energy. There was no means of analysing the frequency structure, time variation of frequency structure, or the behaviour of separate regions of the beam cross-section.
There were two "bright" patches, well off axis, symmetrically placed above and below the main beam. The angular relationships demonstrated their origin with a mode using the electrode surfaces in addition to the cavity reflectors.
References.

Section 3 Development of a CO₂ T.E.A. Laser.


References section 3 cont.


22. A.F. Gibson and M.F. Kimmitt: Photon drag detectors Physics Bulletin


Section 4  Laser Damage in Germanium.

4.1 The etalons are damaged.

Following a period of operation (~10^5 shots) of the laser Mk.III, the germanium exit mirror (etalon) showed surface damage on the inside (cavity) face (Fig. 1). This unplanned event was to determine the character of the work throughout the rest of the project. Determining a model for the mechanisms producing the damage led into several major specialist subject areas; field theory, radio frequency antenna design, wave mechanics of the solid-state, electric breakdown of dielectrics and hot-electron theory of semiconductors.

Whilst the laser was in use for experiments involving damage to thin films, several etalons were damaged. Initial examination revealed well defined patterns which will be described later. The pattern orientation with respect to the laser, and to the etalon were noted. The damage occasionally occurred on the etalon exit face in addition to the cavity face. The same pattern characteristics were seen. The extent and severity of the damage was always much less than that on the cavity face.

Section 4 describes the damage, and derives a hypothesis to explain its observed characteristics. The ground has been covered in a publication. Where appropriate, extracts from the publication are used (e.g. sections 4.2 and 4.4). A list of references which contributed to the background of knowledge appears together with those specifically mentioned in the text.

* NOTE: All Figure numbers in section 4 are those used in Willis & Emmony(ref. 1), a copy of which is attached.
A detailed account of the damage features is now given.

4.2 Description of the damage.

"Several germanium mirrors have been damaged, and all the mirrors examined show similar features. Electron microscope examination of the germanium surfaces shows evidence of melting and large thermal stresses. Where the damage was not so severe as to cause obliteration, two periodic patterns were visible. The period of the larger pattern is \( \sim 10.6\mu m \) (Fig.2); (the laser free space wavelength is 10.6\mu m). This pattern will be referred to here as the '\( \lambda \)-pattern'. The smaller pattern, which will be termed the 'fine pattern', occurs perpendicular to the \( \lambda \)-pattern when the two are in association (Fig.3), although the \( \lambda \)-pattern is not always in evidence (Fig.4). The period of the fine pattern is not constant even over distances as short as 10\mu m, but is in the range 1.4\mu m to 2.1\mu m with a usual value \( \sim 1.7\mu m \).

It will be seen in Fig.1 that the damage occurs with regions of heavy damage and of less severe damage, and that a tendency to form in bars is apparent. The bar structure is parallel to the laser electrode surface and is not a function of crystal orientation.

Magnification reveals the \( \lambda \)-pattern bars extending some hundreds of wavelengths (several millimetres), the bar pattern direction being perpendicular to the laser electrode surface (Fig.2 and 3). The \( \lambda \)-pattern is seen in moderately damaged regions and becomes increasingly difficult to distinguish in severely damaged regions where melting and thermal stresses disrupt the regular surface pattern (Fig.5).
The fine pattern is most easily observed in regions where damage is very slight. It takes the form of lines separated by $\sim 1.7 \mu m$, parallel to each other, and extending up to a few tens of micrometres (Fig. 6). They are sometimes in association with a surface mark (for example, a shallow scratch) on the mirror surface (Fig. 7). The direction of the fine pattern on the laser mirror was parallel to the laser electrode surfaces and largely independent of the direction of the surface mark. A surface scratch nearly parallel to the fine pattern direction may 'capture' and deflect a line of the fine pattern (Fig. 7). A feature of interest is the fine pattern line termination where it merges into the undamaged surface. Fig. 8 is an electron micrograph of the tips of the fine pattern lines. The central region is raised above the mirror surface level, while the adjacent regions are slightly depressed. The appearance is similar to that of a 'spearhead'. Some areas of the damage clearly show the $\lambda$-pattern and the fine pattern in co-existence (Fig. 11). The two patterns are orthogonal. The fine pattern is not necessarily continuous across adjacent $\lambda$-pattern ridges. In regions in which the damage is not severe, the $\lambda$-pattern can take the form of variations in thickness of the pattern central ridge (Fig. 12). Note that the thickness variations are co-ordinated across the fine pattern line structure. The $\lambda$-pattern has also been observed as a series of melted and dispersed fine line ridges (Fig. 13). Another region with $\lambda$-pattern and fine pattern together, but more severely damaged, is shown in Fig. 14. Fig. 15 shows an area which has been heavily damaged. Deep fissures in the surface making acute angles to the $\lambda$-pattern can be seen. The fissures are due to cleavage along the crystal
planes to relieve thermal stresses in the surface following absorption of laser radiation. There is no relationship between the orientation of the $\lambda$-pattern and the cleavage cracks. The edges of the cracks are rounded, suggesting melting. A grey powder collects on the surface on and around the severely damaged areas. Individual particles are re-solidified droplets of germanium (Fig.16). There is just a hint of facets on some of them.

4.3 Some hypotheses.

A few of the ideas that were considered and rejected will be outlined.

Initially, when only optical micrographs (low resolution) were available, surface wrinkling and/or cracking was considered. The fine pattern marks (seen on a thin Ge film on this occasion) showed greater spacing in regions of higher light flux - against expectation. The arrival of the scanning electron micrographs (S.E.M) disposed of this hypothesis. An obvious candidate for consideration where a (fairly) regular pattern is produced is interference or diffraction. The linear nature of the pattern suggests "Lloyd's mirror" with the laser electrode plane surface as the mirror. The expected fringe spacing would be $\sim 500\mu m$. The fine pattern dimension is $\sim 2\mu m$. Idea rejected.

Interference between adjacent laser oscillator modes was considered. Available for consideration are longitudinal modes, transverse modes, and those deriving from the vibrational spectrum of CO$_2$. These are all grouped around $\sim 10\mu m$. Spatial beats between them in the plane of
the etalon face could hardly produce a 2\mu m spacing - more nearly 100\mu m minimum.

Wedge fringes due to the etalon faces' mutual inclination (parallelism to within 5 seconds of arc - manufacturer) produce a fringe spacing \( \sim 5\mu m \) when \( \lambda = 2.5\mu m \) (allowing for the refractive index of Ge; \( n = 4 \)). Additionally the fringe pattern would follow rotation of the etalon. The observed pattern was stable against etalon rotation.

There is no reasonable way radiation of \( \sim 10\mu m \) can produce a pattern of 2\mu m spacing by interference or diffraction. To do so would imply the possibility, under its illumination, of resolution of distances less than a wavelength, a situation known to be untenable.

Interaction between the laser beam and an acoustic wave set up across the Ge surface is a possibility (photog. ref. 16).

The strain produced on the lattice by the crest of an acoustic wave may be sufficient additional inducement in the presence of the laser field for the lattice to rupture (melt). An intense field would have to meet acoustic wave crests in particular regions of the Ge surface to produce the localised melting observed. The laser pulse is almost certainly amplitude modulated (multimode operation) with a crest separation \( \sim 5ns \) (= 2L/c). These "flashes" might "photograph" and freeze the instantaneous position of the acoustic wave crests. If the repeatability were excellent (phenomenal), a regular pattern would be produced. The snags to the idea are that (a) the pattern spacing is \( \sim 23\mu m \) (if velocity of sound in Ge is \( 5.4 \times 10^3 m/s \)) and (b) where would linear acoustic wavefronts be generated?
The preferred hypothesis will now be discussed.

A careful examination of the S.E.M. Fig. 7 shows a characteristic cross-section of the damage marks. These may be interpreted as the result of melting by an electric current driven in Ge by the laser field, and followed by re-freezing of the Ge. The details of the melt-refreeze cycle are described in 4.4.1. Section 4.4.2 shows how, if the marks in Fig. 7 are considered the result of an array of linear electric conduction currents originating by impact ionization in the laser field, the observed pattern of damage marks could be formed.

4.4 The proposed hypothesis.

4.4.1 Melt-refreeze cycle.

The cross-section which is shown in Fig. 9 results from a process of melting and refreezing (Fig. 10). The germanium within the boundary of the mark is melted by the laser flux, and because of the higher density of the liquid, occupies a smaller volume (Fig. 10a). Re-solidification begins at the perimeter, locking a depression into the surface contour (Fig. 10b).

As re-solidification is completed, a central ridge is formed enabling the former volume of solid to be regained. The central ridge is then above the original surface level. The density of germanium at $25^\circ C$ is $5.323 \text{ kg m}^{-3}$ (solid) and at $960^\circ C$ is $5.571 \text{ kg m}^{-3}$ (liquid). (ref. 4)

Evidence for this interpretation of Fig. 7 was sought in two ways:

a) Experiments with ice and wax.

b) Mathematical analysis with computer aided evaluation.
Both water and paraffin wax expand on freezing. They may therefore be used as analogues of Ge. Linear melts were produced by plunging hot metal strips into the solid and withdrawing. The shapes in Fig. 7 were reproduced on a large scale (centimetre). By varying the depth to width ratio of the melt, interesting variations of scale of profile were achieved. But the "spearhead" characteristic was retained in all cases.

The mathematical analysis was the subject of a publication (ref. 3) which is appended. The results support the interpretation of the S.E.M photographs.

4.4.2 Antenna theory adapted.

If the surface marks on the etalon are interpreted as refrozen linear melts, then an account has to be given of the periodicity. If each melt was interpreted as registering the presence of a linear geometry avalanche current path, then presumably the current would be alternating at $\sim 10^{-13}$ Hz under the influence of the laser field. Thus, under these assumptions, the problem becomes one of interpreting the significance of the geometry of an array of "R.F." currents. It seemed natural to turn to the literature on antenna arrays for help. An extract from the publication explains the theory.

" The observed dimensions of the periodicities show good agreement with those predicted by the field theory for radio antennae, when the dimensions are expressed in terms of wavelengths. The use of antenna theory is justified if the marks in the mirror surface are interpreted as indicating the paths of alternating electric currents induced in the
germanium mirror surface region by the laser cavity radiation fields. The frequency of the induced currents is $2.3 \times 10^{13}$ Hz, the CO$_2$ laser output frequency. An analysis of the field interactions resulting from the presence of the induced avalanche currents is given.

The mechanism relevant to the growth of periodic damage of the type discussed above is the formation of electron avalanches. This involves the existence of low ionization energy centres such as scratches, dislocations, etc., in the germanium surface. A defect acts as a source of carriers which enables the avalanche current to form and grow in the direction of the exciting electric vector of the radiation field.

The laser radiation was partially plane polarized with the maximum electric field intensity perpendicular to the cavity electrode surfaces. This was due to the existence of whisper modes (Fig.17) which involved reflections from the electrode surfaces and a consequent enhancement of $E_\perp$ (the electric intensity normal to the plane of the incidence) over $E_\parallel$. The reflectivity for $E_\perp$ is greater than for $E_\parallel$ for glancing angles at a metal surface. The interaction of the whisper modes with the main cavity beam gave rise to a beam intensity which was not uniform over its cross-section. This is indicated by the damage structure (Fig.1). It follows that particular areas, somewhere between maximum damage and no damage, were irradiated with an intensity just at the threshold level for avalanche formation. In these areas only the maximum field intensity occurring during a laser pulse
will be sufficient to generate an avalanche. The maximum field strength will occur in the direction of \( \mathbf{E}_1 \). The avalanche currents are therefore in the direction of \( \mathbf{E}_1 \), which is parallel to the laser electrode surfaces. The periodic damage has been observed in such threshold regions, where the damage is slight.

The avalanche current excited by the laser radiation reradiates energy at \( \sim 10^{13} \text{Hz} \). The most usual case dealt with in the radio antennae literature is that of an oscillating doublet radiating into free space. Here the situation is that of a radiating doublet in the interface separating two seminfinite dielectrics (considering the dimensions of the germanium mirror as very large in comparison to a radiation wavelength of 10.6/\( n \) \( \mu \)m in the germanium, where \( n = 4 \) is the refractive index). The radiation from the oscillating doublet interferes with the laser radiation, and in regions of constructive interference the probability of forming a new avalanche current is increased.

The constructive interference patterns which give rise to a regular array of avalanche currents, and therefore to surface damage with structured appearance, will be discussed in some detail. The doublet near field inside the germanium gives rise to the fine pattern, whilst the surface wave in the interface causes the \( \lambda \) pattern.

**Near field effects.**

The fine pattern has a spacing of approximately 1.7\( \mu \)m with some variation about this value, (spacings from 1.4\( \mu \)m to about 2.1\( \mu \)m have been observed). Since there is a selfreinforcing pattern, the individual currents must be
in phase, and therefore maintain a consistent phase relationship with the incident laser radiation (in this case the reactive component of the current element impedance only influences the phase slightly). The simplest condition for this to occur for a row of short doublets is with a spacing of \( 0.7\lambda \). At this distance the near field of a doublet (Fig.13) would induce an in-phase current in a resistive element. The length of the current track, and the associated melt in the germanium surface, increases with each laser pulse. Over regions where the irradiating laser intensity is just below breakdown threshold, the electric field enhancement at \( 0.7\lambda_{\text{Ge}} \) provided by the near field of the linear current is likely to produce a new avalanche current parallel to the first. This represents pattern growth in a 'broadside' direction (Figs 19 and 23). Since a progressive wave with an electric field component in the plane of the interface cannot be sustained due to the boundary conditions, only the near field of a doublet is significant in new broadside avalanche formation. Consequently, in the broadside direction only the adjacent current influences the growth path of a fresh avalanche.

**Surface wave effects.**

The fine pattern represents an array of co-phased currents oscillating at the frequency of, and in phase with, the incident laser field. In accord with electro-magnetic field theory, a surface wave will be launched in the dielectric interface formed by the mirror and gas. The direction of maximum intensity is along the axis of the current track.
The polar diagram for a doublet is shown in Fig. 20a. An array of such doublets will modify the polar diagram so as to increase the electric intensity of the surface wave in the direction of the current axis (Fig. 20b). A surface wave has an electric vector $E_n$ perpendicular to the interface and a component $E_L$ in the direction of propagation (Fig. 21). A surface wave is an inhomogeneous electromagnetic wave guided along the interface. The lines of constant phase and of constant amplitude are shown in Fig. 22.

For a surface wave travelling over germanium the angle of tilt $\Theta$ is $14^{\circ}$, and the longitudinal component of the electric field in the direction of propagation, $E_L$, has a magnitude of $0.25E_n$. Consequently $E_L$ has a significant magnitude, and is correctly oriented to influence the current magnitude in the avalanche tracks. The phase of the incident laser radiation relative to that of the surface wave is important. The phase will enhance at intervals of $\approx \lambda_0$, the free space wavelength, across the surface. At these locations an existing current may be increased (Fig. 12), or a new avalanche may be created as the field strength is raised over threshold (Fig. 23). In either case, surface damage due to melting will be greater and display a periodic interval of $\approx \lambda_0$. This is the $\lambda$-pattern, which is observed in regions of moderate damage.

The exact interval for the $\lambda$-pattern will be the distance $AB$ in Fig. 22 which will be given by $\lambda_0 \sec \Theta$. For a germanium interface, the pattern interval is:

$$x=10.6\mu m \cdot \sec 14^{\circ}$$

$$10.9\mu m.$$
Summary.
Structured damage patterns have been observed on germanium mirrors used in TEA CO₂ lasers. Two regular pattern intervals occur orthogonally. The patterns result from melting of the germanium following the formation of avalanche currents in response to the electric field of the incident laser radiation. The orientation of the linear current tracks follows the predominant polarization of the laser radiation. The proposed sequence of pattern growth is avalanche formation, linear melting, constructive interference between the incident radiation and the field of the induced current doublet, followed by initiation of new avalanches conforming to a regular array. The near field within the germanium gives rise to broadside pattern growth ($\sim 1.7 \mu m$ spacing), whilst a surface wave produces new avalanches and/or increased damage at a spacing close to the free space wavelength ($\lambda_0=10.6 \mu m$).

4.5 An observation.
There were two sudden strides forward during the development of this theory. One was the recognition of the existence of a surface wave, of which the key feature (here) is a component of electric field in the direction of propagation. The thickening in Fig. 4.12 to form the $\lambda$-pattern required it. Until this penny dropped, electric fields were 90° "wrong".

The second leap came on realising that the polar diagram for a current doublet launching a surface wave is end-fire (rather than the familiar space launch which is broadside). The jig-saw was fitting together.

An examination of the avalanche breakdown of Ge in a strong electric field is undertaken in section 5.
With the Compliments of

Illegible text

Loughborough University of Technology
References.

Laser damage in germanium


5.1 Introduction.

The nature of an avalanche breakdown in germanium, which is subjected to intense laser light, is considered from first principles. The philosophy is essentially that of the "microscopic" school; that is, to consider the life history of a typical electron (and/or hole), and attempt to take into account all the factors affecting its behaviour.

The section falls naturally into two parts. Together they represent a step-by-step progress toward understanding a complex phenomenon.

The unit comprising sections 5.2 to 5.5 deals with the free electron case. Even whilst considering the thermal distribution of conduction electrons in germanium, the free electron mass \( m \) is used rather than effective mass \( m^* \), and trajectories free of phonon interaction are considered. These sections represent the construction of a basic framework of thought which supports the following development. Although written much earlier than the second part of section 5, the unit is retained for its value as a foundation.

Section 5.6 to section 5.12 assemble from the literature present thinking relating to electrical breakdown, with especial reference to the case of germanium. The topic of 'hot electrons' is pursued at some length using available data.

Bass & Barratt's adaptation (for optical frequency fields) of Shockley's "lucky electron" approach to impact ionization, was used as the basis of a computer programme. The purpose was to examine the effect of various material parameters on the
5.2 **Electron dynamics.**

It is proposed that particular forms of the damage (described elsewhere) on the germanium output mirror of the laser may be attributed to the formation of electron avalanches and a progressive pulse by pulse growth in extent of the damaged region. It is worth examining some aspects of the behaviour of electrons in electromagnetic fields. We shall commence with the more straightforward situations, and worst case numerical values relevant to the laser damage under investigation to indicate where greater sophistication is required, and is not required. Some aspects of electron avalanching in optical fields will be approached.

The motion of a free electron in vacuo acted upon by crossed \( \mathbf{E} \) and \( \mathbf{B} \) fields will be considered. It will be demonstrated that the effect of the \( \mathbf{B} \) field may safely be ignored for the cycle time of radiation at 28.3 THz. Thereafter only the action of the electric field is taken into account, and conditions prevailing at the gas-germanium interface are considered.

5.2.1 **Case 1. Free electron in electromagnetic field.**

The electron in vacuo starts from rest at \( t=0 \) from the origin \( O \), static electric and magnetic fields are maintained with \( \mathbf{E} \) along \( OY \), \( \mathbf{B} \) along \( OZ \).

Free electron trajectory in crossed \( \mathbf{E} \) and \( \mathbf{H} \) fields.
Equation of motion:-

\[ \frac{dy}{dt} = \frac{e}{m} \left( \mathbf{E} + (\mathbf{v} \times \mathbf{B}) \right) \]  

The solution of this equation is a common cycloid for the initial conditions assumed (1).

Transpose to a set of axes \( X', Y', Z' \) translating in the direction \(OX\) with a velocity \( u \), given by

\[ u = \frac{E}{B} \quad \quad \quad u = \frac{1}{B^2} (\mathbf{E} \times \mathbf{B}) \]  

Thus \( u \times \mathbf{B} = \frac{1}{B^2} (\mathbf{E} \times \mathbf{B}) \times \mathbf{B} \)

Then the velocity \( \mathbf{v}' \) relative to \( X', Y', Z' \) is obtained from

\[ \mathbf{v} = \mathbf{u} + \mathbf{v}' \]  

and

\[ \frac{dv'}{dt} = \frac{dv'}{dt} \]

so substituting into 1:-

\[ \frac{dv'}{dt} = \frac{e}{m} (\mathbf{E} + (u \times \mathbf{B} + \mathbf{v}' \times \mathbf{B})) \]

But \( u \times \mathbf{B} = \frac{1}{B^2} (\mathbf{E} \times \mathbf{B}) \times \mathbf{B} \)

Thus

\[ \frac{dv'}{dt} = \frac{e}{m} (\mathbf{v}' \times \mathbf{B}) \]

This says that the acceleration is always perpendicular to the velocity. Hence the speed \( v' \) is constant and the orbit is a circle in the \( X', Y' \) plane of radius \( \rho \) and angular velocity \( \omega \) :-

In scalar form

\[ (v')^2 = \frac{-Be v'}{m} \]

\[ \rho = \frac{-v'}{e/m B} \]
\[ \omega = \frac{1}{\rho} = \frac{e}{m} B \]

The trajectory relative to XYZ is the locus of a point on the circumference of a notional wheel of radius a rolling along OX with axle velocity \( u \).

\[ a = \frac{u}{\omega} \]
\[ a = -\frac{E}{e/m} B^2 \]

For the special case \( v = 0 \) when \( t = 0 \),

\[ a = \rho \]

and the trajectory is a common cycloid.

The aspect of eventual interest is the behaviour of conduction electrons in germanium under the influence of 10.6 \( \mu \)m wavelength radiation.

For the moment we consider magnitudes for static fields when \( E \) is of the order of \( 10^3 \) V/m (typical of dielectric breakdown), but restricted to times corresponding to a cycle at 28.3 THz. It will be shown that the electron acceleration due to the magnetic field is insignificant in comparison to that due to the electric field, and that the motion produced is for practical purposes parallel to the direction of \( E \). These results follow from the fact that in the time available the electron is only able to traverse a minute arc segment of the cycloid. So far we are still concerned with D.C. fields acting on an electron in vacuo, though the time of field application has been restricted. The ratio of \( E \) to \( H \) will be the same as of an electromagnetic wave in vacuo.

One cycle time \( \Delta t = \) reciprocal \( 2.33 \times 10^{13} \) \( = T \)

\[ = 3.5 \times 10^{-14} \text{ s} \]

\[ \therefore T/2 = 1.76 \times 10^{-14} \text{ s} \]
Thus

\[ E = 10^3 \frac{v}{m} \]

\[ H = \frac{\mathcal{E}}{120 \pi} = 2.6 \times 10^5 \]

\[ B = \frac{\mathcal{E}}{m} = 0.33 \text{ T} \]

Thus

\[ \omega = \frac{m}{e} B \]

\[ \omega \Delta t = -5.7 \times 10^{10} \text{ radian} \]

and

\[ \omega \Delta t = -1 \times 10^{-3} \text{ radian} \]

The angle is so small that displacement is substantially along OY.

To evaluate the displacement, note that

\[ |v'| = |u| \text{ when } v = 0 \text{ at } t = 0 \]

and

\[ |u| = \frac{m \mathcal{E}}{q} \]

so

\[ |u| = 3.03 \times 10^3 \text{ m/s} \]

which is greater than the velocity of light c, but is only notional because during the short time being considered the electron only achieves a small fraction of u.

\[ y = a - a \cos \omega \Delta t \]

\[ = a(1 - \cos \omega \Delta t) \]

\[ = \frac{u}{2}(1 - \cos \omega \Delta t) \]

\[ = 3.3 \times 10^8 \times \frac{5.7 \times 10^{10}}{1 - \cos \omega \Delta t} \]

\[ = 2.6 \times 10^{-9} \text{ metre} \]

\[ x = a \Delta t - a \sin \omega \Delta t \]

\[ = a(\Delta t - \sin \omega \Delta t) \]

\[ = 8.9 \times 10^{-13} \]

\[ \div 10^{-12} \text{ metre} \]

Thus for the time under consideration, the displacement is substantially along OY, and is effectively that which would have been obtained by an electric field alone. This remains
true for times extending to several tens of cycles, long enough for the electron to reach ionizing energy. It takes approximately three cycle times at 23.3 THz for the electron to move a distance equivalent to one interatomic spacing along OX.

5.2.2 Case 2 Time dependent electric field.
The electron is subject to a sinusoidal e-m radiation field, characterised by the peak electric field $E_0$. The parameter of interest is the electron energy at the end of one half cycle. The effect of $H$ will be ignored. Note that $\omega$ takes on a different significance, the radian velocity of the electromagnetic field.

Since the displacement of an electron is restricted to the OY direction, the equation of motion may be written

$$\ddot{y} = -\frac{eE}{m}$$

$$E = E_0 \sin \omega t \quad \text{if } E=0 \text{ when } t=0$$

$$\ddot{y} = -\frac{e E_0 \sin \omega t}{m}$$

$$\dot{y} = \frac{e E_0 \cos \omega t + C}{m \omega}$$

if $\dot{y} = 0$ when $t = 0$, $C = \frac{e E_0}{m \omega}$

$$\dot{y} = \frac{e E_0 \cos \omega t - \frac{e E_0}{m \omega}}{m \omega}$$

The electron energy is maximum when $t = T/2$, where $T$ is the period of the electric field.

Thus

- peak electron velocity $=-2 \frac{e E_0}{m \omega}$

and electron energy $\frac{mv^2}{2} = \frac{m}{2} \left(\frac{e E_0}{m \omega}\right)^2 \omega$
Electric field

Velocity

Displacement

Fig. 5.2.2 - 1
when \( E = 10^8 \text{ V/m} \) and \( f = 2.33 \times 10^{13} \text{ Hz} \)
electron energy \( \Delta 0.11 \text{ eV} \)

This result confirms that Relativity need not be taken into account, as departures from classical relationships are only significant at energies greater than about 1000 eV.

Also of interest is the displacement:
\[
y = \frac{e}{m} \frac{E_0}{\omega} \sin \omega t - \frac{E_0 e}{m} t + C \quad T/2 \geq t \geq 0
\]

If \( y = 0 \) when \( t = 0 \), \( C = 0 \)

Thus
\[
y = \frac{E_0 e}{\omega m} \left\{ \frac{\sin \omega t}{\omega} - t \right\}
\]

When \( t = T/2 \), term in brackets is just \( T/2 \)
and
\[
|y_{T/2}| = \frac{E_0 e}{\omega m} \frac{T^2}{2} = \frac{E_0 e}{\pi} \frac{T^2}{4}
\]

When \( E_0 = 10^8 \text{ V/m} \), \( f = 2.33 \times 10^{13} \)
\[
|y_{T/2}| = 1.7 \times 10^{-9} \text{ m}
\]

5.2.3 Case 3. Quasi-free electrons in germanium.

Electromagnetic radiation incident on a germanium interface.

The electron acted upon by the fields is considered to be in the germanium conduction band, not far from the surface, capable of acquiring energy from an impressed electric field according to a classical model (5). The interest is in radiation of frequency 28.3 THz.

Consider what modifications are necessary to the foregoing to take account of the presence of the germanium. Electric fields of \( 10^8 \text{ V/m} \) may still be postulated, provided account is taken of the field variation through the surface and into the outside space. If it be postulated that in the times
considered no lattice scattering events take place (reasonable since in germanium at room temperature the mean free path is about $10^{-3}$ m), then the above results for electron energy and displacement occurring in a half-cycle time still hold. It is interesting to note that the half-cycle time displacement $1.7 \times 10^{-9}$ m corresponds to about three times the lattice constant, whereas the mean free path is twenty or so atomic spacings (or more according to ref. 2 page 25-27). It must be remembered that the quoted data for germanium relate strictly to thermal equilibrium at 300 K.

Again Shockley showed that the carrier mobility in germanium saturates with high impressed fields - the Gunn diode is based upon the effect. But since mobility is a function of the dependence of drift velocity on lattice scattering, it is regarded here as not pertinent to this problem. We are considering the dynamics in the absence of collisions on the way. So velocity saturation will be ignored for the moment.

The effect on the cycloid trajectory is worthy of review. If the arbitrary field of $10^3$ V/m is retained for the purpose of gauging magnitudes, the intrinsic impedance $E/H$ of germanium is $1/4$ that of free space. $B$ (taking $u_r = 1$) is thus proportionately greater ($x 4$) and the cycloid curvature is greater. To check whether the B field may still be neglected in this problem, evaluate and compare the $x$ and $y$ displacements over the time of one half-cycle of the radiation. We revert momentarily to the static field arithmetic.

($a$ is reduced to $1/16$ its former value, viz $3.2 \times 10^{-4}$ m.)

($w$ is increased to $4 \times$ its former value, viz $2.2 \times 10^{11}$ rad/s.)
\[ y = a(1 - \cos \omega dt) \]
\[ = 2.6 \times 10^{-9} \text{ m.} \]
\[ x = a(\omega dt - \sin \omega dt) \]
\[ = 4 \times 10^{-12} \text{ m.} \]

Thus the B field again need not be considered.

### 5.3 Conclusions to be drawn from the cited cases.

The problem of the behaviour of "free" conduction electrons in the germanium under the influence of electromagnetic radiation of frequency 28.3 THZ and of high intensity has been approached using classical concepts. It has been demonstrated that the significance of the B field on electron trajectories limited by time to acquiring energies of the order of 0.1 eV only is minimal. In the following discussion no further account will be taken of its presence, and only the E field will be taken into account.

The overall purpose of the discussion is to assess the possibility of the formation of electron avalanches in the germanium. The structure of the observed damage is to be explained in terms of such avalanches forming, producing melts in the germanium surface, and also influencing the location of adjacent avalanche formation.

The energy gained by an electron accelerated in the field for one half cycle is of the order of 0.1 eV. Electron-hole pair formation in germanium requires about 0.7 eV. Thus either electrons must be available from a source of lower ionization energy, or the electron initiating an avalanche must be able to use more than one half cycle of radiation, despite the field direction reversal.
It must be remembered that once initiated, the avalanche must be sustained if visible damage is to be produced on the germanium surface.

Both of these possibilities seem feasible.

5.4 Sources of lower ionization energy.

Impurities, surface states and surface defects.
Electrons may be released more easily from impurities and surface states, especially from surface defects such as scratches etc. Observations (Fig.4.7) confirm that the damage concerning us here definitely initiates along microscopic scratches. It is not possible to assess whether such a surface defect is essential to the formation of the damage.

Chemical change following melting.
When an avalanche has produced a melt in the surface, the possibility exists of chemical combination of the germanium with the laser gases and conceivably trace gases such as oxygen. The succeeding laser pulse may be more readily able to remelt this area and facilitate a pulse-by-pulse growth of the damaged region.

Stressed states following freezing.
At the end of the pulse, the surface melts will re-freeze. The surface contour is permanently changed (4) and may include regions of frozen in stress. These may enable a progressive extension by providing a readily ionizable local region of lattice for the next pulse.

Thermal electrons.
The conduction band will contain a distribution of electronic energies. Due to the high 'density of states' available in
the germanium conduction band in relation to the density of conduction electrons at room temperature, the distribution is close to the Maxwell-Boltzmann for free electrons (ref. 2, page 27). The mean kinetic energy is \( \frac{3}{2} kT \). The 'high energy tail' might provide electrons capable of ionization after further acceleration by a half-cycle of field.

5.5 Examination of the high energy tail (thermal distribution).
In this section, the number of electrons in the high energy tail capable of accelerating to \( E_1 \) in a field of \( 10^3 \text{V/m} \) during an optical half-cycle is estimated. The cumulative effect of resulting ionizations over the available optical cycles of the laser pulse is estimated. The increased conductivity is assessed from a damage viewpoint.

5.5.1 The intrinsic electron density.
To find the electron density in intrinsic germanium (5):

\[
\text{Band gap } = 0.72 \text{ eV} \quad (\text{ref.} 2)
\]

\[
n_e = \int_{E_c}^{E_1} Z(E) \, dE \quad (\text{ref.} 5)
\]

where \( n_e \) electron density; \( n_j \) occupation number for state \( j \) (i.e. mean no. of electrons in state \( j \); \( Z(E) \) density of states function; \( E \) electron energy; \( E_c \) electron energy at bottom of conduction band;

If electrons at the bottom of conduction band are considered to behave as free electrons,

\[
Z(E) = 2\pi \xi L^3 (2\pi/m^2)^{3/2} E^{3/2}
\]

where \( \xi \) = degeneracy; \( L \) = dimension of specimen; and if classical statistics are applicable

\[
n_e = N_c \exp\left\{ \frac{-(E_c - \xi F)}{kT} \right\}
\]

\( \xi \) is the Fermi level. \( N_c \) is the 'effective density of states', which for free electrons is (ref. 5, page 134):

\[
N_c = 4.83 \times 10^{21} \text{ T}^{3/2} \text{ m}^{-3}
\]

Which leads, with an equal number of holes, to
\[ n_i = N \exp \left( - \frac{\xi}{a} / 2kT \right) \]

\[ n_i \text{ electron density in conduction band} \]

Putting in values for germanium at 300K

\[ n_i = 2.24 \times 10^{19} \text{ m}^{-3} \]

Horant quotes \[ 2.5 \times 10^{19} \text{ at 300 K} \]. (ref.2)

5.5.2 The thermal distribution.

The distribution of velocities above the bottom of the conduction band where \( v = 0 \) is given by a Maxwell-Boltzmann distribution:-

\[ f(v) dv = 4\pi \xi^3 v^2 \exp \left( -mv^2/2kT \right) dv \]

(ref. 5 equation 4,9)

\[ C = \left( m/2\pi kT \right)^{3/2} \]

Putting in \( C \), and rearranging

\[ f(v) dv = 4 \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left( -mv^2/2kT \right) dv \]

The distribution function \( f(v) dv \) gives the fraction of the total population of \( N \) particles to be found on average with velocities lying in the range \( v \) to \( v + dv \). The actual population is found from \( N \times f(v)dv \).

In this problem, it is of little concern to know the velocity per se. Of more interest is a kinetic energy distribution function \( f(\xi) d\xi \). (To avoid further subscripts, the symbol \( \xi \) will be used here for thermal kinetic energy as opposed to total energy, without introducing ambiguity).

Manipulating \( f(v)dv \):

\[ \xi = \frac{mv^2}{2} \quad d\xi = mv \ dv \]

and

\[ f(\xi) d(\xi) = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \xi^{3/2} \exp(-\xi/kT) \ d\xi \]
As a check:
\[ \int_0^\infty \varepsilon^{\frac{3}{2}} \exp \left( -\frac{\varepsilon}{kT} \right) d\varepsilon = \frac{\sqrt{\pi (kT)^3}}{2} \] (ref. 6 page 101)

which means
\[ \int_0^\infty f(\varepsilon) d\varepsilon = 1 \]
and the number of particles with an energy lying in the range between \( \varepsilon \) and \( \varepsilon + d\varepsilon \) is \( N. f(\varepsilon) d\varepsilon \).

An alternative form may be expressed in terms of the energy possessed by the particle relative to the quantity \( kT \).

Defining the relative energy \( R \),
\[ R = \frac{\varepsilon}{kT} \]
and
\[ f(\varepsilon) d\varepsilon \]
Again
\[ \int_0^\infty f(R) dR = 1 \]

The function \( f(R) dR \) might be termed the UNIVERSAL DISTRIBUTION FUNCTION for indistinguishable particles in thermal equilibrium. From it may be deduced the details of any particular case given \( m \) and \( T \).

At this point, a digression to examine a feature of interest which arises from changing the viewpoint from \( f(v) dv \) to \( f(\varepsilon) d\varepsilon \). The velocity distribution \( f(v) dv \) has a maximum at a velocity corresponding to \( \varepsilon = \frac{mv^2}{2} = kT \) from which Roberts (6) states that the most probable velocity is given by
\[ v = \left( \frac{2kT}{m} \right)^{\frac{1}{2}} \]

whilst \( f(\varepsilon) d\varepsilon \) peaks when \( \varepsilon = \frac{kT}{2} \) presumably giving the most probable energy.
Thus the "most probable velocity" and the "most probable energy" do not correspond. The apparent discrepancy stems from the definitions of the classes of particle "dν" and "dE" which are not linearly related. However, the point leads to a careful consideration of the meaning of the phrase "the most probable" in this context.

5.5.3 Accelerating the high energy tail to $E_i$.

Returning to the main theme, the "universal distribution" is used to examine the population of electrons in the conduction band of germanium at 300 K with kinetic energies approaching 0.7 eV. The object is to assess how many electrons might be raised to ionizing capability by one half-cycle of applied field.

The number of electrons per unit volume $n'$ capable of being raised to ionizing $E_i$ is given by

$$n' = \frac{2}{\sqrt{\pi}} \int_{-E_{\text{min}}}^{E_i} e^{R^2} \exp(-R)dR \times n_1 \times f'$$

where $n_1$ is electron density at 300K for intrinsic germanium, $f'$ is the fraction with a thermal velocity acceptably oriented for acceleration by the electric field of the half-cycle in question, and $E_{\text{min}}$ is the minimum electron energy capable of being raised to $E_i$ by one half-cycle of the field. It has been shown:-

$$\dot{y} = \frac{e}{m} \frac{E_0}{\omega} \cos \omega t + c$$

If the velocity is $-v_0$ (in the direction of acceleration)

when $t = 0$, $$\dot{y} = \frac{e}{m} \frac{E_0}{\omega} (\cos \omega t - 1) - v_0$$

When $t = T/2$: $$\dot{y}_{\text{max}} = - \frac{e}{m} \frac{E_0}{\pi} T - v_0$$
Thus each half cycle will increase the velocity of the electron
by
\[ \frac{e}{m} \frac{E_0}{k} T \]
when \( E_0 = 10^3 \text{ V/m} \) and \( f = 23.3 \text{ THz} \), increase in \( v \approx 2 \times 10^5 \text{ m/s} \).
The ionizing energy for germanium is 0.7 eV which corresponds

to \( 5 \times 10^5 \text{ m/s} \). Therefore \( \epsilon_{\text{min}} \) corresponds to a velocity

of \( 3 \times 10^5 \text{ m/s} \).
Thus \( \epsilon_{\text{min}} = 0.25 \text{ eV} \) and \( \epsilon_{\text{min}}/kT = 10 \)

Therefore:
\[ n' = \frac{2}{\sqrt{\pi}} \int_{R}^{\infty} \exp(-R)dR \times n_\perp \times f' \]

Since only an estimate is required, it may be noted that in

the region \( 10 \ll \epsilon < \epsilon_\perp \), \( \exp(-R) \) is the dominant term, and

the value \( \exp(-10) \) may be taken to be

sufficiently close to the value of the integral.

thus
\[ n' = 5.1 \times 10^{-5} \times 2.5 \times 10^{13} \times 0.1 \text{ (taking } f' \approx 0.1) \]

= \( 1.3 \times 10^8 \text{ electrons per cm}^3 \text{ (very approximately).} \)

This is the number of electrons per cm\(^3\) with thermal
velocity correctly oriented with respect to the optical
electric field to accept energy approaching \( \epsilon_\perp \) within one
half cycle. It is a further condition that collision does
not take place before \( \epsilon_\perp \) is reached, but does soon after.

If \( l \) is the mean free path, \( y \) the distance travelled from
the commencement of the optical field half cycle to the
point at which \( \epsilon = \epsilon_\perp \), and \( dy \) is the further distance
before optical field reversal (or more strictly, to the
point at which the next optical half cycle has reduced
the electron energy to \( \epsilon_\perp \) once more), then the probability \( p(y) \)
of a successful ionizing event is

\[ p(y) = \exp(-y/l) \left( 1 - \exp(-dy/l) \right) \]

An estimate of \( p(y) \) may be obtained for a "particular electron" given the thermal velocity at the commencement of the optical half cycle (and \( E_0 \)) so that \( y \) and \( dy \) may be evaluated. That is, both

\[ y, \quad dy = F(\text{initial thermal velocity, } E_0, \quad \epsilon_i) \]

For germanium \( l \) is approximately \( 10^{-7} \text{m} \), or 200-300 atomic spacings. *(1 might be expected to be a function of temperature, applied field \( E \), and particular sample of germanium, as well as proximity to sample surface. These aspects will not be taken into account here).

*(this value was taken from ref.2 page 25 - but now seems high).

5.5.4 Expected conductivity modulation.

Of more interest is the probable number \( n'' \) of ionizing events per \( \text{cm}^{-3} \) during each half-cycle. In principle this could be obtained by integrating over the number of electrons with acceptable initial velocity:

\[ n'' = n_i \int_{T'}^{2} \frac{2}{\pi(kT)^{3/2}} \frac{\epsilon^2}{\epsilon_{\text{min}}} \exp(-\epsilon/kT) \exp\left\{ -y(\epsilon)/l \right\} \left[ 1 - \exp\left\{ -dy(\epsilon)/l \right\} \right] d\epsilon \]

An impression of magnitudes may be gained by using the data in Fig.5.6 - 1 to consider a thermal electron commencing the half cycle with an energy of about 0.45 eV.

From the figure,

\[ y = 7.6 \times 10^{-9} \text{m.} \quad \text{the equality is co-incidental} \]
\[ dy = 7.6 \times 10^{-9} \text{m.} \]
\[ l = 10^{-7} \text{m.} \]

thus

\[ p(y) = \exp(-y/l) \left( 1 - \exp(-dy/l) \right) \]

\[ = 0.9 \times 0.1 \]
This says that the nature of crystalline germanium is such that the required acceleration from 0.45 eV to 0.7 eV is very probable, whilst the dominant term is that describing the likelihood of an ionizing event before the energy is reduced by the next optical half cycle to less than $E_i$. To the order of precision here, the overall probability of a successful ionizing event is

$$p(y, \text{ initial thermal energy } 0.45 \text{ eV }) \approx 0.1$$

The number of ionizing events per cm$^3$ originating from thermal electrons with energies between 0.44 and 0.46 eV (i.e., $dE = 0.02$) at the commencement of an optical half cycle is:

$$n''(0.45 \text{ eV}) = \frac{N_i}{\sqrt{\pi (kT)^2}} \frac{E^{1/2}}{E} \exp(-E/kT)p(y)dE$$

$$= 2.5 \times 10^{13} \times 0.1 \times 2.85 \times 10^2 \times (0.45)^{1/2} \times 1.5 \times 10^{-8} \times 0.1 \times 0.02$$

$$= 1.5 \times 10^4 \text{ ionizations/cm}^3 \text{ optical half cycle.}$$

(based on $E_0 = 10^8 \text{ V/m, } f = 28.3 \text{ THz}$)

This result would indicate that of the $10^8$ thermal electrons/cm$^3$ capable of reaching $E_i$, a reasonable proportion, say $10^5$/cm$^3$ will produce an ionizing event, with an additional $10^5$/cm$^3$ electron density.

The laser pulse is about 100 ns duration with near peak field, i.e., ~$10^6$ cycles. If each half cycle produced $10^5$ electrons/cm$^3$ independent of the preceding half cycle, the net increase in electron density would be

$$n \approx 10^5 \times 10^6 \times 2$$

$$= 10^{11} \text{ electrons/cm}^3.$$
This would make an insignificant contribution to the intrinsic conductivity (where \( n_1 = 2.5 \times 10^{13}/\text{cm}^3 \)).

When the ionizing collision takes place, the ionizing electron may well possess enough energy to produce a post-event pair, each with a substantial fraction of \( \epsilon_1 \) (typically 0.3 - 0.4 eV). If a lucky elastic collision occurs to reverse the velocity to keep it in phase with the field, the possibility of avalanche multiplication exists. This possibility is further examined in a subsequent section.

If "lucky elastic collisions" be excluded from consideration, a significant increase in the conductivity of the illuminated germanium due to ionizing events in each half-cycle and utilizing electrons in the "high energy tail" of the thermal distribution seems remote.

5.5.5 Dependence of modulation on field strength.

The numerical values relate to a particular \( E_0 \) (=10^8 V/m) and frequency of radiation (23.3 THz). To assess the effect on \( n'' \) of varying these parameters, note

\[
n'' = f(y, dy) = f(E_0, T^2)
\]

The relevant factors

\[
\exp \left(-\frac{y}{l}\right) \rightarrow \left(1 - \frac{y}{l}\right) \rightarrow 1 \text{ if } y/l \text{ is small}
\]

\[
\left\{1 - \exp \left(-\frac{dy}{l}\right)\right\} \rightarrow \frac{dy}{l} \text{ if } dy/l \text{ is small.}
\]

The factor representing the probability of a successful ionizing event approximates

\[
p(y) = \exp \left(-\frac{y}{l}\right) \left(1 - \exp(- \frac{dy}{l})\right) \rightarrow \frac{dy}{l}
\]

and

\[
n'' = \text{const} \times \int_{\epsilon_{\text{min}}}^{\infty} \frac{\epsilon^{\frac{3}{2}}}{\epsilon_{\text{min}}} \exp(- \epsilon/kT) \left(dy/l\right) \; d\epsilon
\]

*This section was based on \( l = 10^{-7} \text{m} \) from ref.2.
using
\[ y = \frac{E_o}{\omega_m} \left( \frac{\sin \omega t}{\omega} - t \right) - \sqrt{\omega t} \]

for guidance, observe that \( y \) (and also \( dy \)) is the sum of two parts, essentially both \( y \) and \( dy \) = \( F \left\{ f(E_o, T^2) + f(\epsilon) \right\} \)

Putting this into the expression for \( n'' \):
\[ n'' = \text{const.} \int_{\epsilon_{\text{min}}}^{\epsilon_{\text{max}}} \epsilon^{\frac{1}{2}} \exp\left( -\frac{\epsilon}{kT} \right) F \left\{ f(E_o, T^2) + f(\epsilon) \right\} d\epsilon \]

Note that \( l \) has been included in the constant.

The thermal energy \( \epsilon \) of the electrons is of course independent of \( E_o \) and \( T \). After integration, \( n'' \) is linearly related to \( E_o \) and \( T^2 \). For a \( \text{CO}_2 \) laser, \( T \) is not at issue. Once again emphasising the assumption that the electron thermal distribution has no "memory" of the previous optical half-cycle, a linear dependence of \( n'' \) upon \( E_o \) is too "slow" to satisfactorily describe an increase in conductivity amounting to an avalanche. But the experimental evidence in support of avalanche formation is considerable.

5.5.6 Observations on lattice temperature effects.
The analysis above assumes a constant lattice temperature at about room temperature. It is worth noting that as energy is absorbed by the germanium from the laser radiation, by whatever mechanism, the electron density will increase as a rapid function of material temperature rise. Germanium can transform from a transparent medium at room temperature into a highly absorbing medium at about 300°C. Once the process is established, a thermal runaway can occur where the surface of the germanium is able to absorb a large fraction of the incident energy.
In an external (to the laser cavity) component, rapid melting and (possibly) vaporisation will take place. When the germanium surface is an integral part of the laser cavity, presumably an equilibrium condition would establish itself where the germanium would absorb energy at just the rate that would reduce the mirror reflection to a value that just maintained the beam intensity at such level as produced the rate of energy absorption aforementioned.

The consequence of local heating (say due to an inclusion) would be to produce local "holes" or partial "holes" in the beam cross section.

5.5.7 Summary.

The possibility of producing a significant increase of conductivity in a germanium surface has been examined. The consideration has been restricted to finding the necessary additional carriers from the product of thermal electrons subject to an accelerating field for one half optical cycle effecting an ionizing event. Such thermal electrons would necessarily originate in the "high energy tail" of the thermal distribution. The host lattice was considered to remain at room temperature. The possibility of electrons being kept in phase with the alternating field by a mechanism of "lucky" elastic collisions has been excluded from this analysis. The mean free path was considered invariant.
Under these conditions it was estimated that a field of peak intensity $E_0 = 10^8$ V/m within the germanium would increase the conductivity of intrinsic germanium by about 1% during a typical laser pulse. This was based upon the idea that the thermal distribution of electrons for room temperature exists at the commencement of each optical half cycle. Carrier diffusion and recombination would reduce the excess (over thermal equilibrium value) electron density. Even if a consideration of the ionizing capability of holes would double the result, an increase in conductivity amounting to avalanche has been shown not to derive from "straight forward" (that is unidirectional) acceleration followed by ionization under the influence of the optical field.

5.6 THE "LUCKY" ELECTRON APPROACH.

Shockley (29) has suggested that for D.C. fields applied to semiconductors, ionization is produced mainly by "lucky electrons" that happen to be accelerated to ionization energy $E_i$ without undergoing a single collision with phonons, even though the distance required $E_i/eE$ may be many times the mean free path $l$. If $l$ is independent of energy, then the probability of this occurrence is:

$$p(y)_{DC} = \exp\left(-\frac{E_i}{eEl}\right)$$

Bass and Barrett (7) extended Shockley's treatment to high frequency fields by considering a lucky electron. In an optical frequency field a lucky electron is one which undergoes just the right collisions to keep it in phase with the field. Such an electron requires about 3 half cycles for a field $E_0 = 10^8$ V/m within the material at a
DETAILS OF A "LUCKY" ELECTRON IN GERMANIUM
DRIVEN BY FIELD $E_0 = 10^8 \text{V/m}$ AND $f = 2.83 \times 10^3 \text{Hz}$. 

Fig. 5.6 - 1
frequency of 23.3 THz to reach $\epsilon_1$ (Fig. 5.6). The sequence of about 2 special collisions has a low probability, but then so does Shockley's collisionless sequence for D.C. fields. Indeed, the D.C. and optical ionization probabilities would be expected to show the same field dependence according to this model. (7).

5.7 EXPERIMENTAL SUPPORT FOR AVALANCHES.

Before discussing the lucky sequence of collisions in more detail a brief review is given of some experimental evidence in the literature for the existence of optical avalanches. Bass and Barrett (7) produce experimental evidence that at least at Nd:YAG laser frequencies (23 THz) the measured damage probabilities can be represented by:

$$p(E) = \exp\left(-\frac{K}{E}\right)$$

where $E$ is the r.m.s. optical field. The D.C. ionization coefficient (which is defined as the number of ionization events produced by an electron or hole drifting unit length in the direction of the field) has the same functional field dependence. Ten materials were tested, including glass and SrTiO$_3$. They noted that amorphous materials were more damage resistant, which could be due to short mean free paths of the order of a mean atomic spacing. The short path would render a lucky sequence very unlikely. Among the crystalline materials tested, those with a large band gap have a high damage resistance as compared with those with a lower $\epsilon_1$. SrTiO$_3$ which is known to have a high mobility (implying a large $l$ to the extent that "hot" electrons are scattered by the same mechanism as thermal electrons) is relatively easily damaged.
Thus experimental fact is in accord with the hypothesis that breakdown can occur by avalanche, at least to the extent that amorphous materials and crystalline materials with large band gap are difficult to breakdown, whilst a high mobility material damages relatively easily. Further, optical and D.C. breakdown probabilities exhibit a similar functional dependence on electric field strength.

Yablonovitch (11) showed that at 28.3 THz, the bulk intrinsic breakdown thresholds of ten alkali-halide crystal materials where "intimately related to the corresponding d.c. dielectric strengths", from which he concluded that "the same mechanism is operative in both types of experiment".

Other workers (12,13) extended the investigation to cover the frequencies 283 THz (glass laser) and 454 THz (ruby laser). Their results again suggest an avalanche mechanism, with signs of a frequency dependence coming into operation above $\sim 450$ THz.

Y. Yasojima et al conducted pre-breakdown charge collection experiments with alkali-halide crystals from which they deduced a breakdown mechanism: "free electrons produced by multiphoton ionization from shallow donor levels such as colour centres are accelerated by the laser electric field and cause avalanche impact ionization".

Wang et al (14) observes that Cd Te has one of the lowest absorption coefficients, yet exhibits a relatively low resistance to damage (corresponding to electric field $\sim 10^5 V/cm$). They are led to consider whether 'hot electron runaway' and possibly 'some other collective form of instability is involved'. They considered some form of
power dependent avalanche breakdown mechanism the most likely to account for their observations, rather than thermal models. Interestingly J.E.Carroll(57) states that CdTe forms "domains" for $E \sim 10$ kV/cm (D.C.).

In the case of the breakdown of gases by laser fields, Chan (15; March 73) tests a number of gases against a theoretical model based upon classical microwave cascade theory, and concludes that "the gas breakdown threshold is, in general, defined in terms of threshold power density in units of MW/cm$^2$." Later Tulip and Seguin (16; Aug.73) published measurements of pre-breakdown plasma which gave "insight into breakdown mechanism and pointed to the importance of multiphoton ionization for initiation of breakdown with visible lasers". They note that cascade breakdown alone is insufficient to account for their observations.

Any doubt that the electric field intensity was responsible for certain forms of damage by dielectric breakdown must have been allayed by the quantitative success of Boling et al (17) in explaining the asymmetry in damage thresholds of the entrance and exit surfaces of a sample in terms of the electric field intensity just inside the surface.

Previous attempts to explain the facts of surface damage by Giuliano (18) in terms of the formation of acoustic phonons failed to produce quantitative predictions.

Thus it is fair to say that by 1973, the role of avalanche breakdown in producing laser damage of a variety of materials ranging from gases to wide band-gap alkali-halide crystals had been established beyond reasonable doubt.
Despite difficulties in constructing a model for avalanche breakdown, further consideration is justified. The difficulties stem from the rapid alternations of field direction, and the need to accelerate an electron (or hole) to energies \( \sim \) 1 eV. It is probable that in many materials multiphoton processes are able to provide an initial supply of electrons which the laser field is then able to accelerate. The initial supply of electrons in a Ge etalon, which is part of a laser cavity, is not the main problem, since at room temperature we may expect \( n_i \sim 2.5 \times 10^{13} \) per cm\(^3\), a figure which would be enhanced by photo electron-hole pairs generated by light from the discharge. Thus the acceleration of electrons by laser light to ionizing energy through a sequence of lucky collisions which keep it in phase with the laser field will be considered.

### 5.8 Avalanche due to the "lucky electron"

According to Bass and Barrett (7), an electron destined to produce ionization undergoes a sequence of elastic collisions with phonons, which effectively change the direction of the electron momentum such as to remain in phase with the optical field (Fig. 5.8.1). Suppose that an electron, starting from rest, will remain "acceptably" in phase with the field provided it travels a distance \( x_1 - \Delta x_1 \), during one half-cycle, undergoes a "proper" collision somewhere between \( x_1 - \Delta x_1 \) and \( x_1 + \Delta x_1 \), then travels to \( x_2 - \Delta x_2 \) without collision, etc. The necessary turning points \( x_m \) are determined by the field zero-crossing times. Suppose further
Fig. 5.8.1 "Lucky electron" velocity held in phase with driving field $E$ by collisions close to field zero crossing times.
that of those electrons experiencing an elastic collision at
about the right time, only a fraction $f$ find their post-
collision momentum correctly oriented for further acceleration.
For a (supposed) isotropic scattering, $f$ might be expected
to be about 0.1 or 0.2. The overall probability per unit
time of the electron being accelerated to $E_i$ is the trial
rate times the probability of this sequence of events. The
trial rate is the collision frequency $1/\tau_{\text{coll}}$.

$$P(E_i) = \frac{1}{\tau_{\text{coll}}} \prod_{M=1}^{M} \left\{ \exp\left(-\frac{|x_m - x_{m-1}|}{l}\right) \right\} \left(1 - \exp\left(-2\Delta x_m/l\right)\right) f$$

where $M$ is the approximate number of half cycles of the
field required for the electron energy to reach $E_i$. Now,
if $l$ is sufficiently small, $\exp(-2\Delta x_m/l) \ll 1$, so that any
electron that makes the range $x_m \pm \Delta x_m$ undergoes some
collision with high probability, then

$$P(E_i) \approx \frac{1}{\tau_{\text{coll}}} \prod_{M=1}^{M} \exp\left(-\frac{|x_m - x_{m-1}|}{l}\right) \times f$$

$$\approx \frac{1}{\tau_{\text{coll}}} x M \exp(-x_1/l)$$

where $x_1$ is the total path length needed to attain energy
$E_i$, i.e.

$$x_1 = \sum_{M=1}^{M} |x_m - x_{m-1}| = \frac{E_i}{lE}$$

with $\Sigma$ being the time average of the absolute magnitude of
the optical electric field.
It has been assumed that the fraction of favourable collisions \( f \) is constant throughout the process. Also other sequences of events leading to ionization, but including less favourable stages in the process, have been omitted from consideration. In fact, the inadequacies of this theory are the same as for Shockley's d.c. model, which nonetheless has been successful in describing the experimental data. (7, 29).

5.9 Damage by Avalanche.

The probability of obtaining one ionizing event from the acceleration of available electrons in an optical field has been obtained. To produce damage to the material, many such events must occur (2^43 free electrons produced has been suggested as a criterion in relation to gas breakdown). However that maybe, sufficient plasma must be present to absorb enough energy to show damage. It happens that the electrons produced by an ionizing event have energies of the order of the band-gap. Thus the probability of producing a second generation of ionization, and subsequent generations, is very much higher than that for the first. The process of plasma production by avalanche is mainly determined by the initial stages.

Bass and Barrett (7) find (for a range of different materials) that the probability of damage with a given r.m.s. field \( E \) \( p(E) \) is directly proportional to the probability \( P(\epsilon_1) \) per unit time of a thermal electron reaching ionizing energy \( \epsilon_1 \).

\[
p(E) \propto P(\epsilon_1)
\]

This relationship could be expected to hold if the avalanche statistics were governed by the first stage or two of the avalanche. In the next section, the 'lucky electron' model is
applied to the case of Ge using a computer aided calculation.

5.10 'Lucky Electron' in germanium.

5.10.1 The computer programme.

To examine the lucky electron model in relation to Ge illuminated by a CO₂ laser, a computer programme was written to evaluate \( P(\varepsilon_1) \). Numerical evaluations were obtained for a range of parameter values; in particular \( \varepsilon_1 (0.7 \text{ to } 1.3 \text{eV}) \) and mean free path \( l \) (1nm to 100nm).

The numerical technique rendered unnecessary Bass's approximation requiring a short mean free path to ensure a high probability of momentum reversal during field zero-crossing. It is not a very satisfactory assumption in a high mobility semiconductor.

Some assumptions and arbitrary choices were made. The main ones were:

- a) m.f.p. independent of electron energy \( \varepsilon \).
- b) collision rate constant.
- c) momentum reversal within \( 1/10 \) optical cycle time \( T \) of actual zero crossing.
- d) full \( 1/2 \) cycle available energy taken up between collisions, irrespective of collision time.
- e) collision with phonons is isotropic.
- f) energy lost by electron in collision negligibly small.

Note that (a) and (b) are mutually exclusive. That \( l \) is independent of \( \varepsilon \) is generally accepted. Seitz (25) gives \( 1/\tau_{\text{COLL}} \) as a function of electron energy. He finds that collision rate ranges from \( 10^{13} \) to \( 10^{15} \). A figure of \( 10^{14} \)
is used here. Assumption (c) is arbitrary, but probably reasonable. Assumptions (e) and (f) are the same as made by Bass (7). To assess these, reference may be made to
Shockley (27) and others (25, 28, 30). The probability \( P(\epsilon_i) \) of an electron existing in a volume \( 1(\mu m)^3 \) with an energy \( \epsilon_i \) is calculated (for field strengths \( E = 10^7 \) to \( 10^8 V/m \)) from:

\[
P(\epsilon_i) = N \frac{\gamma_{las}}{\gamma_{coll}} \int \exp \left( -\frac{x_i}{\ell} \right) \int \left\{ 1 - \exp \left( -\frac{\Delta x_i}{\ell} \right) \right\}
\]

where \( N \) is the number of conduction band electrons in the element of volume \( 1(\mu m)^3 \). The volume is thought appropriate to the damage marks in Fig. 4.7.

5.10.2 Discussion of results.
To interpret the results the crude idea that 'when \( P(\epsilon_i) > 1 \), then breakdown avalanches are considered to have formed' may be used. Breakdown fields \( \sim 4 \times 10^7 V/m \) are obtained. This needs to be compared with available experimental data. But since absolute values of breakdown field are notoriously difficult to derive (due to the extremely rapid dependence upon field strength), the variation of threshold as a function of m.f.p. is more significant. The programme reveals a (relatively) deep minimum in \( E_{BR} \) for \( l = 10nm \) at the \( \text{CO}_2 \) laser frequency. This is about the value Miller (37) measured for Ge (13nm). Once shown, the existence of such a minimum at optical frequencies is "obvious".
It would be a useful test of the model to look at its predicted dependence of \( E_{BR} \) on \( l \) and also of \( E_{BR} \) on optical frequency (with \( \epsilon_i \) and \( l \) as parameters). Comparison
with published experimental values could be made both for 
Ge and other materials. If these results looked promising, 
the model is capable of considerable refinement. Comparison 
of this model with that of Molchanov (48), and with the work 
of Keldysh (31) might lead to significant progress in 
understanding the interaction of intense light fluxes with 
materials; in particular with semiconductors.
5.11 Wave mechanical treatment

Thus far the problem of electron (and hole) dynamics under the influence of high fields in germanium has been treated as though the electron is a classical particle moving essentially as if it were in a free space containing obstacles (the lattice) capable of reversing momentum by collision. The only concession to the electron environment has been acknowledgement of the reduction of the field strength due to the dielectric constant. In fact, the electron moves in the periodic potential of the lattice. Wave mechanics is the best descriptive tool presently available to handle this situation. Starting with the Schrödinger equation, and expressing the periodic potential of the lattice, Bloch produced solutions in terms of electron energy ($\hbar \omega$) and electron wave number $k$. This may be expressed in the form of an $E$-$k$ diagram. By interpreting the slope in terms of velocity, the curvature in terms of (reciprocal) effective mass, and the quantity $p = \hbar k$ as electron momentum (Shockley, ref. 55, page 143, prefers the name 'crystal momentum'), the mathematical formalism of classical Newtonian mechanics can be retained. The problem can frequently be treated as a particle problem if the proper values of parameters (e.g. effective mass $m^*$), and certain restrictions observed (e.g. energy bands), Hyde (63) gives a useful summary.
5.12 Hot electrons in germanium: a literature review.

The damage which occurred in our laser exit mirror, and of which we have sought to gain an understanding, appears to be the result of increased electron density in the germanium. The resulting energy absorption from the laser beam is enough to permanently damage the crystal. Two mechanisms are candidates for the electron density enhancement, Zener emission (23,33), and avalanche multiplication.

The interests of the solid state electronic industry has resulted in a considerable literature concerned with the properties of semiconductors - in particular germanium. A selection of papers (refs.24 to 31 and 35 to 39,41,42) have been studied in relation to such topics as 'hot electrons', drift velocity saturation, avalanche formation, time dependence of avalanche formation, filamentary currents, and surface effects. Note that these papers deal mainly with D.C. fields applied from electrodes (or pseudo-electrodes such as p-n junctions). There is interest in fields up to microwave frequencies. Our interest is with strong fields at optical frequencies (28.3 THz) applied without resort to electrodes. In this section, an attempt is made to summarise the work done on germanium under the stated conditions, and draw such inferences as we may in relation to hot electrons in germanium driven by strong optical fields. The pattern of the enquiry is shown in Fig.5.12.1.
D.C. fields with electrodes

- Zener
- Avalanche?

Shockley et al 1951
narrow junctions

McKay & McAffee 1953
broad junctions

How does the electron gain energy?

Ballistic
Shockley, 1961
Bass & Barratt, 1972

Distribution

- displaced Maxwellian
- Wolff V. high field
- pointed
- Shockley low field
- compromise
- Baraff medium field

How much energy required for impact ionisation?

- Carroll
- McKay & McAffee 1953
- 1.5 eV
- Miller
- 1955
- 3 eV
- Shockley (by optical absorption, by Vavilov)
- 1959
- 1.1 eV
- Ge
- Si
- McKay & McAffee 1953
- 3.6 eV

What constitutes breakdown?

How long does it take?

- McKay & McAffee 1953
- <20 ns

When formed, is the current filamentary?

Optical fields ??

Fig. 5.12.1. Hot electrons in Ge - planform of enquiry
5.12.1 Zener Emission or Avalanche?

The consensus of opinion is that both mechanisms have been observed. Zener emission is only observed in narrow specimens ($\sim 500 \mu m$ wide (33)). Wider specimens exhibit avalanche breakdown. The field strength required for avalanche breakdown increases as the specimen width decreases due to the finite length required for the charge multiplication process. Presumably in narrow junctions the Zener threshold field is encountered before the avalanche threshold field, whilst in broad specimens ($\geq 0.1 \mu m$) the reverse is the case. Although precise data is not available, Miller (37) states that the Zener threshold field is greater than $3.2 \times 10^7 V/m$; McAfee et al (33) state the threshold to be $\sim 2.2 \times 10^7 V/m$ (expt.) whilst their equation predicts $9 \times 10^7 V/m$. Gunn's measurements (33) indicate an avalanche breakdown field as low as $6 \times 10^6 V/m$. It seems safe to say that avalanche multiplication can occur for fields about an order of magnitude lower than that required for Zener emission. In the case of breakdown in our etalon, "specimen size" information may be interpreted (in the absence of electrodes) into the question "is there room for an avalanche to develop?" to which the response is "YES - plenty!" Thus the evidence seems to support the idea that the optical damage is by the agency of avalanche multiplication.

A crucial question concerns time. If the Zener emission is a very rapid process ($< optical half cycle)$, this mechanism would be favoured against a slower avalanche process, even at higher field threshold. However, information which
would resolve this is not presently at hand. Interestingly I do not recall any reference in the laser damage literature to charge multiplication by Zener emission leading to destruction. Further, it seems to me, a more or less uniform charge distribution would be available for absorption, leading to a featureless damage mark. It would be difficult to explain filaments as observed in the etalon. The balance of evidence thus supports the proposition that the damage marks owe their origin to avalanche by impact. We shall accordingly further discuss the observations on the assumption that avalanche ionisation by impact is a key feature. The processes by which the carriers are "heated", and become capable of ionization, are of considerable interest.

5.12.2 Production of "hot carriers"

To produce ionization requires a minimum carrier energy $E_i$.

At room temperature the average carrier energy $\frac{3}{2}kT$ is $\approx 0.025eV$, whilst $E_i \approx 2eV$ for Ge. The net gain of energy from the field is the result of the competing processes—energy input from the field, and dissipation of energy to the lattice by phonon interaction. The nature of the phonon interaction is a function of electron energy (and is thus related to applied field) and lattice temperature, and has been the subject of debate (Von Hippel, Fröhlich, Seitz, Shockley, 24,25,26,27). Information regarding electron-phonon interaction may be obtained experimentally by measuring drift velocity as a function of applied field (Ryder, Gunn, Chang 34,35,42). The results of Gunn are shown in Fig. 5.12.2.1. Following (mainly) Shockley's lucid
Gunn

The variation of drift velocity with electric field.

(a) Current density in n-type germanium as a function of electric field. (b) Current density in p-type germanium as a function of electric field. (From Ryder, E. J. (1963) Mobility of holes and electrons in high Electric Fields. Phys. Rev., 90, 766-769.)

Fig. 5.12.2 - 1
The results of Gunn, Ryder & Chang (refs. 38, 34, 42).
treatment (27), the initial linear dependence of $v_d$ upon $E$ is due to the ability of the LA phonons to maintain the electrons at the lattice temperature $T_L$. As $E$ is increased, the electron temperature $T_e$ rises above $T_L$ and the collision rate $1/\tau_{ee}$ increases (assuming mean free path independent of electron energy). The mobility is reduced with $v_d$ increasing as $E^3$. Further increase of $E$ raises the electron energy to a level sufficient to stimulate optical phonons ($h\omega_{opt} = 0.037\text{eV}$ for Ge (29)). Under the assumptions that electrons lose an energy $h\omega_{opt}$ at each collision, irrespective of collision geometry, the drift velocity $v_d$ saturates. Further increase of field eventually leads to avalanche breakdown. Seitz (25) pointed out the importance of the acoustic phonons in electron energy regions of a few eV, where hitherto only optical phonons were considered to be effective in energy transfer to the lattice. A basic understanding of electron-phonon interactions contributes toward a model of impact ionisation in germanium.

A model of carrier multiplication requires a knowledge of the number of electrons raised to energies greater than $E_i$ at a given field. Thus the energy distribution function $f(E)$ is needed. Many authors have approached this subject (e.g. Seitz, Wolff, Shockley, Baraff, Keldysh 25, 29, 30, 31). The simplest proposal is of a displaced Maxwellian distribution shifted to an origin on $\frac{1}{2}m\nu_d^2$. It depends for its validity on predominance of $(e-e)$ scattering, which does not apply to a semiconductor.

Gibson (40) maintains however, that results of calculations
of some parameters (mobility for example) are not at all sensitive to inclusion of \((e - e)\) scattering. It is mathematically tractable and therefore attractive. Shockley has suggested a spherical distribution with an elongated appendage in the direction of the field. Electrons reach \(E_1\) in a ballistic flight. Wolff proposed a distribution essentially isotropic (in fact a Maxwellian) in which the energy \(E_1\) is reached, or is "diffused toward" through the usual collision processes. Neither author took account of the semiconductor band structure, the details of which were unknown at the time. Baraff harmonised the two approaches by noting that Shockley's distribution was appropriate to 'low fields' \(\alpha \sim e^{-\text{const} E}\), while Wolff's was appropriate to 'high fields' \(\alpha \sim e^{-\text{const} E^2}\). Baraff solved the Boltzmann transport equation by numerical techniques. His results therefore pertained to a series of chosen values of the parameters, and to temperatures sufficiently close to zero. Keldysh extends the work by solving the problem of impact ionization analytically, with the advantage of the ability to select arbitrary values of field \(E\) and temperature \(T\). To use his expressions, a variety of materials data is required (in this case for germanium). No numerical comparisons are made between his expressions and published experimental data. It would be informative if this were done. The writer is presently unaware of subsequent publications as there may be dealing with this matter.

The processes by which electrons become 'hot' in germanium, at least under the influence of D.C. applied fields, is
fairly well modelled. The "bones" seem to be in place. Though there is room for continued refinement in correlating experimental values with predictions derived from the models.

5.12.3 What is the value of $E_i$?

Conservation of momentum and energy demands that $E_i$ is greater than the bandgap energy $E_g$ for ionization by a hot carrier.

If the (effective) masses and velocities of electrons and holes are designated $m_e$, $m_h$, $v_e$, $v_h$, with the incident ionizing electron initial and final velocity $v_i$ and $v_f$ respectively, then conservation gives:

Momentum: $m_e v_i = m_e v_f + m_e v_e + m_h v_h$

Energy: $\frac{1}{2}m_e v_i^2 = E_g + \frac{1}{2}m_e v_f^2 + \frac{1}{2}m_e v_e^2 + \frac{1}{2}m_h v_h^2$

Incident energy is minimized when $v_e = v_h = v_f$, when:

for ionization by electron: $E_i(E) = \frac{2m_e + m_h}{m_e + m_h} E_g$

for ionization by hole: $E_i(E) = \frac{2m_h + m_e}{m_h + m_e} E_g$

That both electrons and holes could ionize was demonstrated experimentally by McKay et al (35). In general the values for ionization by electron and by hole will have differing values. For a given applied field the corresponding ionization coefficients $\alpha(E)$ and $\beta(E)$ will differ. Nevertheless much of the earlier work was carried out under the assumption that $\alpha(E) = \beta(E)$ in germanium. McKay (35) found $\alpha \approx \beta$.

In this case, the mathematics is more straightforward, and it was considered that the theory for avalanche breakdown
would not be too sensitive to differences in $\alpha$ and $\beta$. Later, Miller (37) measuring avalanche breakdown in germanium (1955), found that the ionizing rate for holes is larger than that for electrons by a factor of about 2. Miller's results were in close accord with the theory of Wolff (23), implying Baraff's (30, in 1962) high field condition. The expressions (above) for $\varepsilon_1$ suggest (assuming $m_e \approx m_h$) that the minimum carrier energy required for impact ionization $\sim 1.5$ to 2 times $\varepsilon_6$. Thus for Ge the expected value for $\varepsilon_1 = 1.5$ to 1.6eV. Miller (37) obtained a value $\varepsilon_1 = 1.5$eV for Ge by interpreting his results against Wolff's theory. Shockley (29) reviewing experiments carried out by several experimenters, in particular McKay and McAfee (35) with $\alpha$-particle bombardment, and by Vavilov on the photo-production of electron-hole pairs, obtains values of $\varepsilon_1$ for Ge in the range 2.8 to 3.8 eV. This data, however, includes energy taken up by phonons during the pair production process.

There is reasonable agreement between expectation and experiment. The minimum impact ionization energy is considerably higher than $\varepsilon_6$ - of a few electron-volts.

5.12.4 What constitutes breakdown?

Producing an electron-hole pair does not constitute breakdown. Enough energy has to be transferred from the carrier population to the lattice to disrupt it before visible (permanent) damage is produced. Seitz (25 - page 1379) argues cogently that a suitable criterion for breakdown is that one primary electron should produce $10^{12}$ secondaries in a field $\sim 10^5$V/m - i.e. 40 generations of pair production. Each lattice point would receive $\sim 10$eV ($10^6$ J per mole), more than enough to
melt Ge ($\sim 5.5 \times 10^4$ J per mole). The argument is conducted for a specimen $\sim 1$ cm between electrodes; the specimen dimensions affect the result through the "diffusion-diameter" of the current path. Seitz does not appear to allow for the ionizing and energy dumping capacity of the holes produced, as was the case with many of the earlier papers. However, the criterion of $2^{40}$ electrons produced is a useful guide for our purpose.

5.12.5 How long does avalanche formation take?

Our problem of the damage tracks in Ge involves two short time parameters - the optical field $\frac{1}{2}$ cycle time of $\sim 10^{-14}s$, and the laser pulse duration time $\sim 10^{-7}s$. It is therefore relevant to examine the relation of avalanche formation time to these orders of magnitude. The equations for $\epsilon_1$ (above) show that for minimum initial energy, the ratio of pair energy (each carrier) to impact energy is $\sim 1/9$.

From momentum conservation

$$\frac{v_f}{v_i} = \frac{m_e}{2m_e + m_h} \sim \frac{1}{3}$$

$$\therefore \frac{v_f^2}{v_i^2} \sim \frac{1}{9}$$

Therefore the carrier has to gain $\epsilon_1$ between each ionizing event. The individual carrier velocity drops from $10^6m/s$ to $\sim 3 \times 10^5m/s$, both figures appropriate to the saturation drift velocity (velocity average) of $10^5m/s$ in Ge (34,37,42). Therefore, in the direction of the (d.c.) field, we can reckon a constant velocity of $10^5m/s$, and a gain of energy of $EeL_1$ where $L_1$ is the free path between ionizing collisions. Setting $\epsilon_1 \sim 2eV$, and $E_{BR} \sim 2 \times 10^7V/m$ (37,41 35 is higher, 38 is lower) gives $L_1 = 10^{-7}m$ and a time
between ionizing collisions $\gamma_1 \sim 10^{-12}$s. Forty generations in cascade would require $4 \times 10^{-11}$s. ($\gamma_{AVAL}$). This could be shorter by a factor of $\sim 2$ if it be conjectured that the avalanche leader moved at an individual hot electron's average speed between collisions rather than at the group drift velocity.

Turning to the literature for evidence, McKay (36) mentions $10^{-10}$s. (though not quite identical circumstances); ref.35 quotes $\gamma_{AVAL} < 2 \times 10^{-8}$s., their oscilloscope rise time; Shockley (29) fits an avalanche theory to six sets of experimental data from four independent experiments to come up with $L_1/L_r = 57$ where $L_r$ is the phonon mean free path. He does not use a value of $L_r$ for germanium (only for silicon derived from curve fitting to Chynoweth's measurements (39, and another paper 1960). So taking Miller's $L_r = 130^2$ for germanium based on curve fitting his measurements to Wolff's theory (28), the ionization free path becomes $L_1 = 7.4 \times 10^{-7}$m. Interpreting McKay and McAfee's (35) graphical data for Ge, $L_1 = l_{BR} \sim 10^{-6}$m. Considering the rather hybrid deduction from different theories and measurements, this seems in fair agreement with the "knock-about" figure of $L_1 \sim 10^{-7}$m deduced above. This corresponds to $\gamma_{AVAL} \approx 10^{-10}$s. again. If we required greater precision for $\gamma_{AVAL}$ we could interpret the above references more carefully, and bring in further evidence from Lee (32) and Whitehead (ref.56 section 2.8 page 95). But for the moment this will suffice.

It seems clear that, in terms of the laser radiation damage problem, the avalanche formation time is of the order of $\sim 3000$ optical cycles, whilst remaining only $\sim 1/100$
of the laser pulse length. Alternatively stated:

\[ T \ll \gamma_{AVAL} \ll \gamma_{LAS} \]

The relevant field strength in the data is the threshold field, which is also the relevant field experienced by the etalon in the areas under study.

5.12.6 The Avalanche Track.

It might be expected that if a uniform field were applied to a homogenous specimen, the ionization coefficient \( \lambda \) (and \( \beta \)) would be uniform resulting in overall avalanche breakdown. However, a negative resistance characteristic would produce entirely different results. That semiconductors may possess an intrinsic negative resistance property has been suggested and subsequently observed in some cases.

Krömer (65) has suggested that the negative mass that the carriers would acquire at the top of the band might, under the correct circumstances, provide a useful negative resistance (Nemag amplifier). Ridley and Watkins (43) first suggested the form of negative resistance associated with a particular conduction band structure, from which the Gunn diode has developed. This is a voltage controlled characteristic giving rise to domain formation.

Ridley in 1963 (44) examined the concepts of voltage controlled negative resistance, and current controlled negative resistance in semiconductors. He showed that for current control, a uniform field applied to a homogenous semiconductor specimen would result in a transient instability leading to the formation of a current filament. The current
density would naturally concentrate into a non-uniform current flow. This is not a magnetic pinch, as in the case of discharge through a gas, but is a consequence of space charge formation in avalanche, and resulting radial field component. The properties of Ge and Si will give rise to a current controlled negative resistance. The filaments were probably first observed by McKay in 1954 (36), although he did not recognise them as such. The reported properties of his avalanching diode, and his resulting deductions all fit Ridley's discussion. Further work and observations of current filaments have been made by Muller (45) and Barnett (46).

This aspect is of particular interest in the optical damage problem. Wang (14) reported "some sort of instability" in CdTe at \( \sim 10^7 \text{V/m} \) of laser field. CdTe has been shown to exhibit the Gunn effect (formation of Ridley and Watkins' domains with D.C. applied field) at about the same field \( (1.3 \times 10^6 \text{V/m}; \text{Carroll (57) page 72 reporting Ludwig}) \).

We are more interested in filament formation, which the damage marks strongly indicate were formed. Given that filament formation is natural under a D.C. field, the questions raised by the laser damage in Ge are:-

(a) Might filaments be expected with rapidly reversing fields \( (T \ll \gamma_{AVAL})? \)
(b) What may be said concerning the size dimensions of the current filaments?
(c) Why do they occur in a particular direction?
(d) Why do they show a more or less characteristic filament-to-filament spacing?
Further remarks will be made concerning these subjects later.

5.12.7 **Plasma effects in semiconductors.**

The quasi free carriers in a semi-conductor may support a number of wave types, for example helicon waves & Alfvén waves (58). These waves are charge bunching effects, not to be confused with quantum-mechanical waves. Some wave types require both electric and magnetic fields for support, whilst others require only an electric field producing a drift stream of carriers (see also Carroll(57), chap.4). In seeking the mechanism behind the etalon damage, the possibility that an interaction between the laser light and plasma waves and/or acoustic waves might be a candidate should be borne in mind. The periodicities of the damage might be explained naturally by such interactions. A further periodicity occurring in the problem is the amplitude modulation of the laser beam with a period \( \omega 2L/c \) corresponding to \( \omega 150 \text{MHz} \) arising from the multimode operation. Searching this area for possibilities with some 'back of envelope' sums, as far as I can determine these waves have no role in producing the observed etalon damage. As always in scientific inquiry, an open mind may be retained as this conclusion is my judgement based on a limited knowledge of the subject of plasma waves. This topic will not be taken up again here.

5.12.8 **The Surface Physics of Ge.**

The work so far has considered only the physics of Ge in bulk. But the observed damage is on the surface. No evidence for
the condition of the bulk material has been obtained, but the evidence from the S.E.H. photographs suggest a damage depth of penetration of 1 or 2 μ. It is well known that surface states exist within the band gap (60, 66). The previous numerical work was based upon C = 0.7eV, but in the surface it may be much less. Assumptions that the recombination rate of electrons and holes (lifetime in bulk ≈ 100 μs) is too slow to be considered may not be valid; the influence of the etalon surface polishing (during manufacture) on the parameters is unknown. The electric field strength over the first few atomic layers of the etalon as a function of the free space value (just outside) warrants careful consideration (17).

Finally it has been shown (21) that unless very special precautions are taken, heat cycling introduces acceptor centres into the germanium, thought to be due to the presence of Cu as an impurity. Quenching the hot material enhances the effect, with as many as 10^17/ cm^3 acceptors introduced. These are precisely the conditions being postulated as occurring in the linear melts (section 4 of this work, also ref. 4.2). The hypothesis offered in section 4 required a pulse-by-pulse growth of the linear melt. The copper circumstance would aid growth by rendering the melted region permanently more conductive by a factor of up to 10,000 times. These regions would then rapidly re-melt in the early part of the next laser pulse allowing time to "work on" the boundary of the melt and extend it. The pattern of linear melts is able to "grow".

Summarising, the 'hard' knowledge concerning the surface is scant.
Where the facts are unknown, their existence been ignored (there are many good precedents for this procedure in the cited references!). Such hard data as is available (21) tends to support the hypothesis of section 4. The Cu acceptor centres, the reduced energy gap $E_g$, the higher electric field at the etalon surface, would all contribute to the hypothesis about the damage formation.

5.13 Conclusion to section 5.
In section 4, a hypothesis was presented to explain the observed damage marks made by CO$_2$ laser "light" on the surface(s) of germanium etalons used as exit mirrors in a pulsed laser. The hypothesis required that linear melts were caused by avalanching current filaments driven by the radiation electric field. Section 5 has been devoted to examining the details and plausibility of impact ionization currents of a linear geometry driven by an optical frequency electric field. The approach has been a step-by-step analysis starting with the dynamics of a free electron in an electro-magnetic field of optical frequency, and working up to a full review of recent literature dealing with impact ionization in semiconductors (mainly for D.C. excitation) and related topics. A computer programme was written to examine an idea put forward in ref.7., inserting appropriate parameters for Ge.
References.

Section 5 Avalanche Breakdown in Germanium.

References section 5 cont.


Properties of Germanium.


Avalanches and Zener Breakdown in Ge and Si.

Theoretical:-


References section 5 cont.


Experimental:


References section 5 cont.


Current Filaments.


At Optical Frequencies.

47. R.W.Hellwarth: 
   Role of Photo-Electrons in Optical Damage. 


50. S.I.Anisimov et al: 
   Effect Of Powerful Light Fluxes On Metals. 
References section 5 cont.


Miscellaneous.


6.1 General introduction to Chapters 6, 7 and 8.

It has become clear that no further substantial progress can be made in quantitatively understanding the formation of the surface patterns without a more profound knowledge of the thermal and optical properties of Ge. The next three chapters, 6, 7 and 8 will be dedicated to this purpose.

It is therefore proposed to go right back to first principles and construct a working (mathematical) model of Ge. The model needs to work over the full temperature range 300K - 1210K, that is from room temperature up to melting point temperature.

There are then two clear requirements which may be identified.

The first is to assemble together the relevant aspects of existing theory, from the many separate areas of knowledge to which they properly belong. The second is to assign numerical values to all the Ge material parameters of interest over the full temperature range. Some of the main parameters are \( \rho, C, k, \sigma', \sigma'', \epsilon, \epsilon', \epsilon'', \alpha, \tau, n, R, \ldots \) for which magnitudes are required from 300K to 1210K.

When such a data base is assembled, many different circumstances of laser interaction with Ge may be modelled by solving a suitable partial differential equation, such as will be defined early in chapter 6. It is not expected that analytic solutions will be available for most realistic laser interactions of
interest. Resort may be made to numerical techniques for solution.

A few remarks will be made on each of these two requirements to assemble the relevant theory, and to construct a numerical data base describing Ge.

To illustrate how widely the required theory is dispersed, and the consequent need to collect it together here, one or two specific aspects will be mentioned.

The behaviour of the thermal conductivity of Ge over the temperature range 300K - 1200K needs to be established. It may be suspected that the lattice conductivity will fall while the electronic conductivity of the semiconductor may rise. But by how much? What does present theory say about this?

And from an entirely different branch of science, how (for Ge) does \( \varepsilon \) vary, how does \( n \) vary, and how does \( \sigma \) change over this temperature range? And what are the properties of surface waves, and how do they change as the temperature of the solid interface changes? What theoretical framework exists? What does it have to say about these matters?

Why concern ourselves too much with the theoretical framework? By definition there can be nothing new to find there. It is all well established. Why not look up the required data for germanium, plug it into the appropriate formula to see what the answer is?
There are a number of objections to this superficial approach. An ever present pitfall is the danger of using an expression outside its range of applicability, because the constraints, approximations, etc., associated with its derivation are not being observed and respected. It's simply not possible to avoid this pitfall totally by tracing everything one does back to source, thereby becoming properly aware of limitations operating on each situation. But anything which maximises one's defense against slipping into this abuse must be desirable. Therefore in Chapters 6 and 7, close attention is given to systematically putting together the required theory, built from first principles wherever possible. Critical appraisal is made to clarify meaning and significance wherever it is needed.

Completion of this exercise, the construction of a sound framework, will enable the use of the material to be very flexible. Not only will the potential of dealing with a wide range of circumstances involving laser interaction with Ge be realised, but with modest adaptation the behaviour of other materials might also be encompassed.

The other matter for comment was the construction of a numerical data base for Ge. It is anticipated that information on so many properties are required over such a temperature range that the required data is not likely to be available in its entirety. Therefore the approach to be adopted is to use the theoretical framework which will be established to extrapolate from known experimental values (taken from the literature) into the unknown regions where data is not to the hand of the author.
The purpose of this procedure is to enable quantitative modelling to be done even where parameter values are unavailable - that is to extend the range of the behaviour model. Clearly this process cannot be taken too far without reference to some experimental data for validation.

Validation will be performed where available experimental data overlaps the model range. But the present purpose will be considerably furthered if trends and general patterns of behaviour can be simulated. And as further data within range becomes available, the model may be updated and adapted to take account of it. The precision of predictions based on the model may therefore be continually refined.

The main framework of the approach will be to deal with the more straightforward, and less sensitive parameters such as $\rho$, $C$, $k$ (thermal conductivity) first. To obtain the optical properties, the experimental values of d.c. electrical conductivity $\sigma^e$ (available throughout the temperature range, and into the liquid phase), and the quantities $\mu$, $\tau$, $m^*$, $n_1$ will be established.

The optical properties are only of interest for the moment at the CO$_2$ laser frequency of 28.3 THz. Therefore the high frequency conductivity $\sigma' - j\sigma''$ at this frequency will be calculated, leading to values for $\varepsilon' - j\varepsilon''$ and $n$ and $k$ over the full temperature range. From these the coefficient of absorption $\alpha$, and the internal heat source $q_v$ follow. These complete the required numerical model for Ge.
With regard to the operating conditions of the laser, the peak electric field strengths are computed, based on a peak power measurement. The laser cavity (and etalon) supports standing waves, which are taken into account. The heating at any location may be evaluated.

To summarise, the basic direction of investigation is to set up a fully numerical model of Ge over the temperature range 300K-1200K. This will be derived from a judicious amalgamation of experimental data and extrapolation based on a theoretical framework. The approach allows continuous amendment as more experimental data comes to hand.

The model is intended for use in simulating conditions of interaction between a laser beam and materials such as Ge. The laser beam may be C.W., or pulsed. A numerical solution of material temperature as a function of position and time \( T = T(x,t) \) should be available given a definition of beam intensity \( I = I(x,t) \) and a boundary condition describing the cooling arrangements.

Some insights into the nature of the formation of the surface patterns observed on Ge etalons and on thin films of Ge mounted on a glass substrate are to be looked for.

It should be realised that the scope of the projected work outlined above exceeds the capacity of this present project alone. Whilst the overall objectives have been defined, some realistic estimate must be made of the likely progress towards
It is thought that the theoretical framework will be laid down. That numerical values will be assigned to the Ge material parameters over the full temperature range. That a modest level of validation will be carried out, and some small scale trial runs of sections of the model executed.

Any research investigation is open ended...... potentially infinite. A project such as this must be finite, must terminate. This study will provide all the necessary data with which simulations of laser interactions with Ge may be carried out using numerical analysis.

Someone once said, "when a problem has been defined, it is practically solved." The next three chapters 6,7 and 8 set out to define the problem in detail.
Section 6.2 Introduction.

In this section, the thermal aspects of the problem are the subject of consideration. The detailed mechanisms involving coupling of energy from the laser beam into the germanium etalon are, for the moment, circumnavigated. These aspects are taken up again in section 7. Discussion commences with a quantity of energy $Q$ deposited as a "thin disk" within the material at a specified time $t$. The time interval of interest contains the whole laser pulse, and extends just beyond its termination.

An aspect of major interest is the phenomenon of thermal runaway in germanium. When the heat deposition in an elementary volume exceeds the rate of heat diffusion from that volume, it leads to a local temperature rise. As the temperature of the volume element increases, the rate of loss of heat increases leading usually to the establishment of an equilibrium at some temperature $T_{eq}$.

However, in the case of semiconductors, the rate of heat take up from the laser beam increases with material temperature. This leads to thermal instability when the rate of increase of absorption with temperature exceeds the rate of increase of heat loss with temperature. If, for an elementary volume $dV$, the heat deposited per unit time per unit volume is $q_v$ and the heat lost per unit area per unit time is $q_s$, then equilibrium is established at $T_{eq}$ when

$$\iiint q_v dV = \iint q_s ds$$
For most materials

\[
\frac{d}{dT} \left\{ \iiint q_v \, dV \right\} = 0
\]

if the heat source \(q_v\) is due to the absorption of electromagnetic radiation. Thus for a given laser beam intensity, The R.H.S. can always find a temperature \(T_{eq}\) for which it is equal to the L.H.S.; since

\[
q_v \alpha \frac{dT}{d\tilde{n}} \quad \text{where } \tilde{n} \text{ is the normal to the surface } S
\]

which is usually an increasing function of the temperature of the volume element, given that the element is situated in a finite specimen having a more or less stable heat sink temperature (e.g. ambient temperature at the specimen surface).

For Ge, the absorption coefficient is a strongly increasing function of temperature, so that it becomes possible to find circumstances for which

\[
\frac{d}{dT} \left\{ \iiint q_v \, dV \right\} > \frac{d}{dT} \left\{ \iint q_s \, dS' \right\}
\]

so that thermal runaway occurs. An equality in expression 4 represents an unstable equilibrium in which the temperature might assume any value (within the range for which the equality holds) under a stable set of external conditions.

The phenomenon of thermal runaway is clearly involved in the etalon surface pattern formation, enabling the material temperature to be raised to melting point (at least) at well
defined localities. The likelihood is that the material adjacent to the pattern marks (undamaged on the photograph) remains more or less at ambient temperature. The temperature rise if the pulse energy (4J) were completely absorbed uniformly over the beam cross section throughout the etalon depth would only be

\[ \rho A d x c x \theta = E_p \]

where \( \rho \) is density, \( A \) is beam X-sectional area, \( d \) is the etalon depth, \( c \) is the specific heat of the etalon material, \( \theta \) is the temperature rise and \( E_p \) is the laser pulse energy.

\[ 5323 \times 4 \times 10^{-4} \times 6 \times 10^{-3} \times 310 \times \theta = 4 \]

\[ \theta = 10^0 \]

As a temperature rise of 10\(^0\) is a gross overestimate, since most of the pulse energy is transmitted to rather than absorbed, there has to be a very strong positive feedback process to achieve localised temperature rises of over 900 \(^0\) within a (seemingly) homogenous crystalline material of remarkable chemical purity.

The L.H.S of expression 4

\[ \frac{d}{dT} \left\{ \iiint q_v \, dV \right\} \]

is a function of material temperature alone (for given laser beam parameters).

The R.H.S. of 4

\[ \frac{d}{dT} \left\{ \iiint q_d \, ds \right\} \]

is a function of temperature gradient at the point of consideration, which in turn is a
function of the temporal and spacial characteristics of the laser beam, and the thermal conductivity \( K(T) \) of the material. Note that thermal diffusion will take place both by lattice phonon diffusion, and by charge carrier diffusion.

An attempt is made in the following section to examine some of the factors contributing to \( q_v(T) \), and \( q_s(T) \).

The aim is to estimate some of the values in expression 4 for germanium to obtain some insight into beam intensities which could be expected to produce thermal runaway.

The internal heat source \( q_v \) is governed by the local electromagnetic intensity, and the local carrier density. These two quantities are strongly interdependent in a semiconductor like germanium. The carrier density contributes to the optical properties of the material - reflectivity, absorptivity. These in turn determine the radiation intensity reaching any locality in the beam path by affecting how much energy has been reflected and/or absorbed from the beam prior to its encountering the locality in question.

To set up a model for thermal runaway will therefore require a detailed knowledge of the dependence of \( q_v \) on carrier density, and a relation expressing beam intensity as a function of beam penetration into the germanium.

To obtain the latter, the temperature profile of the beam path through the germanium will have to be obtained, since carrier density is a function of material temperature. This will require a solution of the heat diffusion equation; the appropriate equation will be discussed in Section 6.3.
There seem to be two essentially separable steps in setting up a model for the interaction of an intense electromagnetic beam with the semiconductor:

(a) examine the detailed functional relationships involving $q_v$ and the material parameters; also will be required the detailed functional relationships between the material parameters and thermal conductivity, specific heat, and density. The behaviour of all these relationships as a function of material temperature will be a requirement for progress with a model for thermal runaway.

(b) feed the detailed data into a suitable partial differential equation, and seek solutions. The desired solutions are visualised as a sequence of temperature profiles through the material at convenient time intervals (say 10ns) which correspond to a specified incident beam intensity. Initially the incident beam would have to be idealised to a rectangular pulse time profile; if feasible, it might be later substituted by a triangular idealisation, or an even closer representation might be obtained using a look up table prepared from an oscilloscope record. An assessment of the "investment" of extra complexity will have
to be weighed against potential return of more precise data; a decision as to worth of the extra stages will be made later.

The following sections will discuss the partial differential equation describing the heating (temperature profile) of the material by the radiation; the terms and relationships needed to set up the equation for solution will then be discussed item by item - e.g. the behaviour of $\tau$, the absorption coefficient as a function of carrier density as a function of temperature, thence ultimately of position in the beam path.
Section 6.3 The differential equation.

This section seeks a description of the heating of the germanium in the beam path as a function of time. For the moment, a macroscopic view is adopted, using material parameters

\[ \rho, c, k \]

\( \rho \) \quad \text{density}

\( c \) \quad \text{specific thermal capacity}

\( k \) \quad \text{thermal conductivity}

First the standard heat conduction equation will be derived based on Fourier's heat conduction law

\[ \frac{dQ}{dt} = -k \frac{dT}{dx} \quad ---6.3(1) \]

where

\( Q \) \quad \text{is a quantity of heat}

\( t \) \quad \text{is time}

\( A \) \quad \text{is area normal to heat flow}

\( T \) \quad \text{is temperature}

\( x \) \quad \text{is the coordinate of direction of heat flow.}

The condition for conservation of thermal energy in an elementary volume \( A \delta x \) may be expressed as net heat conducted in + heat source output = increase of internal energy. This is illustrated in Fig. 6.3(1).

Considering the heat flow to be in the x-direction for the moment,

\[ \frac{dQ_x}{dt} - \frac{dQ_{x, dx}}{dt} + q_v A \delta x = \rho C \frac{dT}{dt} \]

where \( q_v \) is the rate of production of heat within the volume element \( A \delta x \).

Fig 6.3(1)
Hence
\[
\frac{dQ_x}{dt} - \left( \frac{dQ_x}{dt} + \frac{d}{dx} \left( \frac{dQ_x}{dt} \right) \delta x \right) + q_v A \delta x = \rho A \delta x C \frac{dT}{dt}
\]
\[
- \frac{d}{dx} \left\{ - k A \frac{dT}{dx} \right\} dx + q_v A \delta x = \rho A \delta x C \frac{dT}{dt}
\]
removing \( A \delta x \)
\[
\frac{d}{dx} \left\{ k \frac{dT}{dx} \right\} + q_v = \rho C \frac{dT}{dt}
\]
--- 6.3(2)

Clearly, if \( k \) is a constant, the first term may be written \( k \frac{d^2T}{dx^2} \), but in germanium, this is not an obvious step.

The thermal conductivity \( k \) depends on phonon transport and transport by electrons and holes. Since the carrier density is a strong function of \( T \), it follows that \( k = k(T) \), and the form of equation 6.3(2) stands. If \( k \) turns out to be a slow function of \( T \), then it may be possible over adjacent steps of a numerical analysis evaluation to take the simpler form. We shall return to consider the behaviour of \( k = k(T) \) for germanium in section 6.6.

Meanwhile we note that in 3 dimensions, and using partial derivatives:
\[
\left\{ \frac{\partial}{\partial x} \left[ k \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial y} \left[ k \frac{\partial T}{\partial y} \right] + \frac{\partial}{\partial z} \left[ k \frac{\partial T}{\partial z} \right] \right\} + q_v = \rho C \frac{dT}{dt}
\]
--- 6.3(3)
For the initial simplification of the germanium etalon case, we choose to consider that a very thin disk of material (\(\sim 1\mu m\) in depth and 1 cm radius) is raised in temperature to melting. Thus the etalon, of thickness 6mm, may be considered as infinite in extent, and filling the half-space \(x > 0\). It is a reasonable assumption that heat will only conduct in the positive \(x\)-direction; the loss of heat by any mechanism across the gas solid interface will be considered negligibly small. The simplified problem is shown in Fig. 6.3(2).

The appropriate equation is therefore the one-dimensional form equation 6.3(2). It is re-written below with the temperature dependence of \(k\) and \(q_v\) emphasised:

\[
\frac{\partial}{\partial x} \left\{ k(T) \frac{\partial T}{\partial x} \right\} + q_v(T) = \rho c \frac{\partial T}{\partial t}
\]

\[6.3(4)\]
Incidently, let us establish the upper limit of disk thickness $d'$. Suppose all of the pulse energy just raises the disk uniformly to melting. Taking the pulse energy as $\sim 4J$, then

$$Q = \pi (0.01)^2 \times d' \times 5.3 \times 10^{-2} \times 310 \times 916 \left[ \frac{\text{m}^2 \text{J} \cdot \text{K}}{\text{m}^3 \text{J} \cdot \text{K}} \right]$$

$$4J = 4.73 \times 10^5 \times d' \text{ J/m}$$

$$d' = 8.5 \mu m$$

Under these assumptions the melt cannot exceed $8 \mu m$ in depth.

The observations indicate a depth $\sim 1 \mu m$ implying an interception of $\sim 10\%$ of the pulse energy for melting, the majority being transmitted before the runaway renders the germanium opaque.

The criterion by which the specimen may be regarded as infinite in extent is whether or not heat is able to diffuse from the hot spot to the boundary in the time available. Tuck (ref.4) expresses this in the form $4.3 \sqrt{D t}$ is the minimum thickness of a semi-infinite specimen, where $D$ is the coefficient of diffusion. In this problem, the diffusivity $\alpha$ is the appropriate quantity. Putting in numerical values (and using room temperature values), the minimum specimen depth $d_{min}$ is, if the event time is $\sim 1 \mu s$

$$d_{min} = 4.3 \sqrt{\alpha t}$$

$$= 4.3 \sqrt{3.5 \times 10^{-5} \times 10^{-3} \left[ \frac{\text{m}^2 \text{s}}{\text{s}} \right]}$$

$$= 25 \mu m$$

At $25 \mu m$ (using the low value of $\alpha$), the temperature rise is $1\%$ of that at the incident surface after $1 \mu s$ (Tuck's criterion). Clearly the etalon at $6 \mu m$ thickness may be regarded as semi-infinite here.
The heat diffusion length is minute. Certainly regarding the etalon as a semi-infinite half space is acceptable. The temptation might be to ignore thermal conductivity in the model. But there are two points to note:

a) the diffusion length quoted is apposite the solution of the equation form in which $k$ is treated as constant.

b) the thermal diffusivity $\alpha$ value at $20^\circ$C was used. As the material $T$ rises, the diffusion length will certainly increase as $k$ increases due to increasing carrier concentration. The behaviour of $k(T)$ is discussed in section 6.6. But the assessment of the possibility of regarding the etalon as a semi-infinite half space is considered adequate as it stands.

The conclusions drawn here then are

1) the thin melt disk in a semi-infinite slab of germanium is a satisfactory initial model with which to make progress in understanding thermal runaway. It reduces the problem to one spatial dimension, $x$.

11) the appropriate equation is

$$\frac{d}{dx}\left\{k(T) \frac{\partial T}{\partial x}\right\} + q_v(T) = \rho c \frac{\partial T}{\partial t}$$

6.3(4)
Because of the dependence of $k(T)$ and $q_v(T)$ on temperature, an analytic solution valid over the full temperature range of interest is not thought possible. Hence the potential of numerical techniques will be examined. It may be possible to solve the problem in temperature bands, over which $k$ and $q_v$ are regarded as constant; they would then be updated for the next solution segment. The following sections are devoted to evaluating the behaviour of $k(T)$, and of $q_v(T)$ over the temperature range of interest.
Section 6.3.1 "Second sound"

The heat conduction equation based on the Fourier conduction relationship and established as useful to this problem was quoted in the previous section. For the purpose of discussing "second sound" and its possible relevance here, the more compact form made possible by constant material parameters will be used in this section. This should not prejudice the considerations. Should it be judged necessary to take account of "second sound" in the laser germanium interaction model, variable material parameters will be re-introduced. We start then with

\[
\nabla^2 T = \frac{1}{\alpha^2} \frac{dT}{dt} \quad (1)
\]

Many observers (ref.1) have pointed out that this parabolic equation implies an infinite velocity of propagation of effect - i.e. that a portion of the solution extends to infinity. That the effect at a large distance is very small (negligible) does not negate the philosophical objection that thermal effects are experienced at great distance from the causal disturbance instantaneously. To take account of this, it has been proposed that the damped wave equation (the telegraph equation) is a better description, particularly when dealing with transient phenomena.

\[
\frac{1}{\alpha^2} \frac{\partial^2 T}{\partial t^2} + \frac{1}{\alpha} \frac{\partial T}{\partial t} = \nabla^2 T \quad (2)
\]

where \(v_c^2\) is the velocity of propagation of the thermal disturbance - often referred to as 'second sound' by virtue of the fact that it is an (ordered) phonon propagation effect.
A relaxation time may be defined by
\[ \tau_0 = \frac{\alpha}{\mathcal{U}_2^2} \]
---6.3.1(3)
which characterises the decay time of the damped thermal disturbance.

For most practical problems, the effect of the first term (containing \( \mathcal{U}_2 \)) is negligible. Usually \( \alpha \) (the thermal diffusivity) is 10 orders of magnitude smaller than \( \mathcal{U}_2^2 \), the square of the velocity of propagation of second sound. Put another way, if the equation is re-written
\[ \frac{\alpha^2}{\mathcal{U}_2^2} \cdot \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \alpha \nabla^2 T \]
---6.3.1(4)
it can be seen that \( \frac{\partial^2 T}{\partial t^2} \) needs to be \( \sim 10^{-10} \) times the value of \( \frac{\partial T}{\partial t} \) for the first term to contribute effectively.

The "temperature acceleration" \( \frac{\partial^2 T}{\partial t^2} \) has to be very large compared to the rate of change of temperature \( \frac{\partial T}{\partial t} \). The only circumstance for this to occur is during a very short time duration transient. The laser produced melt in the germanium surface is a clear candidate.

For the sake of completeness, the value of \( 10^{-10} \) (relevant at room temp.) for \( \frac{\alpha^2}{\mathcal{U}_2^2} \) may be reduced if \( \mathcal{L} \) becomes larger. The thermal conductivity \( k \) for a very pure crystal at low temperature \((0 \rightarrow 40K)\) may be up to \( 100 \) times the value at room temperature. For these conditions the first term of equation 6.3.1(2) may well become significant. Experimental work has been done in this regime (ref. 2 and ref. 3). These regimes are only of interest in the circumstances of the laser-germanium interaction in so far as they are able to suggest a suitable value of \( \mathcal{U}_2 \) for use in assessing the
significance of the first term (equation 6.3.1(2)) magnitude. Some broad estimates may be made to establish whether the "second sound" term is significant in the construction of a model for thermal runaway during a laser pulse. To do this, assume that the surface temperature of the germanium rises mainly during the peak laser power. This is of duration $\sim 100\text{ns}$. Assume that the "take off" and "levelling out" time occupy the remainder of the laser pulse. At threshold laser intensity, the surface just melts. This data is put into Fig. 6.3.1(1).

Fig 6.3.1(1)

It is emphasised that the data in the figure are "guestimates" - but probably not out by as much as a factor of 2; hopefully not out by an order of magnitude.

The maximum rate of temperature rise:

$$\frac{dT}{dt} \sim \frac{900-100}{100\text{ns}}$$

$$\sim 8 \times 10^9 \text{ K/s}$$
A possible evaluation of the second differential coefficient:

\[ \frac{\partial^2 T}{\partial t^2} \sim \left\{ \left( \frac{\partial T}{\partial x} \right)_{\text{max}} - \left( \frac{\partial T}{\partial x} \right)_{\text{min}} \right\} / 100 \; \text{s} \]

\[ \sim \frac{3 \times 10^9}{10^{-7}} \quad \text{K/s} \]

\[ \sim 10^{17} \quad \text{K/s}^2 \]

For the second sound term to be significant:

\[ \frac{1}{\mathcal{V}_2^2} \cdot \frac{\partial^2 T}{\partial t^2} \geq \frac{1}{100} \cdot \frac{1}{\mathcal{V}_1} \cdot \frac{\partial T}{\partial x} \quad \text{(arbitrary factor = 100)} \]

--- 6.3.1(5)

To make progress requires a value of \( \mathcal{V}_2 \). Peshkov (ref.5) says that \( \mathcal{V}_2 \) for Helium \( \Pi \) is an order of magnitude less than first sound velocity \( s (s = 250 \text{m/s}; \mathcal{V}_1 \approx 20 \text{m/s}) \).

Chester (ref.3) states the relationship

\[ \mathcal{V}_2 = \frac{s}{\sqrt{3}} \]

for any dielectric material. That does not seem to agree with Peshkov, but for the purpose of this estimate, let's take \( \mathcal{V}_2 \) to be less than \( s \), the worst case say \( s/10 \).

For germanium \( s = 5 \times 10^3 \text{m/s} \)

\[ \mathcal{V}_2 = 500 \text{ m/s} \quad \text{(say)} \]

\[ \frac{1}{\mathcal{V}_2^2} \cdot \frac{\partial^2 T}{\partial t^2} \sim \frac{1}{500^2} \quad 10^{17} \quad \left[ \frac{\mathcal{E}^2}{\varepsilon} \cdot \frac{K}{\varepsilon} \right] \]

\[ \sim 4 \times 10^{11} \quad \text{K/m}^2 \]

and

\[ \frac{1}{100} \cdot \frac{1}{3.5 \times 10^5} \cdot \frac{\partial T}{\partial t} \sim 300 \times 9 \times 10^9 \quad \left[ \frac{\mathcal{E}^2}{\varepsilon} \cdot \frac{K}{\varepsilon} \right] \]

\[ \sim 24 \times 10^{11} \quad \text{K/m}^2 \]

These values are close. An arbitrary factor of 100 has already been allowed, and still the L.H.S term of 6.3.1(5) is less than R.H.S. The L.H.S. needs to be larger if second sound
plays a significant part in the phenomenon. So on the face of it, we may rule out second sound.

Analysis will be continued on this supposition. The pressure to exclude second sound effects arises from the need to keep the complexity of the model equation down - to keep the prospect of a solution in sight. We already know that \( k(T) \) and \( q_v(T) \) are complicated variables. In all likelihood, this fact will require the use of numerical methods. In that case it may turn out that to include the term \( \frac{1}{\kappa^2} \frac{\partial^2 T}{\partial t^2} \) will not worsen the magnitude of the difficulties.

The case for keeping second sound under review is that the above criterion turned out to be very nearly met. The uncertainty in what value should be used for \( V_2 \), together with a much larger uncertainty in the appropriate value of \( \frac{\partial T}{\partial t} \) leaves a strong element of doubt about the validity of rejecting second sound. Remember also that second sound effects are more likely to be present in very pure crystalline dielectrics.

Semiconductor crystals like germanium (at least at temperatures around room temperature) should meet this requirement.

The effect of the second sound term in equation 6.3.1(2) is to prescribe an upper limit to the heat flux which it is possible for the crystal to transmit. This value would be obtained if a temperature step function were "clamped" on to the crystal (ref.1,p 25). Where a rapid change of temperature gradient occurs, the heat flux \( q \) is less than would normally be expected. Usually

\[
\hat{\vec{Q}} = - k \bigtriangledown \vec{T} \quad \quad \quad \quad \quad --6.3.1(6)
\]
but including second sound effects, the heat flux is diminished

\[ \frac{\partial}{\partial x} \frac{\partial \dot{q}}{\partial x} + \dot{q} = -k \nabla T \]

---6.3.1(7)

The importance of equation 6.3.1(7) to the problem of a melting surface would be that the rate of loss of energy to the body of the crystal would be reduced, allowing the surface temperature rise to be more rapid than otherwise expected.

It is just possible to envisage that at the onset of runaway, the rates of change of \( T \), \( \frac{\partial T}{\partial x} \) and \( \frac{\partial q}{\partial t} \) could be so large that the actual flux \( \dot{q} \) into the crystal body would be quite small. There might occur a very temporary thermal isolation of the surface allowing a melt, and even evaporation of the surface layers.

![Fig 6.3.1(2)](image)

The sketch (Fig.6.3.1(2)) represents a feasible temperature-time behaviour of a surface irradiated by a strong laser pulse.
The salient features where second sound is most likely to be significant are indicated. Another approach to estimate the significance of second sound to this problem is to use Chesters' equation 11 (ref. 3) expressing a minimum frequency $f_c$ of temperature fluctuation below which temperature waves cannot propagate through a material:

$$f_c = \frac{s^2}{6\pi} \sqrt{\frac{\rho C}{k}}$$

---6.3.1(3)

Inserting values for germanium ($k, \rho$, and $C$ at room temperature for the moment)

$$f_c = \frac{(5.4 \times 10^3)^2}{6\pi} \frac{1}{3.5 \times 10^{-5}} \left[ \frac{m^2}{s^2} \cdot \frac{s}{m^2} \right]$$

$$= 4.4 \times 10^{10} \text{ Hz}$$

Which corresponds to a temperature rise time $\sim 10^{-11}$ s.

Although the temperature "runs away" over a fraction of the pulse time, the intense part of which lasts $\sim 10^{-7}$ s, it would seem unlikely at this stage that the rapid heating would occur in times as short as $10^{-11}$ s.

The situation with pico-second pulse lasers would appear quite different. The appraisal of second sound above would indicate that potentially observable effects might occur. Combining this approach with low temperature might bring second sound effects in germanium into an observable regime. Very fast temperature detectors such as pyroelectric radiation devices might offer means of detecting and measuring effects.

But in conclusion, in this section the role of second sound in the present problem has been estimated. The decision at this stage is that it is not significant, and will therefore be
dropped from the analysis. Because the evaluation has been carried out with room temperature parameters (e.g. k for germanium), as opposed to those at the high temperatures in the problem, it would be wise to hold this decision under review. In dielectrics, low temperatures are more favourable to second sound effects, because k increases. For a semiconductor, k increases with temperature - but this is not due to phonon effects. Therefore any apparent increase in the possibility of second sound effects due to higher values of k must be treated with caution.
Section 6.4. General discussion of Temperature dependence.

The thermal conductivity (k) and the heat source (qv) appear in the differential equation which describes the energy transport in a material. In most practical situations, these parameters may be considered as constant. In the case of a semiconductor, they are functions of the temperature (T). This fact greatly complicates the search for a solution of the differential equation, and may rule out the possibility of an analytical solution. It certainly means that a "standard case" solution is not available. Numerical methods provide the most likely route to solution.

The main factor influencing the temperature dependence of k and qv is the rapid increase of carriers with temperature in semiconducting materials.

The thermal conductivity has a lattice contribution and a carrier contribution. Both vary with T, but the carrier contribution is likely to be very significant at temperatures approaching melting point.

The heat source qv represents the thermal energy per unit volume "originating" within the material. In the case of germanium "conducting" a beam of infra-red light, qv represents the electromagnetic radiation energy intercepted by the material, the absorption. Once again there is a lattice contribution and a carrier contribution. For radiation of free space wavelength 10.6 μm and germanium, the lattice contribution is negligible for temperatures much above room temperature. The carrier contribution is dominant, and proportional to carrier density. The hole contribution is markedly larger than that of the electronic contribution.
For both the parameters above, the carrier density plays a major role in the temperature dependence. Incidentally the beam intensity at any point in the beam path depends on the reflection and the absorption that has occurred "upstream" of the point. Thus the intensity reaching such a point is too a strong function of temperature; the absorption varies with temperature; the reflection may also be expected to vary with temperature since it is influenced by the carrier density.

The preceding general discussion serves to underline the need to establish the way in which the carrier density varies with temperature. Upon this behaviour depends the behaviour of $k$ and $q_v$ (through both the local beam intensity $I$, and the coefficient of absorption $\mathcal{C}$). The next section sets out to establish the behaviour of carrier density with temperature, and succeeding sections examine $k = k(T)$ and $\mathcal{C} = \mathcal{C}(T)$. 
Section 6.5 Intrinsic carrier concentration; \( n_i = n_i(T) \).

6.5.1 Introduction.

The carrier concentration of intrinsic germanium as a function of temperature is the king-pin of the phenomena of interest here. It dominates the changes in absorption (of radiation) behaviour of germanium over the temperature range 300-1200K. It also enters into the behaviour of the thermal conductivity, and the dielectric constant (hence reflection/transmission ratio at the etalon boundaries). Consequently, this section sets out to determine \( n_i = n_i(T) \) as exactly as possible from the available evidence. Theoretical expressions and empirical results are compared and compounded to arrive at an expression which may be used to evaluate \( n_i \) at any temperature within the range of interest. An expression (as opposed to a "look up" table) was considered the more desirable for use in a computer model if a satisfactory one could be devised. Following the framework set out by Morin and Maita (ref.18), and using some more recent numerical data, an expression representing \( n_i = n_i(T) \) is determined.

6.5.2 The theoretical expression.

The theoretical expression is (ref.18,24,25);

\[
n_i = 4 \times 10^5 \times \frac{m_n m_p}{m_e^2} \frac{1}{2} T^{-3/2} \exp \left( - \frac{\xi_g}{2kT} \right)
\]

where

- \( n_i \) (cm\(^{-3}\)) is the intrinsic carrier concentration (electrons or holes)
- \( m_n \) is the density of states effective electron mass
- \( m_p \) = - - - - - - - hole -
- \( m_0 \) = - - electron rest mass
- \( T \) is the absolute temperature
- \( \xi_g \) is the intrinsic ionization energy.
- \( k \) is Boltzmann's constant.
The expression is shown plotted for a number of semiconductors in Fig. 6.5.2-1 (ref. 25).

Of particular interest in this problem are the values of $n_i$ as the melting point (1210K) is approached. At these temperatures $n_i$ has values which are optically significant, and are in the region of the required density to bring the plasma frequency into coincidence with the laser frequency. It is therefore desirable to estimate $n_i$ as closely as possible at the higher temperatures.

The expression above (6.5.2-1) has limitations in this range. In particular the intrinsic ionization energy $E_i$ reduces with temperature, and is further reduced by the electrostatic interaction of charge carriers as their density increases. This represents a substantial under-estimate of $n_i$ at 1200K by expression 6.5.2-1, unless these factors are taken into account.

As an illustration of the caution required when consulting texts (even standard texts) for numerical data (as opposed to theoretical framework), Smith's (ref. 24) plot of $n_i$ is
presented as Fig. 6.5.2 - 2. Comparing the two authors, the value of $n_i$ at 1000K is in good agreement at $\sim 2 \times 10^{18} \text{cm}^{-3}$, but at 300K there is an order of magnitude difference ($2 \times 10^{12}$ & $2 \times 10^{13}$).

![Graph showing variation of $n$ and $p$ with temperature for Ge.](image)

Further, Smith states that the factor $T^{3/2}$ does not cause significant divergence from a straight line of the Log $n_i - 1/T$ plot. Looking at his plot, one would be convinced. For interest the equation 6.5.2 - 1 has been evaluated, using parameter values cited by Smith, both with and without the $T^{3/2}$ term active. The values in Table 6.5.2 - 1. They are superimposed on Smith's plot in Fig. 6.5.2 - 3.

Although it is broadly true that $T^{3/2}$ is of small significance compared to $\exp(-\frac{\xi}{k_BT})$, there is again an order of magnitude difference in the data at one end of the temperature range as
Fig. 6.5.2 - 3

Variation of \( n \) and \( p \) with temperature for Ge. (Full line curves give \( n \), dotted curves give \( p \)) \( N_d - N_e = 0 \) (intrinsic line)

\[ \n \begin{align*} 
\text{\( \n \leq \frac{1}{3} \).} 
\end{align*} \]

<table>
<thead>
<tr>
<th>( T ) K</th>
<th>( \text{Column 2 of table 6.5.2 - 1} )</th>
<th>( n_i \text{ Cm}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.2</td>
<td>13</td>
</tr>
<tr>
<td>400</td>
<td>8.4</td>
<td>14</td>
</tr>
<tr>
<td>500</td>
<td>8.1</td>
<td>15</td>
</tr>
<tr>
<td>600</td>
<td>3.8</td>
<td>16</td>
</tr>
<tr>
<td>700</td>
<td>1.2</td>
<td>17</td>
</tr>
<tr>
<td>800</td>
<td>2.9</td>
<td>17</td>
</tr>
<tr>
<td>900</td>
<td>6.0</td>
<td>17</td>
</tr>
<tr>
<td>1000</td>
<td>1.1</td>
<td>18</td>
</tr>
</tbody>
</table>

Equation 6.5.2 - 1 evaluated.
1 is with \( T^2 \) included
2 is with \( T^2 \) set constant at \( 10^4 \)
Other values as in Smith; \( E_g = 0.665 \); mass-term \( \approx 1/3 \).
compared to the other. Normally this would be of little consequence, but because of the significance of the plasma frequency resonance - and its sensitivity to \( n_1 \), it is desirable to obtain as close an estimate for \( n_1 \) as possible. In subsequent section, some published empirical values are examined.

Section 6.5.3 Variation of \( \varepsilon_g \).

The intrinsic ionization energy \( \varepsilon_g \) is a function both of temperature, and of electrostatic interaction of carriers.

\[
\varepsilon_g = \varepsilon_g(n_1, T)
\]

The variation with temperature has been measured by G.G. Macfarlane (ref. 26), and is expressed graphically in Fig. 6.5.3 - 1, after ref. 24.
Although the data is for a temperature range adjacent to that of interest here, the value of $\varepsilon_q$ may be taken to be represented by an extrapolation of Fig. 6.5.3 - 1, and expressed.

$$\varepsilon_q = 0.782 - 3.9 \times 10^{-4} T \text{ electron volts} \quad 6.5.3 - 2$$

As the carrier density becomes significant with rising temperature, the value of $\varepsilon_q$ will be reduced by electrostatic interaction. An expression has been proposed by Hering and is referred to in ref.18. The increment $\Delta \varepsilon_q$ expressed as a function of the concentration $n_i$ is:

$$\Delta \varepsilon_q = -4.61 \times 10^{-10} (n_i)^{1/2} T^{-1/2} \quad 6.5.3 - 3$$

Using approximate values of $n_i$ taken from section 6.5.2, this expression is tabulated and plotted below to establish the relative magnitude of the correction:

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta \varepsilon_q$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-1.3</td>
</tr>
<tr>
<td>500</td>
<td>-1.8</td>
</tr>
<tr>
<td>700</td>
<td>-6.0</td>
</tr>
<tr>
<td>900</td>
<td>-1.2</td>
</tr>
<tr>
<td>1100</td>
<td>-1.9</td>
</tr>
</tbody>
</table>

It will be seen that the electrostatic is small at $\sim 1100K$ compared to the lattice temperature correction ($0.02eV$; $0.43eV$), about 1:20. Combining the two corrections, $\varepsilon_q$ may be expressed:
\[ \varepsilon_g = 0.782 - 3.9 \times 10^{-4} T - 4.61 \times 10^{-10} (n_i)^{2.5 T^{-3}} \]  

This expression will be used in equation 6.5.2 - 1 to estimate \( n_i \) at elevated temperatures.

Section 6.5.4 Empirical \( n_i = n_i(T) \).

Morin and Maita (ref.18) have used measured conductivity parameters up to 500K to deduce \( n_i(250K - 500K) \). Extrapolating these behaviours up to 1000K, and allowing for calculated effects at high temperature (such as electrostatic reduction of \( \varepsilon_g \)), an estimate of \( n_i(500K - 1000K) \) was made. The conductivity (500K - 1000K) could then be computed, and compared with experimental values. The agreement was good. Therefore, their function \( n_i = n_i(T) \) may be used with some measure of confidence. The data is presented graphically in Fig.6.5.4 - 1.
The section \( n_1(250K - 500K) \) may be expressed as an empirical relation (adapted form of ref. 18 equin (12)):

\[
n_1 = 1.76 \times 10^{16} T^{3/2} \exp \left( -\frac{0.785}{2kT} \right)
\]

For higher temperatures, \( \varepsilon_0 \) may be modified according to equation 6.5.3 - 4. Note that the multiplying constant is significantly higher than the theoretical \( 4.82 \times 10^{15} \left( \frac{m_n m_p}{m_0^2} \right)^{3/4} \).

This compensates for the rather high value of \( \varepsilon_0 \) at 0.785 eV, which is close to Macfarlane's value at absolute zero (0.782 eV).

It will be shown later that the theoretical constant may be retained if all factors so far mentioned are taken into account.

Section 6.5.5 A satisfactory expression synthesised.

By combining all the factors so far discussed, the author has assembled an expression which reproduces Morin and Maita's empirical \( n_1(T) \) very closely. The density of states effective mass term was used as an adjustable parameter. The two relevant equations are repeated below:

\[
n_1 = 4.82 \times 10^{15} \left( \frac{m_n m_p}{m_0^2} \right)^{3/4} T^{3/2} \exp \left( -\varepsilon_0/2kT \right)
\]

\[
\varepsilon_0 = 0.782 - 3.9 \times 10^{-4} T - 4.61 \times 10^{-10}(n_1)^{2/3} T^{-1/3}
\]

Morin and Maita took \( m_n = m_p = 0.6 \) (1954).

Present published data (ref. 19) quotes \( m_n = 0.35; m_p = 0.56 \)

The table 6.5.5 - 1 below summarises these values, and the value of the term \( \left( m_n m_p/m_0^2 \right)^{3/4} \):

<table>
<thead>
<tr>
<th>( m_n )</th>
<th>( m_p )</th>
<th>( (m_n m_p/m_0^2)^{3/4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.6</td>
<td>0.465</td>
</tr>
<tr>
<td>0.35</td>
<td>0.56</td>
<td>0.295</td>
</tr>
<tr>
<td>(0.53)</td>
<td>(0.53)</td>
<td>0.387</td>
</tr>
</tbody>
</table>

Used as an adjustable parameter.
If the two equations quoted are used to compute $n_i$, and the value $n_i(300K) = 2.5 \times 10^{13} \text{cm}^{-3}$ is taken as well established, then the effective mass term needs to have the value 0.387. As will be seen from the table, this is intermediate between previously used values. As an aside, it suggests (if it is taken $m_n = m_p$) $m_n = m_p = 0.53$. This step is proposed as a matter of convenience rather than as a statement about the physics of semiconductors. It does produce a striking correspondence with the empirically derived data. The equations above are tabulated in Table 6.5.5-2 beside Morin and Maita's empirical results to enable easy comparison.

Table 6.5.5-2

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\tau_g$ (eV)</th>
<th>$n_i$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.675</td>
<td>5.0 12</td>
</tr>
<tr>
<td>290</td>
<td>0.669</td>
<td>1.4 13</td>
</tr>
<tr>
<td>300</td>
<td>0.665</td>
<td>2.56 13</td>
</tr>
<tr>
<td>400</td>
<td>0.625</td>
<td>1.7 15</td>
</tr>
<tr>
<td>500</td>
<td>0.584</td>
<td>2.4 16</td>
</tr>
<tr>
<td>600</td>
<td>0.542</td>
<td>1.5 17</td>
</tr>
<tr>
<td>700</td>
<td>0.498</td>
<td>5.6 17</td>
</tr>
<tr>
<td>800</td>
<td>0.452</td>
<td>1.6 18</td>
</tr>
<tr>
<td>900</td>
<td>0.406</td>
<td>3.7 18</td>
</tr>
<tr>
<td>1000</td>
<td>0.357</td>
<td>7.4 18</td>
</tr>
<tr>
<td>1100</td>
<td>0.308</td>
<td>1.3 19</td>
</tr>
<tr>
<td>1200</td>
<td>0.258</td>
<td>2.2 19</td>
</tr>
</tbody>
</table>

For the purposes of this analysis, the synthesis of the theoretical and empirical is considered to have produced expressions which generate $n_i = n_i(T)$ for the range 300K - 1200K with reasonable confidence.
Section 6.6 Thermal Conductivity $k = k(T)$.

6.6.1 Introduction

The purpose of this section is to establish the nature of $k = k(T)$ for germanium. The theoretical framework is discussed, and some experimental values are extracted from the literature. Following the discussion, an assessment is made of the options available for inserting the data into the equation describing the heating process during laser irradiation (equation 6.3(4)).

The macroscopic view of thermal conductivity is embodied in the definition based on the Fourier heat conduction law

$$k = \frac{q}{\frac{\partial T}{\partial n}} = \frac{\frac{W}{mK}}{\partial n}$$

which says that $k$ is the amount of heat conducted per unit time per unit area per unit negative temperature gradient. Values range from 12200 W/mK for copper at 20.3 K to 0.1 W/mK for liquid carbon dioxide at 273 K. Values for gases are in general an order of magnitude lower again (ref.1 p.31-32). A table of values of $k$ for selected materials appears below to establish typical magnitudes.

<table>
<thead>
<tr>
<th>Material</th>
<th>W/m K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic solids:</td>
<td></td>
</tr>
<tr>
<td>Silver (purest)</td>
<td>418</td>
</tr>
<tr>
<td>Copper (pure)</td>
<td>387</td>
</tr>
<tr>
<td>Aluminum (pure)</td>
<td>203</td>
</tr>
<tr>
<td>Zinc (pure)</td>
<td>112.7</td>
</tr>
<tr>
<td>Iron (pure)</td>
<td>73</td>
</tr>
<tr>
<td>Tin (pure)</td>
<td>66</td>
</tr>
<tr>
<td>Lead (pure)</td>
<td>34.7</td>
</tr>
<tr>
<td>Nonmetallic solids:</td>
<td></td>
</tr>
<tr>
<td>Periclase, MgO</td>
<td>41.6</td>
</tr>
<tr>
<td>Quartz (parallel to axis)</td>
<td>19.1</td>
</tr>
<tr>
<td>Corundum, Al₂O₃</td>
<td>10.4</td>
</tr>
<tr>
<td>Marble</td>
<td>2.78</td>
</tr>
<tr>
<td>Ice, H₂O</td>
<td>2.22</td>
</tr>
<tr>
<td>Quarts (fused)</td>
<td>1.91</td>
</tr>
<tr>
<td>Pyrex glass</td>
<td>1.05</td>
</tr>
<tr>
<td>Liquids:</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>8.21</td>
</tr>
<tr>
<td>Water</td>
<td>5.54</td>
</tr>
<tr>
<td>Sulfur dioxide, SO₂</td>
<td>2.12</td>
</tr>
<tr>
<td>Methyl chloride, CH₃Cl</td>
<td>1.79</td>
</tr>
<tr>
<td>Carbon dioxide, CO₂</td>
<td>0.185</td>
</tr>
<tr>
<td>Freon, CCl₃F₃</td>
<td>0.0728</td>
</tr>
<tr>
<td>Gases:</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.175</td>
</tr>
<tr>
<td>Helium</td>
<td>0.141</td>
</tr>
<tr>
<td>Air</td>
<td>0.0243</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.0126</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.0066</td>
</tr>
</tbody>
</table>
The thermal conductivity of a material depends upon its physical character at an atomic level. It represents the attempt of the elementary particles to regain thermal equilibrium from disturbed condition. Energy transport mechanisms are called into play. The value of thermal conductivity is an expression of the efficiency of energy exchange processes between the fundamental particles constituting the material. The lattice contributes to $k$; in electrical conductors the charge carriers contribute to $k$. Electrical conductivity and thermal conductivity (due to carriers) are related, and described by the Wiedemann–Franz law. For dielectrics the lattice component is dominant; for conductors the carrier component is dominant; and for semiconductors there is an intermediate situation, moving toward carrier dominance at elevated temperatures when the charge carrier density is at its highest.

The effectiveness of the lattice in transporting heat energy is largely determined by its crystalline perfection. Thus chemical purity is very important. Chemical purity in this context embraces isotopic purity.

6.6.2 Thermal transport by the lattice.

Energy is carried through the lattice structure by elastic vibrations. These may be described in terms of the superposition of wave trains transporting energy quanta (phonons). Thermal resistance ($R = 1/k$) is provided by scattering mechanisms within the lattice which tend to randomise the direction of travel of the energy quanta. Less scattering means less resistance, higher conductivity. Any discontinuity in the crystalline structure is capable of scattering the phonons.
impurity atoms (including the presence of isotopes), crystal defects, specimen boundaries. Amorphous materials are poor thermal conductors.

If phonon scattering was limited to the mechanisms already mentioned, a large well grown pure single crystal could be expected to exhibit a high value of $v$. A perfect crystal would have an infinite $v$. The present problem is concerned with germanium, a material which can be grown in large single crystals with excellent chemical purity. But very large $v$ values are not observed. Phonon-phonon scattering holds $v$ finite.

For a linear crystal, there can be no phonon-phonon scattering. Were the force-displacement relationship for the atoms of the crystal strictly proportional, the lattice could support any number of wavetrains, with interleaved paths, without mutual interference. At each phonon-phonon encounter, energy and crystal momentum would be conserved, and any net energy transport in one direction would proceed unhindered.

Any actual crystal exhibits an asymmetry about the atomic equilibrium position of the force displacement curve (Fig. 6.6.2-1).

![Diagram showing harmonic nature of crystal interatomic forces](image)

*Fig. 6.6.2-1*

*Showing an harmonic nature of crystal interatomic forces.*
There is an anharmonic component, which leads to mutual modification of character of the interacting phonons. Two main classes of encounter may be distinguished; the normal process, and the Umklapp process. In the normal encounter, the total wave vector $\vec{K}_1$ of the pair of phonons is conserved, and may be described:

$$\vec{K}_1 + \vec{K}_2 = \vec{K}_3$$  \hspace{1cm} 6.6.2 - 1

The normal process does not directly lead to phonon scattering. On the other hand the Umklapp process (ref.12) does result in a net change of direction of energy flow, and leads directly to phonon scattering (randomisation of direction). It is essentially a "Bragg reflection" type of process in which crystal momentum may be "reflected". There is no analogous process in particle dynamics. It may be described

$$\vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{G}$$  \hspace{1cm} 6.6.2 - 2

where $\vec{G}$ is $2\pi$ times a reciprocal lattice vector.

The Umklapp process only occurs where the participating phonons are relatively energetic ($E \sim \frac{k_b (\Theta)}{2}$ where $E$ is the phonon energy, $k_b$ is Boltzmann's constant, $\Theta$ is the Debye temperature).

One consequence of this is that Umklapp events are relatively rare at low temperatures, governed by the Boltzmann probability factor $\exp\left(-\frac{\Theta}{2T}\right)$; that is, proportional to the number density of suitable phonons. At high temperatures, the population of suitable phonons $\sim \frac{2T}{\Theta}$, so that Umklapp events are proportional to $T$.

The concept of phonon mean free path, $\ell$, before scattering is useful. A shorter $\ell$ means higher thermal resistance $R$, a lower thermal conductivity $k$.

$$R \propto \frac{1}{\ell} \hspace{1cm} k \propto \ell$$  \hspace{1cm} 6.6.2 - 3
The number density $n$ of phonons capable of undergoing an Umklapp process determines $\ell$, where Umklapp scattering is the dominant mechanism. Thus

$$\ell \propto \frac{1}{n} \quad 6.6.2 - 4$$

The energy transport, and hence the thermal conductivity $k$, may be expressed in terms of the mean free path. It may be shown to be (ref.1, page 35):

$$k = \frac{1}{3} \rho C_v \overline{v} \ell \quad 6.6.2 - 5$$

where $\rho$ is the material density, $C_v$ is the specific thermal capacity at constant volume, and $\overline{v}$ is the mean phonon velocity. This expression has the general form shared by the transport coefficients of the kinetic theory (ref.13 pages 45 - 48).

The total lattice thermal resistance of a material is usually taken to be the sum of the resistive contributions of all the relevant scattering mechanisms. Thus

$$R_{Total} = R_B + R_U + R_I + R_D + R_M \quad 6.6.2 - 6$$

where:

- $R_B$ is resistance due to boundary scattering
- $R_U$ " " " Umklapp "
- $R_I$ " " " impurity "
- $R_D$ " " " defect "
- $R_M$ " " " mosaic "

For a pure well formed crystal (such as the germanium etalon), $R_I$, $R_D$, $R_M$ may be taken as negligible in relation to $R_B$ and $R_U$. Further $R_B$ is only relevant at very low temperatures where the specimen boundaries determine the phonon mean free path. These points are illustrated in Fig.6.6.2 - 2 (ref.9 page 14)
To predict $k$ from a calculated behaviour of the mean free path $l$, a knowledge of the temperature dependence of $C_v$, the specific heat capacity at constant volume is required (see equation 6.6.2-5). Also required is the behaviour of $\rho(T)$ and $\overline{\omega}(T)$. The specific heat is a measure of the rate of change of the aggregate phonon energy with temperature, and as such is concerned with the number density and the frequency distribution of the phonon population. There is an intimate connection between the temperature behaviour of $C_v$ and that of $k$. The next section 6.6.3 examines the temperature behaviour of $C_v$.

Fig. 6.62 - 3

(FROM REF. 1 PAGE 66)
Section 6.6.3 The specific thermal capacity.

The specific thermal capacity, and its behaviour with temperature enters this problem in two ways; the Debye temperature \( \Theta \), important in describing lattice conductivity, is defined in terms of \( C_v = C_v(T) \); and \( C_v \) enters into the equation to be solved - equation 6.3 - 4. Thus this problem requires a knowledge of \( C_v \) over the range 300 K \( \rightarrow \) 1200 K.

The distinction between \( C_v \) (the specific thermal capacity at constant volume) and \( C_p \) (the specific thermal capacity at constant pressure) must be examined. The theory requires the use of \( C_v \), while measurements (and quoted values) are of \( C_p \).

Dulong and Petit in 1819 enunciated their law for the atomic heat of all solids (ref.14 page 210). "The product of the specific thermal capacity at constant volume and the atomic weight, that is, the atomic heat, is the same for all substances, and is equal to 24.94 joules per gram-atom per degree".

As was shown later, this result follows from the principle of equipartition of energy. For an atom situated in a crystal lattice, there are 6 degrees of freedom, 3 of potential energy, 3 of kinetic energy. Equipartition requires \( \frac{1}{2}k_B T \) of energy per degree of freedom; thus for one gram-atom, the total vibrational energy \( E \) at temperature \( T \) is:

\[
E = N_0 \times 6 \times \left( \frac{1}{2}k_B T \right) = 3RT
\]

where \( N_0 \) is Avogadro’s number

and here \( R \) is the universal gas constant \( = k_B N_0 \)

\( k_B \) is Boltzmann’s constant.
The atomic heat at constant volume $C_v$ is therefore

$$C_v = \frac{dE}{dT} = 3R$$

Experiment shows that at ordinary and high temperatures, $C_v$ for "simple substances" converge toward the Dulong and Petit value. Over the full range of temperature, the $C_v(T)$ curves for these substances are of similar shape, and may be expressed as

$$C_v = F\left(\frac{T}{\Theta}\right)$$

where $F$ is a function, the same for all materials, and $\Theta$ is a parameter particular to each substance, known as the Debye temperature. A universal curve of $C_v$ may be plotted (Fig.6.6.3 -1).
Better descriptions of these experimental data invoke quantisation of the phonon energy (ref.14 Chap.XXII).

Before interpreting these facts in terms of germanium, the difference between $C_v$ and $C_p$ will be estimated for germanium.

One relationship which may be used is (ref.14 page 209):

$$C_p - C_v = \frac{9 \alpha^2 \gamma}{k} - \frac{1}{3} \gamma$$

where $\alpha$ is the coefficient of linear expansion

$\gamma$ - - volume of 1 kg ($\gamma = \rho \varepsilon$)

$k$ - - isothermal compressibility.

Substituting the values for $G_e \approx 300$ K:

$$C_p - C_v = \frac{9 \times (6.1 \times 10^{-6})^2}{5323 \times 1.3 \times 10^{-6}} \times 300 \left[ \frac{m^3 \gamma}{kg \cdot m^2} \right]$$

$$= 1.45 \text{ J/kgK}$$

which when compared to quoted $C_p \sim 310$ J/kgK, it is seen that the error in regarding $C_v \approx C_p$ is less than 1% at 300K.

Insufficient data is available for evaluation at $\sim 1200$K.

There seems some doubt about this last figure in terms of data presently available to the author, as it leads to a ratio

$$\frac{C_p}{C_v} \approx \frac{311.45}{310} \approx 1.005$$

This is much smaller than the ratio for many other materials ($Al, Cu, NaCl, KCl$ etc) which all have values of $C_p/C_v \approx 1.04$ (ref.14 page 210). A value 1.04 leads to $C_p - C_v = 12 \frac{J}{kgK}$, an order of magnitude higher than previously. The approximate formula (due to Nernst & Lindemann) related to the material
melting point temperature gives an order of magnitude lower result:

\[ C_p - C_v = \frac{0.0071}{T_{mp}} C_T^2 \]  

(in c.g.s units)

leading for Ge at 300K to:

\[ C_p - C_v = 0.122 \ \frac{J}{kgK} \]

This difficulty may be resolved for our purpose without resort to further published data. First note that germanium is one of the group of zinc blende structure crystalline substances with a coefficient of linear expansion which is abnormally low, a matter discussed by W.B. Daniels (ref.17 page 482 ff.). He notes that at high temperatures these semiconductors have \( \alpha \sim 10 \times 10^{-6} \text{K}^{-1} \) whereas the alkali halides have \( \alpha \approx 100 \times 10^{-6} \text{K}^{-1} \). Thus discrepancies with various formulae for \( C_p - C_v \) might be expected. Use of a small \( \alpha \) in eqn. 6.6.2 - 4 will lead to a small difference \( C_p - C_v \). Second, note that in all evaluated expressions, \( C_p - C_v \) is always small compared to \( C_p \), even though differing by an order of magnitude. The thermal runaway of germanium under irradiation is not likely to be sensitive to small variations in the value of \( C_v \) used in the equation 6.3 - 4.

Therefore, in this work, reliance is placed in the thermodynamic expression for \( C_p - C_v \), repeated below for convenience, together with the evaluation at 300 K for germanium:

\[ C_p - C_v = \frac{9 \alpha^2 T}{K} \]

\[ \rightarrow 1.45 \ \frac{J}{kgK} \ \text{for Ge} \gtrsim 300K \]

and \[ C_v \approx C_p \approx 310 \ \frac{J}{kgK} \ \text{at} \ 300K \].
Finally, in this section dealing with the thermal capacity, a check is made to find the contribution to the specific thermal capacity due to rupturing covalent bonds, and the subsequent thermalisation of the carriers produced in intrinsic germanium material. For dielectrics, and for metals, the carrier contribution to $C_v$ is nil. For semiconductors, the largest contribution will be made at temperatures near melting; the significance of this contribution will be evaluated. An approximate evaluation should be sufficient.

There will be three elements to the carrier contribution to $C_v$:—

1) raise the temperature of existing carriers by one degree,
2) thermalise newly formed electrons & holes,
3) supply the ionization energy for electron-hole formation.

Regarding the carriers as free to gain thermal energy $\sim 3/2k_BT$ (contrast case of a metal), which implies low concentrations in the available band structure, then the contribution to $C_p$ is

$$\frac{d}{dT} \left( \frac{3}{2} k_B T \right) \rightarrow \frac{3}{2} k_B \text{ per carrier, for the existing carriers} \rightarrow 1.5 n'_i k_B \text{ in all, where } n'_i \text{ is number of electrons (or holes) in 1kg of material.}$$

To thermalise each carrier formed requires $3/2k_BT$ per carrier, or allowing for both electrons and holes, $2 \times \Delta n'_i \times 1.5 k_B T \rightarrow 3\Delta n'_i k_B T$, where $\Delta n'_i$ is the change of concentration appropriate to a change of 1 K at the temperature $T$.

The ionization energy required will be $\Delta n'_i \times \varepsilon_g$ where $\varepsilon_g$ is the band gap energy.

Thus writing the carrier contribution as $C_c$,

$$C_c = 1.5 n'_i k_B + 3 \Delta n'_i k_B T + \Delta n'_i \varepsilon_g$$

$$= 1.5 n'_i k_B + \Delta n'_i (3k_B T + \varepsilon_g)$$
Two approaches may be adopted for evaluating 6.6.3 - 5. Both will be tried, one providing a cross check on the other (though they are not independent routes). The first, reading values of \( n_i \rightarrow n_i' \) and \( \Delta n_i \rightarrow \Delta n_i' \) from the graph published by Morin and Maita (ref.18 Fig.4) over the temperature range 900K - 1000K, is the more approximate:

\[
\begin{aligned}
\xi_g &= 0.67 \text{ eV} \\
C_p &= 310 \text{ J/kgK}
\end{aligned}
\]

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( n_i \times 10^9 / \text{cm}^3 )</th>
<th>( \Delta n_i \times 10^9 / \text{cm}^3 )</th>
<th>( n_i' \times 10^8 / \text{kg} )</th>
<th>( \Delta n_i' \times 10^8 / \text{kg} )</th>
<th>( 1.5 \pi n_i k_B )</th>
<th>( 3 \pi n_i' k_B T )</th>
<th>( \Delta n_i \xi_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.8</td>
<td>0.4 \times 10^2</td>
<td>1.5</td>
<td>0.75 \times 10^2</td>
<td>3 \times 10^2</td>
<td>0.31</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Values taken from Fig.6.5.4.- 1

Summing the final three columns give \( C_c \sim 1.1 \text{ J/kgK} \), insignificant against \( C_p \sim 310 \text{ J/kgK} \). (Note that the room temperature density \( \rho = 5.323 \text{ g/cm}^3 \) was used in obtaining \( n_i' \) and \( \Delta n_i' \)).

The second approach is to differentiate Morin and Maita's empirical equation for \( n_i \) to obtain \( \Delta n_i \), then use equn. 6.6.3 - 5. The equation is (strictly) only valid for \( T = 250 - 500 \text{ K} \). No allowance is made for \( \xi_g = \xi_g(T) \), and \( \rho_{200K} \) is again used. None of these points should lead to an erroneous final decision (that \( C_c \) is to be ignored).

From Morin and Maita's equation 12 (ref.18):

\[
n_i = 1.76 \times 10^{16} T^{3/2} \exp \left( - \frac{0.785}{2 k_B T} \right) \text{ cm}^{-3} \quad 6.6.3 - 6
\]

\[
\frac{dn_i}{dT} = 1.76 \times 10^{16} T^{3/2} \left\{ \frac{3}{2} \cdot \frac{1}{T} + \frac{0.785}{2 k_B} \cdot \frac{1}{T^2} \right\} \exp ( )
\]

\[
\Delta n_i = \left\{ \frac{3}{2} \cdot \frac{1}{T} + \frac{1550}{T^2} \right\} n_i
\]

6.6.3 - 7
Substituting into 6.6.3 - 5:-

\[ n_i = \frac{1000}{5.523} \]  

\( n_i \) to convert to particles/kg,

\[ C_c = n_i \left\{ 1.5 k_B + \left( \frac{1.5}{T} + \frac{4.550}{T^2} \right) \left( 3k_B T + \ell g \right) \right\} \]

using \( n_i \) from graph:-

\[ = 1.5 \times 10^{21} (2 \times 10^{-23} + (1.5 \times 10^{-3} + 4.55 \times 10^{-3})(4.14 \times 10^{-20} + 11 \times 10^{-20})) \]

\[ = 1.4 \text{ J/kg K} \leq 1000 \text{ K.} \]

This is in good agreement with the former estimate of 1.1 J/kg K.

The higher value would be expected from an "instantaneous" value at 1000 K as opposed to an average over the range 800 K - 1000 K.

This section concludes that for the problem being considered, the observed values of \( C_p \) will serve as \( C_v \). For germanium \( C_p \) at 300 K is \( \sim 310 \text{ J/kg K} \), and the Debye temperature is \( \Theta = 374 \text{K} \).

This leads to the behaviour \( C_v = C_v(T) \) predicted by the theory shown in Fig. 6.6.3 - 2.

---

**Fig. 6.6.3 - 2.**
6.6.4 Temperature dependence of $k_{\text{LATTICE}}$.

The dominant thermal resistance in a good quality crystal (at the higher temperatures) is dominated by the Umklapp processes (section 6.6.2). This point is graphically made in Fig. 6.6.4 - 1 in which the various contributions to $k$ are shown separately, and combined (for $S_1$).

![Diagram](image)

Comparison of the low-temperature $K$ results for Si with the theory in which various phonon scattering mechanisms are considered.

Fig. 6.6.4 - 1.

Detailed analysis of the relaxation time $\tau$ to be expected from the spectrum of three-phonon Umklapp events is extensive (ref. 10 page 62). The required results relevant to the problem under consideration are extracted, and shown in table 6.6.4 - 1 below.
Table 6.6.4 - 1.

<table>
<thead>
<tr>
<th>Class</th>
<th>Scattering process</th>
<th>$\omega$ and $T$ dependence of $\tau^{-1}$</th>
<th>N-processes</th>
<th>U-processes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L+L \rightarrow L$</td>
<td>$\omega T$ (high temp.)</td>
<td>$\omega^2 T$</td>
<td>no U-processes</td>
</tr>
<tr>
<td></td>
<td>$L \rightarrow L+L$</td>
<td>$\omega^4 T$ (low temp.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$T+L \rightarrow L$</td>
<td>$\omega T$ (high temp.)</td>
<td>$\omega^3 T$ (high temp.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\omega^4 T$ (low temp.)</td>
<td>$\omega^6 T^{-1} \exp(-\hbar \omega_D / k_B T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$L+T \rightarrow L$</td>
<td>$\omega^4 T$ (low temp.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that the table shows $\tau^{-1}$ dependence on phonon radian frequency $\omega$ and temperature $T$. The lattice thermal conductivity $k_L$ should be proportional to $\tau$ for the Umklapp processes Class II.

At low temperatures $\left(\frac{0}{30} \leq T \leq \frac{0}{10}\right)$,

$$k_L \propto \frac{T}{\omega^2} \exp\left(\frac{\hbar \omega_D}{k_B T}\right)$$

6.6.4 - 1

where $\hbar = 2\pi h$, $h$ is Planck's constant, and $\omega_D$ is a characteristic parameter, which may be expressed in terms of the Debye temperature, $\Theta$. The temperature dependence expressed in 6.6.4 - 1 is not undisputed. Expressed alternatively,

$$k_L \propto T^{\frac{5}{\delta}} \exp\left(\frac{\Theta}{bT}\right)$$

6.6.4 - 2

where both $\delta$ and $b$ are of the order of unity (first proposed by Peierls), would be in accord with most authors. Although $\delta$ as high as 8 has been proposed by Julian (1965), the exact value is unlikely to be determined by experiment due to the dominance of the exponential term (ref.9, page 53 ff) (See both Fig. and Table 6.6.4 - 2).
TABLE 6.6.4-2

Different forms of the temperature dependence of U-process-limited thermal conductivity which fit experimental results equally well

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<thead>
<tr>
<th></th>
<th>NaF</th>
<th>LiF</th>
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<tr>
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<td>$T^2 \exp(\theta/6 \cdot T)$</td>
<td></td>
</tr>
<tr>
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<td>$T^2 \exp(\theta/4 \cdot T)$</td>
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</tr>
<tr>
<td>$T^2 \exp(\theta/2 \cdot 2T)$</td>
<td>$T^2 \exp(\theta/2 \cdot 4T)$</td>
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</tr>
</tbody>
</table>

FI G. 6.6.4—2
Plots of thermal conductivity multiplied by various powers of the temperature as a function of inverse temperature for NaF. The absolute values of the ordinate change by 10 between each curve. (Data from Jackson and Walker 1971.)

To observe this low temperature dependence requires extreme chemical purity. Although germanium may be prepared to a chemical purity better than 1 atom in $10^{10}$ atoms, it occurs as a mixture of isotopes in the proportions noted below (ref. 21) $^{70}\text{Ge}$ 20.55%; $^{72}\text{Ge}$ 27.37%; $^{73}\text{Ge}$ 7.67%; $^{74}\text{Ge}$ 36.74%; $^{76}\text{Ge}$ 7.67% (to digress for a moment, it is interesting to note that germanium from meteorites has the same isotopic composition). The results of several authors showing experimental and calculated $k_L$ over the temperature range 1 K → 100 K are shown in Fig. 6.6.4—3 (ref. 10 page 99).
The two sets of curves represent natural and isotopically enriched germanium. The R.H.S of the diagram shows $k_L$ dipping toward the 60 W m$^{-1}$ K$^{-1}$ room temperature value, and the range of major interest in the present problem.

At high temperatures (a term which embraces 300K—1200K for germanium), the temperature dependence of $\tau$, and hence $k_L$ is:

$$k_L \propto \frac{1}{\omega^2 \tau} \quad \ldots \quad 6.6.4 - 3$$

This may be expressed for germanium in terms of constant $A$, which will be quantified from published data $6.6.7$.

$$k_L \propto A \frac{1}{\tau} \quad \ldots \quad 6.6.4 - 4$$

Expressions for $k_L$ embodying this temperature law have been proposed (refs listed ref.9 page 47), which relate $k$ to other measureable material parameters:

$$k_L \propto \frac{M_a a^3 \Theta}{\gamma^2} \cdot \frac{1}{\tau} \quad \ldots \quad 6.6.4 - 5$$

$M_a$ is the atomic weight (proportional to the mass of the atom, $M$)
$a^3$ is the volume occupied by one atom
$\Theta$ is the Debye temperature
$\gamma$ is the Gruneisen constant.

The Gruneisen constant is an anharmonicity measure. For a perfectly harmonic crystal, $\gamma = 0$. There are a number of definitions for $\gamma$; one is in terms of the rate of change of the mode frequency with the volume of the crystal. In terms of the $i$th mode

$$\gamma_i = \frac{\partial \ln \omega_i}{\partial \ln V} \quad \ldots \quad 6.6.4 - 6$$
Then $\gamma$ is the mean of all the $\gamma_i$s weighted toward the $\gamma_i$s for the important modes at any given temperature.

Another approach is in terms of the coefficient of expansion. Were the crystal perfectly harmonic, there would be no thermal expansion. The expansion which does take place depends on the anharmonicity ($\gamma$), and the changes in the excited modes of vibration as the temperature changes (of which $C_v$ is a measure).

The experimental definition of $\gamma$:

$$\text{coefficient of expansion} = \gamma C_v K$$

Inserting the values for germanium,

$$\gamma = \frac{6.1 \times 10^{-6}}{310 \times 53.23 \times 1.3 \times 10^{-11}} \left[ \frac{1}{k} - \frac{k_g k}{J} \frac{m^3}{kg} \right]$$

$$\gamma = 0.284$$

The value of the Gruneisen constant for many semiconductor crystals as derived from measurements of $k$ and the use of relation 6.6.4 - 5 is $\approx 2$ (ref. 16). The discrepancy between the thermal expansion derived $\gamma$ and the conductivity derived $\gamma$ is reduced when normal three phonon processes are taken into account (ref. 29). Also Barron (ref. 30) pointed out that different averaging processes are involved in calculating $\gamma$ from thermal expansion and the thermal conductivity respectively.

Measurement shows that in practice the thermal conductivity for germanium (and silicon) varies approximately as $T^{-1.3}$. A small correction to the $T^{-1}$ law of about 0.02 in the power of the temperature can be ascribed to the effects of thermal expansion. At the higher temperatures, an additional resistivity proportional $T^2$ should be taken into account. Empirical data for $k_L$ are presented in 6.6.7.
Section 6.6.5: The carrier contribution to thermal conductivity.

The carriers in a metal or semiconductor may pick up energy in a high temperature region of the lattice, and carry it away to a cooler region. Energy is transported down a temperature gradient by this mechanism, and will make a contribution to the total thermal conductivity of the crystal. As the carrier density increases (with rising temperature) in a semiconductor, the carrier contribution will become increasingly significant in comparison to the lattice conductivity.

The purpose of this section is to review the theoretical framework, and to evaluate the relevant expressions in terms of germanium over the temperature range (300K - 1200K). In 6.6.7 some published empirical data is presented.

It might be expected that the electrical conductivity should be related to the carrier thermal conductivity, since both are using the same transport mechanism subject to the same scattering processes. For a pure metal, the carrier thermal conductivity $k_e$ is dominant, so that the measured conductivity $k_{\text{meas}}$ is:

$$k_{\text{meas}} \approx k_e$$

6.6.5 - 1

Then the Wiedemann - Franz law applies

$$\frac{k_{\text{meas}}}{\sigma T} = L$$

6.6.5 - 2

where $L$ is constant

$$L = \frac{1}{3} \pi^2 k_e^2 \quad 6.6.5 - 3$$

$$= 2.45 \times 10^{-8} \text{ W} \Omega \text{ deg}^{-2}$$

The value $\frac{1}{3} \pi^2$ depends upon $E_F \gg kT$, which for a metal at normal temperatures is true ($E_F > 5eV; kT \sim 0.03eV$).
In an intrinsic semiconductor, there are two components to the carrier transport of energy. There is transport of kinetic energy, and the transport of the energy of ionization, which is given up to the lattice on recombination downstream. The latter term is the larger in an intrinsic material. The Weidemann-Franz law may only be applied to the kinetic energy term. The value \( \frac{1}{3} \pi \rho \) may be modified for a degenerate semiconductor tending to the value 2 depending on the appropriate value of \( E_F/kT \), and assuming the relaxation time \( \gamma \propto E^{-\frac{1}{2}} \) (\( E \) is the carrier kinetic energy). For a non-degenerate semiconductor for which \( \gamma \propto E^{-\frac{3}{2}} \), the value is 2.

For the purpose of this section, it is assumed that carrier transport is in response to temperature gradients alone; zero electric field is assumed. In the case of the laser beam giving rise to the temperature gradients, as in the problem under consideration, the material is bathed in very strong electric fields. They are alternating at 28.3 THz (\( \lambda_e = 10.6 \mu m \)). For the moment, these will be treated as averaging zero over a time scale very short compared with thermal transport effects. Thus the zero field condition is considered to apply in the following paragraphs. This will enable the analysis to be based on Smith Ch.6 (ref.24).

When there is a temperature gradient, the equilibrium distribution function \( \mathcal{f}(\mathbf{k}) \), giving the distribution of the electrons between allowed energy levels with various values of the wave vector \( \mathbf{k} \), will be disturbed from its equilibrium value. In this case, a simple averaging of the equations of motion over the equilibrium distribution is not satisfactory. To obtain
equations for electric current density and of heat flow, the variation of $\mathcal{f}(k)$ given by Boltzmann's equation must be used.

The result for current density due to electrons is:

$$ J_x = \frac{ne}{m_e} \left\{ e \xi_x + T \frac{\partial}{\partial T} \left( \frac{E_T}{T} \right) \frac{dT}{dx} \right\} \langle \gamma \rangle + \frac{ne}{m_e} \frac{dT}{dx} \langle \gamma E \rangle \quad 6.6.5 - 4 $$

To obtain the heat current $W_x$, replace $-e$ by $E$ before averaging:

$$ W_x = -\frac{n}{m_e} \left\{ e \xi_x + T \frac{\partial}{\partial T} \left( \frac{E_T}{T} \right) \frac{dT}{dx} \right\} \langle \gamma E \rangle - \frac{n}{m_e} \frac{dT}{dx} \langle \gamma E^2 \rangle \quad 6.6.5 - 5 $$

*N.B. Some brackets have been moved in 6.6.5 - 4 as compared to ref. 24.

If no current flows, $\xi_x$ may be eliminated between the equations 6.6.5 - 4 & 6.6.5 - 5 (Note that if $\frac{dT}{dx} \neq 0$, $\xi_x \neq 0$):

$$ W_x = \frac{n}{m_e T} \frac{dT}{dx} \frac{\langle \gamma \rangle \langle E^2 \gamma \rangle - \langle E \gamma \rangle^2}{\langle \gamma \rangle} \quad 6.6.5 - 6 $$

The thermal conductivity $k_e$ due to electrons is then

$$ k_e = -\frac{W_x}{\frac{dT}{dx}} = \frac{n}{m_e} \frac{1}{T} \left\{ \langle \gamma \rangle \langle E^2 \gamma \rangle - \langle E \gamma \rangle^2 \right\} \quad 6.6.5 - 7 $$

But

$$ \sigma = \frac{ne^2}{m_e} \frac{\langle \gamma \rangle}{\langle \gamma \rangle} \quad 6.6.5 - 8 $$

Therefore

$$ k_e = \frac{ne^2}{m_e} \frac{1}{T} \frac{1}{e^2} \frac{1}{\langle \gamma \rangle} \left\{ \langle \gamma \rangle \langle E^2 \gamma \rangle - \langle E \gamma \rangle^2 \right\} \quad 6.6.5 - 9 $$

$$ = \sigma \frac{T}{k^2 T^2} \left( \frac{e^2}{k^2} \right) \left\{ \frac{\langle \gamma \rangle \langle E^2 \gamma \rangle - \langle E \gamma \rangle^2}{\langle \gamma \rangle^2} \right\} \quad 6.6.5 - 10 $$

But $\frac{k_e}{\sigma T} = L$ (the Lorentz ratio)
To evaluate the averages $\gamma, E^2\gamma$ and $E\gamma$ over the electronic energy distribution, first write for $\langle \gamma \rangle$ (ref. 24 page 117):-

\[
\langle \gamma \rangle = \frac{\int_0^\infty E N(E) \exp\left(-\frac{E}{kT}\right) \tau(E) \, dE}{\int_0^\infty E N(E) \exp\left(-\frac{E}{kT}\right) \, dE}
\]  

where equation 6.6.5 - 12 includes the use of the weighting function for the averaging process of (ref. 24 page 116);

\[
E N(E) \int_0^\infty \left[(E-E_F)/kT\right] \, dE
\]  

with the function $\int_0^\infty$ being replaced by an exponential to give

\[
E N(E) \exp\left(-\frac{E}{kT}\right)
\]  

This weighting function is required to give sufficient weight to the more energetic electrons, rather than (as might have been expected):-

\[
N(E) \int_0^\infty \left[(E-E_F)/kT\right] \, dE
\]  

where $f_0$ is the fermi function $f(x) = 1/(\exp(x)+1)$

$E$ is the electron energy (note not the band gap energy $E_g$)

$E_f$ is the Fermi energy

$N(E)dE$ is the number of energy levels per unit volume with energy between $E$ and $(E + dE)$

For a non-degenerate semi-conductor, having "spherical" energy bands

\[
N(E) \propto E^\frac{3}{2}
\]  

Substituting back into 6.6.5 - 12;
To progress further requires a knowledge of $\gamma = \gamma(E)$. For many semiconductors, it is satisfactory to write:

$$\gamma = a e^{-s}$$  \hspace{1cm} 6.6.5 - 18

where $s$ is a constant, and $a$ is temperature dependent.

For lattice scattering alone, $s = \frac{1}{2}$. Substituting 6.6.5 - 18 into 6.6.5 - 17:

$$\langle \gamma \rangle = \frac{\int_0^\infty E^{\frac{3}{2} - s} e^{c} \exp \left( - \frac{E}{kT} \right) dE}{\int_0^\infty E^{\frac{3}{2}} \exp \left( - \frac{E}{kT} \right) dE}$$  \hspace{1cm} 6.6.5 - 19

The integrals may be evaluated using the properties of the Gamma function, defined by:

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt$$  \hspace{1cm} 6.6.5 - 20

The properties are (ref 32 p.10 ff):

$$\Gamma(x + 1) = x \Gamma(x)$$

$$\Gamma(n + 1) = n! \quad n \text{ integer}$$

$$\Gamma \left( \frac{1}{2} \right) = \sqrt{\pi}$$

Substituting $t = E/kT$ into 6.6.5 - 19, it reduces to:

$$\langle \gamma \rangle = a(kT)^{-s} \Gamma \left( \frac{5}{2} - s \right) / \Gamma \left( \frac{5}{2} \right)$$  \hspace{1cm} 6.6.5 - 21

For a pure semiconductor, with predominantly lattice scattering, $s = \frac{1}{2}$, so that

$$\langle \gamma \rangle = a(kT)^{-\frac{1}{2}} \frac{3}{2} \sqrt{\pi}$$

$$= \frac{4a}{3\sqrt{\pi} kT}$$  \hspace{1cm} 6.6.5 - 22
To evaluate the weighted averages \( \langle r E \rangle \), \( \langle E^2 r \rangle \), of the equation 6.6.5 - 11, the weighting factors are the same as for \( \langle r \rangle \); multiply eqn. 6.6.5 - 19 by \( E \) (and \( E^2 \)) before averaging. Using the same procedure gives:

\[
\langle r E \rangle = a(kT)^{-s} kT \left[ \frac{7}{2} - s \right] / \left[ (5/2) \right]
\]
(for \( s = \frac{1}{2} \))

\[
= \frac{4a}{3 \sqrt{\pi kT}} \]

and

\[
\langle r E^2 \rangle = a(kT)^{-s} k^2 T^2 \left[ \frac{9}{2} - s \right] / \left[ (5/2) \right]
\]
(for \( s = \frac{1}{2} \))

\[
= \frac{4}{3 \sqrt{\pi kT}} a x 3! x k^2 T^2
\]

Therefore in equation 6.6.5 - 11

\[
\frac{1}{k^2 T^2} \left\{ \frac{\langle r \rangle \langle E^2 r \rangle - \langle E r \rangle^2}{\langle r \rangle^2} \right\}
\]

reduces to:

\[
\left\{ 3! - (2!)^2 \right\} = 2 \quad \mp \left( \frac{5}{2} - s \right)
\]

Therefore, in the case of a non-degenerate n-type semiconductor, the electric heat conductivity \( k_e \) is related to the electrical conductivity by

\[
\frac{k_e}{\sigma T} = L \left( \frac{k}{e} \right)^2
\]

and \( L = 2 \) or in general \( L = (5/2 - s) \)

When holes participate predominantly in the heat conduction, a similar expression is obtained (ref.24 page 150):

\[
\frac{k_h}{\sigma T} = \left( \frac{5}{2} - s' \right) \left( \frac{k}{e} \right)^2
\]

where \( s' \) is the power appropriate to hole scattering.
When both electrons and holes participate to give a mixed conductivity $k_m$, an extra term is introduced which represents the transport of the intrinsic ionization energy $\xi_g$ down the thermal gradient (ref. 24 page 150):

$$\frac{k_m}{\sigma T} = \left\{ \frac{(S_2 - S) n \mu_e + \left( \frac{S_2 - S}{S} \right) \rho \mu_h}{\left( n \mu_e + \rho \mu_h \right)} \right\} + \left\{ \frac{(S - S') + \xi_g}{kT} \right\}$$

6.6.5 -28

For a non-degenerate semiconductor for which $s = s' = \frac{1}{2}$, if a small contribution due to the temperature variation of $\xi_g$ is neglected:

$$\frac{k_m}{\sigma T} = \frac{k^2}{e^2} \left\{ \frac{(S_2 - S) n \mu_e + \left( \frac{S_2 - S}{S} \right) \rho \mu_h}{\left( n \mu_e + \rho \mu_h \right)} \right\}$$

6.6.5 -29

This result (first quoted by E.H. Putley (ref. 33)) may be put into various forms for convenience (ref. 10 page 86).

$$\frac{k_m}{\sigma T} = \frac{k^2}{e^2} \cdot \frac{\sigma_e \sigma_h}{\sigma^2} \left\{ \frac{\xi_g}{kT} \left( \frac{S_2 - S}{S} \right) + \left( \frac{S - S'}{S} \right) \right\}$$

6.6.5 -30

where $\sigma_e, \sigma_h, \sigma'$ are conductivity, electron, hole and total.

$L_e, L_h$, are the separate Lorentz numbers for electrons holes.

If $s = s' = \frac{1}{2}$

$$\frac{k_m}{\sigma T} = \frac{k^2}{e^2} \left\{ \frac{\sigma_e \sigma_h}{\sigma^2} \cdot \left( \frac{\xi_g}{kT} + 4 \right)^2 + \frac{4 \sigma_e + \sigma_h}{\sigma} \right\}$$

6.6.5 -31

For an intrinsic semiconductor $n = p = n_i$, so that $\sigma_e/\sigma_h = \mu_e/\mu_h = b$, the ratio of electron to hole mobilities, and (ref. 28):

$$\frac{k_m}{\sigma T} = \frac{k^2}{e^2} \left\{ 2 + \frac{b}{(1 + b)^2} \left( \frac{\xi_g}{kT} + 4 \right)^2 \right\}$$

6.6.5 -32
This last form is the one which will be evaluated for germanium, taking \( t \text{g} \), \( \mu_e \), \( \mu_h \) and hence \( b \) from the work of Morin and Maita (ref. 18).

In their work, the lattice mobility is extrapolated to the higher temperatures from measurements over $100K-300K$. At the higher temperatures, an additional calculated allowance was made for electron-hole scattering which, as the carrier concentration increases with temperature, further reduces the mobility (see dotted entry Fig.6.6.5 - 1).

![Graph showing the relationship between conductivity mobility and temperature.]

**Fig. 6.6.5 - 1**

The lattice mobility may be expressed (ref.18):

\[
\begin{align*}
\mu_e &= 4.90 \times 10^7 \ T^{-1.66} \\
\mu_h &= 1.05 \times 10^9 \ T^{-2.33}
\end{align*}
\]
For temperatures above 500K, the combined effect of the lattice scattering and electron-hole scattering lead to:

\[
\begin{align*}
\mu_e(500K) & = 4.84 \times 10^9 T^{-2.4} \\
\mu_h(500K) & = 1.56 \times 10^{10} T^{-2.76}
\end{align*}
\]

These expressions for \( \mu \) above 500K were extracted from the graph ref. 18 Fig. 1, and a straight line fitted to the values read out. The fits had correlation coefficients of -.998 (equn 35) and 0.9997 (equn 36).

The values for \( \xi_g \) are derived from the expression developed in section 6.5.3:

\[
\xi_g = 0.782 - 3.9 \times 10^{-4} T - 4.61 \times 10^{-10} (n_e)^{0.5} T^{-0.5}
\]

The electrical conductivity values used in table 6.6.5 - 1 are taken from Glassbrenner and Slack (ref.28) with some interpolated points. Their values had been obtained from a review of several authors, including ref.18. They fit a straight line \( \ln \sigma = \frac{1}{T} \) with great precision, correlation - 0.9999. It is concluded that this therefore broadly represents a linear regression line fit to the empirical values of Morin and Maita (ref.18). The line used in ref.28 is:

\[
\ln \sigma = -4120/T + 14.8
\]

Morin and Maita's data shows a distinct curve, which clearly is not represented by equn.37. Some error is therefore introduced into the calculation of \( k_m \). Since \( k_m \) cannot be measured directly, and since \( k_m \) is small compared to the total thermal conductivity over the greater part of the temperature range, these minor discrepancies are considered of no consequence in the present context.
<table>
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<tr>
<th>T</th>
<th>μ_e</th>
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<th>( \sigma )</th>
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**Table 6.6.5 - 1**

**Fig. 6.6.5 - 2.**
The evaluation of $k_m$ for germanium using equation 6.6.5 - 32 is tabulated Table 6.6.5 - 1 and plotted in Fig. 6.6.5 - 2.

Section 6.6.6 Thermal transport by radiation.
Since electromagnetic radiation can propagate through a material, in particular germanium, there will be a net thermal transport away from a high temperature region. If the radiation is intercepted (absorbed) "downstream" of the source, it will constitute a contribution toward the thermal conductivity. The energy flow is randomised in a succession of photon emissions and absorptions. A diffusion of energy characterised by the radiative heat conductivity coefficient $k_r$ results.
Such a radiative contribution to $k$ has been observed in Ge - Si alloys (ref.16). The thermal conductivity due to photons is given by (ref.10 page 87);

$$k_r = \frac{16}{3} \sigma_R n^2 T^3 \langle \alpha^{-1} \rangle$$

where $k_r$ Thermal conductivity by photon diffusion

$\sigma_R$ Stefan-Boltzmann radiation constant

$n$ refractive index

$T$ temperature degrees K

$\alpha$ coefficient of absorption

$\langle \alpha^{-1} \rangle$ an average taken over the spectral range of the black body radiation appropriate to the lattice temperature (ref.10 page 87).
The temperature dependence of $k_r$ in the case of germanium is determined by two opposing terms:

a) a rapid increase with temperature due to $T^3$

b) a rapid decrease with temperature due to $\langle \alpha^{-1} \rangle$

Therefore, at some temperature, a peak will be exhibited (Fig. 6.6.6 - 1). The most important contribution to $\langle \alpha^{-1} \rangle$ is made by $\alpha$ in the neighbourhood of the peak of the blackbody radiation distribution. For intrinsic germanium, with a rapid increase of carriers with temperature, $\langle \alpha^{-1} \rangle$ decreases rapidly from about 500K upward. A peak in the value of $k_r$ occurs for a temperature $\sim 600$K (Fig. 6.6.6 - 2).

![Diagram](image)

**Fig. 6.6.6 - 2**

The peak contribution is only $\sim 1$ W/mK. For pure germanium, with a lattice contribution over the temperature range from 60W/mK to 10W/mK, $k_r$ is difficult to observe experimentally.
To observe $k_r$, a crystal with low lattice conductivity is required (GaAs, Ge-Si alloy). Additionally, a large energy-gap material is required to "hold-off" the $\langle \alpha^{-1} \rangle$ term long enough for the $T^3$ term to be significant.

At temperatures high enough for carrier conductivity to be appreciable, due to large carrier concentration, the carriers will ensure that $\langle \alpha^{-1} \rangle$ is very small. Thus $k_r$ is not likely to be significant in temperature ranges where $k_e$ or $k_m$ are significant.

It is generally agreed that radiation makes no significant contribution to $k$ at any temperature in intrinsic germanium (ref.10, page 111). For the problem under investigation, $k_r$ is a factor that does not need to be further considered.
Section 6.6.7 Germanium - thermal conductivity, \( k \).

The previous sections have examined the nature of thermal conductivity for a crystalline material. It has been observed that there are essentially three possible contributions worth considering; lattice, carrier and photon. The theoretical framework for these quantities has been reviewed and examined to establish the expected temperature dependence of each. Here, the empirical magnitudes relevant to germanium over the temperature range 300K → 1200K will be extracted from the literature, and a general conformity to expectation noted. Finally forms of the function \( k = k(T) \) suitable for use in the laser heating model are discussed.

A photon contribution \( k_r \) is too small in comparison with the high conductivity of the lattice to be measureable for intrinsic germanium. Therefore, over the range 300K → 1200K, \( k_r = 0 \), and will not be further considered.

The lattice conductivity \( k_L \) is \( \sim 60 \text{W/mK} \) at 300 K, and conforms approximately to the theoretically expected \( \frac{1}{T} \) dependence for higher temperatures. The results of Beers et al (ref:16) for a near intrinsic specimen "Ge - 1810" are shown in Fig.6.6.7 - 1.

![Fig.6.6.7 - 1](image)

The ratio of thermal resistivities to absolute temperature, \( \frac{R}{T} \), as a function of temperature in silicon and germanium. The types of the impurity additions and the extrinsic carrier concentrations are indicated in the figure.
If over the temperature range 300K---600K:

\[ k_L \times k_{\text{meas}} = \frac{A}{T} \]  \hspace{1cm} 6.6.7 - 1

then the product of thermal resistance \( W = \frac{1}{k} \) with reciprocal temperature \( \frac{1}{T} \):

\[ \frac{W}{T} = \frac{1}{A} = \text{constant} \]  \hspace{1cm} 6.6.7 - 2

Beers et al., using a thermal diffusivity method to measure \( k \), found this to be approximately so, with the constant \( A \approx 6.2 \times 10^{-3} \text{ W}^{-1} \text{ cm} \). Using this to evaluate \( A \) of equation 6.6.7 - 1:

300K → 600K:  \[ k_L \sim k_{\text{meas}} = \frac{1.62 \times 10^4}{T} \text{ W m}^{-1} \]  \hspace{1cm} 6.6.7 - 3

giving a value of \( k = 54 \text{ W/mK} \) @ 300K. This is somewhat lower than the generally accepted value for intrinsic Ge. The values of interest to the present problem have been interpreted from the graph Fig.6.6.7 - 1, and presented in Table 6.6.7 - 1 & Fig.6.6.7 - 2.

The isotope resistivity, \( W_I \), due to the isotope mix in Ge (see section 6.6.4) is given by an expression for weak point defect scattering due to Ambegaokar (ref.35):

\[ W_I = 4.4 \times 10^4 \int \delta \Theta^{-1} \text{ W}^{-1} \text{ deg cm} \]

where

\[ \int = \sum_i f_i \left[ (M_i - M)/M \right]^2 \]  \hspace{1cm} 6.6.7 - 4

is the point defect parameter due to isotopes \( M_i \) of concentration \( f_i \). \( \Theta \) is the Debye temperature (K), and \( \delta \) is the cube root of the atomic volume in ångstroms. For germanium, \( \int = 59 \times 10^{-5} \) (ref.16), which means that the increased resistivity
**Germanium - Intrinsic Thermal Conductivity - Temperature**

Data deduced from graph Beer et al. [Ref 7]

**Thermal Resistance** $W$ expressed in cm $K$/W

**Lattice Thermal Res** $W_{ph}$

To convert data to $K$ W/mK, read value of $W/T$ from graph, then

$$k\frac{W}{mK} = \frac{1}{(W/T)_{graph}} \times (T)_{graph} \times \frac{1}{100 cm} \frac{cm}{W} [K]$$

**Table 6.6.7 - 1**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$W/T$ (cm/W)</th>
<th>$W_{ph}/T$ (cm/W)</th>
<th>$k$ (W/mK)</th>
<th>$k_{ph}$ (W/mK)</th>
<th>$k_{carrier}$ (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$6.2 \times 10^{-2}$</td>
<td>$6.2 \times 10^{-3}$</td>
<td>54</td>
<td>54</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>$6.2 \times 10^{-3}$</td>
<td>$6.2 \times 10^{-4}$</td>
<td>32</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>$6.2 \times 10^{-3}$</td>
<td>$6.3 \times 10^{-4}$</td>
<td>24</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>800</td>
<td>$6.2 \times 10^{-3}$</td>
<td>$6.7 \times 10^{-4}$</td>
<td>20</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>1000</td>
<td>$5.8 \times 10^{-3}$</td>
<td>$7.1 \times 10^{-4}$</td>
<td>17.1</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>1100</td>
<td>$5.8 \times 10^{-3}$</td>
<td>$7.3 \times 10^{-4}$</td>
<td>17.6</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>1200</td>
<td>$4.5 \times 10^{-3}$</td>
<td>$7.6 \times 10^{-4}$</td>
<td>18.5</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

N.B. Beer et al. measured $W/T$; $W_{ph}$ obtained by subtraction. (Values of $k_{carrier}$ were not explicit in Ref 7)

**Fig. 6.6.7 - 2**
due to isotopes is $\approx 10\%$ at 300K. At higher temperatures, this contribution becomes less significant since it is temperature independent.

Glassbrenner and Slack (ref. 28) measured the thermal conductivity for germanium over a wide temperature range (3K - 1190K). To achieve this range, two apparatus sets were used; with no "adjustments" to results, the two sets joined smoothly Fig. 6.6.7 - 3.

![Graph](image)

**Fig. 6.6.7 - 3**

For the lattice conductivity, they took into account Umklapp, isotope, and **four phonon** relaxation times ($\tau_u, \tau, \tau_H$ respectively). These are given by:

$$\tau_u^{-1} = Bu w^2 T$$

$$\tau_I^{-1}(w) = 3 V_o \sqrt{\frac{w}{\pi}} v^3$$
where $\omega$ is the phonon frequency

$V_c$ "" average volume per atom in the crystal

$\nu$ "" sound velocity

$H$ subscript stands for higher order phonon interaction processes.

and

$$B_u = \frac{\hbar \nu^2}{2 \pi m \omega^2} \exp\left(\frac{\omega}{3T}\right)$$

independent of $T$ when $T > \Theta$

$m$ is the average mass of a single atom

$\gamma$ is Gruneisen's constant assumed to equal 2

$B_H$ is a constant.

When $T > \Theta$, the quantity $x = (\hbar \omega / k_B T)$ is small, and an approximate expression may be used to express the lattice conductivity $k_L$:

$$k_L = \frac{k_B}{2 \pi^2 \nu} \left(\frac{k_B \omega}{\hbar}\right)^3 \int_0^{\infty} \gamma_c x^2 \text{d}x$$

in which $\gamma_c$, a combined relaxation time is:

$$\gamma_c^{-1} = \gamma_u^{-1} + \gamma_I^{-1} + \gamma_H^{-1}$$

$$= (B_u T + B_H T^2) \omega^2 + A \omega^4$$

When isotope scattering is much less significant than phonon-phonon scattering ($T > \Theta$), Ambegaokar (ref.35) proposes that equations 6.6.7 - 8 & 10 may be reduced to:

$$W_u = \frac{\pi \nu \hbar B_u}{\omega} T$$

$$W_H = \frac{\pi \nu \hbar B_H}{\omega} T^2$$

$$W_I = \frac{4 \pi^2 \nu V_c}{\hbar \omega^2}$$

and $k_L^{-1} = W_L = W_u + W_H + W_I$
The quantity $W_I$ is (except for a factor of 12 in the definition of $T$) the same as that given by Ambegaokar. For germanium (values used in ref.28),

- $V_0 = 2.26 \times 10^{-23}$ cm$^{-3}$
- $v = 3.94 \times 10^5$ cm/sec
- $H = 395K$ (source quoted)
- $\gamma = 4.90 \times 10^{-5}$ (source quoted)

so that $W_I = 0.17$ cm deg/W.

Now the thrust of the argument here is that using the value for $W_I$, and remembering that over the range $300K - 600K$

- $W_L = k_{\text{meas}}^{-1} = (W_u + W_H) + W_I$
- $(W - W_I) = W_u + W_H$

The function $(W - W_I)T^{-1}$ versus $T$ for Ge as a means of determining the extrapolated lattice thermal resistivity at high temperatures.

Fig. 6.6.7 - 4.
A plot of \( \frac{W - W_L}{T} \) versus T should be a straight line from which \( B_u \) and \( B_H \) may be experimentally determined (to see this, note temperature dependence of \( W_u \) & \( W_H \) in 6.6.7 - 11, and remember \( W_L \) is independent of temperature). Also, an extrapolation of the line may be (it is assumed) used to determine \( k_L \) in the temperature range 600K - 1200K.

The results of Glassbrenner and Slack are shown in Fig.6.6.7 - 4. From the graph Fig.6.6.7 - 4, the empirical expression for \( k_L \) may be deduced (ref.28):-

\[
k_L^{-1} = W_L = (3.95 \times 10^{-3} T + 3.38 \times 10^{-6} T^2 + 0.17)\text{cm deg/W}
\]

Values calculated from 6.6.7 - 13 are in table 6.6.7 - 2 together with measured values from ref.28, and a difference column which represents the carrier contribution to thermal conductivity. The final column of Table 6.6.7 - 2 shows the carrier contribution calculated in section 6.6.5 for comparison.

**Table 6.6.7 - 2**

<table>
<thead>
<tr>
<th>T k</th>
<th>( k_L ) W/mk</th>
<th>( k_{\text{measured}} ) W/mk</th>
<th>( k_m ) (by difference) W/mk</th>
<th>( k_m ) calc. W/mk</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>60.3</td>
<td>60.0</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>400</td>
<td>43.7</td>
<td>44.0</td>
<td>-</td>
<td>2.7</td>
</tr>
<tr>
<td>500</td>
<td>33.4</td>
<td>33.8</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>600</td>
<td>26.6</td>
<td>26.9</td>
<td>-</td>
<td>5.6</td>
</tr>
<tr>
<td>700</td>
<td>21.8</td>
<td>21.9</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>800</td>
<td>18.2</td>
<td>19.3</td>
<td>1.1</td>
<td>2.1</td>
</tr>
<tr>
<td>900</td>
<td>15.5</td>
<td>17.1</td>
<td>3.1</td>
<td>4.3</td>
</tr>
<tr>
<td>1000</td>
<td>15.3</td>
<td>17.1</td>
<td>3.8</td>
<td>4.3</td>
</tr>
<tr>
<td>1100</td>
<td>11.6</td>
<td>16.9</td>
<td>5.3</td>
<td>5.8</td>
</tr>
<tr>
<td>1200</td>
<td>10.2</td>
<td>17.3</td>
<td>7.1</td>
<td>6.8</td>
</tr>
<tr>
<td>1210</td>
<td>10.1</td>
<td>17.3</td>
<td>7.2</td>
<td>6.8</td>
</tr>
</tbody>
</table>
The carrier contribution to the thermal conductivity $k_m$, as deduced experimentally, and as calculated, show reasonable agreement. It is probably not possible to get closer to the truth than this. Experimentally, $k_m$ is determined by subtracting an extrapolated $k_L$ from $k_{\text{meas}}$ - a difference between two relatively large quantities. Theoretically the expressions used are derived under a number of simplifying assumptions; the semiconductor is taken to be intrinsic, possess simple parabolic valence and conduction bands, and in which the charge carriers suffer only acoustic mode lattice scattering where the scattering probability varies with the carrier energy $\varepsilon \propto \sqrt{\varepsilon}$. In fact germanium has multiple minima conduction bands, multiple valence bands, and both acoustic and intervalley scattering occur. The correlation is therefore taken as satisfactory for present purposes. The way is now open to look at alternative models of $k = k(T)$ which may be used for computational purposes.

There are several models for $k = k(T)$ which should prove satisfactory for this problem. A decision between them will not be made at this stage. We note possibilities, and keep options open.

Intuitively, we feel that a description of the behaviour of germanium under intense radiation in thermal runaway conditions will only be weakly influenced by $k = k(T)$. The expectation would be that the absolute value of $k$ at the ambient temperature, together with the experimental geometry, would dominate the "take off" into thermal runaway. But once into runaway, dependence on $k$ would be weak, due to the rapidity of
change. From these comments, we may draw the inference that it is not necessary for the model to reproduce experimental \( k = k(T) \) with precision. Again intuitively, values to \( \pm 10\% \) are probably more than adequate. Even \( \pm 20\% \) over the temperature range \( 400K \rightarrow 1200K \), where change is rapid is probably more than acceptable.

The models available then to represent \( k = k(T) \) for germanium will be labelled \( k_1, k_2, k_3 \) etc.

**Model \( k_1 \):** A "look up" table \( (\pm 5\% \text{ absolute}) \)

The precision is the estimated precision of the experimental measurements (ref.28). The table may be obtained from Tables 6.6.7 - 1 or - 2, or from Figs. 6.6.7 - 2 or - 5 as required.

---

**Fig. 6.6.7 - 5**

\( k \) versus \( T \) for Ge showing the experimental points and the extrapolated lattice component \( k_e \). The Debye and melting temperatures are \( \theta \) and \( \text{MP} \), respectively.
Model $k_2$:  

\[ k = k_L + k_m \]

Combined theoretical and empirical expressions

\[ k_L = \left( 3.95 \times 10^{-5}T + 3.33 \times 10^{-3}T^2 + 1.7 \times 10^{-3} \right) \]

\[ k_m = \left\{ 2 + \frac{b}{1 + b} \right\}^2 \left( \frac{\varepsilon g}{k_B T} + 4 \right)^2 \left[ \frac{k_B}{e} \right]^2 \sigma_T \]

\[ \sigma' = n_i e \left( \mu_e + \mu_h \right) \]

\[ \varepsilon g = 0.782 - 3.9 \times 10^{-4} T - 4.61 \times 10^{-13} (n_i)^{1/2} T^{-1/2} \]

\[ n_i = 1.86 \times 10^{21} T^{3/2} \exp \left( -\frac{\varepsilon g}{2k_B T} \right) \]

\[ b = \frac{\mu_e}{\mu_h} \]

300K ≤ T ≤ 500K:

\[ \mu_e = 4.90 \times 10^3 T^{-1.66} \]

\[ \mu_h = 1.05 \times 10^5 T^{-2.33} \]

500K ≤ T ≤ 1200K:

\[ \mu_e = 4.84 \times 10^5 T^{-2.4} \]

\[ \mu_h = 1.56 \times 10^6 T^{-2.76} \]

Note that all the constants in the equations listed have been adjusted to express the quantities in S.I units rather than the mix resulting from deriving the data from a multitude of sources and retaining the authors' units in each case. The original equation labels have been retained to facilitate cross reference.
The units of the quantities are then:

\[ k, k_L, k_m \] \text{ W/mK}

\[ \ell_g \] \text{ eV}

\[ n_i \] \text{ m}^{-3}

\[ \mu_e, \mu_h \] \text{ m}^2/\text{Vs}

\[ \sigma' \] \text{ (S m)}^{-1}; \text{ S}

The values have to be computed in reverse order of listing; the bracketed equations have to be iterated because of the implicit relationship between \( n_i \) and \( \ell_g \).

**Model \( k_2 \approx \text{a1:} \)\(^{\cdots} \text{ (w.r.t. } k_1)\)**

This full procedure may be acceptably shortened by noting that a considerable proportion of the work is in evaluating \( k_m \), which over most of the range is a small correction term. The precision required is therefore relaxed.

For example, although \( \mu_e \) and \( \mu_h \) vary over the full temperature range very considerably, the quantity \( b/(1 + b)^2 \) is a slowly varying quantity (Table 6.6.5 - 1). It may be expressed

\[
\frac{b}{(1 + b)^2} = -4.5 \times 10^{-5}T + 0.215
\]

6.6.7 - 16

The conductivity \( \sigma' \) may be expressed:

\[
\ln \sigma' = -4120/T + 14.8
\]

\[ \sigma' = \exp(14.8 - 4120/T) \]

6.6.5 - 37

Use of these two expressions would lead to a speedier evaluation of \( k_m \). The worst errors occur around 300K, where it matters least due to the very small value of \( k_m \) at 300K.
Even more economical would be to treat \( k_m \) as a linear function of \( T \) with a programme instruction to treat negative values as zero (see Fig. 6.6.5 - 2)

\[
k_m = 1.17 \times 10^{-2} T - 7.21
\]

In TABLE 6.6.7 - 2, the full evaluations of the quantities discussed are compared with those derived from the empirical approximations 6.6.7 - 16 and 17 and 6.6.5 - 37.

**TABLE 6.6.7 - 2**

<table>
<thead>
<tr>
<th>( T )</th>
<th>( b )</th>
<th>( (1 + b)^2 )</th>
<th>( \sigma )</th>
<th>( k_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( (A_m)^{-1} )</td>
<td>( W/mk )</td>
<td></td>
</tr>
<tr>
<td>full</td>
<td>Equin.6.6.7-16</td>
<td>full</td>
<td>Equin.6.6.5-37</td>
<td>full</td>
</tr>
<tr>
<td>300</td>
<td>0.22</td>
<td>0.20</td>
<td>3.0 2.9 0</td>
<td>0.001 0</td>
</tr>
<tr>
<td>400</td>
<td>0.20</td>
<td>0.20</td>
<td>9.0 9.0 1</td>
<td>0.03   0</td>
</tr>
<tr>
<td>500</td>
<td>0.19</td>
<td>0.19</td>
<td>7.0 7.1 2</td>
<td>0.2    0</td>
</tr>
<tr>
<td>600</td>
<td>0.19</td>
<td>0.19</td>
<td>3.0 3.2 3</td>
<td>0.6    0</td>
</tr>
<tr>
<td>700</td>
<td>0.18</td>
<td>0.18</td>
<td>7.6 7.4 3</td>
<td>1.1    1.0</td>
</tr>
<tr>
<td>800</td>
<td>0.18</td>
<td>0.18</td>
<td>1.6 1.6 4</td>
<td>2.1    2.1</td>
</tr>
<tr>
<td>900</td>
<td>0.17</td>
<td>0.17</td>
<td>2.8 2.3 4</td>
<td>3.1    3.3</td>
</tr>
<tr>
<td>1000</td>
<td>0.17</td>
<td>0.17</td>
<td>4.4 4.4 4</td>
<td>4.3    4.5</td>
</tr>
<tr>
<td>1100</td>
<td>0.17</td>
<td>0.17</td>
<td>6.5 6.3 4</td>
<td>5.8    5.6</td>
</tr>
<tr>
<td>1200</td>
<td>0.16</td>
<td>0.16</td>
<td>8.7 8.6 4</td>
<td>6.8    6.8</td>
</tr>
</tbody>
</table>

As may be seen, the approximate empirical expressions perform well over the full temperature range.

A very good model, economic in computer time may be obtained from:

\[
k = k_L + k_m
\]

\[
k = (\text{equn 6.6.7 - 13}) + (\text{equn 6.6.7 - 17})
\]

\[
k = \left\{ (3.95 \times 10^{-5} T + 3.38 \times 10^{-8} T^2 + 1.7 \times 10^{-3}) \right\} -1 + 1.17 \times 10^{-2} T - 7.21
\]
This expression uses only the variable T. A comparison between equation 6.6.7 - 18 and the measured values is shown in the Table 6.6.7 - 3.

### Table 6.6.7-3

<table>
<thead>
<tr>
<th>T [deg K]</th>
<th>k(W/mK) measured</th>
<th>k(W/mK) eqn 6.6.7 - 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>60.0</td>
<td>60.3</td>
</tr>
<tr>
<td>400</td>
<td>44.0</td>
<td>43.7</td>
</tr>
<tr>
<td>500</td>
<td>33.8</td>
<td>33.4</td>
</tr>
<tr>
<td>600</td>
<td>26.9</td>
<td>26.6</td>
</tr>
<tr>
<td>700</td>
<td>21.9</td>
<td>22.8</td>
</tr>
<tr>
<td>800</td>
<td>19.3</td>
<td>20.4</td>
</tr>
<tr>
<td>900</td>
<td>17.7</td>
<td>18.8</td>
</tr>
<tr>
<td>1000</td>
<td>17.1</td>
<td>17.3</td>
</tr>
<tr>
<td>1100</td>
<td>16.9</td>
<td>17.3</td>
</tr>
<tr>
<td>1200</td>
<td>17.3</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Model k₃: Piecewise linear approximation ($\sim \pm 5\%$ of $k_{\text{meas.}}$)

$$\ln k \quad (W/mK)$$

Fig 6.6.7 - 6

$$300K \leq T \leq 820K: - \quad k = 6.3 \times 10^4 \cdot T^{-1.22}$$

$$820K \leq T \leq 1210K: - \quad k = 17.56$$

6.31
Model k 4:

Simple expression \( (\sim \pm 15\% \text{ of } k \text{ measured}) \)

\[
\frac{k}{(W/mK)} \sim 60 \\
\sim 15 \\
300 \text{ K temp} \\
\]

\[k = 1.8 \times 10^4/T \quad W/mK\]

The table 6.6.7 - 4 enables a comparison of the models to be made.

Table 6.6.7 - 4

<table>
<thead>
<tr>
<th>T (deg K)</th>
<th>Model k1 ( \pm 5% ) absolute</th>
<th>Model k2 ( \pm 5% ) of k1</th>
<th>Model k3 ( \pm 5% ) of k1</th>
<th>Model k4 ( \pm 15% ) of k1</th>
<th>Error % w.r.t. k1</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>60.0</td>
<td>60.3</td>
<td>59.9</td>
<td>60.0</td>
<td>+1 0 0</td>
</tr>
<tr>
<td>400</td>
<td>44.0</td>
<td>43.7</td>
<td>42.0</td>
<td>45.0</td>
<td>-1 -5 +2</td>
</tr>
<tr>
<td>500</td>
<td>33.8</td>
<td>33.5</td>
<td>32.0</td>
<td>36.0</td>
<td>-1 -5 +6</td>
</tr>
<tr>
<td>600</td>
<td>26.9</td>
<td>27.1</td>
<td>25.7</td>
<td>30.0</td>
<td>+1 -5 +12</td>
</tr>
<tr>
<td>700</td>
<td>21.9</td>
<td>22.9</td>
<td>21.3</td>
<td>25.7</td>
<td>+5 -3 +17</td>
</tr>
<tr>
<td>800</td>
<td>19.3</td>
<td>20.3</td>
<td>18.1</td>
<td>22.5</td>
<td>+5 -6 +17</td>
</tr>
<tr>
<td>900</td>
<td>17.7</td>
<td>18.6</td>
<td>17.56</td>
<td>20.0</td>
<td>+5 -1 +13</td>
</tr>
<tr>
<td>1000</td>
<td>17.1</td>
<td>17.6</td>
<td>17.56</td>
<td>18.0</td>
<td>+3 +3 +5</td>
</tr>
<tr>
<td>1100</td>
<td>16.9</td>
<td>17.4</td>
<td>17.56</td>
<td>16.4</td>
<td>+3 +4 -3</td>
</tr>
<tr>
<td>1200</td>
<td>17.3</td>
<td>17.0</td>
<td>17.56</td>
<td>15.0</td>
<td>-2 +2 -13</td>
</tr>
</tbody>
</table>

In this section, empirical values of the thermal conductivity of germanium over the temperature range 300K - 1200K have been
extracted from the literature. Some models have been prepared which will generate \( k = k(T) \) to various levels of precision. The purpose of the models is to facilitate the numerical solution of thermal problems, in particular problems involving the "thermal runaway" of germanium through which laser radiation is passing. The choice of model used will involve the assessment of the required precision of \( k \) value at any temperature, and considerations of computer storage and of computer time. Such assessment in relation to the present problem is to be made at the time of synthesis of the separate problem parts, when a clearer picture of total computer requirement is available.
Section 6.7  Electrical conductivity $\sigma' = \sigma'(T)$.

6.7.1 Introduction.

The electrical conductivity is central to this problem. The conductivity provides a mechanism which transfers energy from the laser beam into the semiconductor material. The conductivity is partially responsible for the re-distribution within the germanium crystal of the deposited heat energy. And it is the conductivity variation over the surface of the crystal which interacts with the laser beam in a fashion leading to the self-reinforcing growth of the etalon damage patterns.

To construct a description of these features, a mathematical model which reproduces the behaviour of the electrical conductivity $\sigma'$ with temperature $T$ is sought. Also the variation of $\sigma'$ with optical frequency is examined to determine the relationship between the zero frequency conductivity $\sigma_0$, and corresponding value at the laser frequency 23.3THz.

6.7.2 The theoretical background of $\sigma'$.

Conductivity may be defined as the ratio of current density $\mathbf{J}$ produced by a casual field $\mathbf{E}$:

$$\mathbf{J} = \sigma \mathbf{E} \quad \text{6.7.2 - 1}$$

But the current density $I/A$ is given by:

$$I = Anev \quad \text{6.7.2 - 2}$$

for particles of number density $n$ and charge $e$ with an average drift velocity under the field of $v$. 
For low values of D.C. field \( E \leq 10^5 \text{ V/m for germanium} \), the drift velocity is proportional to \( E \):

\[
\tau = \mu E
\]

where \( \mu \) is the mobility.

Combining these equations, we may write

\[
\sigma = ne \mu
\]

For mixed conduction by electrons \( n \) (unit vol) and holes \( p \) (unit vol) with mobilities \( \mu_e \) and \( \mu_h \) respectively,

\[
\sigma = ne \mu_e + p e \mu_h
\]

and for intrinsic material, \( n = p = n_i \), so

\[
\sigma = n_i e (\mu_e + \mu_h) = n_i e \mu_e (1 + b)
\]

where \( b = \mu_e / \mu_h \)

The temperature dependence of the quantities on the R.H.S of equation 6.7.2 - 6 will lead to \( \sigma_0 = \sigma(T) \). Basic theory leads to a simple exponential relationship:

\[
n_i \propto T^{3/2} \exp(-\frac{\xi_g}{2kT})
\]

\[
\mu \propto T^{-3/2}
\]

Hence

\[
\sigma \propto \exp\left(-\frac{\xi_g}{2kT}\right)
\]

The mobility dependence is based upon the assumption that the mobility is predominantly determined by acoustic phonon scattering. The argument supporting the \( T^{-3/2} \) dependence will be outlined.

Phonon scattering is isotropic; that is, there is an equal probability of motion in any direction after collision. This leads to the mobility in terms of the average time between collisions \( \tau := \frac{e \tau_e}{m_n} \) for electrons and \( \tau := \frac{e \tau_h}{m_p} \) for holes.
where \( m_n \) and \( m_p \) are the effective masses of the electron and the hole respectively. The relaxation time \( \tau \) may be different for the two carriers. In general, \( \tau \) will depend on carrier velocity, and hence on carrier energy \( \varepsilon \) and temperature \( T \).

The mean free path \( l \) may be defined as the average distance covered by the carrier between scattering events.

Therefore

\[
\tau = \frac{l}{\nu}
\]

or in general:

\[
\tau(\nu) = \frac{l(\nu)}{\nu}
\]

Now for a semiconductor with spherical constant energy surfaces it may be shown that the mean free path \( l \) due to scattering by the lattice vibrations is independent of the carrier velocity (ref. 24, § 8.5). Thus, under these conditions

\[
\tau \propto \frac{1}{\nu} \quad \text{or} \quad \tau \propto \frac{1}{\sqrt{\varepsilon}}
\]

Writing the proportionality constant \( = a \),

\[
\tau = a \varepsilon^{-\frac{1}{2}}
\]

When using equation 6.7.2 - 8, \( \tau \) must be averaged over the velocity distribution, to give \( \langle \tau \rangle \). The required average, expressed in terms of the \( \Gamma \) function, was dealt with in section 6.6.5. The result was equation 6.6.5 - 22:

\[
\langle \tau \rangle = \frac{L \cdot a}{3 \sqrt{\pi} kT}
\]

Using 6.7.2 - 9 and 11, and \( \varepsilon = \frac{1}{2} m_n \sigma^2 \), substituting for \( a \) in 6.6.5 - 22 gives:

\[
\langle \tau \rangle = \frac{L \cdot m_n \sigma^2}{3 \sqrt{2\pi} kT}
\]
Combining 6.7.2 - 12 with 6.7.2 - 8, and using the subscript \( L \) to indicate lattice dominance:

\[
\mu_L = \frac{e\langle \tau \rangle}{m_n} = \frac{4eL}{3(2\pi\sigma_n kT)^{1/2}} \quad \ldots \quad 6.7.2 - 13
\]

The mean free path \( l \) is a function of temperature. The probability of scattering is proportional to the energy carried by the lattice displacement wave. For long acoustic waves the energy \( \sim kT \). The scattering cross-section \( \sigma \) is therefore \( \sim T \); whence the mean free path \( l \) for scattering by the longitutinal acoustic modes is (ref.24, page 246):

\[
l = \frac{A}{T} \quad \text{where } A \text{ is constant} \quad 6.7.2 - 14
\]

The value of \( A \) has been calculated using a full wave mechanical treatment by W. Shockley and J. Bardeen. From equation 6.7.2 - 14 it follows that dependence of the relaxation time \( \tau \) may be expressed:

\[
\tau = a' e^{-\frac{1}{2} \frac{A}{T}} \quad 6.7.2 - 15
\]

where \( a' \) is a constant.

Returning to the temperature dependence of \( \mu_L \), we see from equation 6.7.2 - 13 & 14:

\[
\mu_L \propto T^{-3/2} \quad 6.7.2 - 16
\]
Therefore, under the restrictions of the argument, the lattice mobility $T^{-3/2}$ dependence cancels with the density of states $T^{3/2}$ dependence factor in $n_1$ to give an exponential dependence for the conductivity - as expressed in equation 6.7.2 - 7.

We shall compare this expression for $\sigma^\prime$ (which would be economic of computer time) against empirical values for $\sigma^\prime$ in section 6.7.4.
6.7.3 **Empirical values of conductivity $\sigma'$.**

Measured conductivity over the temperature range 300K-1200K has been extracted from the literature. The work of Morin and Maita (ref.16) is used as a base reference. Measurements by other authors are also included for comparison.

A table 6.7.3 - 1 has been drawn up with values read from the published data; The graphs used are Figs.6.7.3 - 1 and 2 (from refs. 18 & 16). The precision is limited by the resolution possible on the rather small diagrams.

Clearly, from inspection of the tables, it would be unwise to place better than $\sim \pm 10\%$ reliance on the data. One suspects that the data from refs 16 & 28 are essentially linear idealizations on the Log $\sigma'$ vers.(1/T) axes. Morin and Maita's data are probably intrinsically better than 10% (they do not actually say), but processing the data off the small graph degrades the data.

To aid the process of reading out Morin & Maita's graph, some of the most easily estimated points were tabulated (Table 6.7.3 - 2) and using these the three enlarged graphs were made (Figs. 6.7.3 - 3, 4 and 5). To some extent, the process resembles the improvement of a signal-to-noise ratio by utilising the regular properties of the signal. The conductivity values so obtained are probably good to $\sim \pm 10\%$ absolute, and greater weight is attached here to these values.

To take the data into the just melted range, Domenicali's values (ref.36) are used, which "marry" to M & M 's value at 1200K quite well.
Table 6.7.3 - 1

<table>
<thead>
<tr>
<th>T (deg K)</th>
<th>Morin</th>
<th>Beers</th>
<th>Glassbrenner</th>
<th>Domenicali</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maita</td>
<td>Cody et al</td>
<td>Slack</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2.2</td>
<td>6.8</td>
<td>9.0</td>
<td>1</td>
</tr>
<tr>
<td>400</td>
<td>8.6</td>
<td>2.9</td>
<td>3.0</td>
<td>3</td>
</tr>
<tr>
<td>500</td>
<td>7.5</td>
<td>7.5</td>
<td>1.6</td>
<td>4</td>
</tr>
<tr>
<td>600</td>
<td>1.7</td>
<td>1.8</td>
<td>2.8</td>
<td>4</td>
</tr>
<tr>
<td>700</td>
<td>2.8</td>
<td>4.5</td>
<td>9.6</td>
<td>4</td>
</tr>
<tr>
<td>800</td>
<td>4.4</td>
<td>4.4</td>
<td>8.7</td>
<td>4</td>
</tr>
<tr>
<td>900</td>
<td>4.4</td>
<td>4.4</td>
<td>8.7</td>
<td>4</td>
</tr>
<tr>
<td>1000</td>
<td>6.1</td>
<td>4.4</td>
<td>8.7</td>
<td>4</td>
</tr>
<tr>
<td>1100</td>
<td>8.2</td>
<td>9.6</td>
<td>8.7</td>
<td>4</td>
</tr>
<tr>
<td>1200</td>
<td>8.3</td>
<td>1.6</td>
<td>8.7</td>
<td>4</td>
</tr>
<tr>
<td>M.P.Solid</td>
<td></td>
<td></td>
<td></td>
<td>8.3</td>
</tr>
<tr>
<td>M.P.Liquid</td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
</tr>
</tbody>
</table>

The electrical conductivities of Ge, Si and Ge-Si alloys as functions of temperature.

---

**Fig.6.7.3 - 1**

**Fig.6.7.3 - 2**

Conductivity is reciprocal temperature.
Table 6.7.3 - 2

<table>
<thead>
<tr>
<th>$1/T$</th>
<th>$\sigma$</th>
<th>$1/T$</th>
<th>$\sigma$</th>
<th>$1/T$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-4}K^{-1})</td>
<td>(\Omega \cdot cm)^{-1}</td>
<td>(10^{-4}K^{-1})</td>
<td>(\Omega \cdot cm)^{-1}</td>
<td>(10^{-4}K^{-1})</td>
<td>(\Omega \cdot cm)^{-1}</td>
</tr>
<tr>
<td>35.0</td>
<td>1.0 -2</td>
<td>25.8</td>
<td>6.0 -1</td>
<td>16.0</td>
<td>4.0 1</td>
</tr>
<tr>
<td>33.5</td>
<td>2.0 -2</td>
<td>24.3</td>
<td>1.0 0</td>
<td>13.7</td>
<td>1.0 2</td>
</tr>
<tr>
<td>32.0</td>
<td>4.0 -2</td>
<td>23.0</td>
<td>2.0 0</td>
<td>12.0</td>
<td>2.0 2</td>
</tr>
<tr>
<td>29.7</td>
<td>1.0 -1</td>
<td>21.5</td>
<td>4.0 0</td>
<td>10.2</td>
<td>4.0 2</td>
</tr>
<tr>
<td>28.2</td>
<td>2.0 -1</td>
<td>19.1</td>
<td>1.0 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.8</td>
<td>4.0 -1</td>
<td>17.5</td>
<td>2.0 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.7.4 Computer models for $\sigma^\prime$.

The three basic approaches:

1) "look up" table
2) Sequence of equations base on theory/measurement mix.
3) Linear regression on Log $\sigma^\prime$ - $1/T$ axes of empirical data.

We shall refer to these as model $\sigma^\prime 1, \sigma^\prime 2, \sigma^\prime 3$.

Model $\sigma^\prime 1$

Compile from table 6.7.3 - 1

Estimated precision $\pm 10\%$.

Model $\sigma^\prime 2$

$$\sigma = n_i e \left( \mu_e + \mu_h \right)$$

$$n_i = 1.86 \times 10^{21} T^{3/2} \exp(-E_g/2kT)$$

$$E_g = 0.732 - 3.9 \times 10^{-4}T^{-1} - 4.61 \times 10^{-13}(n_i)^{1/2} T^{-1/2}$$

$300K \leq T \leq 500K$:

$$\mu_e = 4.90 \times 10^3 T^{-1.66}$$

$$\mu_h = 1.05 \times 10^5 T^{-2.33}$$

6.7.2 - 6
6.5.2 - 1
6.5.3 - 4
6.6.5 - 33
6.6.5 - 34
The equations are computed in reverse order. The braced pair are iterated.

Model \( \sigma_3 \)

Referring to the graphs (Figs. 6.7.3 - 2, 3, 4, 5), they are visually very close to a straight line. A very good fit is

\[
\sigma' = 2.68 \times 10^6 \exp(-4120/T)
\]

These three models are tabulated in Table 6.7.3 - 3

<table>
<thead>
<tr>
<th>T degK</th>
<th>( \sigma'^1 ) (( \Omega m )^{-1})</th>
<th>( \sigma'^2 ) (( \Omega m )^{-1})</th>
<th>( \sigma'^3 ) (( \Omega m )^{-1})</th>
<th>Error % w.r.t ( \sigma'^1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.2 0</td>
<td>2.2 0</td>
<td>2.9 0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>8.6 1</td>
<td>8.9 1</td>
<td>9.0 1</td>
<td>+ 4</td>
</tr>
<tr>
<td>500</td>
<td>7.5 2</td>
<td>8.2 2</td>
<td>7.1 2</td>
<td>+ 9</td>
</tr>
<tr>
<td>600</td>
<td>2.9 3</td>
<td>3.2 3</td>
<td>2.8 3</td>
<td>+ 10</td>
</tr>
<tr>
<td>700</td>
<td>7.9 3</td>
<td>8.4 3</td>
<td>7.4 3</td>
<td>+ 6</td>
</tr>
<tr>
<td>800</td>
<td>1.7 4</td>
<td>1.7 4</td>
<td>1.6 4</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>2.8 4</td>
<td>3.0 4</td>
<td>2.8 4</td>
<td>+ 7</td>
</tr>
<tr>
<td>1000</td>
<td>4.4 4</td>
<td>4.7 4</td>
<td>4.4 4</td>
<td>+ 6</td>
</tr>
<tr>
<td>1100</td>
<td>6.1 4</td>
<td>6.7 4</td>
<td>6.3 4</td>
<td>+ 10</td>
</tr>
<tr>
<td>1200</td>
<td>8.2 4</td>
<td>9.0 4</td>
<td>8.6 4</td>
<td>+ 10</td>
</tr>
</tbody>
</table>
Conclusions

As before, an expression is considered more "economic" than a "look up" table (with subroutine for interpolation if thought necessary).

Although model $\sigma^3$ is attractive because of its simplicity, difficulties are encountered due to the log (and reciprocal) scales required for linear relationship. A very small shift of the line used results in substantial changes in $\sigma'$, especially at the extremes of range. This is illustrated in the sketch Fig. 6.7.3 - 6. The line fit will give values too high at 300K and 1200K.

This is likely to be a serious deficiency for the present purpose. Whether or not the radiation produces runaway is likely to be very sensitive to $\sigma'$ (which determines $\alpha$ the coefficient of absorption) over the lower temperature range 300K - 350K). Once runaway is established, change is so rapid that the solution of the model should be relatively insensitive to error in $\sigma'$.

The proper policy then should be to reproduce $\sigma' = \sigma'(T)$ as closely as possible between 300K-400K; from 400K-1200K, a progressively relaxed precision would be satisfactory.
The physical model $\sigma^2$ offers no advantage in precision, and is uneconomic of computing time. Its value lies in the insights provided, which point toward the class of relationship between $\sigma$ and $T$ most likely to yield results. A piecewise model based on the model $\sigma^3$ approach is the most useful here, and will be adopted.

Model $\sigma^3A$.

300K $\leq$ $T$ $\leq$ 400K: $\sigma = 5.66 \times 10^6 \exp(-4439/T)$

400K $\leq$ $T$ $\leq$ 1200K: $\sigma = 2.68 \times 10^6 \exp(-4120/T)$

$\sigma$ given in ($\Omega \cdot m$)$^{-1}$.

Equation 6.7.3 - 1 is compared with values from graph Fig.6.7.3 - 4 in table 6.7.3 - 4

<table>
<thead>
<tr>
<th>$T_{K}$</th>
<th>$\sigma$ (graph) ($\Omega \cdot m$)$^{-1}$</th>
<th>$\sigma^3A$ ($\Omega \cdot m$)$^{-1}$</th>
<th>$T_{K}$</th>
<th>$\sigma$ (graph) ($\Omega \cdot m$)$^{-1}$</th>
<th>$\sigma^3A$ ($\Omega \cdot m$)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>2.2 -1</td>
<td>2.25 -1</td>
<td>350</td>
<td>1.80 -1</td>
<td>1.76 -1</td>
</tr>
<tr>
<td>270</td>
<td>4.1 -1</td>
<td>2.12 -1</td>
<td>360</td>
<td>2.55 -1</td>
<td>2.50 -1</td>
</tr>
<tr>
<td>280</td>
<td>7.38 -1</td>
<td>3.60 -1</td>
<td>370</td>
<td>3.60 -1</td>
<td>3.49 -1</td>
</tr>
<tr>
<td>290</td>
<td>1.25 0</td>
<td>1.27 0</td>
<td>380</td>
<td>4.90 1</td>
<td>4.78 1</td>
</tr>
<tr>
<td>300</td>
<td>2.15 0</td>
<td>2.12 0</td>
<td>390</td>
<td>6.40 1</td>
<td>6.45 1</td>
</tr>
<tr>
<td>310</td>
<td>3.50 0</td>
<td>3.42 0</td>
<td>400</td>
<td>8.50 1</td>
<td>8.58 1</td>
</tr>
<tr>
<td>320</td>
<td>5.60 0</td>
<td>5.35 0</td>
<td>410</td>
<td>1.10 2</td>
<td>1.12 2</td>
</tr>
<tr>
<td>330</td>
<td>8.60 0</td>
<td>8.15 0</td>
<td>420</td>
<td>1.40 2</td>
<td>1.46 2</td>
</tr>
<tr>
<td>340</td>
<td>1.27 1</td>
<td>1.21 1</td>
<td>430</td>
<td>1.80 2</td>
<td>1.86 2</td>
</tr>
</tbody>
</table>
6.7.5 Conductivity at the laser frequency.

The electrical conductivity is a function of frequency.

As the frequency of the electric field becomes comparable with the carrier collision time $\tau$, a number of effects become apparent. The transfer of energy from the driving field to the material lattice becomes less effective, and the current lags in phase.

At low frequencies (meaning those for which the cycle time $\gg \tau$), the carrier scattering is able to hold the particle current in phase with the driving field. For germanium, $\tau \approx 10^{-12} \text{s}$, so that low frequencies are those below $\approx 10^{10} \text{Hz} = 10\text{GHz}$. These frequencies may be regarded (from the point of view of the carriers) as pseudo - D.C. The normal D.C. conductivity $\sigma_0$ is the appropriate parameter.

At high frequencies, the scattering events over a cycle time are rare, and the carrier behaviour resembles the free space behaviour. That is, the particle velocity (and hence the current) lags the field $E$ in phase by an angle tending toward $90^\circ$. A significant quadrature component exists for frequencies above $\approx 10\text{GHz}$ for germanium (if $\tau = 10^{-12}\text{s}$).

There can exist circumstances when, at a certain frequency, the lagging quadrature component of current is exactly equal in magnitude to the leading quadrature component (displacement current). The condition of the material at this frequency might be referred to as "material resonance". An electromagnetic wave can travel from free space into the material without change,
i.e. the refractive index is equal to unity. The critical frequency is normally called the "plasma frequency".

The plasma frequency is of interest in this problem, since it could assist the thermal runaway of the germanium by "letting in" stronger fields as the material temperature rose. When the incident laser beam heats the etalon, the carrier density increases with temperature, the refractive index falls, with consequently less reflection, allowing more of the incident field into the material to further heat it. Approach toward the plasma frequency could be a powerful mechanism to deposit energy into the material at the interface very rapidly once runaway had been established. A later section deals with this possibility in more detail.

To establish some of the points so far made more quantitatively, we follow the argument presented by Kruse (ref. 37 page 125f.f.). Consider the equation of motion for a free carrier (charge q) having an effective mass $m_e$, driven by a sinusoidally varying electric field $\mathbf{E}$ of radian frequency $\omega$:

$$qE_0 \sin \omega t = \left\langle \frac{d}{dt} \left( m_e \mathbf{v} \right) \right\rangle_{\text{net}}$$

where $\mathbf{v}$ is the average carrier velocity.

The factor in braces is the net rate of change of momentum, to which there are two contributions. The one is the rate of gain of momentum from the field; the other is the rate of loss of momentum by scattering.
On the assumption that the rate of loss is proportional to the net momentum, the latter term may be written:

\[
\frac{d}{dt} (m_e \overline{v}) = (m_e \overline{v})_0 \exp\left(-\frac{t}{\tau}\right)
\]

which describes the time rate of decay of momentum from an initial value \((m_e \overline{v})_0\). The constant \(\tau\) may be identified with the time between collisions (ref.13 page 100) providing the scattering is isotropic (predominantly due to phonons). In the context of equn.6.7.5 - 2, \(\tau\) may be regarded as the characteristic time required for the carriers to acquire a new equilibrium velocity distribution. The momentum loss rate may therefore be written:

\[
\frac{d^2}{dt^2} (m_e \overline{v}) = -\frac{1}{\tau} (m_e \overline{v}) \quad 6.7.5 - 3
\]

The gain of momentum from the field will simply be expressed as:

\[
rate\ of\ gain\ of\ momentum = \frac{d}{dt} (m_e \overline{v}) = m_e \frac{d\overline{v}}{dt} \quad 6.7.5 - 4
\]

Substituting the elements 6.7.5 - 3 & 4 back into 6.7.5 - 2;

\[
q_e \frac{\varepsilon_0}{m_e} \sin \omega t = \frac{d\overline{v}}{dt} = (\frac{-\overline{v}}{\tau}) \quad 6.7.5 - 5
\]

The solution of this equation is

\[
\overline{v} = \frac{q_e \varepsilon_0 \tau (\sin \omega t - \omega \tau \cos \omega t)}{m_e (1 + \omega^2 \tau^2)} \quad 6.7.5 - 6
\]
Note that the first term on the R.H.S represents the in-phase drift velocity (current). The velocity \( \bar{U} \) is "held" in phase by the scattering, and provides the energy transfer mechanism between the radiation and the material. The second term represents the phase lagging quadrature term. The current flow represented by this term may be regarded as inductive, and tending to cancel the capacitative displacement current of the material. It is a non-dissipative term.

Writing

\[
\sigma^* = \sigma' - j \sigma'' \quad \text{for the complex conductivity,}
\]

\[
\sigma^* = n q \sigma / \varepsilon = n q \left( q \tau / (m e (1 + \omega^2 \tau^2)) \right) (1 - j \omega \tau) \quad 6.7.5 - 7
\]

\[
= n q (\mu' - j \mu'')
\]

where \( \mu^* = \mu' - j \mu'' \) is introduced as the complex mobility.

The dissipative component is:

\[
\mu' = \frac{q \tau}{m_e (1 + \omega^2 \tau^2)}
\]

\[
= \mu_o \frac{1}{(1 + \omega^2 \tau^2)} \quad 6.7.5 - 8
\]

where \( \mu_o \) is the ordinary D.C. mobility.

The "inductive" mobility \( \mu'' \) is given by:

\[
\mu'' = \frac{q \tau}{m_e} \frac{\omega \tau}{(1 + \omega^2 \tau^2)}
\]

\[
= \mu_o \frac{\omega \tau}{(1 + \omega^2 \tau^2)} \quad 6.7.5 - 9
\]
There are several ways of presenting graphically the information in equations 6.7.5 - 3 & 9. The particular interest is in the behaviour of Ge at the CO₂ frequency 23.3 THz (ω = 1.73 x 10^{14} \text{ rad/s.}). The value of \gamma changes as the Ge temperature rises, so we look for a "universal" plot, in terms of which the ω scale can be interpreted given a value of \gamma.

We write \( x = \omega \gamma \), and note that:

\[
\sigma' = \left( \frac{1}{1 + x^2} \right) \sigma_0 \quad 6.7.5 - 10
\]

\[
\sigma'' = \left( \frac{x}{1 + x^2} \right) \sigma_0 \quad 6.7.5 - 11
\]

where \( \sigma_0 \) is the D.C. conductivity.

The two factors determining in-phase and quadrature components are plotted:

a) on linear scales over a restricted range (Fig.6.7.5 - 1)

b) on logarithmic scales (Fig.6.7.5 - 2)

c) on an Argand or Bode type presentation (Fig.6.7.5 - 3)

The data, and the Figs.6.7.5 - 1,2,3 show that the quadrature conductivity reaches a peak of \( \frac{1}{2} \sigma_0 \) when \( \omega \gamma = 1 \); and that the change from in-phase current to quadrature current is confined to \( \sim 2 \) decades in \( \omega \gamma \).
Table 6.7.5-2

<table>
<thead>
<tr>
<th>T</th>
<th>$\mu_e$</th>
<th>$\langle \tau \rangle_e$</th>
<th>$\mu_h$</th>
<th>$\langle \tau \rangle_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>m$^2$/Vs</td>
<td>s</td>
<td>m$^2$/Vs</td>
<td>s</td>
</tr>
<tr>
<td>300</td>
<td>0.38</td>
<td>3 - 13</td>
<td>0.18</td>
<td>4.0 - 13</td>
</tr>
<tr>
<td>600</td>
<td>0.1</td>
<td>7 - 14</td>
<td>0.03</td>
<td>6.3 - 14</td>
</tr>
<tr>
<td>1000</td>
<td>0.03</td>
<td>2.1 - 14</td>
<td>0.008</td>
<td>1.7 - 14</td>
</tr>
<tr>
<td>1200</td>
<td>0.02</td>
<td>1.4 - 14</td>
<td>0.005</td>
<td>1.0 - 14</td>
</tr>
</tbody>
</table>
The data for the plots is tabulated in Table 6.7.5 - 1:

Table 6.7.5 - 1

<table>
<thead>
<tr>
<th>\omega \tau \equiv \chi</th>
<th>\langle \chi \rangle</th>
<th>\frac{1}{1 + x^2}</th>
<th>\frac{x}{1 + x^2}</th>
<th>\text{Angle of phase lag}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\omega = 1.73 \times 10^{14} \text{ s}^{-1}</td>
<td>s</td>
<td>\text{in phase}</td>
<td>\text{quadrature}</td>
<td>\text{degrees}</td>
</tr>
<tr>
<td>0.01</td>
<td>6.0</td>
<td>-17</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>0.1</td>
<td>6.0</td>
<td>-16</td>
<td>0.99</td>
<td>0.1</td>
</tr>
<tr>
<td>0.5</td>
<td>2.8</td>
<td>-15</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>0.6</td>
<td>3.4</td>
<td>-15</td>
<td>0.74</td>
<td>0.44</td>
</tr>
<tr>
<td>0.7</td>
<td>3.9</td>
<td>-15</td>
<td>0.67</td>
<td>0.47</td>
</tr>
<tr>
<td>0.8</td>
<td>4.5</td>
<td>-15</td>
<td>0.61</td>
<td>0.49</td>
</tr>
<tr>
<td>0.9</td>
<td>5.1</td>
<td>-15</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>1.0</td>
<td>6.0</td>
<td>-15</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>2.0</td>
<td>1.1</td>
<td>-14</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>3.0</td>
<td>1.7</td>
<td>-14</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>4.0</td>
<td>2.2</td>
<td>-14</td>
<td>0.06</td>
<td>0.24</td>
</tr>
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<td>5.0</td>
<td>2.8</td>
<td>-14</td>
<td>0.04</td>
<td>0.19</td>
</tr>
<tr>
<td>10</td>
<td>6.0</td>
<td>-14</td>
<td>0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>100</td>
<td>6.0</td>
<td>-13</td>
<td>0.0001</td>
<td>0.01</td>
</tr>
<tr>
<td>1000</td>
<td>6.0</td>
<td>-12</td>
<td>10^{-6}</td>
<td>0.001</td>
</tr>
</tbody>
</table>

That Fig. 6.7.5 - 3 is a semi-circle needs to be demonstrated.

In the auxiliary diagram Fig. 6.7.5 - 4, if the figure is a semi-circle, then $\angle ACB$ is a right angle (angle in a semicircle).

It follows that

$\angle CAD = \angle DCB = \beta$

But $\tan \beta$ may be expressed in two ways; one from $\triangle ADC$ and the other from $\triangle CDB$. 

![Fig. 6.7.5 - 4](image)
From $\triangle ADC$, $\tan \beta = \frac{x}{(1 + x^2)^{1/2}} \cdot \frac{1 + x^2}{1} = x$

From $\triangle CDB$, $\tan \beta = \frac{1 - \frac{1}{(1 + x^2)^{1/2}}}{\frac{x}{(1 + x^2)^{1/2}}} = \frac{1 + x^2 - 1}{(1 + x^2)} \cdot \frac{(1 + x^2)}{x} = x$

Therefore $\angle CAD$ does equal $\angle DCB$; $\angle ACB = \angle t$, and the figure is a semi-circle.

To interpret the diagram in terms of germanium, the value of $\gamma$, and its behaviour with $T$ is required.

Equation 6.7.2 - 8 is recalled:

$$\mu_c = \frac{e \gamma}{m_c}$$  \hspace{1cm} 6.7.5 - 12

where the subscripts $c$ refer to conductivity, i.e., $m_c$ is the conductivity effective mass of the carrier concerned.

For a semiconductor with ellipsoidal constant energy surfaces in the conduction band (such as germanium), $m_c$ is given (by ref. 24 page 104):-

$$\frac{1}{m_c} = \frac{1}{3} \left( \frac{1}{m_L} + \frac{2}{m_T} \right)$$  \hspace{1cm} 6.7.5 - 13

Where $m_L$, $m_T$ are the longitudinal and transverse effective masses respectively. This gives a value somewhat different from the density of states effective mass previously used. For
electrons in germanium,

\[ m_{l} = 1.538 \, m_{o} \]

\[ m_{T} = 0.08152 \, m_{o} \]

which gives

\[ m_{c} = 0.119 \, m_{o} \]

where \( m_{o} \) is the free electron mass.

For holes

\[ m_{c} = 0.36 \, m_{o} \]

The equation 6.7.5 - 12 is derived under the assumption that \( \gamma \) is not a function of carrier energy. For germanium, since the mean free path \( l \) is independent of energy, it follows that

\[ \gamma = \alpha \varepsilon^{-\frac{1}{3}} \] (see equation 6.7.2 - 11).

In this case (ref.25 page 46),

\[ \mu_{c} = \frac{e \overline{\tau}}{m_{c}} + \frac{e}{3 \hbar^{2}} \left\langle k^{2} \frac{\partial \gamma}{\partial \varepsilon} \right\rangle \] 6.7.5 - 14

where \( k \) is the electron wave number, with \( \overline{\tau} \) and \( \left\langle \right\rangle \) representing a statistical average.

The mobility may be formally written

\[ \mu_{c} = \frac{e \left\langle \tau \right\rangle}{m_{c}} \] 6.7.5 - 15

where \( \left\langle \tau \right\rangle \) is an equivalent relaxation time, not equal to \( \overline{\tau} \).

It can be shown that for a non-degenerate spherical band where \( \tau \) varies with energy as

\[ \tau = \alpha \varepsilon^{-s} \]

then:

\[ \tau = \alpha \left( kT \right)^{-s} \frac{\Gamma(\frac{5}{2} - s)}{\Gamma(\frac{5}{2})} \] 6.7.5 - 16

where \( k \) is here Boltzmann's constant, and \( \Gamma \) is the Gamma function. (see section 6.6.5).
To find values of equivalent relaxation time $\langle \tau \rangle$, the values of mobility in Table 6.6.5 - 1 are used in equation 6.7.5 - 15, and the values tabulated in Table 6.7.5 - 2.

Smith quotes a figure of $\tau = 6 \times 10^{-13}$ s (ref. 24 page 101) with a value of 0.3 for the effective mass. Both the concept of $\langle \tau \rangle$ and of $m_c$ leave some considerable uncertainty as to the numerical value that should be assigned to them. Two of the difficulties will be mentioned; the first is that the effective mass $m_c$ is measured usually in a cyclotron experiment which implies a material temperature of $\approx 4$ K and $m_c$ is temperature dependent. The other is that germanium has multiple valance bands giving rise to light holes, heavy holes and split-off holes, each with a characteristic effective mass. The value of conductivity mass used in equation 6.7.5 - 15 is therefore an average. Further no allowance for the variation of $m_c$ with temperature can be made in calculating $\langle \tau \rangle$.

It follows that the values for $\langle \tau \rangle$ in Table 6.7.5 - 2 are indicative rather than precise.

But it is quite clear from figure 6.7.5 - 3 that the conductivity in germanium at 28.3THz is essentially in quadrature lagging the driving field.

A numerical value for $\langle \tau \rangle$ has been established for the temperature range of interest. Now the laser frequency conductivity as determined by the theoretical expressions, and the experimental values of D.C conductivity $\sigma_0$ will be tabulated. Values of $\sigma_0$ are taken from Table 6.7.3 - 3.
6.109

effective mass; electron \( m_c = 0.12\ m_0 \)
hole \( m_c = 0.36\ m_0 \)

Table 6.7.5 - 3

<table>
<thead>
<tr>
<th>( T )</th>
<th>( \langle \tau \rangle )</th>
<th>( \sigma_0 )</th>
<th>( \frac{1}{1 + \chi^2} )</th>
<th>( \sigma' )</th>
<th>( \frac{x}{1 + \chi^2} )</th>
<th>( \sigma'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>( 10^{-14}\ s )</td>
<td>(( \Omega\ m ))^{-1}</td>
<td>in phase</td>
<td>(( \Omega\ m ))^{-1}</td>
<td>quadrature</td>
<td>(( \Omega\ m ))^{-1}</td>
</tr>
<tr>
<td>300</td>
<td>30</td>
<td>2.2 0</td>
<td>4.7 -4</td>
<td>1.0 -3</td>
<td>2.2 -2</td>
<td>4.8 -2</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
<td>8.6 1</td>
<td>1.3 -3</td>
<td>1.1 -1</td>
<td>3.6 -2</td>
<td>3.1 0</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>7.5 2</td>
<td>2.6 -3</td>
<td>2.0 0</td>
<td>5.1 -2</td>
<td>3.9 1</td>
</tr>
<tr>
<td>600</td>
<td>7</td>
<td>2.9 3</td>
<td>7.0 -3</td>
<td>2.0 1</td>
<td>8.3 -2</td>
<td>2.4 2</td>
</tr>
<tr>
<td>700</td>
<td>5</td>
<td>7.9 3</td>
<td>1.4 -2</td>
<td>1.2 2</td>
<td>1.2 -1</td>
<td>9.3 2</td>
</tr>
<tr>
<td>800</td>
<td>3</td>
<td>1.7 4</td>
<td>2.8 -2</td>
<td>4.7 2</td>
<td>1.6 -1</td>
<td>2.8 3</td>
</tr>
<tr>
<td>900</td>
<td>3</td>
<td>2.8 4</td>
<td>4.5 -2</td>
<td>1.3 3</td>
<td>2.1 -1</td>
<td>5.3 3</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
<td>4.4 4</td>
<td>7.0 -2</td>
<td>3.1 3</td>
<td>2.6 -1</td>
<td>1.1 4</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>6.1 4</td>
<td>1.1 -1</td>
<td>6.9 3</td>
<td>3.2 -1</td>
<td>1.9 4</td>
</tr>
<tr>
<td>1200</td>
<td>1</td>
<td>8.2 4</td>
<td>1.6 -1</td>
<td>1.3 4</td>
<td>3.7 -1</td>
<td>3.0 4</td>
</tr>
<tr>
<td>1210</td>
<td>1</td>
<td>8.3 4</td>
<td>1.7 -1</td>
<td>1.4 4</td>
<td>3.7 -1</td>
<td>3.1 4</td>
</tr>
</tbody>
</table>

It must be remembered that the conductivity \( \sigma' \) is the sum of electron and hole conductivities \( (\sigma'_e + \sigma'_h) \). At any temperature, if the relaxation time \( \langle \tau \rangle_e \) is different from that of \( \langle \tau \rangle_h \), the separate high frequency ratios \( \sigma''/\sigma_0 \) and \( \sigma''/\sigma_0 \) will have to be calculated for both electrons and holes, in order to arrive at the correct sum terms \( (\sigma'_e + \sigma'_h) \) and \( (\sigma''_e + \sigma''_h) \) for the high frequency conductivity. But looking at the values for \( \langle \tau \rangle_e \) and \( \langle \tau \rangle_h \) in Table 6.7.5 - 2, there is insufficient evidence of widely different \( \langle \tau \rangle \) values; certainly the case for
the more lengthy procedure cannot be justified. The $\sigma_0$ term is treated therefore as a single entity in calculating the entries for Table 6.7.5 - 3.

Note as the temperature rises toward the melting point of germanium, the change in $\langle \tau \rangle$ produces approximately a 360 fold increase in the ratio of high frequency (in-phase) conductivity to D.C. conductivity over the range 300K - 1200K. The D.C. conductivity $\sigma_0$ changes by a factor of $\sim 4 \times 10^4$ over the same temperature range; it follows that the high frequency conductivity changes in the ratio $4 \times 10^4 \times 360 = 1.4 \times 10^7 \sim 10^7$ i.e. about a ten million to one increase over the temperature range.

It is worth considering the physical significance of that result. Is it a reasonable conclusion that as the temperature of the germanium increases from 300K - 1200K, the D.C. conductivity increases by $4 \times 10^4$ times, while the infra-red conductivity increases more than $10^7$ times? This, when $\langle \tau \rangle$ is decreasing with a stronger than $T^{-3/2}$ dependence?

It is a reasonable conclusion. The reducing value of $\langle \tau \rangle$ pulls the driven current more into phase, so that a greater proportion of the carrier K.E. is transferred to the lattice. The reduction in $\sigma_0$ brought about by decreasing $\langle \tau \rangle$ is far outweighed by the increase in $\sigma_0$ due to increasing $n_i$ (as always in semiconductors). Therefore, at the I.R. frequency, taking a higher proportion of the $n_i$ increased $\sigma_0$ leads to $d\sigma_0/dT$ being considerably larger than $d\sigma_0/dT$.

This result is of considerable significance. It means that the runaway condition can occur at lower beam intensities than would otherwise have been expected.
Section 6.7.6 Computational model for I.R. conductivity $\sigma'$. 

The previous section has established the calculated behaviour of $\sigma' = \sigma'(T)$ based on measured D.C. conductivity $\sigma_c = \sigma_c(T)$, and estimates of $\langle \tau \rangle$ using extrapolations of $\mu = \mu(T)$. The I.R. conductivity $\sigma'$ is required as a step toward the coefficient of absorption $\alpha = \alpha(T)$, and then to the internal heat source, $q_v = q_v(T)$ of equation 6.3 - 4.

As before, a computational model may be based on the physics by retracing at any prescribed temperature the steps outlined over the last few sections.

Previously, it has been possible to find an expression through a process of being guided to the required form by the theory, and fitting the empirical results as closely as possible to this. This will be done again.

The final expression(s) will be two or three steps beyond the nearest empirical results, since values of $\sigma'(\text{measured})$ are not available. In the chain of steps from $\sigma_c$ to $\sigma'$ are mobility $\mu$ and effective mass $m_e$, both of which are inferred quantities. Consequently the absolute precision is less certain. The effective mass value could be up to a factor of $\sim 5$ in error over the temperature range. This will be directly reflected in $\langle \tau \rangle$. Reference to Fig.6.7.5 - 3 and to Table 6.7.5 - 1 shows that an estimate of $\langle \tau \rangle = 1 \times 10^{-14}\text{s}$ instead of (say) $6 \times 10^{-14}\text{s}$ would in $\sigma'$ be a $20 : 1$ error. When $\langle \tau \rangle \approx 10^{-12}\text{s}$, an order of magnitude error in $\langle \tau \rangle$ would give rise to two orders of magnitude error in $\sigma'$. 
The I.R. conductivity value $\sigma'$ is sensitive to $\langle \tau \rangle$ as $1/\langle \tau \rangle^2$. The temperature dependence of $\sigma'$ should be reasonably well represented by the models.

The point has been made before that the models should be at their best over the temperature range 270K - 350K, since whether a given circumstance is a "runaway" condition or not will be decided by the physical parameters over this temperature range. Consequently the physical model described in section 6.7.5 is evaluated over the restricted temperature range and tabulated in Table 6.7.6 - 1 as a guide for model performance.

Table 6.7.6 - 1

<table>
<thead>
<tr>
<th>T</th>
<th>$\langle \tau \rangle$</th>
<th>$\sigma^*$</th>
<th>$\frac{1}{1 + x^2}$</th>
<th>$\sigma'$</th>
<th>$\frac{x}{1 + x^2}$</th>
<th>$\sigma''$</th>
<th>$j(\Omega m)^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>(10^{-13}s)</td>
<td>(\Omega m)^{-1}</td>
<td>(10^{-4})</td>
<td>(\Omega m)^{-1}</td>
<td>(10^{-2})</td>
<td>(\Omega m)^{-1}</td>
<td></td>
</tr>
<tr>
<td>260</td>
<td>3.3</td>
<td>0.22</td>
<td>2.9</td>
<td>6.4 -5</td>
<td>1.7</td>
<td>3.7 -3</td>
<td></td>
</tr>
<tr>
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<td>3.1</td>
<td>0.41</td>
<td>3.3</td>
<td>1.4 -4</td>
<td>1.8</td>
<td>7.5 -3</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>2.9</td>
<td>0.73</td>
<td>3.8</td>
<td>2.3 -4</td>
<td>1.9</td>
<td>1.4 -2</td>
<td></td>
</tr>
<tr>
<td>290</td>
<td>2.7</td>
<td>1.3</td>
<td>4.2</td>
<td>5.4 -4</td>
<td>2.1</td>
<td>2.6 -2</td>
<td></td>
</tr>
<tr>
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<td>2.12</td>
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<td>2.2</td>
<td>4.6 -2</td>
<td></td>
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<td>5.3</td>
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<td>7.9 -2</td>
<td></td>
</tr>
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<td>5.4</td>
<td>5.9</td>
<td>3.1 -3</td>
<td>2.4</td>
<td>1.3 -1</td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>2.2</td>
<td>8.2</td>
<td>6.5</td>
<td>5.3 -3</td>
<td>2.5</td>
<td>2.1 -1</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>2.1</td>
<td>12</td>
<td>7.2</td>
<td>8.7 -3</td>
<td>2.7</td>
<td>3.2 -1</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>2.0</td>
<td>18</td>
<td>7.9</td>
<td>1.4 -2</td>
<td>2.3</td>
<td>4.9 -1</td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>1.9</td>
<td>25</td>
<td>8.7</td>
<td>2.2 -2</td>
<td>2.9</td>
<td>7.4 -1</td>
<td></td>
</tr>
<tr>
<td>370</td>
<td>1.8</td>
<td>35</td>
<td>9.5</td>
<td>3.3 -2</td>
<td>3.1</td>
<td>1.1 0</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>1.7</td>
<td>48</td>
<td>10</td>
<td>5.0 -2</td>
<td>3.2</td>
<td>1.5 0</td>
<td></td>
</tr>
<tr>
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<td>1.7</td>
<td>65</td>
<td>11</td>
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<td>3.4</td>
<td>2.2 0</td>
<td></td>
</tr>
<tr>
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<td>86</td>
<td>12</td>
<td>1.1 -1</td>
<td>3.5</td>
<td>3.0 0</td>
<td></td>
</tr>
</tbody>
</table>

*Represented by expression 6.7.3 - 1 = 5.66 x 10^6 exp(-4439/T).
To guide the search for a function to represent $\sigma'$, follow through the temperature dependence of the physical model.

\[
\mu_c \propto T^{-b} \quad ; \quad \langle \tau \rangle \propto T^{-b}
\]

\[
\sigma_c \propto e^{\exp(-C/T)} \quad 6.7.6 - 1
\]

\[
\sigma' \propto \left( \frac{1}{T^{-b}} \right)^2 e^{\exp(-C/T)} \quad 6.7.6 - 2
\]

Over this range $b = 1.66$, and it is reasonable to expect the $\exp(-C/T)$ term to dominate. Dropping the $T^{2b}$ dependence introduces (a max $\sim 10\%$) deviation from the tabulated $\sigma'$ values in such a direction as to tend to compensate the deviations from empirical values introduced by the idealization for $\sigma$ equation 6.7.3 - 1. Therefore equation 6.7.6 - 3 below can be used to represent $\sigma'$ over the range 260K-430K.

\[
\sigma' = 1.09 \times 10^5 \exp(-5543/T) \quad 6.7.6 - 3
\]

At the price of slightly increased complexity, the $T^{2b}$ term may be retained. As this embraces the physical model from which Table 6.7.6 - 1 is prepared, the agreement is exact:

\[
\sigma' = 1.555 \times 10^{-5} T^{-3.32} \exp(-4428/T) \quad 6.7.6 - 4
\]

The range is limited to 500K, because the mobility dependence moves over to a $T^{-2.4}$ dependence above 500K (equn. 6.6.5 - 35).

Therefore,

\[
\sigma' = 6.447 \times 10^{-10} T^{4.8} \exp(-3929/T) \quad 6.7.6 - 5
\]
Although the $T^{4.8}$ dependence is that of the upper temperature range, the expression has been made to serve the lower range (300K-400K) to better than 5% divergence from the tabulated values. It therefore reproduces the whole range of $\sigma'$ very satisfactorily.

Equation 6.7.6 - 5 is the preferred expression for reproducing $\sigma'(300K-1210K)$.

Since the coefficient of absorption is directly related to $\sigma'$, and since the unstable condition of runaway is determined by a number of factors*, one of which is $\frac{d\sigma}{dT} (\propto \frac{d\sigma'}{dT})$, it is useful to have an expression capable of reproducing $d\sigma'/dT = d\sigma'/dT(T)$.

To obtain the expression, the differences $\Delta \sigma'$ over 10 degree increments were tabulated using Table 6.7.6 - 1 values. These were then fitted to the expression below. To guide the search, the analysis below was used. To fit the values well for 300K-400K is considered important, because of the solution sensitivity here.

In general:-

$$\sigma' = AT^{2b} \exp(-C/T)$$

where A & C are constants.

$$\frac{d\sigma'}{dT} = A \left[ 2b T^{(2b-1)} + \frac{C T^{-2b}}{T^2} \right] \exp \left( -\frac{C}{T} \right)$$

*discussed in more detail in subsequent sections.
The power $b$ is 1.66 below 500K; call it 1.5 for convenience, and:

$$\frac{d\sigma'}{dT} = A \left[ 3T^2 + CT^{3/2} \right] \exp\left( -\frac{C}{T} \right)$$

$$= AT^{3/2} \left[ 3\sqrt{T} + C \right] \exp\left( -\frac{C}{T} \right) \quad 6.7.6 - 8$$

at 400K, $3\sqrt{T} = 60$, while $C \approx 5000$.

$$\frac{d\sigma'}{dT} \approx AT^{3/2} \exp\left( -\frac{C}{T} \right)$$

As usual, it is worth trying the straightforward exponential relationship: An excellent reproduction is obtained (300K-400K) with:

$$\frac{d\sigma'}{dT} = 855 \exp\left( -\frac{4931}{T} \right) \quad 6.7.6 - 9$$

At the higher temperatures this expression is expected to serve, since solution sensitivity to $d\sigma'/dT$ is expected to be very weak.

Expression 6.7.6 - 9 will be used to reproduce $d\sigma'/dT$.

Confidence in the expression over the range 300K-400K is the same as that for the $\sigma'$ expression.
Section 6  Material parameters - their temperature dependence.


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References section 6 cont.


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Section 7 Electromagnetic wave propagation.

7.1 Introduction.

The aim of this work is to set up a computer model which describes the heating of a specimen of germanium by a beam of I.R. radiation at the CO₂ laser frequency.

The beam passes from free space (in fact gas at atmospheric pressure) into the germanium, involving reflection and transmission at the interface. Once in, the beam is absorbed with a consequent reduction of intensity along its path.

Given an incident intensity, I₀, a detailed knowledge of the intensity I along the beam path (co-ordinate z) is required. The relationships between the parameters describing e-m wave propagation, and the material parameters are required. In a semiconductor, the parameters of interest change rapidly with temperature, and so it is expected that the optical parameters of the problem will vary over a wide range.

In section 7, these relationships are described.

As well as radiation passing through the germanium specimen, it is of interest to investigate the possibility of surface waves being stimulated and supported in the interface. The temperature range of interest (300K-1200K) covers a wide range of magnitudes in the parameters of interest, so that the details concerning surface waves may also cover a variety of conditions. These will be examined.

The work of this section is based firmly in Moss et al 1973,
Smith (2nd Edn) 1978, Kruse 1962, and Waldron 1970 (refs.40,24,37,38). The books concern visible, IR, and microwave radiation. There is a large area of common ground between microwave specialists and optical/IR specialists.

The common ground in symbol usage is much less obvious; in fact, it is a minefield. So much so, this author has decided to devote the next section 7.2 to listing the symbols used in section 7, at least those where different usages are most prevalent. The approach of optimum value in the present problem has been adopted; the best has been distilled from the sources mentioned, and combined with some ideas of the author.

Maximum clarity with maximum precision has been sought. The text is intended to be to the point rather than comprehensive in its coverage. The aspects required for this problem are noted; adjacent and lead-in topics are omitted.
7.2 Symbol assignment.

Because of the variety of usage in the literature, and the need to use symbols for more than one entity, the meaning of symbols used in section 7 are detailed here for easy reference.

<table>
<thead>
<tr>
<th>Quadrature operator ($\sqrt{-1}$)</th>
<th>$j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In free space; velocity, wavelength</td>
<td>$C_0$, $\lambda_0$</td>
</tr>
<tr>
<td>In material; velocity, complex velocity, wavelength</td>
<td>$C$, $C^*$, $\lambda$</td>
</tr>
<tr>
<td>Electric field; instantaneous, peak</td>
<td>$E$, $E_0$</td>
</tr>
<tr>
<td>Electric induction (usual)</td>
<td>$D_u$</td>
</tr>
<tr>
<td>Generalised electric induction (complex)</td>
<td>$D$</td>
</tr>
<tr>
<td>Electric dipole moment per unit vol.</td>
<td>$P$</td>
</tr>
<tr>
<td>Electric susceptibility</td>
<td>$\chi$</td>
</tr>
<tr>
<td>Electric permittivity; absolute, relative, free space</td>
<td>$\varepsilon_0$, $\varepsilon_r$, $\varepsilon_0$</td>
</tr>
<tr>
<td>Generalised relative permittivity (complex)</td>
<td>$\varepsilon = \varepsilon' - j\varepsilon''$</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>$H$</td>
</tr>
<tr>
<td>Magnetic induction</td>
<td>$B$</td>
</tr>
<tr>
<td>Magnetic permeability; absolute, relative, free space</td>
<td>$\mu\mu_0$, $\mu_r$, $\mu_0$</td>
</tr>
<tr>
<td>Current density</td>
<td>$J$</td>
</tr>
<tr>
<td>Conductivity at zero frequency</td>
<td>$\sigma_0$</td>
</tr>
<tr>
<td>Conductivity (complex) at frequency of interest</td>
<td>$\sigma - \sigma' - j\sigma''$</td>
</tr>
<tr>
<td>Charge; general, electronic, density of</td>
<td>$q$, $e$, $\rho$</td>
</tr>
<tr>
<td>Mass; free electron, effective conductivity, electron, hole</td>
<td>$m_0$, $m_e$, $m_h$</td>
</tr>
<tr>
<td>Carrier relaxation time; simple, averaged</td>
<td>$\tau$, $\langle \tau \rangle$</td>
</tr>
<tr>
<td>Number density; electrons, holes, intrinsic</td>
<td>$N_e$, $N_h$, $n_i$</td>
</tr>
<tr>
<td>Energy dissipation constant</td>
<td>$g$</td>
</tr>
<tr>
<td>Wave propagation; direction, constant (complex)</td>
<td>$z$, $\nu$</td>
</tr>
<tr>
<td>Frequency; radian, normal</td>
<td>$\omega$, $\nu$</td>
</tr>
<tr>
<td>Generalised refractive index (complex)</td>
<td>$n^* = n - jk$</td>
</tr>
<tr>
<td>Refractive index</td>
<td>$n$</td>
</tr>
<tr>
<td>Absorption constant (amplitude)</td>
<td>$k$</td>
</tr>
<tr>
<td>Extinction coefficient (amplitude)</td>
<td>$K$</td>
</tr>
<tr>
<td>Coefficient of absorption (power)</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Reflection; power, amplitude</td>
<td>$R$, $r$</td>
</tr>
<tr>
<td>Transmission; power, amplitude</td>
<td>$T$, $t$</td>
</tr>
<tr>
<td>Time (distinguished by context)</td>
<td>$t$</td>
</tr>
<tr>
<td>Radiation intensity; local, incident</td>
<td>$I$, $I_0$</td>
</tr>
<tr>
<td>Time differential operator for monochromatic disturbance</td>
<td>$j\omega$</td>
</tr>
<tr>
<td>Conductivity mobility at zero frequency; electrons, holes</td>
<td>$\mu_e$, $\mu_n$</td>
</tr>
</tbody>
</table>
Section 7.3 **Electromagnetic waves.**

This problem requires that the interaction between e-m radiation at \( \nu = 23.3 \text{THz} \) and germanium at various temperatures be characterized. The material properties, particularly free carrier density \( n_i \), are a fast function of temperature, and it may be expected that the optical properties change, also as a rapid function of temperature.

Germanium, particularly at elevated temperatures, may be classed optically as a lossy semiconductor. That is, both the lattice and the free carriers play a significant role in determining the optical properties. The material lies optically between a loss free dielectric and the case of a metal. The theory describing these two cases is therefore inadequate for the present case.

We shall develop a generalised theory which, by extending the meanings of relative permittivity, conductivity, and electric induction, enables Maxwell's equations, as simplified for a loss free dielectric, to be retained. The plane wave standard solution is also retained. The mathematical formalism is retained, and looks familiar, but the extended symbolic meaning has to be continually borne in mind during interpretation.

First, the extended meanings of terms will be described and explained. It will then be shown that the Maxwell equations are still true using the generalised quantities. The standard
plane wave solution is presented, followed by a statement of relationships that derive from the wider interpretation and which concern attenuation of the wave by the material.

7.3.1 Generalised $D_u$ and $\varepsilon_L$.

Using $D_u$ to represent the electric induction with the usual meaning, and $\varepsilon_L$ to represent the relative permittivity with the usual meaning, then:

$$D_u = \varepsilon_L \varepsilon_0 E$$  \(7.3.1 - 1\)

The subscript $L$ has been appended to $\varepsilon_L$ to indicate that $\varepsilon_L$ is a parameter which describes the behaviour of the bound electrons in the material, predominantly the valence electrons. The bound electron contribution is frequently referred to as the lattice contribution.

The parameter $\varepsilon_L$ contains information about the displacement from an equilibrium position of the bound charges in response to an applied field $E$. The sequence of relationships below confirm the point:

$$P = \chi \varepsilon_0 E$$  \(7.3.1 - 2\)

$P$ is clearly a direct function of bound charge displacement. $D_u$ is defined as:

$$D_u = \varepsilon_0 E + P$$  
$$= \varepsilon_0 (1 + \chi) E$$  \(7.3.1 - 3\)

If we write:

$$\varepsilon_L = (1 + \chi)$$  \(7.3.1 - 4\)
then

\[ D_u = \varepsilon_L \varepsilon_0 E \]

so that both \( \varepsilon_L \) and \( D_u \) are parameters defined to take account of the displacement of bound charges from an equilibrium position by an electric field.

These quantities are defined in terms of static fields. We wish to treat alternating fields. The most convenient time dependence to consider is \( e^{\text{exp} j \omega t} \). In optical terms that corresponds to a monochromatic signal. It is sufficiently general, since any time dependence may be represented by a Fourier series of similar terms.

If the bound electrons are driven by an alternating field \( E = E_0 e^{\text{exp} j \omega t} \), the charge displacement will be in phase with \( E \) for low frequencies. But at higher frequencies a quadrature component will become evident lagging the field \( E \). Then \( \varepsilon_L \) properly requires the in-phase and the quadrature terms:

\[ \varepsilon_L = \varepsilon'_L - j \varepsilon''_L \]

There is no reason to consider only bound charges. Driven by an alternating field, the "free" carrier gas will execute a net simple harmonic motion about an equilibrium charge distribution. In this case, for low frequencies, the drift velocity is in phase with \( E \), so that the displacement lags \( E \). We show later that this may be taken into account by adding \( (-j \sigma/\omega \varepsilon_0) \) to the relative permittivity:

\[ \varepsilon = \varepsilon_L - j \sigma/\omega \varepsilon_0 \]
The conductivity as normally understood is the ratio $J/E$, both in phase. The carrier scattering ensures that the carrier drift velocity (hence $J$) is in phase with $E$, provided there are a large number of scattering events per cycle of field alternation. For frequencies approaching optical frequencies ($\sim 10^{15}$ Hz), this limitation no longer holds, since $\langle \tau \rangle = 10^{-13}$ s typically. Scattering events during a cycle time are rare. The carrier response to the driving field then resembles the free space behaviour, for which the acceleration is in phase with $E$. The velocity (hence $J$) then lags $E$ by $90^\circ$.

Account may be taken of this by defining a complex conductivity:

$$\sigma = J/E = \sigma' - j\sigma'' \tag{7.3.1-7}$$

which takes account of the phase of $J$ with respect to $E$. Only $\sigma'$ is dissipative, $\sigma''$ may be described as inductive.

Now an electric induction $D$, and a relative permittivity may be defined which takes account of all the foregoing points. Using equations 7.3 - 5 and 7.3 - 7 in 7.3 - 6:

$$\varepsilon = \varepsilon_L - j\sigma'\omega\varepsilon_0 \tag{7.3.1-6}$$

$$\varepsilon = \langle (\varepsilon' - j\varepsilon'') - j/\omega\varepsilon_0(\sigma' - j\sigma'') \rangle \tag{7.3.1-7}$$

$$\varepsilon = \langle (\varepsilon'_L - \sigma''/\omega\varepsilon_0) - j(\varepsilon'' - \sigma'/\omega\varepsilon_0) \rangle \tag{7.3.1-8}$$

and

$$D = \varepsilon_0 E \tag{7.3.1-1}$$

$$D = \langle (\varepsilon'_L - \sigma''/\omega\varepsilon_0) - j(\varepsilon'' - \sigma'/\omega\varepsilon_0) \rangle \varepsilon_0 E \tag{7.3.1-9}$$
The reader will note the use of symbols. The deliberate decision was made to use the traditional quantity symbol with a generalised meaning. The attentive reader should not encounter difficulty - a constant awareness of the bound - and free - electron (hole) contribution, both in-phase and in-quadrature, is all that is required.

The symbol usage keeps subscripts and 's to a minimum, maintaining a simple uncluttered appearance. The overwhelming beauty of describing the intricate complexity of the e-m wave interaction with a lossy semiconductor using Maxwell's equations reduced to handle a lossless dielectric is the reward.

Whilst making these points concerning usage, let it be understood that the quantities E, D, H, B, P, J are all vector quantities. It was decided not to clutter them with bars-over, or arrows. No heavy typeface was available. The experienced reader will not find difficulty. Consideration is limited to linear isotropic materials, so that the vectors in any one equation are (usually) parallel. The treatment as given is for homogenous materials, though it may be extended to inhomogenous materials if the vector operators div and curl are allowed to operate on the scalars \( \sigma, \epsilon, \) etc., as appropriate.

The final caveat; the extended usages, and the particular forms of Maxwell's equations that follow using the operation \( \nabla \times \frac{\partial \mathbf{E}}{\partial t} = j \omega \mathbf{J} \) are only valid for the time dependence \( \exp(j \omega t) \).
7.3.2 **Maxwell's equations.**

Electromagnetic theory is based on Maxwell's equations.

\[
\begin{align*}
(1) \quad \text{div } D &= \rho \\
(11) \quad \text{div } B &= 0 \\
(111) \quad \text{curl } E &= -\frac{\partial B}{\partial t} \\
(1IV) \quad \text{curl } H &= \frac{\partial D}{\partial t} + J
\end{align*}
\]

Alternative statements in vector and cartesian form are noted, using \( \mathbf{A} \) as a dummy vector:

\[
\text{div } \mathbf{A} = \nabla \cdot \mathbf{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}
\]

\[
\text{curl } \mathbf{A} = \nabla \times \mathbf{A} = \hat{\mathbf{x}} \left( \frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial z} \right) + \hat{\mathbf{y}} \left( \frac{\partial A_y}{\partial z} - \frac{\partial A_z}{\partial x} \right) + \hat{\mathbf{z}} \left( \frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial y} \right)
\]

where \( \hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}} \) are the usual unit vectors in the \( x,y,z \) directions.

In matrix form:

\[
\text{curl } \mathbf{A} = \nabla \times \mathbf{A} = \begin{bmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{bmatrix}
\]

Two of the four Maxwell's equations contain \( D \). First it will be shown that the R.H.S of the fourth may be written \( \partial D/\partial t \) when \( D \) carries its extended meaning. Secondly, it will be shown that 7.3.2 - 1(i) may be simply written \( \text{div } D = 0 \).
Take equation 7.3.2 - 1 (IV):

\[ \text{curl } H = \frac{\partial D_u}{\partial t} + J \]

\[ = \frac{\partial}{\partial t} \left( \varepsilon L \varepsilon_o E \right) + \sigma \varepsilon E \]

\[ = (j \omega \varepsilon L \varepsilon_o + \sigma \varepsilon) E \]

\[ = j \omega \varepsilon_o (\varepsilon - \frac{j \sigma}{\omega \varepsilon_o}) E \]

\[ = j \omega \varepsilon D \]

Therefore we may write 7.3.2 - 1 (iv) in either of the two forms:

\[ \text{curl } H = j \omega D \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 7.3.2 - 2 \]

\[ \text{curl } H = \frac{\partial}{\partial t} \left( D \right) \quad \quad \quad 7.3.2 - 3 \]

where \( D, \varepsilon, \) and \( \sigma \) carry the meanings described in section 7.3.1, and \( \frac{\partial}{\partial t} \neq j \omega. \)

For equation 7.3.2 - 1(i), it has to be shown that the equation holds in the extended meaning,

\[ \text{div } D = 0 \]

Commence with the standard equation 7.3.2 - 1 (IV):

\[ \text{curl } H = \frac{\partial D_u}{\partial t} + J \]

Take the divergence:

\[ \text{div } \text{curl } H = \frac{\partial}{\partial t} (\text{div } D_u) + \text{div } J \]
But div curl = 0;

\[ \text{div } J = \frac{\partial}{\partial t} (\text{div } D) \]

and using the first standard equation 7.3.2 - 1 (i):

\[ - \text{div } J = \frac{\partial}{\partial t} (\rho) \]

which is a general statement of the continuity of current, of which Kirchhoff's law at a junction of several conductors is a particular case, with \( \rho = 0 \) at all times. Replacing \( \frac{\partial}{\partial t} :- \)

\[ - \text{div } J = j \omega \rho \]

Using \( J = \sigma E \);

\[ \rho = j \frac{\sigma}{\omega} \text{ div } E \]

Substituting for \( \rho \) in 7.3.2 - 1(i), the standard equation:

\[ \text{div } D = j \frac{\sigma}{\omega} \text{ div } E \]

\[ \text{div } (\varepsilon_L \varepsilon_0 E) = j \frac{\sigma}{\omega} \text{ div } E \]

\[ \varepsilon_L \varepsilon_0 \text{ div } E = j \frac{\sigma}{\omega} \text{ div } E \]

or \( \varepsilon_0 (\varepsilon_L - j \frac{\sigma}{\omega \varepsilon_0}) \text{ div } E = 0 \)

or \( \varepsilon_0 (\varepsilon_L - \frac{\sigma''}{\omega \varepsilon_0} - j(\varepsilon'' + \frac{\sigma'}{\omega \varepsilon_0})) \text{ div } E = 0 \)

The L.H.S is just the extended meaning of \( D \) discussed in section 7.3.1, and has been derived using only the standard Maxwell equations, and the standard definitions as starting points.
It has been shown that using the generalised meanings of $D$, $\mathbf{E}$, and $\sigma'$, the first and fourth Maxwell equations hold:

\[
\begin{align*}
\text{div } D &= 0 \\
\text{curl } \mathbf{H} &= \frac{\partial D}{\partial t}
\end{align*}
\]

In the next section the plane wave solution of Maxwell's equations will be discussed.

### 7.3.3 Plane waves in a lossy semiconductor.

The symbols $D, \mathbf{E}, \sigma'$ are used with their generalised meanings discussed in section 7.3.1. Also the operator $j\omega = \frac{\partial}{\partial t}$ is freely used as required.

The standard Maxwell form has now been generalised to:

\[
\begin{align*}
(1) & \quad \text{div } D = 0 \\
(\text{II}) & \quad \text{div } B = 0 \\
(\text{III}) & \quad \text{curl } E = -\frac{\partial B}{\partial t} \\
(\text{IV}) & \quad \text{curl } H = -\frac{\partial D}{\partial t}
\end{align*}
\]

Take the curl of the equation (III):

\[
\text{CURL CURL } E = -\frac{\partial}{\partial t} (\text{CURL } B)
\]

\[
= -\frac{\partial}{\partial t} (\mu \mu_0 \text{CURL } H)
\]
Use the vector identity:

\[ \text{CURL CURL } E = \text{grad div } E - \nabla^2 E \]

\[ = - \nabla^2 E \quad 7.3.3 - 3 \]

Since \( \text{grad div } E \equiv 0 \) by equation (i).

Substitute from 7.3.3 - 3 into 7.3.3 - 2; and using 7.3.3 - 1(iv)

\[ \nabla^2 E = \mu \mu_0 \frac{\partial^2}{\partial t^2} (D) \]

\[ \nabla^2 E = \mu \mu_0 \epsilon \epsilon_0 \frac{\partial^2}{\partial t^2} (E) \quad 7.3.3 - 4 \]

Similarly in \( H \):

\[ \nabla^2 H = \mu \mu_0 \epsilon \epsilon_0 \frac{\partial^2}{\partial t^2} (H) \quad 7.3.3 - 5 \]

which are the wave equations for waves travelling with a (complex) velocity:

\[ C^* = \frac{1}{\sqrt{\mu \mu_0 \epsilon \epsilon_0}} \quad 7.3.3 - 6 \]

For waves in vacuo:

\[ C_0 = \frac{1}{\sqrt{\mu_0 \epsilon_0}} \quad 7.3.3 - 7 \]

Take the direction of travel to be \( O_x \), and look for solutions of the form \( \exp(j \omega t + \gamma z) \).

Then:

\[ \frac{\partial}{\partial z} = \gamma; \quad \frac{\partial^2}{\partial z^2} = \gamma^2; \quad \frac{\partial}{\partial t} = j \omega; \quad \frac{\partial}{\partial t} = -\omega \quad 7.3.3 - 8 \]
and in cartesian co-ordinates,

$$\nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

Therefore equations 7.3.3 - 4 & 5 become:

$$\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \omega^2 \mu \mu_o \varepsilon \varepsilon_o \right) \begin{bmatrix} E_x \\ H_y \end{bmatrix} = 0$$

In an infinite medium, there is a plane wave solution;

Therefore \( \frac{\partial}{\partial x} = \frac{\partial}{\partial y} = 0 \)

and equation 7.3.3 - 9 reduces to

$$\gamma^2 = -\omega^2 \mu \mu_o \varepsilon \varepsilon_o$$

$$\gamma = j \omega \sqrt{\mu \mu_o \varepsilon \varepsilon_o}$$

$$\gamma = j \omega / c$$

\( \gamma \) is known as the propagation constant, and is complex.

The plane wave equations are:

$$\begin{bmatrix} E_x \\ H_y \end{bmatrix} = \begin{bmatrix} E_{ox} \\ H_{oy} \end{bmatrix} e^{\gamma \left( j \omega t \pm \frac{\omega}{c} \right)}$$

Since the whole derivation is premised upon the time dependence \( e^{\gamma j \omega t} \), it will be hence-forth be regarded as implicit in all appropriate expressions. Concentrating upon the space \( (\gamma) \) dependence of the electric field, and taking only the wave in the + \( Oz \) direction for the moment;
equation 7.3.3 - 11 becomes:

\[ E = E_0 \exp\left(-j\left(\frac{\omega}{C^*}\right)z\right) \]  

7.3.3 - 12

The refractive index is defined as:

\[ n = \frac{C_0}{C} \]  

7.3.3 - 13

If a complex refractive index is defined as the ratio of the free space velocity to the complex velocity \( C^* \),

\[ n^* = (n - jk) = \frac{C_0}{C^*} \]  

7.3.3 - 14

Then eqn. 7.3.3 - 12 becomes:

\[ E = E_0 \exp\left(-j\frac{\omega}{C^*}(n-jk)z\right) \]  

7.3.3 - 15

\[ = E_0 \exp\left(-\frac{\omega}{C_0} kz\right) \exp\left(-j\frac{\omega}{C_0} n z\right) \]  

7.3.3 - 16

where \( n \) describes the phase velocity

\[ C = \frac{C_0}{n} \]  

7.3.3 - 17

and the absorption constant \( k \) describes the rate of decay of amplitude.

The decay of the radiation, and the consequent material heating are of prime interest in this problem. A short digression to record some inter-relationships between the several descriptive parameters follows.
We note in passing that some writers (e.g. Smith ref. 24) use a parameter $\kappa$ in place of $k$ where:

$$\kappa = \frac{k}{n} \quad \ldots \quad 7.3.3 - 18$$

usually termed the extinction coefficient $\kappa$, although Smith refers to $\kappa$ as the absorption index (ref. 24 page 292).

The coefficient of absorption $\alpha$ describes the loss of radiation power:

$$I = I_o \exp(-\alpha z) \quad \ldots \quad 7.3.3 - 19$$

Comparing this with equn. 7.3.3 - 16, and remembering that intensity $\propto$ (amplitude)$^2$, then

$$\exp(-\alpha) = \left\{\exp\left(-\frac{2}{c_0} k\right)\right\}^2$$

$$\alpha = \frac{2}{c_0} k$$

or

$$\alpha = \frac{4 \pi}{\lambda_0} k \quad \ldots \quad 7.3.3 - 20$$

Now relationships between the complex dielectric constant, the refractive index, and the absorption constant will be established. For a loss free dielectric,

$$n = \sqrt{\epsilon^\prime} \quad \ldots \quad 7.3.3 - 21$$

in the general case:

$$n^* = \sqrt{\epsilon} \quad \ldots \quad 7.3.3 - 22$$

Substituting for $n^*$, and squaring

$$(n - jk)^2 = \mathcal{E} = \mathcal{E}^\prime - j\mathcal{E}^\prime\prime \quad \ldots \quad 7.3.3 - 23$$
Separating real and imaginary parts:-

\[ n^2 + k^2 = \varepsilon' \]
\[ 2nk = \varepsilon'' \]

It is the case that \( \varepsilon' \) and \( \varepsilon'' \) may be related to basic measurable material parameters such as \( N_e, m_0, m_e, e \), and \( \sigma \). On the other hand, for the e-m wave we are interested in phase velocity (and \( \lambda \)), and attenuation. Then if \( n \) and \( k \) are to be related to material properties, they are required in terms of \( \varepsilon' \) and \( \varepsilon'' \):

\[ n = \frac{1}{\sqrt{2}} \left( \sqrt{\left( \varepsilon'^2 + \varepsilon''^2 \right)} + \varepsilon' \right)^{\frac{1}{2}} \]
\[ k = \frac{1}{\sqrt{2}} \left( \sqrt{\left( \varepsilon'^2 + \varepsilon''^2 \right)} - \varepsilon' \right)^{\frac{1}{2}} \]

In this section, the parameters required to characterize an e-m wave in a semiconductor have been set out. The use of standard symbols, but with an extended meaning, is contentious. The author commends it for consideration, as it enables a further level of generalisation to be achieved, whilst maintaining a simplicity in notation.

In the next section, the material parameters are related to \( n \) and \( k \). The aim is to predict from the theoretical relationships the optical properties of germanium over the temperature range \( 300K - 1200K \) from known properties e.g. \( n_i = n_i(T) \) and \( \sigma' = \sigma'(T) \).
7.4 $n, k,$ and $\varepsilon$ related to the material properties.

At the end of the previous section, $n$, $k$, and $\varepsilon$ were connected in equations 7.3.3 - 25 & 26. This section obtains expressions for $\varepsilon_L$, $\varepsilon_L'$, and $\varepsilon_c$ where $\varepsilon_L$ represents the relative permittivity due to bound electrons, and $\varepsilon_c$ represents the relative permittivity due to the mobile carriers (electrons and holes). A later section discusses the evaluation of these properties for germanium over the range 300K-1200K.

7.4.1 The lattice contribution, $\varepsilon_L$.

A detailed quantum mechanical account of $\varepsilon_L$ has been given by a number of authors (references quoted p.28 ref.9), and the results differ little from the classical treatment. It is usual therefore to approach this subject from a classical point of view.

An expression for the (alternating) polarisation produced by a radiation field is required.

Assume for a bound electron a displacement $x$, a restoring force $m_0 w_0^2 x$ and a damping force $m_0 g \frac{dx}{dt}$ where $w_0$ and $g$ are angular frequencies. Then the equation of a bound electron is:

$$m_0 \frac{d^2x}{dt^2} + m_0 g \frac{dx}{dt} + m_0 \omega_0^2 x = -\epsilon E_x \exp(j\omega t)$$

where $E_x \exp(j\omega t)$ is the impressed electric field.
The solution for the complex amplitude $x_o$ is:-

$$x_o = - \frac{e E_x}{m_o} \cdot \frac{1}{\omega_o^2 - \omega^2 + j \omega g}$$

But

$$\varepsilon \varepsilon_o E = \varepsilon_o E + P$$

For a one dimensional system,

$$\varepsilon_L = 1 + \frac{P_x}{\varepsilon_o E_x}$$

But the polarisation $P_x$ is the dipole moment per unit volume.

$$P_x = N_e e x_o$$

Substituting back for $\varepsilon_L$:

$$\varepsilon_L = 1 - \frac{N_e e}{\varepsilon_o} x_o$$

To relate to $\eta$ and $k'$,

$$\varepsilon_L = (n - jk)^2$$

$$\varepsilon_L = 1 + \frac{N_e e^2}{m_o \varepsilon_o} \left\{ \frac{1}{\omega_o^2 - \omega^2 + j \omega g} \right\}$$

Separating in-phase and quadrature parts:-

$$\varepsilon'_L = n^2 - k^2 = 1 + \frac{N_e e^2}{m_o \varepsilon_o} \left\{ \frac{\omega^2 - \omega_o^2}{(\omega_o^2 - \omega^2)^2 + \omega^2 g^2} \right\}$$

$$\varepsilon''_L = 2nk = \frac{N_e e^2}{m_o \varepsilon_o} \left\{ \frac{\omega g}{(\omega_o^2 - \omega^2)^2 + \omega^2 g^2} \right\}$$
The main properties of $\varepsilon_L'$ and $\varepsilon_L''$ will be outlined. The sketch Fig. 7.4.1-1 shows the behaviour of $n$ and $k$.

For a lattice characterized by a single frequency $\Omega_0$, $2n\kappa\omega$ is a maximum at $\Omega_0$. The maximum absorption ($\propto k$) occurs for $\omega \sim \Omega_0$, but $\omega$ slightly greater than $\Omega_0$.

The damping factor $g$ is defined such that when $2n\kappa\omega$ is half the peak value, the frequency displacement from resonance is $\frac{1}{2}g$. That is, $g$ is the bandwidth of the resonance curve.

As $\omega \to 0$, $k$ is low, so that $n^2 - k^2 = n_0^2$, and from 7.4.1 - 7

$$n_0^2 = 1 + \frac{N_e e^2}{m_0 \varepsilon_0 \omega_0^2}.$$  

7.4.1 - 9

To check the theory, note that for Ge, $2n\kappa\omega$ peaks sharply at 0.295 $\mu$m (ref. 4 page 25) ($\omega_0 = 6.39 \times 10^{15}$ s$^{-1}$). If $N_e$ is put equal to four times the atomic density (as Ge has four valence electrons per atom ($N_e = 1.766 \times 10^{29}$ n$^{-3}$)), then:

$$n_0 = 3.9$$

which is close to the observed value $n_0^2 = 15.98$. The dielectric
constant $\varepsilon'_L$ measured at 1MHz (ref.4 page 26) is 15.8 ± 0.2.
These data indicate two things; (a) the classical theory is in satisfactory accord with experiment, and (b) since for germanium, $n_o^2 = n^2$ at 28.3 THz = $\varepsilon'_L$ at 1MHz, then there is no lattice resonant frequency $\omega_0$ close to $2 \times 10^{14} \text{ s}^{-1}$. Therefore the lattice absorption at the laser frequency, should be very small.

7.4.2 Free carrier contributions.

For a non-degenerate band, the quantum mechanical analysis yields essentially the same results as the semi-classical approach. For Ge at 300K, the conduction band (C.B.) electrons meet this criterion. However, for holes, the bands are degenerate, and the semi-classical theory fails.

The theory to be outlined therefore only strictly applies to the conduction band electrons in Ge.

The equation of motion for a C.B. electron is eqn. 7.4.1 - 1 in which the restoring force (and hence $\omega_0$) is zero:-

$$m_e \frac{d^2x}{dt^2} + q \frac{dx}{dt} = -eE_x \exp(j\omega t)$$  \hspace{1cm} 7.4.2 - 1

Note that now the conductivity effective mass $m_e$ is required.

The solution for the complex amplitude is:-

$$x_o = -\frac{eE_x}{m_e} \frac{1}{-\omega^2 + j\omega g}$$  \hspace{1cm} 7.4.2 - 1a
Since this problem is concerned with intrinsic Ge, the density of electrons may be written \( n_i \), so that eqn 7.4.1 - 6 becomes:

\[
\varepsilon_e = 1 - \frac{n_i e^2}{m_e \varepsilon_0} \left\{ \frac{1}{\omega^2 - j\omega q} \right\} \tag{7.4.2 - 2}
\]

where the relative permittivity, due to C.B. electrons is written \( \varepsilon_e \). Separating in-phase and quadrature parts:

\[
\varepsilon_e' = n_i^2 - k^2 = 1 - \frac{n_i e^2}{m_e \varepsilon_0} \left\{ \frac{1}{\omega^2 + q^2} \right\} \tag{7.4.2 - 3}
\]

\[
\varepsilon_e'' = 2nk = \frac{n_i e^2}{m_e \varepsilon_0 \omega} \left\{ \frac{q^2}{\omega^2 + q^2} \right\} \tag{7.4.2 - 4}
\]

The parameter \( \frac{1}{\varepsilon} \) may be identified with the momentum relaxation time. Following Moss et al (ref.4 page 36), integrate eqn 7.4.2 - 1 over a time \( T \) in which many collisions occur:

\[
\left[ \frac{m_e}{d\tau} \right]_0^T + \left[ m_e \mu_e \tau \right]_0^T = -eE \tag{7.4.2 - 5}
\]

Following ref.4 exactly, he says that the first term is zero at each collision. He then implies and uses

\[
\left[ \frac{m_e}{d\tau} \right]_0^T = 0 \tag{7.4.2 - 6}
\]

The term \( \left[ \tau \right]_0^T \) is the total distance travelled \( = E_\mu_e \tag{7.4.2 - 7} \)

(against the field since \( e \)) from the definition of mobility.

Therefore

\[
\varepsilon m_e \mu_e E T = eFT \tag{7.4.2 - 7}
\]
This derivation seems unsound. If it is to stand up at all, \( T \) has to be very short indeed compared to a cycle time, so that \( E \) is quasi-D.C. Only then can the R.H.S. integral be \( -eET \). At the same time the argument requires \( T \gg \tau \). For Ge, frequencies \(~100\text{ MHz}\) and \( T \sim 10^{-10}\text{ s}\) represent reasonable limits to these quantities, since \( \tau \sim 10^{-12}\text{ s}\). Some doubt about its validity at \( 28.3\text{ THz} \) then remains. This doubt may be removed by an alternative approach which avoids involving the mobility \( \mu_e \).

Rewrite eqn. 7.4.2 - 1 in a form emphasising momentum:

\[
\frac{d}{dt} (n_e \frac{dx}{dt}) + g(n_e \frac{dx}{dt}) = -e E_{\infty} \exp(\gamma \omega t)
\]

The first term represents rate of gain of momentum from the driving field. The second term represents rate of loss of momentum due to scattering. Both are instantaneous values, so there is no time restriction as there was previously. Following the arguments which are summarised by equations 6.7.5 - 2 and 3, the second term of 7.4.4 - 1a may be identified with the R.H.S. of 6.7.5 - 3:

\[
g(n_e \frac{dx}{dt}) \equiv \frac{1}{\gamma} \left( m_e \bar{v} \right)
\]

Hence

\[g \equiv \frac{1}{\gamma}
\]
The parameter \( \gamma \) is the momentum relaxation time defined under the assumptions discussed in section 6.7.5. Strictly \( \gamma \) should be averaged over the electron energy distribution and written \( \langle \gamma \rangle \).

The equations for \( \epsilon_e' \) and \( \epsilon_e'' \) are re-expressed in terms of \( \gamma \):

\[
\epsilon_e' = \eta - k^2 = 1 - \frac{n_i e^2}{m_e \varepsilon_o} \left\{ \frac{\gamma^2}{1 + \omega^2 \gamma^2} \right\} 
\]

7.4.2 - 3a

\[
\epsilon_e'' = 2n_k = \frac{n_i e^2}{m_e \varepsilon_o \omega} \left\{ \frac{\gamma}{1 + \omega^2 \gamma^2} \right\} 
\]

7.4.2 - 4a

When \( \omega \gamma \gg 1 \) (as it is for Ge 300K - 1200K when \( \omega \approx 2 \times 10^{14} \, \text{s}^{-1} \)), the first equation reduces to:

\[
\epsilon_e' = 1 - \frac{n_i e^2}{m_e \varepsilon_o \omega^2} 
\]

7.4.2 - 3b

and, since \( \gamma \) has vanished, \( \epsilon_e' \) is independent of the precise scattering mechanism.

Some alternative forms of the second equation are of interest:

\[
\epsilon_e'' = \frac{1}{\omega \varepsilon_o} \frac{n_i e^2 \gamma}{m_e} \frac{1}{1 + \omega^2 \gamma^2} 
\]

7.4.2 - 4c

\[
= \frac{1}{\omega \varepsilon_o} \cdot \sigma \cdot \frac{1}{1 + \omega^2 \gamma^2} 
\]

7.4.2 - 4d

\[
= \frac{\sigma'}{\omega \varepsilon_o} 
\]

7.4.2 - 4e

When \( \omega^2 \gamma^2 \gg 1 \), 7.4.2 - 4d may be rearranged to give:

\[
\epsilon_e'' \omega = 2n_k \omega = n c_o \alpha = \frac{\sigma'}{\varepsilon_o \omega^2 \gamma^2} 
\]

7.4.2 - 10
This last form illustrates the well known $\alpha \propto \lambda_0^2$ law which holds when $n = n_0$ is independent of wavelength. This condition is met for Ge at $\lambda_0 = 10.6\ \mu m$.

For the purposes of this work, the form 7.4.2 - 4e is the most useful, since $\sigma'$ takes into account the variations with temperature (300K - 1200K) of both $\sigma_0'$ and $\tau'$, and is tabulated for Ge in section 6.7.5. Both electron and hole conductivity have been taken into account in the expression. However it is worth noting the separate contributions below.

When both electrons and holes are present, the separate contributions are taken as linearly additive, and proportional to the number density of each $N_e, N_h$. First, the relative permittivity due to the free carriers $\varepsilon'_c$:

$$\varepsilon'_c = 1 - \frac{N_e e^2 \tau_e}{n_e \varepsilon_0 \omega \left(1 + \omega^2 \tau_e^2 \right)} - \frac{N_h e^2 \tau_h}{m_h \varepsilon_0 \omega \left(1 + \omega^2 \tau_h^2 \right)}$$

and using equn. 6.7.5 - 11:-

$$\varepsilon'_c = 1 - \left( \frac{\sigma''_e}{\omega \varepsilon_0} + \frac{\sigma''_h}{\omega \varepsilon_0} \right)$$

$$\therefore \varepsilon'_c = 1 - \frac{\sigma''}{\omega \varepsilon_0}$$

For the case of intrinsic material ($N_e = N_h = n_i$), when $\omega \tau' \gg 1$ (as for Ge at 10.6 $\mu m$), equation 7.4.2 - 11 reduces to:-

$$\varepsilon'_c = 1 - \frac{n_i e^2}{\omega^2 \varepsilon_0 \left( \frac{1}{m_e} + \frac{1}{m_h} \right)}$$

which is independent of the scattering mechanisms for electrons or holes.
Similarly using 7.4.2 - 4e and 7.4.2 - 10, the electron and hole contribution to absorption may be written:

\[
\alpha = \frac{\sigma'}{\hbar c_0 \varepsilon_0} = \frac{1}{\hbar c_0 \varepsilon_0} \left( \sigma_e' + \sigma_h' \right)
\]  

7.4.3 Combining \( \varepsilon_L \) and \( \varepsilon_c \) to give \( \varepsilon \).

This section shows that when a material has a susceptibility due to bound electrons \( \varepsilon_L \), and also due to free carriers \( \varepsilon_c \), it is the susceptibilities that are additive.

\[
\chi_L + \chi_c = \chi
\]  

It is then shown how to obtain \( \varepsilon \) from \( \varepsilon_L \) and \( \varepsilon_c \).

We start from the definition of \( D \):

\[
D = \varepsilon_0 E + P
\]  

where the equation is taken to be perfectly general; it takes account of bound and free electrons, as well as quadrature and in-phase components. If the polarization due to bound electron is \( P_L \), and that due to free carriers is \( P_c \), then:

\[
D = \varepsilon_0 E + P_L + P_c
\]  

But we may write:

\[
P_L = \varepsilon_0 \chi_L E \quad \text{and} \quad P_c = \varepsilon_0 \chi_c E
\]  

Therefore:

\[
D = (1 + \chi_L + \chi_c) E_0 E
\]  

\[
\leq \varepsilon \varepsilon_0 E
\]  

where \( \varepsilon \) is used in the generalised meaning of this work.
Then
\[ \epsilon = 1 + \chi_L + \chi_c \]

It is customary to bracket the 1 with \( \chi_L \), and write
\[ \epsilon = (1 + \chi_L) + \chi_c \]
\[ \epsilon = \epsilon_L + \chi_c \]

where \( \epsilon_L \) is the lattice relative permittivity. Equation 7.4.3 - 8 is the underlying form used in standard texts, although it is usually implicit rather than explicit.

The term \( \epsilon_L \) is usually comprehensively dealt with in texts, and has been discussed here in section 7.4.1. No further remarks are required.

On the other hand, the free carrier contribution is usually arrived at without much discussion of its physical meaning, or that it is really \( \chi_c \) that is being tacked on to \( \epsilon_L \) to give \( \epsilon \).

So consider the charge movements described by \( \chi_c \).

Figure 7.4.3 - 1 represents (arbitrarily) a cylindrical part of conductor, length \( l \), in which the carrier density is \( N \).

Under the influence of an electric field \( E_x = E_0 \exp(jwt) \), the free charges are displaced from their equilibrium by an amount \( \chi \).
The dipole moment = \( N A x e \) \( \hat{L} \)

dipole moment/unit vol = \( N e x \) \( \ldots 7.4.3 - 9 \)

Now \( x \) varies with \( t \) as \( \exp(j\omega t) \) and with amplitude quoted in

equation 7.4.2 - 1a

\[
x_o = \frac{e E_o}{m} \frac{1}{\omega^2 - j\omega g}
\]

\( 7.4.2 - 1a \)

Substituting \( x = x_o \exp(j\omega t) \) into 7.4.3 - 9,

\[
P_o \exp(j\omega t) = N e x
\]

\[
= \frac{N e^2}{m} \left( \frac{1}{\omega^2 - j\omega g} \right) E_o \exp(j\omega t)
\]

\( 7.4.3 - 10 \)

The susceptibility is

\[
\frac{P}{\epsilon_o E} = \frac{P_o \exp(j\omega t)}{\epsilon_o E_o \exp(j\omega t)} = \frac{N e^2}{\epsilon_o m} \left( \frac{1}{\omega^2 - j\omega g} \right)
\]

\( 7.4.3 - 11 \)

and has in-phase and quadrature components. Separating these out:

\[
\chi_c = \chi_c' - j \chi_c''
\]

\( 7.4.3 - 12 \)

\[
\chi_c' = -\frac{N e^2}{\epsilon_o m} \left( \frac{\gamma^2}{1 + \omega^2 \gamma^2} \right)
\]

\( 7.4.3 - 13 \)

\[
\chi_c'' = \frac{N e^2}{\epsilon_o m \omega} \left( \frac{\gamma}{1 + \omega^2 \gamma^2} \right)
\]

\( 7.4.3 - 14 \)

The latter two expressions may be put in terms of the conductivity

\( \sigma_o \), or in terms of \( \sigma = \sigma' - j \sigma'' \):

\[
\chi_c' = -\frac{\sigma_o}{\omega \epsilon_o} \left( \frac{\gamma}{1 + \omega^2 \gamma^2} \right)
\]

\( 7.4.3 - 13a \)

\[
\chi_c'' = \frac{\sigma_o}{\omega \epsilon_o} \left( \frac{1}{1 + \omega^2 \gamma^2} \right)
\]

\( 7.4.3 - 14a \)
or
\[ \chi_c' = -\frac{\sigma''}{\omega \varepsilon_0} \]
\[ \chi_c'' = \frac{\sigma'}{\omega \varepsilon_0} \]

The values for \( \sigma' \) and \( \sigma'' \) for Ge over the temperature range of interest, and at the CO\(_2\) laser frequency have been tabulated in section 6.7.5.

It is worth noting that \( P_L' \) and \( P_c' \) are in antiphase. \( P_L' \) leads \( E \) by 90° (capacitative), and \( P_c' \) lags \( E \) by 90° (inductive). \( P_c' \) is only significant when \( \omega > \gamma \), or the conductivity \( \sigma_0 \) is substantial, as is the case for Ge for temperatures \( \approx 1000K \).

We now wish to combine the contributions to \( \varepsilon \) from bound and mobile electrons.

\[ \varepsilon = (1 + \chi) \]
\[ \varepsilon' - j\varepsilon'' = 1 + \chi' - j\chi'' \]
\[ = 1 + \chi_L' + \chi_c' - j\chi_L'' - j\chi_c'' \]

Therefore:
\[ \varepsilon' = 1 + \chi_L' + \chi_c' \]
\[ \varepsilon' = \varepsilon_L' + \chi_c' \]

and
\[ \varepsilon'' = \chi_L'' + \chi_c'' \]

The optical parameters \( n, k, \) and \( \chi \) may be obtained from \( \varepsilon' \) and \( \varepsilon'' \) by using equations 7.3.3 - 25, and 26, and 7.3.3 - 20.
7.4.4 The Plasma frequency

Under certain conditions, the free electron contribution to \( \epsilon' \) may exactly cancel the bound electron contribution. Then \( \epsilon' \) becomes zero, and the frequency at which it occurs is known as the plasma frequency \( \omega_p, \omega_p \).

For conduction electrons, the plasma frequency is given by:

\[
\omega_p^2 = \frac{N e^2}{\epsilon'_L \epsilon_o m_e}
\]

For intrinsic Ge, electrons and holes are present in equal concentration \( n_i \). Starting from equation 7.4.3 - 15:

\[
\epsilon' = \epsilon'_L + \chi_c
\]
\[
\epsilon' = \epsilon'_L + \chi'_e + \chi'_h
\]

We may now use equation 7.4.3 - 13 adapted to the condition \( \omega \gg 1 \), and for both electrons and holes:

\[
\chi'_c = - \frac{N e^2}{m_e \omega^2 \epsilon_o} - \frac{N h e^2}{m_h \omega^2 \epsilon_o}
\]

\[
= - \frac{n_i e^2}{\omega^2 \epsilon_o} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)
\]

Substituting this back into 7.4.4 - 2:

\[
\epsilon' = \epsilon'_L - \frac{n_i e^2}{\omega^2 \epsilon_o} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)
\]
When $\omega = \omega_p$, $\varepsilon' = 0$, therefore:

$$\omega_p^2 = \frac{n_i e^2}{\varepsilon_L' \varepsilon_0} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)$$

and the only modification to 7.4.4 - 1 required is to the mass term.

For the problem under consideration, the value of $n_i$ required to correspond to the CO$_2$ laser frequency is of interest. Putting the numerical values appropriate for Ge:

$$\omega_p = 1.78 \times 10^{-14} \text{ s}^{-1}$$

$$\varepsilon_L' = 16 \quad m_e = 0.12 \, m_o \quad m_h = 0.36 \, m_o$$

and $n_i = 1.4 \times 10^{25} \text{ m}^{-3}$

Consulting Table 6.5.5 - 2, we see that $n_i$ reaches this value at $\approx 1100\text{K}$, a little lower than the melting point (1210K). The estimated temperature for plasma resonance in Ge is therefore within the range of temperature of interest in this study.

The dispersion relationships may be expressed in terms of $\omega_p$;

$$\varepsilon' = \varepsilon_n^2 k^2 = \varepsilon_L' \left( 1 - \frac{\omega_p^2}{\omega^2 + q^2} \right)$$

$$\varepsilon' = 2 n k = \frac{1}{\omega} \cdot \frac{q \varepsilon_L' \omega_p^2}{\omega^2 + q^2}$$

Briefly, the significance of the plasma frequency may be outlined by considering a lossless material ($\varepsilon' \rightarrow \infty$, $q \rightarrow 0$)

When

$\omega > \omega_p$, \quad $k = 0$, \quad $n \neq 0$

$\omega < \omega_p$, \quad $n = 0$, \quad $k \neq 0$
Refer to Fig. 7.4.4 - 1:

For $\omega > \omega_p$, energy is propagated into the material. As $\omega$ reduces toward $\omega_1$, near $\omega_p$, the refractive index $n \to 1$ and $R$ becomes 0; all the incident energy is propagated into the material. Over a further narrow frequency range from $\omega_1$, to $\omega_p$, $n$ changes from $n = 1$ to $n = 0$ as $R$ rises from $R = 0$ to $R = 1$.

Refer to Fig. 7.4.4 - 1(e)

The physical significance of $\omega_1$ is that the displacement currents (capacitative) due to the bound electrons excited by an incident $\varepsilon - \mu$ wave are exactly cancelled by the response currents (inductive) of the (collisionless) free carriers. The wave environment is then essentially the same as that of free space. Hence $n = 1$, and $R = 0$.

For exciting frequencies between $\omega_1$ and $\omega_p$, the inductive free carrier currents are larger than the bound charge currents; at $\omega_p$ they exactly cancel not only the bound charge displacement current, but also the displacement current of free space. The dielectric constant $\varepsilon'$ becomes zero, which means $n = 0$ and propagation of energy into the material cannot take place. The $H$ field is zero; $R$ becomes unity.

When $\omega > \omega_p$, $n = 0$ and $k$ increases as $\omega$ decreases. $R$ is unity, so no energy is propagated into the material. The wavelength within the material becomes infinite, which means that the plasma moves with the same phase throughout, and a progressively reducing amplitude from the boundary. Since the material is lossless, the $E$ field and the resulting current density (also $H$) are in phase quadrature.
Fig. 7.4.4 - 1
Parameter behaviour around the plasma frequency for a lossless material.
Fig. 7.4.4 - 2
Parameter behaviour around the plasma frequency for a dissipative material.
Refer to Fig. 7.4.4 - 2.

Germanium is a lossy material. This means the presence of an in-phase component of total material current $\mathbf{J}$ when excited by an $e - m$ field. Figs (c), (d) and (e) illustrate the point.

If the displacement current is $\mathbf{J}_D$, and the current due to free carrier response is $\mathbf{J}_c$ in phase, $\mathbf{J}_c''$ in quadrature lagging, then

$$
\mathbf{J} = j\mathbf{J}_D + \mathbf{J}_c
$$

$$
\mathbf{J} = j\mathbf{J}_D + \mathbf{J}_c' - j\mathbf{J}_c''
$$

$$
= \mathbf{J}_c' + j(\mathbf{J}_D - \mathbf{J}_c'')
$$

At the plasma frequency, the quadrature term is zero, leaving only the in-phase free component $\mathbf{J}_c'$. The wave is promoted into the material, but quickly attenuated.

Whether or not in a given material there exist a set of properties derived from the plasma resonance depends on the presence of a quadrature lagging free carrier conductivity, which at all low frequencies exceeds the capacitative conductivity $\sigma_D$ of the bound charges. This will be determined by the carrier density $N$ and the momentum relaxation time $\tau$ according to the inequality 7.4.4 - 12. The conductivities of interest may be expressed:

- Capacitative conductivity, free space

$$
\sigma_{oo} = j\omega \epsilon_0
$$

Due to bound electrons

$$
\sigma_{oB} = j\omega (\epsilon - 1) \epsilon_0
$$

Total displacement conductivity

$$
\sigma = j\omega \epsilon \epsilon_0
$$

Inductive conductivity due to free carriers

$$
\sigma'' = -j\omega \frac{N^2 e^2 \tau^2}{m} \frac{1}{(1 + \omega^2 \tau^2)}
$$

7.4.4 - 11
Refer to Fig. 7.4.4 - 2(c):

It will be noted that at low frequencies ($\omega \tau \ll 1$), the capacitative conductivity $\sigma'$ and the inductive conductivity $\sigma''$ are both proportional to frequency $\omega$. At frequencies around $\omega \tau = 1$, the inductive component begins to drop until at higher frequencies it is falling with increasing $\omega$ as $1/\omega$. Over this frequency range, in the absence of a bound electron resonance, the capacitative conductivity continues to rise linearly with $\omega$.

The condition that plasma resonance may exist:

$$|\sigma'| < |\sigma''|$$

$$\omega \varepsilon'_L \varepsilon_o < \frac{N e^2 \tau}{m} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

at all low frequencies.

At very low frequencies, $\omega \tau \ll 1$, hence

$$\omega \varepsilon'_L \varepsilon_o < \omega \frac{N e^2 \tau^2}{m}$$

or

$$N \tau^2 > \frac{\varepsilon'_L \varepsilon_o m}{\varepsilon^2} \quad \text{(7.4.4-12)}$$

An alternative view of the plasma resonance is that which equates the material quadrature current to zero:

$$\int (\sigma' - \sigma'') = 0$$

$$\omega_p \varepsilon'_L \varepsilon_o = \frac{N e^2 \tau}{m} \frac{\omega \tau}{(1 + \omega^2 \tau^2)} \quad \text{(7.4.4-13a)}$$

$$\omega_p^2 \tau^2 = \frac{N e^2 \tau^2}{\varepsilon'_L \varepsilon_o m} - 1 \quad \text{(7.4.4-13b)}$$

$$\omega_p = \left\{ \frac{N e^2}{\varepsilon'_L \varepsilon_o m} - \frac{1}{\tau^2} \right\}^{1/2} \quad \text{(7.4.4-13c)}$$
Expression 7.4.4 - 13c reduces to the standard one (7.4.4 - 1) if \( \frac{1}{n^2} \) may be neglected, which may be seen (by inspection of 7.4.4 - 13a) equivalent to the condition \( \omega \ll \omega' \). 

The conditions discussed relating to plasma resonance phenomena are of importance to the analysis of the present problem. As the irradiation heats the Ge, the material plasma frequency \( \omega_p \) increases from a fairly low value at 400K (N small, about the lowest capable of displaying plasma resonance) to move through the CO\(_2\) laser frequency in the region of melting, or just below.

A knowledge of the exact phase relationships between the incident field \( E_i \), and the resulting material currents with the consequent re-radiation, are essential to an understanding of the nature of the surface patterns observed on the Ge etalon.
Section 7.5 At the interface

The germanium etalon on which the damage occurred was part of the laser cavity. The field conditions at the etalon surface are consequently particular.

This section sets out pertinent details concerning reflection of radiation incident normally on a Ge-free-space interface. To be exact, the "free-space" is the laser cavity containing a gas mixture at atmospheric pressure.

The case of a low loss dielectric \((k/n)\) is taken first, as relevant to Ge over temperature range \(300K - 800K\). A summary of relationships applying to a lossy dielectric, which are applicable to Ge over the range \(800K - 1200K\) are covered in sections 7.5.4 - 7.5.5.

7.5.1 At a single surface

\[ n_1 \quad \rightarrow \quad n_2 \]

\[ E_r \]

\[ E_t \]

\[ n_1 < n_2 \]

\[ n_1 > n_2 \]

Fig. 7.5.1 - 1
Fig 7.5.1 - 1 shows the electric vector of a normally incident field, with the reflected and transmitted components. The electric field is continuous across the boundary. Reflection is in antiphase where the radiation enters the dielectric.

The magnitude of the electric field increases as the radiation exits.

The amplitude and power coefficients are given by:

\[ r = \frac{n_1 - n_2}{n_1 + n_2} \quad R = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \quad 7.5.1 - 1 \]

\[ t = 1 + r \quad T = \frac{\frac{1}{n_2} n_1^2}{\left( \frac{1}{n_2} + n_1 \right)^2} \quad 7.5.1 - 2 \]

Field continuity across the boundary demands that the algebraic sum of the incident and the reflected field \((1 + r)\) is equal to the transmitted field magnitude \(t\) on the other side of the interface.

This leads to \( t = 1 + r \).

The expressions work both for passing into, and for emerging from a dielectric, provided the subscript 1 is used on the incident side of the interface, and the sign of \( r \) (which indicates phase relative to \( E_i \)) is retained.

Because concern here is only with the case of normal incidence, the convention is adopted that \( r \) is + ve if the reflected field \( E_r \) is in phase with the incident field \( E_i \), and \( r \) is - ve if \( E_r \) and \( E_i \) are in antiphase.
The power transmission coefficient $T$ takes account of both the amplitude coefficient $t$, and the changed velocity of energy propagation.

Applied to Ge at 300K/free space:-

![Diagram](image)

Fig 7.5.1 - 2

7.5.2 Two faces - incoherent light

When the radiation passes through a slab of dielectric, two interfaces are encountered. The net reflection (reflectance, $R_c$) and the net transmission (transmittance, $T_c$) is consequent upon multiple internal reflections. For incoherent radiation, the powers are additive. The values of $R_c$ and $T_c$ for incoherent radiation are set out in this section, and for coherent light in later sections.

![Diagram](image)

Fig 7.5.2 - 1
\[ 1 = T + R \]  
(conservation of energy)  

The transmittance may be expressed:\n\[ T_c = T^2 (1 + R^2 + R^4 + \ldots) \]
\[ T_c = \frac{T}{2 - T} \quad \text{in terms of } T \text{ alone} \]
\[ T_c = \frac{T}{1 + R} \]
\[ T_c = \frac{1-R}{1+R} \quad \text{in terms of } R \text{ alone} \]

The reflectance may be expressed:\n\[ R_c = R + RT^2 (1 + R^2 + R^4 \ldots) \]
\[ R_c = R \left( \frac{1 + T_c}{1 - R} \right) \]
\[ R_c = R \left( \frac{1 + \frac{1-R}{1+R}}{1 - R} \right) \]
\[ R_c = \frac{2R}{1 + R} \]

For Ge at 300 K, \( R = 0.36 \); \( R_c = 0.53 \)
\( T = 0.64 \); \( T_c = 0.47 \)
7.5.3 Two faces - coherent light

For coherent radiation, the amplitudes of the separate components (which result from multiple reflections) are additive.

The reflectance and transmittance of a slab of dielectric illuminated by coherent radiation is a function of slab thickness/\(\lambda\) since this determines the relative phases of the components.

When the dielectric is used as an active component of the laser cavity, only the values of \(T_c\) and \(R_c\) under the condition \(2d = (2m - 1)\frac{\lambda}{2}\) (\(m\) integer) are of practical interest. This produces the maximum possible value of \(R_c\), and forces the laser frequency (hence \(\lambda\)) to comply through the mechanism of cavity gain.

![Diagram of normal incidence](image)

\[2d = (2m - 1)\frac{\lambda}{2}\]

Fig 7.5.3 - 1
The net transmitted amplitude is:

\[ t_c = \frac{\dot{t}_1 t_2 + \dot{t}_2^2 r^2 \exp \left(-\frac{i 2 \lambda d}{\lambda} \cdot 2 \pi \right) + \dot{t}_1 t_2 r^4 \exp \left(-\frac{i 2 \lambda d}{\lambda} \cdot 2 \pi \right)}{1 + r^2} + \ldots \]

Under the condition \(2d = (2m - 1) \frac{\lambda}{2}\), this becomes:

\[ t_c = t_1 t_2 - t_1 t_2 r^2 + t_1 t_2 r^4 - t_1 t_2 r^6 + \ldots \]

\[ t_c = t_1 t_2 (1 - r^2 + r^4 - r^6 + \ldots) \]

\[ t_c = t_1 t_2 \frac{1}{1 + r^2} \]

Using \( t_1 = (1 - |r|) \); \( t_2 = (1 + |r|) \); \( t_1 t_2 = (1 - r^2) \)

\[ t_c = \frac{(1 - r^2)}{1 + r^2} \] \hspace{1cm} 7.5.3 - 1

\[ T_c = \left( \frac{(1 - r^2)}{1 + r^2} \right)^2 \] \hspace{1cm} 7.5.3 - 2

The net reflected amplitude is:

\[ r_c = -r + t_1 t_2 r \exp \left(\frac{-i 2 \lambda d}{\lambda} \cdot 2 \pi \right) + t_1 t_2 r^3 \exp \left(\frac{-i 2 \lambda d}{\lambda} \cdot 2 \pi \right) \]

Under the condition that \(2d = (2m - 1) \frac{\lambda}{2}\):

\[ r_c = -r - t_1 t_2 r + t_1 t_2 r^3 - t_1 t_2 r^5 + \ldots \]

\[ r_c = -r \left(1 + t_1 t_2 (1 - r^2 + r^5 - r^7 + \ldots)\right) \]

\[ r_c = -r \left(1 + t_c\right) \]

\[ r_c = -r \left(1 + \frac{t_1 t_2}{1 + r^2}\right) \]

Using \( t_1 = (1 - |r|) \); \( t_2 = (1 + |r|) \); \( t_1 t_2 = (1 - r^2) \)

\[ r_c = -\frac{2r}{1 + r^2} \] \hspace{1cm} 7.5.3 - 3
For Ge at 300K,

\[ t_c = 0.47 \quad T_c = 0.22 \]

\[ r_c = -0.88 \quad R_c = 0.78 \]

Note that \( r_c \) is in antiphase w.r.t. the incident radiation, which is coherent. For the Ge laser etalon this means that the inside surface (toward cavity) is at a minimum of the resulting standing wave pattern. It follows from the condition

\[ 2d = (2m - 1)\frac{\lambda}{2} \]

that the outside face (exit) is at a standing wave maximum.

These facts will be used in a later section, to assess working field strengths during cavity operation. The presence of the standing wave pattern means that the heating by absorption is far from evenly distributed throughout the material of the etalon.
7.5.4 When \( k \) is significant

Amplitude reflection

As the Ge is heated up by the radiation, the free carrier concentration \( n_1 \) increases, and with it the rate of absorption of \( e - m \) energy. The optical parameter \( k \) is most significantly affected by these changes; \( k \) influences the coefficients describing reflection and transmission. Absorption and absorptance are also required. The following sections set out the relationships required by the problem under investigation.

At a single boundary between a dielectric of index \( n_o \), and a lossy material of index \( (n - jk) \), phase differences are introduced between the quantities \( E_i \), \( E_r \), and \( E_t \). There are a number of cases to be considered. The detailed phase relationships for each case are established in this section.

The electric field is continuous across the surface. The phasor sum of \( E_i \) and \( E_r \) is equal to \( E_t \). Phasor diagrams are used extensively in this section. Care should be taken not to confuse phasor diagrams with space vector relationships.

Rather than deal with the fields \( E \), the incident magnitude will be taken as unity (used as a reference phasor), and the amplitude coefficients \( r \) and \( t \) will be treated as phasors.

7.5.4.1 From dielectric into absorber

![Diagram showing phase relationships at a boundary between a dielectric and a lossy material](image)

Subscripts:
- \( o \) outside (of absorber)
- \( i \) outside → in
\[ r_1 = \frac{n_1 - n_2}{n_1 + n_2} = \frac{n_0 - (n - jk)}{n_0 + (n - jk)} \]
\[ r_2 = \frac{n_2^2 - (n^2 + k^2) + j2n_0k}{(n_0 + n)^2 + k^2} \]
\[ \tan \theta_o = \frac{2n_0k}{n_o^2 - n^2 - k^2} \]

**QUADRANT:**

By inspection of \( r_o \), \( \theta_o \) is in the 1st or 2nd quadrant.

If \( n_o^2 > (n^2 + k^2) \) then \( \theta_o \) is between 0 and \( \pi /2 \).

This occurs when \( n_o > n \), and \( k \) is small.

If \( n_o > n \), and \( k \) becomes sufficiently large, \( \theta_o \) moves into the second quadrant.

\[ n_o > n \]

\[ \text{Fig 7.5.4 - 2} \]

When \( n_o < n \), the real part of \( r \) is always -ve, and \( \theta_o \) is always in the 2nd quadrant, independent of the value of \( k \).

When \( k \) is small, \( \theta_o \to \pi \); as \( k \) increases, \( \theta_o \) moves toward \( \pi /2 \), hesitates, and moves back to \( \theta_o = \pi \) as \( k \to \infty \).
This latter case is that of light reflected at a metal surface.

\[ 7.45 \]

**Amplitude Transmission**

The coefficient of transmission \( t_{oi} \) into the absorber leads in phase for all cases. That is, \( \phi_{oi} \) is always between 0 and \( \pi/2 \).

\[ t_{oi} = \frac{2n_i}{n_i + n_2} = \frac{2 n_o}{n_o + (n - jk)} \]

\[ t_{oi} = \frac{2n_o (n_o + n + jk)}{(n_o + n)^2 + k^2} \]

\[ \tan \phi_{oi} = \frac{k}{n_o + n} \]

7.5.4.2 **From absorber into dielectric**

\[ n - jk \]

\[ n_o \]

\[ t_{io} \]

\[ \phi_{io} \]

Subscripts: \( i \) inside (of absorber) \( io \) inside to outside

\[ \gamma_i \angle \Theta_i \]

Fig 7.5.4 - 4
Amplitude reflection

\[ r_i = \frac{n_1 - n_o}{n_1 + n_o} = \frac{(n - jk) - n_o}{(n - jk) + n_o} \]

\[ r_i = \frac{n^2 - n_o^2 + k^2 - j2n_o k}{(n_o + n)^2 + k^2} \]

\[ \tan \Theta_i = \frac{-2n_o k}{n^2 - n_o^2 + k^2} \]

\[ = \frac{2n_o k}{n_o^2 - n^2 - k^2} \]

Quadrant:-

- \( n_o > n \)

By inspection of \( r_i \), \( \Theta_i \) is in the 3rd or 4th quadrant.

If \( k \) is small, then \( (n^2 - n_o^2 + k^2) \) is -ve putting \( \Theta_i \) in the 3rd quadrant. As \( k \) increases, the term is rendered +ve, and \( \Theta_i \) moves into the 4th quadrant.

\[ n_o > n \]

\[ 1 + r = t \]

Fig 7.5.4 - 5

When \( n_o < n \), the real part of \( r_i \) is always +ve, and the imaginary part always -ve, putting \( \Theta_i \) between 0 and \((-\frac{\pi}{2})\).
When $k$ is small, $\theta_i = 0$. As $k$ increases $\theta_i$ moves toward $\left(-\frac{\pi}{2}\right)$, hesitates, and returns to $\theta_i = 0$ when $k \to \infty$.

\[
\tan \theta_i = \frac{n_0^2 - n^2 + k^2}{2n_0k}
\]

Fig 7.5.4 - 6

Amplitude transmission

\[
t_{i0} = \frac{2n_1}{n_1 + n_2} = \frac{2(n - jk)}{(n - jk) + n_0}
\]

\[
t_{i0} = 2 \left\{ \frac{n(n_0 + n) + k^2}{(n_0 + n)^2 + k^2} - j \frac{n_0 k}{n(n_0 + n) + k^2} \right\}
\]

\[
\tan \phi_{i0} = \frac{n_0 k}{n(n_0 + n) + k^2}
\]

Fig 7.5.4 - 7

The coefficient of transmission $t_{i0}$ out of the absorber is in all cases lagging in phase. That is $\phi_{i0}$ lies between 0 and $\left(-\frac{\pi}{2}\right)$.

Summary of 7.5.4.1 and 7.5.4.2:
The transmitted wave leads in phase passing into absorber.
The transmitted wave lags in phase passing out of absorber.
The reflected wave phase differs according as to whether
$n > n_o$ or not, and whether $k$ is large or small. The diagram
Fig 7.5.4 - 7 indicates with loci of the tip of a vector to
the centre defining the angle $\Theta$ of the various behaviours.
The relationship between $n$ and $n_o$ is labelled, and the arrows
on the loci indicate direction of increasing $k$.

The full range of conditions shown will encompass circumstances
of little practical significance; a wave emerging from a material
with $k \rightarrow \infty$ for example!
7.8 Surface wave.

It was proposed in our publications (refs. 16, 20) that the \( \lambda \) pattern is caused by e-m surface waves. As will be seen in Fig. 7.8-1, for a linearly polarised plane wave incident normally on a Ge interface to be able to produce interference effects with an e-m wave travelling in the interface, the surface wave must have a field component in the direction of propagation.

An inhomogenous wave exists (the surface wave) which has this property. The term 'inhomogenous' arises from the fact that the "lines of equal amplitude" do not co-incide with the "lines of equal phase" (Fig. 7.8-2).
Let such a wave be propagating in the z direction, in the interface between media of complex permittivities \( \varepsilon \), and \( \varepsilon_2 \).

The co-ordinates of reference are shown in Fig. 7.8 - 2. The relative permeabilities of both media are taken as 1.

From the geometry, \( \partial / \partial y = 0 \); if otherwise, there would be propagation in the y direction, contrary to hypothesis.

Using the solution of Maxwell's equations set out by Waldron (ref. 9) pages 206-211 appropriate to an inhomogenous wave, we have in \( x > 0 \),

\[
\left( \frac{\partial}{\partial x^2} + k_{i}^2 \right) \begin{bmatrix} E_z \\ H_z \end{bmatrix} = 0 \quad \text{7.8 - 1}
\]

where \( k_{i}^2 = \omega^2 \varepsilon_{0} \mu_{0} \varepsilon_{i} - \beta^2 \quad \text{7.8 - 2} \)

and \( \beta = \left( \beta' - j \beta'' \right) \quad \text{7.8 - 3} \)

\[
\beta = \beta_o \left( \beta' - j \beta'' \right)
\]

is the propagation constant. The free space constant \( \beta_o = \frac{2\pi}{\lambda_o} \), and \( \bar{\beta} \) is defined as \( \beta / \beta_o \). The real part \( \beta' \) defines the surface wavelength \( \lambda_z \), while \( \beta'' \) describes attenuation in the z direction. The attenuation distance is \( z_d \).

\[
\begin{align*}
\beta' &= \frac{2\pi}{\lambda_z} = \beta_o \bar{\beta}' = \frac{2\pi}{\lambda_o} \bar{\beta}' \\
\lambda_z &= \frac{1}{\beta'} \lambda_o \\
Z_d &= \frac{1}{\beta_o \bar{\beta}''}
\end{align*}
\]
The solutions are:

\[ E_z = A \exp(\pm j k_1 x) \exp(-j \beta z) \exp(j \omega t) \]  
\[ H_z = B E_z \]

The choice of sign must be exercised to ensure \( k_1 x \) \((k_1 \text{is the imaginary part of } k_1)\) is \(-ve\), so that the field vanishes at infinity.

In the other half space \( x < 0 \), a similar set of relations apply, with further constants \( C \) & \( D \), and

\[ k_2^2 = \omega^2 \epsilon_0 \mu_0 \epsilon_2 - \beta^2 \]

The boundary conditions at \( x = 0 \) determine the relationships between \( A, B, C, D \), leading to:

\[ \epsilon \text{ modes:} \quad \epsilon_2 k_1 = \pm \epsilon_1 k_2 \]  
\[ H \text{ modes:} \quad k_1 = \pm k_2 \]

There can be no solutions to equation 7.8 - 7 under the condition \( \mu_1 = \mu_2 = 1 \). \( H \) modes do not exist in an interface between media of equal permeability. Because \( H_z = 0 \), then \( E_y \) and \( H_x \) are also zero.

For \( E \) waves, equn. 7.8 - 6 gives

\[ \epsilon_2 \sqrt{\epsilon_1 - \beta^2} = \pm \epsilon_1 \sqrt{\epsilon_2 - \beta^2} \]

whence

\[ \beta^2 = \epsilon_1 \epsilon_2 / (\epsilon_1 + \epsilon_2) \]

and putting this result into 7.8 - 2 and 5,

\[ k_1^2 = \omega^2 \epsilon_0 \mu_0 \epsilon_1^2 / (\epsilon_1 + \epsilon_2) \]
\[ k_2^2 = \omega^2 \epsilon_0 \mu_0 \epsilon_2^2 / (\epsilon_1 + \epsilon_2) \]
The field components $E_x$ and $H_y$ are given by:

$$
k_i^2 E_x = -j\beta \frac{\partial E_z}{\partial x}
$$

$$
k_i^2 H_y = -j\omega \varepsilon_0 \varepsilon_i \frac{\partial E_z}{\partial x}
$$

where $i$ is 1 or 2 according to which side of the boundary is considered.

If medium 1 is say Ge with $\varepsilon_i = \varepsilon' - j\varepsilon''$, and medium 2 is free space with $\varepsilon_2 = 1$, then

$$
\beta^2 = \varepsilon / (\varepsilon + 1)
$$

$$
k_{Ge}^2 = \omega^2 \varepsilon_0 \mu_0 \varepsilon^2 / (\varepsilon + 1)
$$

$$
k_0^2 = \omega^2 \varepsilon_0 \mu_0 / (\varepsilon + 1)
$$

These relationships will be used in section 8.13 to characterize surface waves when the interface is defined by Ge near melting point temperature.

Finally, it is observed that if standing waves are formed by a pair of equal amplitude surface waves (propagating in the directions $z$ and $-z$ and generated by a common set of dipoles), the field $E_x$ every $\frac{1}{2} \Lambda$ cancels to zero, leaving only the $E_z$ components which reinforce each other (Fig. 7.8 - 3)

![Fig. 7.8 - 3]
7.7 Conclusion.

Section 7 has set out the essential theoretical base which to establish a quantitative model of the interaction between electromagnetic waves and germanium. The framework presented will be used in section 8 to specify magnitudes for all the parameters of interest describing the optical behaviour of Ge over the temperature range 300K-1210K.
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8.1

Section 8  The optical model for germanium.

8.1 Introduction

The work of the preceding sections is applied to the formulation of an optical model for germanium. The behaviour of the optical parameters over the temperature range from room temperature to the melting point of germanium are calculated using the relationships already discussed.

Comparison with published measurement is made for validation.

A difficulty arises from the fact that the material in which the damage occurred was intrinsic germanium, and as such, some of the free carriers are holes. Whereas it is shown that the optical properties of n-type material may be modelled very closely, the presence of holes in intrinsic specimens introduces a complication.

Of particular interest are the rather special conditions relating to the use of germanium as an active laser cavity element. Representative field strengths are estimated for the conditions of operation pertaining when the damage occurred. The presence of standing wave patterns means that a problem which starts with a L.I.H material very quickly changes to one exhibiting extreme in-homogeneity as localised heating occurs at the antinodes.

Even so, this section deals with the optical properties as those of a homogenous specimen of germanium at a uniform temperature throughout. Only the optical properties at the laser frequency
of 28.3 THz are of major interest in this study.

The model described here is an essential pre-requisite for any detailed computer modelling of the interaction between laser radiation and germanium, whether the specimen is homogenous or, due to local hot spots, inhomogenous.

8.2 Values of \( \varepsilon, n, \) and \( k \)

The values of \( \varepsilon, n, \) and \( k \) are calculated over the full temperature range from the \( \gamma \) and \( \sigma_0 \) data base assembled in sections 6.6.5 (mobility), 6.7.5 (hence \( \omega \)) and 6.7.3 (\( \sigma_0 \)).

The values of \( \varepsilon, n \) and \( k \) are required at the laser frequency (28.3 THz), and are calculated from the high frequency conductivity \( \sigma = \sigma' - \sigma'' \) discussed and tabulated in section 6.7.5.

All the necessary base data for calculating \( \varepsilon, n \) and \( k \) are found in table 6.7.5 - 3; that is \( T, \langle \gamma \rangle, \sigma_0 ', \sigma ', \) and \( \sigma '' \).

For convenience, the necessary relations are collected here:

\[
\sigma' = \sigma_0 \left\{ \frac{1}{1 + \omega^2 \gamma^2} \right\} \quad 6.7.5 - 10
\]

\[
\sigma'' = \sigma_0 \left\{ \frac{\omega \gamma}{1 + \omega^2 \gamma^2} \right\} \quad 6.7.5 - 11
\]

\[
\varepsilon = \varepsilon' - j\varepsilon'' \quad 7.3.3 - 23
\]
\[ \varepsilon' = \varepsilon_L' - \frac{\sigma'}{\omega \varepsilon_0} \quad \text{7.4.4 - 15} \]
\[ \varepsilon'' = \varepsilon_L'' + \frac{\sigma'}{\omega \varepsilon_0} \quad \text{7.4.3 - 16} \]
\[ n = \frac{1}{\sqrt{2}} \left\{ \sqrt{\varepsilon'^2 + \varepsilon''^2} + \varepsilon' \right\}^{1/2} \quad \text{7.3.3 - 25} \]
\[ k = \frac{1}{\sqrt{2}} \left\{ \sqrt{\varepsilon'^2 + \varepsilon''^2} - \varepsilon' \right\}^{1/2} \quad \text{7.3.3 - 26} \]

The lattice absorption parameter \( \varepsilon_L'' \) is regarded as negligibly small compared with the other quantities of interest at 28.3 THz.

It should be noted that if \( k \) is very small (Ge at 300K), 7.3.3 - 26 amounts to the evaluation of a very small difference between two large quantities. A better approach in this case is to rewrite 7.3.3 - 26 in the form:

\[ k = \frac{1}{\sqrt{2}} \left\{ \varepsilon' \left[ 1 + \left( \frac{\varepsilon''}{\varepsilon'} \right)^2 \right]^{1/2} - \varepsilon' \right\}^{1/2} \]

Since \( \varepsilon''/\varepsilon' \) is small, expand this using the binomial theorem, and drop the higher order terms to give:

\[ k = \frac{1}{\sqrt{2}} \left\{ \varepsilon' \left[ 1 + \frac{1}{2} \left( \frac{\varepsilon''}{\varepsilon'} \right)^2 \right] - \varepsilon' \right\}^{1/2} \]

By approximating \( \sqrt{\varepsilon'} = n \), we re-obtain the exact form:

\[ k \approx \frac{n}{2n} \quad \text{7.3.3 - 24} \]

It will now be shown that \( n \approx \sqrt{\varepsilon'} \) holds up to at least 900K.
By a similar line of argument starting from 7.3.3 - 25 and under the same condition \( \varepsilon'' \ll \varepsilon' \),

\[
n = \frac{1}{\sqrt{2}} \left\{ 2 \varepsilon' + \frac{1}{2} \left( \frac{\varepsilon''}{\varepsilon'} \right)^2 \right\}^{\frac{1}{2}}
\]

\( \text{using the binomial again:} \)

\[
n = \sqrt{\varepsilon''} \left\{ 1 + \frac{1}{2} \left( \frac{\varepsilon''}{2 \varepsilon'} \right)^2 + \ldots \right\} \] \[ 8.2 - 2 \]

Consider the significance, and also the limits of validity, of equation 8.2 - 1 and 8.2 - 2. The line of thought is directed toward the need later to decide how to handle the anomalous absorption of holes which is discussed in a following section.

The limits of validity will be considered to extend to the point where the approximations introduce an error in the order of 1%. Not because the calculated parameters are thought to be good to 1%, but rather the 1% due to approximation is not expected to degrade the model significantly.

The largest term dropped from the binomial expansion for \( n \) was

\[
- \frac{1}{6} \left( \frac{\varepsilon''}{2 \varepsilon'} \right)^4 \text{ which is to be compared to 1. For the 1% error } \frac{1}{6} \left( \frac{\varepsilon''}{2 \varepsilon'} \right)^4 \sim 0.01
\]

which leads to:

\[
\varepsilon' \approx \varepsilon''
\]

Only when \( \varepsilon'' \) begins to exceed \( \varepsilon' \) does equation 8.2 - 2 fail.

Furthermore, for the value of \( \varepsilon'' \) to influence \( n \) by more than 1%, the condition

\[
\varepsilon'' > \frac{1}{4} \varepsilon'
\]

must be met, as may be determined by inspection of equation 8.2 - 2.
From the table 8.2 - 1 it will be seen that for Ge, the temperature must exceed \( \sim 1000\text{K} \) before the value of \( \varepsilon'' \) significantly affects \( n \), and must exceed \( 1100\text{K} \) before equation 8.2 - 2 becomes invalid.

The value of \( \varepsilon' \) does alter significantly at temperatures lower than \( 1000\text{K} \). The arguments above show that the change in \( \varepsilon' \) is due to the "inductive" contribution of the free carriers (described by \( \sigma'' \), \( \varepsilon' \)) rather than any loss mechanism associated with the carrier in-phase movements (described by \( \sigma' \), \( \varepsilon'' \)).

Turning back to equation 8.2 - 1, \( k \) is directly proportional to \( \varepsilon'' \), providing \( \varepsilon' \) is essentially constant. This condition holds exactly up to \( 500\text{K} \); for this model, the error is probably not unacceptable up to \( 900\text{K} \).

Relating to the approximation in \( k \), the largest term dropped from the binomial expansion was \(- \frac{1}{8} \left( \frac{\varepsilon''}{\varepsilon'} \right)^4\) to be compared to \( \frac{1}{2} \left( \frac{\varepsilon''}{\varepsilon'} \right)^2 \). Applying the same 1% criterion leads to the requirement

\[
\varepsilon'' \ll 0.2 \varepsilon'
\]

for eqn 8.2 - 1 to be valid. Consulting table 8.2 - 1, it is seen that eqn. 8.2 - 1 is valid up to \( \sim 900\text{K} \). In practice it is probably good enough over the whole temperature range.

Note that if \( n \) has been evaluated, \( k \) may be obtained from \( \varepsilon'' \) using the exact form 7.3.3 - 24.
In the table 8.2 - 1, the first five columns are collected from preceding sections, and the values of $C'$, $C''$, $n$ and $k$ were calculated using the relationships reviewed in this section. The full expressions were used to construct the table. The approximations 8.2 - 1 and 8.2 - 2 were then compared, and the observations concerning validity and temperature range confirmed. Since the determinants of the thermal runaway process occur below 500K, the approximations are more than satisfactory for the modelling.

<table>
<thead>
<tr>
<th>Temp</th>
<th>$\langle \tau \rangle$</th>
<th>$C_0$</th>
<th>$C'$</th>
<th>$C''$</th>
<th>$\epsilon'$</th>
<th>$\epsilon''$</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>$10^{-14}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>30</td>
<td>2.2</td>
<td>7.7</td>
<td>4.1</td>
<td>15.99</td>
<td>4.9</td>
<td>3.99</td>
<td>6.1</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
<td>8.6</td>
<td>6.8</td>
<td>2.4</td>
<td>15.99</td>
<td>4.3</td>
<td>3.99</td>
<td>3.1</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>7.5</td>
<td>2.4</td>
<td>4.2</td>
<td>15.97</td>
<td>1.5</td>
<td>3.99</td>
<td>1.9</td>
</tr>
<tr>
<td>600</td>
<td>7</td>
<td>2.9</td>
<td>1.9</td>
<td>2.3</td>
<td>15.85</td>
<td>1.2</td>
<td>3.98</td>
<td>1.5</td>
</tr>
<tr>
<td>700</td>
<td>5</td>
<td>1.9</td>
<td>3.9</td>
<td>1.8</td>
<td>15.4</td>
<td>6.2</td>
<td>3.93</td>
<td>1.9</td>
</tr>
<tr>
<td>800</td>
<td>3</td>
<td>1.7</td>
<td>4.9</td>
<td>2.3</td>
<td>14.1</td>
<td>3.6</td>
<td>3.75</td>
<td>4.9</td>
</tr>
<tr>
<td>900</td>
<td>3</td>
<td>2.8</td>
<td>4.9</td>
<td>2.5</td>
<td>12.8</td>
<td>6.0</td>
<td>3.6</td>
<td>8.4</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
<td>4.4</td>
<td>4.3</td>
<td>3.1</td>
<td>8.7</td>
<td>2.0</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>6.1</td>
<td>4.5</td>
<td>3.1</td>
<td>5.9</td>
<td>2.8</td>
<td>2.5</td>
<td>5.7</td>
</tr>
<tr>
<td>1200</td>
<td>1</td>
<td>8.2</td>
<td>4.2</td>
<td>4.3</td>
<td>6.2</td>
<td>1.2</td>
<td>2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>12.10</td>
<td>1</td>
<td>8.3</td>
<td>4.2</td>
<td>4.3</td>
<td>6.5</td>
<td>1.3</td>
<td>2.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Approximations good to 900K:

\[ k = \frac{\varepsilon''}{2\sqrt{\varepsilon'}} \] \hspace{1cm} 8.2 - 1
\[ n = \sqrt{\varepsilon'}\left\{1 + \frac{1}{2}\left(\frac{\varepsilon''}{2\varepsilon'}\right)^2\right\} \] \hspace{1cm} 8.2 - 2

Good to 500K:

\[ n = \frac{\sqrt{\varepsilon'}}{2} \] \hspace{1cm} 8.2 - 3

i.e. \( n \) is independent of \( \varepsilon'' \).

8.3 Validation at 300K.

One of the reasons for constructing a mathematical model of the optical behaviour of germanium is to enable the present study to cover regions where there is no available supporting experimental data. The further from "base" this process is extended, the greater the band of uncertainty there is in the final result.

Some available experimental data (ref 19) on \( n \)-type germanium is used here to underpin the work so far done. The data is for a fairly heavily doped \((3.9 \times 10^{24} \text{ m}^{-3})\) specimen at 300K, which in some respects makes it comparable to intrinsic germanium at an elevated temperature \((T \sim 900K, n_i \approx 3.7 \times 10^{24} \text{ m}^{-3}; \text{table 6.5.5 - 2})\).

The data concerns the reflectivity \( R \) as a function of radiation wavelength \( \lambda_0 \) (Fig 8.2 - 1). It shows the plasma edge. It is demonstrated that the theory so far developed can reproduce these experimental results, at least to the precision of interpretation of the available diagram.
An interesting comparison will then be made with a calculated curve of \( R \) for germanium as the free carrier density increases in response to a rising temperature.

\[
R = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}
\]

For germanium of any \( \sigma_0 \), and using the relations reviewed in section 8.2, \( n \) and \( k \) may be determined (and hence \( R \)) as a function of \( \omega \). Using \( \frac{\tau}{m_e} \) as a variable parameter, \( R \) versus \( \lambda_0 \left( = \frac{2\pi c_0}{\omega} \right) \) may be fitted to the experimental results.

The d.c. conductivity \( \sigma_0 \) is calculated from

\[
\sigma_0 = N_D e^2 \frac{\tau}{m_e}
\]
given the donor density \( N_D \).
Table 8.3 - 1 shows the values so obtained; and for comparison, some data interpreted from Spitzer and Fan's experimental results (Fig. 8.3 - 1).

TABLE 8.3 - 1

\[ N_D = 3.9 \times 10^{24} \text{ m}^{-3}; \ \gamma/\mu = 3.0 \times 10^{17} \text{ skg}^{-1}; \ \alpha = 3.0 \times 10^{4}(\Omega \text{ m})^{-1} \]

<table>
<thead>
<tr>
<th>( \lambda_0 )</th>
<th>Calculated</th>
<th>From Graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu \text{m} )</td>
<td>( n )</td>
<td>( R )</td>
</tr>
<tr>
<td>5</td>
<td>3.9</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>3.7</td>
<td>33</td>
</tr>
<tr>
<td>15</td>
<td>3.3</td>
<td>29</td>
</tr>
<tr>
<td>20</td>
<td>2.7</td>
<td>22</td>
</tr>
<tr>
<td>21</td>
<td>2.5</td>
<td>21</td>
</tr>
<tr>
<td>22</td>
<td>2.4</td>
<td>20</td>
</tr>
<tr>
<td>23</td>
<td>2.2</td>
<td>19</td>
</tr>
<tr>
<td>24</td>
<td>2.1</td>
<td>20</td>
</tr>
<tr>
<td>25</td>
<td>1.9</td>
<td>22</td>
</tr>
<tr>
<td>30</td>
<td>1.6</td>
<td>47</td>
</tr>
<tr>
<td>35</td>
<td>1.7</td>
<td>63</td>
</tr>
</tbody>
</table>

The match is striking. At this point theory and practise are in close accord. Further observations may be made.

If \( m_e \) is taken as \( 0.145 m_o \), the corresponding value of \( \gamma \) is \( 4.0 \times 10^{-14} \text{s} \). This probably is reasonable given the high level of doping \( N_D \).
It happens to be close to the value of $\tau$ calculated for intrinsic material with similar carrier density (at 900K) in section 6.7 (see table 6.7.5 - 3; $\tau \approx 3 \times 10^{-14}$ s). The value of effective mass there gives $\tau/m_e = 3.6 \times 10^{17}$ s kg$^{-1}$. An exact correspondence would not be expected, because of the significantly different contribution by holes in the latter case.

However, these two sets of high conductivity properties are so similar, one set measured and one set calculated; at the same time the calculated set are so far from the starting point (intrinsic Ge at 300K) that the high conductivity correspondence between the two sets encourages confidence in the calculated high temperature set. The high temperature calculated value of reflectivity $R$ is now presented.

8.4 $R$ as a function of temperature

As the temperature of germanium increases, so does the carrier density. The values of $n$ and $k$ vary, and so does $R$. The subject of this study concerns a beam of radiation entering a specimen, and heating it up. Clearly the rate of entry of radiant energy depends on $R$; a knowledge of $R$ versus $T$ is important.

It is shown here that as the temperature rises, the calculated $R$ begins to fall at $\sim 700$K, and after reaching a minimum at $\sim 1100$K, rises rapidly toward the melting point value $\sim 60\%$. The general form is similar to $R$ versus $\lambda_0$ in the vicinity of the plasma edge. But of course here $\lambda_0$ is fixed at 10.6 $\mu$m. The similarity is due to the fact that the plasma frequency appropriate to the material temperature moves through the CO$_2$ laser frequency at about 1100K. This point is emphasised with a plot
of calculated plasma frequency versus temperature.

Equation 8.3 - 1 is used with the calculated values of n and k in table 8.2 - 1. R versus T is in table 8.4 - 1, and plotted in Fig. 8.4 - 1. The plasma frequency versus T (calculated using equation 7.4.4 - 6), is shown in Fig. 8.4 - 2.

**TABLE 8.4 - 1**

Calculated R and \( \omega_p \) for Ge as a function of temperature.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>R (%)</th>
<th>( \omega_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>36</td>
<td>-</td>
</tr>
<tr>
<td>400</td>
<td>36</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>36</td>
<td>7.3 12</td>
</tr>
<tr>
<td>600</td>
<td>36</td>
<td>1.7 13</td>
</tr>
<tr>
<td>700</td>
<td>36</td>
<td>3.3 13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T (K)</th>
<th>R (%)</th>
<th>( \omega_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>34</td>
<td>6.3 13</td>
</tr>
<tr>
<td>900</td>
<td>32</td>
<td>8.1 13</td>
</tr>
<tr>
<td>1000</td>
<td>25</td>
<td>1.2 14</td>
</tr>
<tr>
<td>1100</td>
<td>20</td>
<td>1.7 14</td>
</tr>
<tr>
<td>1200</td>
<td>59</td>
<td>2.5 14</td>
</tr>
</tbody>
</table>

These results are extremely interesting. The reflectivity at 10.6 \( \mu m \) appears to dip to a minimum (admitting more radiant energy) just below the melting point temperature. The carrier density within the germanium becomes correct for a plasma resonance at the \( \text{CO}_2 \) laser frequency close to the point of melting.

What significance would such a plasma resonance have on the formation of the observed surface patterns on the germanium laser mirror? How close really is the resonance to the M.P.?
Fig. 8.4 - 1

Calculated R versus T for Ge.

Fig. 8.4 - 2 Calculated (by eqn 7.4.4 - 6) versus T for Ge
Does $\omega_p$ for the hot germanium reach as high as 28.3 THz? - the intersection of $\omega_p$ with $\omega_{\text{LASER}}$ only just occurs in Fig. 8.4 - 2.

The next sections set out to examine these points in closer detail.

8.5 Analysis of plasma resonance effects.

This section is devoted to a short extract from Moss et al [Ref 4]; it is placed here for ease of reference. Moss gives a number of useful relationships, some presented in graphical form. The material is intended to facilitate discussion of the significance of plasma resonance to this study.

The text of the extract has not been amended in any way; in particular the equation numbering and figure numbering is original. The extract is pages 44 - 47.

With reference to the Spitzer and Fan measurements Fig. 8.3 - 1, analysis by the techniques of this section yield the further data:

- $R_{\text{min}} = 0.18$
- $n_0 = 4$
- $n_{\text{min}} = 2$
- $\lambda_{\text{min}} = 22.5 \mu\text{m}$
- $\omega_{\text{min}} = 8.4 \times 10^{13} \text{ s}^{-1}$

whence

\[
\omega_p = 0.9 \omega_{\text{min}} = 7.5 \times 10^{13} \text{ s}^{-1}
\]

and

\[
\omega_p^2 = 5.6 \times 10^{27} \text{ s}^{-2}
\]

\[
m_e = 1.25 \times 10^{-31} \text{ kg}
\]

and $m_0^* = 0.14$
Of particular significance is the value of $\omega_p = 7.5 \times 10^{13}\text{ s}^{-1}$, which is an experimentally derived quantity. As was shown in table 8.4 - 1, the calculated value for hot germanium of similar carrier concentration is $\omega_p = 8 \times 10^{13}\text{ s}^{-1}$ at $\sim 900\text{K}$. A later section refines the evaluation of $\omega_p$, and a value there is $7.3 \times 10^{13}\text{ s}^{-1}$. These facts give further confidence in the calculated optical properties.
Dispersion Theory

of course has a maximum where \( R \) has a minimum — and differentiate with respect to \( k' \). To a very high degree of approximation a relation between \( k' \) and \( n \) at minimum reflectivity is then obtained, namely

\[
k' = \frac{(n_0^2 - n^2)(n^2 - n_0^2)}{5n^2 + 3n_0^2 - 2n_0^6}
\]  
(2.41)

where \( n_0 \) is the undispersed refractive index and \( n_1 \) the index of the initial layer (i.e. air or oxide).

It should be noted that neither \( r \) nor \( \omega_p \) appear in this equation, so that for any given values of \( n_0 \) and \( n_1 \) one can take a series of values of \( n \) and calculate the corresponding values of \( k' \). From these, \( R_{\min}, \tau_{\omega_p\min} \), and \( \omega_p/\omega_{\min} \) can be evaluated and curves plotted relating \( R_{\min} \) to these other parameters. Sets of curves for the usual case of measurements at an air interface (i.e. \( n_1 = 1 \)) are shown in Figures 2.6 and 2.7.

For large values of \( \omega_p/\tau \), the following approximate relations may be derived from the condition of minimum reflection

\[
\begin{align*}
k_{\min} &= 4R_{\min} \\
n_{\min} &= 1 + 5R_{\min} \\
\omega_p^2 &= 1 - n_{\min}^2 \\
\omega_{\min} &= \frac{n_0^2 - n_{\min}^2 + k_{\min}^2}{2n_{\min}k_{\min}}
\end{align*}
\]  
(2.42)

The accuracy with which \( \omega_p/\omega_{\min} \) is given by equation (2.42c) is better than 2% for \( 100R_{\min} \approx 1.5n_0^2 \) and the accuracy of equation (2.42d) is better than 5% for \( 100R_{\min} \approx n_0^2 \).

From equations (2.42) the following may be noted:

1. \( \lambda_p \) is not identical with the wavelength of the minimum reflection; there is a correction factor which becomes considerable if \( \tau_{\omega_p\min} \) is small. With this correction, given by Figure 2.6, precise values of \( N/m^* \) are therefore easily obtainable.

2. \( \tau \) may be evaluated directly, more directly than from mobility measurements for example, by use of Figure 2.7.

† At low values of \( \tau \), the exact expression rather than the approximate one given in equation (2.41) has been used.
3. The minimum value of reflectivity varies roughly as \( \tau^{-2} \) and hence as \((\text{mobility})^{-2}\) when the mobility is large.

The value of the conductivity can be obtained, since

\[
\sigma = N e \mu = N e^2 \tau / m^* = \frac{n^2 e^2}{\omega m^* \varepsilon_0} \quad (2.43)
\]

assuming the usual relation \( \mu = e \tau / m^* \) for the mobility. Measurement of conductivity in this manner should be particularly useful in studying the diffused surface layers used in the fabrication of transistors or integrated circuits, where it is often important to know the conductivity rather than carrier concentration.

It is interesting to note that at a wavelength about 25\% greater than the plasma wavelength the refractive index goes through a broad minimum (where \( n = n_p(\omega, \tau) \) and thereafter rises slowly with increasing wavelength.

When the distribution of scattering times is taken into account, the equations for the real and imaginary parts of the dielectric constant become

\[
n^2 - k^2 = n^2 - \frac{N e^2}{\omega m^* \varepsilon_0} \left( \frac{1}{1 + \alpha^2 \tau^{-1}} \right) \quad (2.44a)
\]

and

\[
2nk = \frac{N e^2}{m^* \varepsilon_0} \frac{1 - \tau^{-1}}{1 + \alpha^2 \tau^{-2}} \quad (2.44b)
\]

where the angular brackets signify averages over the distribution.

These averages have been evaluated for various approximations by Schumann and Phillips (1967). However, for most conditions of interest, \( \omega \tau \) is considerably greater than unity and the \( \omega^{-2} \tau^{-2} \) term is only a small correction. Hence, irrespective of the detailed scattering mechanism, the determination of \( N \) or \( m^* \) from Figure 2.6 will be of good accuracy. The effect on \( 2nk \) and hence on \( \tau_{\text{min}} \) is significant however. Equation (2.42d) shows that \( \tau_{\text{min}} \) is inversely proportional to \( 2nk \), so that what is actually determined by the use of Figure 2.7 is the reciprocal of the average \( (\tau^{-1}/(1 + \omega^{-2} \tau^{-2})) \).

As most of the \( \omega \tau \) values are large, this expression tends to \( 1/(\tau^{-1}) \), whereas the average involved in the expression for the mobility is of course \( (\tau) \). Hence, unless the relevant \( \tau \) values lie in a fairly narrow bracket, precise agreement between \( \tau \) values determined from Figure 2.7 and from Hall-effect mobility would not be expected.

When the energy bands are such that the carrier masses are anisotropic, the mass determined from either dispersion or plasma reflection measurements is the conductivity mass

\[
3/m_{\text{e}} = 1/m_1 + 1/m_2 + 1/m_3
\]

If the energy surfaces are ellipsoids of revolution with longitudinal and transverse masses \( m_l \) and \( m_t \), this becomes

\[
3/m^* = 2/m_t + 1/m_l
\]

If the \( E-k \) curves are non-parabolic, then the effective mass obtained is somewhat greater than that for the band edge.

It is worth pointing out that plasma-edge measurements are usually made at sufficiently long wavelengths for surface effects not to be troublesome and for the results obtained to agree with low-frequency determinations. The method is particularly useful for the study of highly doped or relatively impure materials.

An extension of the treatment to cover layers buried beneath oxide or n-layers under p-layers has been given by Moss, Hawkins, and Burrell (1968a).

A comprehensive review of the advantages and limitations of these techniques for studying semiconductor properties has been given recently by Black, Lanning, and Perkowitz (1970) and measurements of the hole mass in CdSb have been given by Rheinlander (1970). Results for both hole and electron masses in grey tin have been given by Wagner and Ewald (1971), while Thomas and Woolley (1971) have studied Ga/InAs and InAs/Sb alloys.
8.6 Material total conductivity.

In this study, one of the features of special interest about the plasma resonance is the change in phase of the total material conductivity $\sigma_T^*$ (with respect to $E_1$) which occurs in the vicinity of the plasma frequency. The ultimate interest is to establish the nature of the scattering of radiation by the linear melts. Present indications are that the linear melts represent pools of germanium at or near the condition of plasma resonance. The magnitude and phase of the currents in these melts hold the key to the pattern formation.

It must be remembered that the linear melts are surrounded by "normal" germanium, and the physical dimensions of the melts in relation to $\lambda$ might be expected to influence these phase relationships. Nevertheless the discussion for the moment will be confined to consideration of an infinite expanse of homogenous material in which is propagating a plane wave.

To explore the phase of the total conductivity $\sigma_T^*$ in relation to the driving field $E_1$, some results are collected from equations 7.4.4 - 11, and synthesised into:

$$\sigma_T^* = \sigma' + j\sigma''$$

$$= \sigma' - j\sigma'' + \sigma''$$

$$= \sigma' + j(\omega\varepsilon_0 \epsilon' - \sigma'')$$

$$= \omega\varepsilon_0 \epsilon'' + j\omega\varepsilon_0 (\epsilon' - \frac{\sigma''}{\omega\varepsilon_0})$$

$$= \omega\varepsilon_0 (\epsilon'' + j\epsilon')$$

$$= \frac{j\omega\varepsilon_0 (\epsilon' - j\epsilon'')}{\epsilon'' + j\epsilon'}$$

and the phase angle $\phi$ of $\sigma_T^*$ with respect to the driving field is:
These relationships for germanium (300K - 1200K) are shown in Fig. 8.6 - 1. The values of $\varepsilon'$ and $\varepsilon''$ are taken from table 8.2 - 1. When $\varepsilon''$ is negligible, the conductivity leads $E_i$ by 90° (dielectric case); when $\varepsilon' = 0$, the conductivity is in phase with $E_i$ (plasma resonance condition). According to present estimates, this is at $\sim$ 1140 K; the absolute value may be revised in the light of experience.

But far more significant is the staggering rate of change of angle about the plasma frequency temperature. In just 40 K temperature increase, the phase angle moves from $+65°$ to $\sim 0°$! It is this behaviour about the in-phase condition which is of crucial interest in the analysis of the pattern formation.

A brief description of the four main classes of behaviour shown in Fig. 8.6 - 1 follows.

From OK to 900K, the free carrier contribution to $\sigma'$ is so slight that the bound electron conductivity $\sigma_d'$ is dominant and constant at $2.5 \times 10^4$ $(\Omega \cdot m)^{-1}$ leading $E_i$ by 90°.

From 900K to 1100K, $\sigma'$ is small compared to $\sigma_d'$. But the net quadrature magnitude is falling rapidly as the inductive current $\sigma''$ rises to cancel $\sigma_d'$, which remains constant at about $2.5 \times 10^4$ $(\Omega \cdot m)^{-1}$.

Over the range 1100K to 1140K, the net quadrature conductivity is small, and only $\sigma''$ is significant, having reached about $10^4$ $(\Omega \cdot m)^{-1}$. 

At the higher temperatures up to M.P. at 1200K, the net inductive quadrature current increases rapidly, as also does $\sigma''$; this leads to a fast increase in total conductivity to $\sim 2 \times 10^4$ ($\Omega \cdot m$)$^{-1}$.

These results are so interesting, and so important, that an effort will be made to refine the absolute values. It is important to know how close to the actual M.P. the plasma frequency really is.
8.7 Assessment of hole contribution.

The material of the etalon was intrinsic germanium. Holes and electrons are present in equal concentration. The separate contribution of the electrons and holes will now be more fully assessed. This section re-examines the expressions for the optical parameters, and for plasma resonance. The next section deals with the anomalous absorption of holes.

The work of the previous sections has to some extent merged the electron and hole contributions in order to keep the issues discussed clear. This has been done by, for example, regarding the collision parameter $\gamma$ as having the same value for both carriers at any given temperature. At the same time, the hole contribution has been allowed for by taking $\sigma_0$ as a starting point.

The time has come to examine whether a more rigorous analysis produces a significant alteration of the predicted high temperature optical properties of germanium. The approach will be outlined, with most of the detail omitted. The results are tabulated.

The role of the collision parameters $\gamma_e$ and $\gamma_h$ are important, since these influence the magnitude of the quadrature conductivity $\sigma''$, which will control the temperature of coincidence between the radian plasma frequency $\omega_p$, and the laser radian frequency $\omega_L$. The values of $\gamma$ are assessed using as the base the work of section 6.6.5 on mobility, in particular the equations 6.6.5 - 33 to 36. Inserting the values for effective mass yields $\gamma$. 
The values of \( \tau \) and \( \eta \) were checked for self consistency by calculating \( \sigma' \), and comparing with experimental values of \( \sigma'' \) as detailed in section 6.7.3.

With these values of \( \eta \), \( \tau_e \) and \( \tau_h \), the parameters \( \sigma' \), \( \epsilon' \), \( \sigma'' \), \( \epsilon'' \), \( \alpha \), \( k \), \( \text{arc tan} \, \epsilon'/\epsilon'' \), and \( \omega_p \) were calculated over the temperature range 300K - 1200K.

The equations for the conductivities are:

\[
\sigma' = \frac{n_e \epsilon^2}{m_e} \left( \frac{\tau_e}{m_e^*} - \frac{\tau_h}{m_h^*} \right)
\]

\[
\sigma'' = \frac{n_e \epsilon^2}{m_e} \left( \frac{\tau_e}{m_e^* (1 + \omega^2 \tau_e^2)} + \frac{\tau_h}{m_h^* (1 + \omega^2 \tau_h^2)} \right)
\]

\[
\sigma''' = \frac{n_e \epsilon^2}{m_e} \left( \frac{\tau_e}{m_e^* (1 + \omega^2 \tau_e^2)} + \frac{\tau_h}{m_h^* (1 + \omega^2 \tau_h^2)} \right)
\]

8.7 - 1

The remaining relationships are unaltered. The calculated values for 300K to 1200K appear in table 8.7 - 1. This shows a great deal of change between 1100K and 1200K. Therefore table 8.7 - 2 was constructed to detail the transition.

Comparing these values with those obtained from simpler expressions (table 8.2 - 1), the following points appear:

a) the general pattern of behaviour, and approximate magnitudes remain the same,

b) the absolute values obtained for \( \sigma' \) and \( \sigma'' \) are a few percent lower. This would be expected.

c) consequently, the calculated temperature \( T_c \) for concidence of \( \omega \) and \( \omega_\pi \) is really indistinguishable from the M.P temperature (shown on the table as \( \sim 1190\text{K} \)). The error band applicable to these calculations means that it cannot be predicted with certainty whether the co-incidence of \( \omega \) and \( \omega_\pi \) occurs below, at, or above M.P. temperature.
This last point is of considerable importance to the analysis of the pattern formation, because of the very rapid change in the phase relationships around $T_{co}$. This matter will be taken up again later.

The plasma frequency may be calculated in terms of $n_i$ and $\gamma$. The radian frequency $\omega_p$ may be calculated for a lossless material using equation 7.4.4 - 1.

In the case of a lossy material, i.e. a material with a finite $\gamma$, the equation must be modified. The approach is to equate the net quadrature conductivity to zero:

$$\sigma' = \sigma''$$

$$\omega_p e_0 e' \varepsilon_L = \frac{n_i e^2}{m_o} \frac{\gamma}{m^*} \frac{\omega_p \gamma}{(1 + \omega_p \gamma^2)}$$  
7.4.4 - 13a

It will be seen that this reduces to equation 7.4.4 - 1 if $\omega_p \gamma >> 1$ (which means that the loss at $\omega_p$ is very small).

To take account of electrons and holes separately, equation 7.4.4 - 13a may be written:

$$\omega_p e_0 e' L = \frac{n_i e^2}{m_o} \left( \frac{\tau_e}{m_e^*} \frac{\omega_p \gamma}{(1 + \omega_e \gamma^2)} + \frac{\tau_h}{m_h^*} \frac{\omega_p \gamma}{(1 + \omega_h \gamma^2)} \right)$$  
8.7 - 3

It was pointed out in section 7.4.4 that a plasma resonance can only exist if for the terms in 8.7 - 3 the L.H.S $\ll$ R.H.S at low frequencies for which $\omega \gamma << 1$. Putting this condition into 8.7 - 3 and approximating accordingly:
\[
\frac{\varepsilon_0 \varepsilon_r n_0}{\varepsilon^2} \ll n_i \left( \frac{\tau^2}{m_e} + \frac{\tau_h^2}{m_h} \right)
\]

8.7 - 4

It may be shown using the data of table 8.7 - 1 that below \(\sim 600\text{K}\) for intrinsic Ge, a plasma frequency does not exist. The most significant factor on the R.H.S of eqn. 8.7 - 4 is which must exceed a threshold value for a plasma resonance to be possible.

For temperatures above 600K, eqn 8.7 - 3 has been solved for \(\omega_p\) using an iteration technique; \(\omega_p\) is shown plotted in Fig. 8.7 - 1, and tabulated in Table 8.7 - 1.

In this section it has been shown that accounting more rigorously for the hole contribution raises the level of complexity of the expressions to a marked degree, while the change in absolute values calculated is quite small.

But one of those changes is of intense interest; for now \(\omega_p\) becomes equal to \(\omega_L\) at or near the M.P. of Ge. The total material conductivity moves into phase with the driving field just as the Ge melts.

The process of extending the range of modelling by calculating the optical properties has now been carried to the limit of its usefulness. Further refinement of this investigation would have to be accomplished by feeding in experimental data.
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<th>T</th>
<th>n_i</th>
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<th>n_h</th>
<th>ε'</th>
<th>ε''</th>
<th>σ'</th>
<th>σ''</th>
<th>n</th>
<th>k</th>
<th>arctan(ε'/ε'')</th>
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<td></td>
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**TABLE 8.7-1**

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<th>( T_h )</th>
<th>( \epsilon' )</th>
<th>( \epsilon'' )</th>
<th>( \sigma'^{-1} ) (( \alpha \text{m}^{-1} ))</th>
<th>( \sigma''^{-1} ) (( \alpha \text{m}^{-1} ))</th>
<th>n</th>
<th>k</th>
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**TABLE 8.7-2**
8.8 Anomalous absorption by holes.

The Drude-Zener expressions provide a good description of n-type materials. But holes may be excited from the heavy to the light-hole band by photons at $\lambda_s = 10.6 \text{nm}$. The consequent absorption by holes is at least an order of magnitude greater than that predicted by Drude. This must be taken into account if the material is intrinsic. The absorption by holes is so large that it effectively swamps the electronic absorption.

Capron Brill (ref 12) measured the absorption coefficient as a function of material conductivity for both n-type and p-type Ge. Their graphical results are shown Fig. 8.8 - 1a.

Absorption coefficient vs resistivity at 10.6 $\mu$m for anti-monodoped germanium single crystals grown by the natural freeze method. The triangles, open circles, shaded circles, daggers, and crosses represent samples wafered from different single-crystal bars for which the ranges of resistivities overlapped. Conductivity type was determined by a cold-probe method at liquid nitrogen temperature. Below 30 $\Omega$·cm the samples were n-type; above 48 $\Omega$·cm the samples were p-type. From near 42 $\Omega$·cm to near 48 $\Omega$·cm, the samples were neither clearly n-type nor clearly p-type. The vertical bars indicate calculated uncertainties in the absorption coefficient due to an uncertainty of $\pm 0.1\%$ in the transmittance on the 0-100% scale. The solid line is a hand-drawn curve that is presumed to be a reasonable fit to the data.

Fig 8.8 - 1a

Absorption coefficient vs resistivity at 10.6 $\mu$m for stock samples of p-type conductivity. The circles represent gallium-doped samples grown by the horizontal-zone-level method; the triangles represent samples taken from several undoped single crystals grown by the horizontal-zone-level method; the squares represent several undoped samples grown by the Czochralski method. Conductivity type was determined by a cold-probe method at liquid nitrogen temperature. The lower curve has been transferred from Fig. 1, and the upper curve is presumed to be a reasonable fit to the data for the p-type crystals.

Fig. 8.8 - 1b
These results were given a theoretical framework by Bishop & Gibson (ref. 13); their graphical results are displayed in Fig. 8.8-2.

They express the absorption coefficient $\Lambda$ as the sum of the lattice phonon absorption $\Lambda_p$ and that due to the free carriers:

$$\Lambda = \Lambda_p + N_e A_e + N_h A_h$$  \hspace{1cm} 8.8-1

$N_e$ and $N_h$ are the number densities of electrons and holes respectively, and $A_e$ and $A_h$ are the absorption cross-sections for the carriers.
The proportionality expressed in equn 8.8 - 1 of the absorption to number density is well established experimentally (for example ref. 15). The line on Fig. 8.8 - 2a is a computer fit of equation 8.8 - 1 to the experimental points of Capron and Brill. The process yields the values:

\[
\alpha_p = 0.013 \text{ cm}^{-1} \\
A_e = 0.15 \times 10^{-16} \text{ cm}^2 \\
A_h = 6.5 \times 10^{-16} \text{ cm}^2
\]

The values are for Ge at room temperature (ref 12). The hole absorption is \( > 40 \) times that of the electrons. Some previous work had suggested a factor \( \sim 20 \) times.

With these values for equation 8.8 - 1, and using \( N_e = N_h = n_i \) for intrinsic specimens, the coefficient of absorption may be calculated as a function of temperature. The results are in table 8.8 - 1. The values of \( n_i \) are those of table 8.7 - 1. Also shown are the values of \( \alpha \) and \( k \) derived from table 8.7 - 1 for the purposes of comparison.

<table>
<thead>
<tr>
<th>( T ) K</th>
<th>( n_i ) Cm(^{-3})</th>
<th>( \alpha ) ( \text{m}^{-1} )</th>
<th>( k )</th>
<th>( \alpha ) ( \text{m}^{-1} )</th>
<th>( k )</th>
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</table>
It is interesting to note that at room temperature, equation 8.8 - 1 yields $\alpha$ much larger than the Drude theory has been discussed. But at high temperatures the two approaches yield closely similar values for $\alpha$. At room temperature, equation 8.8 - 1 may be taken as reliable, since it is derived directly from measurement. But there is no information to hand concerning the temperature dependence of $\alpha_r$, $A_s$, and $A_h$, which were used as constants. Bishop and Gibson (13) note that the dependence is slight, and quote three further references in support. However their interest was over the narrower range 300K-350K only.

On the other hand, the Drude results fully took account of changes in $\gamma$ with temperature (in so far as data permitted).

There is one other factor to note. Gibson, Rosito, Raffo, and Kimmitt (ref 14) showed that the absorption of p-type Ge at 10.6 $\mu$m ($\lambda_D$) saturates according to

$$\alpha = \alpha_0 \left(1 + \frac{I}{I_s}\right)^{-1}$$

8.8 - 2

where $I_s \approx 10$ MW cm$^{-2}$ at room temperature. The area average of the peak power of our laser was 5 MW/cm$^2$.

The saturation effect is due to partial depletion of the heavy hole band if the radiation is sustained longer than $10^{-11}$s or so. Our laser pulse duration was $10^{-6}$s. It might be expected that following depletion of the heavy hole band, the absorption would revert to that predicted by the Drude expressions.
It would be unwise to attach too much weight to the coming together of the high temperature \( \Delta \) data derived by the two different routes. Clearly there is the benefit that no decision between the two sets is required. No further improvement may now be achieved until new experimental data is to hand. These high temperature data will be considered as satisfactory for the present purpose.

As has been pointed out, the critical phase of a thermal runaway will be at the lower end of the temperature range, say 300K-500K. The equation 8.8 - 1 describes this range well. Above 500K, the runaway model solution is expected to be relatively insensitive to \( \Delta \), so that the tolerances discussed will be quite acceptable.

8.9 Reflection and transmission

The work of section 7.5 is used here to calculate the reflection and transmission characteristics of a single surface of Ge over the temperature range 300K - 1200K. The results are tabulated for the purpose of model assessment.

It will be noted that over the sensitive temperature range 300-500K, the reflectivity \( R \) is essentially constant. Further, just as the M.P is reached, \( R \) is reduced, allowing the incident radiation to more effectively transport energy into the material.
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</table>
Fig. 8.9 - 1 Model of Germanium

Values of $R, R_{10}, t_{01}, t_{10}$ plotted against temperature.

Data is table 8.9 - 1.
8.10 The working field strengths

The Ge etalon, as part of the CO$_2$ laser cavity, supports standing waves at the lasing frequency. Consequently the field strengths are periodic through the thickness of the Ge window. The heating to which it is subject is therefore also periodic, leading to the possibility of local hot regions, and local regions of thermal runaway. When melts occur, the electrical properties which then pertain will scatter the incident radiation strongly.

Therefore the typical field strength magnitudes are assessed in this section. The assessment is based upon an output intensity of 5MWcm$^{-2}$. This value was the peak output power averaged over the 4 cm$^2$ beam section.

The assessment is recorded as diagram 8.10 - 1.

The calculated values are obtained using the work of section 7.5.6 dealing with multiple reflections. The values shown are net.

The upper diagram 8.10 - 1 concerns energy transport. The lower diagram records peak electric field strengths, taking into account the standing waves in the cavity and in the etalon. The field at the exit face is some four times that at the laser cavity face.

Just inside the cavity face, 0.625$\mu$m deep, the field strength has the larger value $\sim 6 \times 10^6$ Vm$^{-1}$. The antinodes represent regions of local heating, and possible thermal runaway.
Fig 8.10 - 1 upper: energy transport through the laser window.
lower: associated peak electric field strengths.
8.11 The value of $q_v$

The heat source $q_v$ within the Oe is required by the equation
6.3 - 4. The source of energy for $q_v$ is the radiation.

Expressions relating $q_v$ to the beam parameters $I$ or $E_o$, and to
any of the material absorption parameters $\varepsilon''$, $\sigma''$, $k$, and $\alpha$
are required. A range of suitable expressions is noted.

The beam intensity $I$, and the peak electric field strength $E_o$
are related:

$$I = \frac{n \cdot E_o^2}{\eta_o}$$  \hspace{1cm} 8.11 - 1

The energy deposited per unit time per unit volume is:

$$q_v = \frac{\text{heat deposited per unit time}}{\text{volume of deposition}}$$

$$q_v = -\frac{dI \cdot A}{A \, d\zeta} = -\frac{dI}{d\zeta}$$  \hspace{1cm} 8.11 - 2

$$q_v = -(-\alpha I)$$

$$q_v = \frac{\lambda \cdot n \cdot E_o^2}{\eta_o^2}$$  \hspace{1cm} 8.11 - 3
\[ q_v = \frac{4\pi k}{\lambda_o} \cdot \frac{n}{\eta_o} \cdot \frac{E_o^2}{2} \]  

\[ q_v = \frac{\pi \varepsilon''}{\lambda_o \eta_o} \cdot \frac{E_o^2}{2} \quad \text{(since } 2nk = \varepsilon'') \]  

substituting \( \varepsilon'' = \frac{\sigma'}{\varepsilon''} \) and \( \frac{1}{\lambda_o} = \frac{\omega}{2 \pi C_o} \)

\[ q_v = \frac{\sigma'}{\varepsilon_o C_o} \cdot \frac{E_o^2}{\eta_o} \]  

\[ q_v = \frac{\sigma'}{\varepsilon_o C_o} \cdot \frac{n}{\eta_o} \cdot \frac{E_o^2}{2} \]  

\[ q_v = \alpha I \]  

Thus closing the circle. Equation 8.11 - 6 contains \( \alpha \) expressed in terms of \( \sigma' \).

\[ q_v = \varepsilon'' \frac{E_o^2}{2} \quad \text{since } \varepsilon_o C_o \eta_o = 1 \]  

and \[ q_v = \varepsilon'' \frac{E_o^2}{2} \]

An alternative way in to these last two expressions is:-

\[ \sigma'' = \varepsilon'' \]  

\[ \sigma' - \sigma'' = \varepsilon' - \varepsilon'' \]  

Dealing with the dissipative terms:-

\[ J' = \sigma' E = \varepsilon'' E \]

\[ q_v = \sigma' E \]

\[ q_v = \frac{\sigma' E_o^2}{2} \]  

\[ q_v = \varepsilon'' \frac{E_o^2}{2} \]
Note that in the general case, $\varepsilon''$ and $\sigma'$ include any dissipation by the bound electrons (described by $\varepsilon''$).

An armory of $q_v$ variants has been assembled to facilitate the selection of a suitable form at any stage of modeling.

### 8.12 Preliminary evaluation.

Some initial quantitative estimates of likely heat flow rates, and minimum intensities required for the observed heating are now possible. These are examined at this stage for general guidance concerning realistic orders of magnitude. The evaluations are made under the assumption of quasi-static conditions rather than transient conditions to obtain straightforward estimates.

Consider first the heat balance for a newly created melt at or near the cavity face of the mirror during a short laser pulse. The melt proposed is about $1\mu m$ thickness, and surrounded by room temperature Ge. The rate of heat loss by thermal conduction is estimated.
\[
\frac{dQ}{dt} = K_{Th} \frac{d\Theta}{d\gamma} = 54 \frac{(1200 - 300)}{10^{-6}} \left[ \frac{W}{mK} \frac{K}{m} \right] \\
\sim 5 \times 10^{10} \text{ W/m}^2
\]

The beam intensity, averaged over the beam X-section, was \(5 \times 10^{10} \text{ W/m}^2\) when at its peak. This result would suggest that if a melt of the proposed dimensions did form, the beam would just sustain it against re-freezing; that is, until the pulse peak passed, when solidification would rapidly ensue.

To estimate the time for solidification, assume a melt of the dimensions above. If the laminar melt area is 1 m\(^2\), the latent heat of fusion is:

\[
Q_f = \rho V \cdot L_f \\
= 5.3 \times 10^3 \times 1 \times 10^{-6} \times 4.8 \times 10^5 \left[ \frac{J}{m^3 \cdot kg} \right] \\
= 2.5 \times 10^3 \text{ J}
\]

with an area for heat conduction of 1 m\(^2\). At the heat loss rate previously estimated, the time for solidification is the time required to remove this heat:

\[
t = \frac{2.5 \times 10^3}{5 \times 10^{10}} \left[ \frac{J}{J/s} \right] \\
= 5 \times 10^{-8} \text{ s}
\]

So that re-solidification takes place during the laser pulse, but after its peak power has passed. The pulse tail is well over \(\sim 1 \mu\text{s}\) long.
Now the rate of heat input will be examined to estimate minimum intensity levels that could raise the temperature quickly enough to produce melting within the laser pulse time profile.

Clearly from the previous estimate, if the beam power of $5 \times 10^{10} \text{ W/m}^2$ is totally absorbed within the lamina, melting would be complete $5 \times 10^{-8}$ s after reaching 1200K. This would imply an absorption coefficient at 1200K which would reduce the radiation amplitude to $\sim \frac{1}{e}$ of its entrance value in a depth $\sim 1 \mu \text{m}$. The energy deposited within the lamina would be $1 - \left(\frac{1}{e}\right)^2 \approx 0.9$ of that available. This requires

$$k \approx \frac{\lambda_s}{2\pi e} = \frac{10.6 \times 10^{-6}}{2\pi \times 10^{-6} \left[\text{m}\right]}$$

$$k \approx 1.7$$

Consulting table 8.7 - 1, at 1200K the value of $k$ shown is 2. Given that no allowance is required for heat loss, then the pulse profile of the laser used would produce melting; allowing for heat conduction would mean that there would not be alot of power to spare.

Starting the heating process from a uniform mirror temperature of 300K requires a very rapid rate of temperature increase to reach M.P. within the time available.

$$\frac{dQ}{dt} = \rho \ C \ \frac{dT}{dt}$$

At 300K, $\rho = 5.3 \times 10^3 \text{ kg/m}^3$; $C = 310 \text{ J/kgK}$. 

8.40
Some representative rates of temperature rise are listed:

**Table 8.12 - 1**

<table>
<thead>
<tr>
<th>$\frac{dT}{dt}$</th>
<th>$\frac{dT}{dt}$</th>
<th>$\frac{dQ}{dt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^8$ deg/10 $\mu s$</td>
<td>$10^8$</td>
<td>$1.6 \times 10^{14}$</td>
</tr>
<tr>
<td>$10^9$ deg/1 $\mu s$</td>
<td>$10^9$</td>
<td>$1.6 \times 10^{15}$</td>
</tr>
<tr>
<td>$10^{10}$ deg/0.1 $\mu s$</td>
<td>$10^{10}$</td>
<td>$1.6 \times 10^{16}$</td>
</tr>
</tbody>
</table>

The beam intensities (expressed in terms of peak electric field strength $E_0$ within the Ge) required to produce these heating rates are listed below. The rate of absorption of energy from the beam depends on $\lambda$, which is itself a function of material temperature. Therefore the required intensity for the specified $\frac{dT}{dt}$ is recorded for material temperatures of 300K, 500K and 1000K. The values for $\rho$ and $C$ are, however, the same throughout, appropriate at 300K.

**Table 8.12 - 2**

<table>
<thead>
<tr>
<th>$\frac{dT}{dt}$</th>
<th>$\frac{dQ}{dt}$</th>
<th>Required Field Intensity $E_0$</th>
<th>$\frac{d}{dQ}$</th>
<th>$\frac{d}{dQ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K/s$</td>
<td>$W/m^3$</td>
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<td>$1000$</td>
</tr>
<tr>
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<td>8</td>
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<tr>
<td>$10^9$</td>
<td>1.6</td>
<td>15</td>
<td>3.2</td>
<td>8</td>
</tr>
<tr>
<td>$10^{10}$</td>
<td>1.6</td>
<td>16</td>
<td>1.0</td>
<td>9</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>m$^{-1}$</td>
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<td>0</td>
<td>1.5</td>
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<td>$n$</td>
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<td>4</td>
<td>3.1</td>
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Equation 8.11 - 3 was used with $\lambda$ taken from Table 3.8 - 1.

Inspection of these estimates reveals that the field strengths available within the Ge ($\sim 6 \times 10^6$ V/m - based on measured peak power averaged over the beam $x$-section) are:

a) about 50 x too low to get a runaway established. This is based on the idea that an initial $dT/dt$ in the order of 100 deg/O.1 s$^{-1}$, which implies $E_0 \sim 3 \times 10^8$ V/m, is required.

b) sufficient to produce melting and maintainance against conductive heat loss once the material reaches $T > 1000$K, given that the field $E_0 \sim 6 \times 10^6$ V/m is still available. But of course the formation of a melt would destroy the standing wave pattern upon which the estimate of $E_0$ is based.

Picking up this last point and digressing for a moment, it is unlikely that the changes in the mirror condition would cause the lasing action to cease around the locality of a melt. As viewed from the cavity side, the reflectivity is likely to be high, especially if a melt is formed, in which case the liquid Ge properties become "metallic". The constraints on the oscillation frequency become relaxed due to the number of reflecting surfaces involved being reduced. Within the etalon, the standing wave pattern will subside due to the absorption of energy forward of the final surface, the exit face. There is on melting some surface deformation, but this is unlikely to be decisive in locally stopping laser action.

The author therefore considers that the required high gain of the laser cavity is maintained despite the mirror melts developing. Using a reverse argument, if the case were otherwise,
the loss of intensity as the cavity died around the impending melt would ensure that melting never took place. Suffice it to say that melting does occur, as the micrographs reveal.

Returning to the information displayed in table 8.12-2, and the apparent inability of the available field to produce the observed runaways, one or two points are worth making.

First, the 5 MW/cm² peak power is an average over 4 cm² beam X-section. That there were 'bright spots' is clear from the "pulse-prints" taken. Could these high spots have been \( \text{average } \times 50 \) in strength?

To support the suggestion that the local peaks may have been 50 x the average, it will be recalled that the evidence deduced from the detailed examination of many micrographs was that the areas represented a threshold situation. The fact that the area of damage was very small (c.f. 4 cm²) means that the average is likely to be substantially below the local highs. It is thus argued that the values shown in table 8.12-2 are consistent with the observations made.

This section has performed an interim examination of magnitudes involved in the present study, and found a high degree of consistency between the mathematical model operated with order-of-size precision, and the observed facts of etalon damage.

In particular, there is support for the idea that the damage areas occurred in regions of field strength only marginally
able to produce observable effects. Recall that it was estimated that some $10^5$ pulses were produced before the damage was examined.

Again, the concept of the linear melt being just produced, with re-freezing taking place during each pulse, has been shown to be quantitatively consistent with the known experimental parameters.

It is consequently worth pursuing the more detailed solution of the many aspects to which the model here constructed has relevance.

8.13 The Surface Wave

It was proposed in our publication (ref. 16) that the surface pattern component with a periodicity of $10.6 \mu m$ originated from an interference between an inhomogenous e-m wave travelling over the surface, and the main laser beam. A quantitative assessment of this proposition is made here under certain simplifying assumptions; the optical parameters used for Ge are those deduced in this study.

It has been seen in the preceeding sections that the optical properties of Ge, in particular $\varepsilon = \varepsilon' - j\varepsilon''$, vary over a very wide range as the temperature increases from 300K to 1210K. For instance $\varepsilon'$ goes from $16 \rightarrow 1.4$, while $\varepsilon''$ goes from $\sim 10^{-6} \rightarrow 10$ ... a range of 7 orders of magnitude. It might be expected therefore that the characteristics of a surface wave supported between free space and such a Ge surface would
also vary widely.

Yet, for the proposition to be tenable, the wavelength of the surface wave as measured along the interface has to be close to the free space wavelength $\lambda_o$. That this should be so over such a wide temperature range would seem very unlikely. But it may be assumed that the sculpturing of the surface can only commence when the surface is thermally softened - at least plastic. That is, interest in the surface wavelength $\lambda_z$ is greater at temperatures near M.P.

Another characteristic of interest is the magnitude of the field component in the direction of propagation $E_z$, the component which will produce the interference with the main beam field. To underline the worry about $E_z$, if the Ge surface becomes "metallic", and the field lines "straighten up" to become perpendicular to the interface, then $E_z$ would be zero, and there could be no interaction with the main beam of the proposed type.

Any surface wave is guided along the interface by virtue of the energy dissipated in one (at least) of the media. Of interest to this study is the distance along the interface $z_d$ required for the amplitude of the wave to decay by the factor $1/e$.

The work of section 7.6 is used to evaluate the quantities of interest.

The model considered is that of a boundary infinite in extent
between two half-spaces. On the one side is free space, and on the other Ge uniformly at a specified temperature \( T \). The direction of propagation is \( O_z \).

\[ \text{Ge at temp } T \]
\[ \varepsilon' - j \varepsilon'' \]

**Fig. 8.13 - 1**

The essential relationships are:

\[ L_z = E_{oz} \exp(\pm j k_0 x) \exp(-j \beta z) \exp(j \omega t) \]

\[ E_{x_1} = \pm \sqrt{\frac{\varepsilon_z}{\varepsilon_1}} E_z, \]

\[ \beta = \beta_e \beta = \frac{2 \pi}{\lambda_0} \beta = \frac{2 \pi}{\lambda_o} (\beta' - j \beta'') \]

\[ \beta = \sqrt{\frac{\varepsilon \varepsilon_z}{\varepsilon_1 + \varepsilon_z}} \]

if \( \varepsilon_1 = 1 \), \( \varepsilon_z = \varepsilon' - j \varepsilon'' \)

\[ \beta = \sqrt{\frac{\varepsilon' - j \varepsilon''}{(\varepsilon' + 1) - j \varepsilon''}} \]

\[ \beta = \beta_e - j \frac{\beta''}{\beta_e} = \frac{2 \pi \varepsilon}{\lambda o} \beta' \]

\[ \lambda_z = \frac{\lambda_0}{\beta} \]
\[ 1 = \beta_o \frac{4}{k} z_d \]
\[ \frac{1}{z_d} = \frac{\lambda_o}{2\pi \beta_o} \]

For the free space side of the interface:
\[ k_o = \beta_o \frac{1}{\sqrt{\varepsilon' + 1} - j\varepsilon''} = \beta_o \left( \bar{k}_o' - j \bar{k}_o'' \right) \]

And on the Ge side:
\[ k_{oc} = \beta_o \frac{\varepsilon' - j\varepsilon''}{\sqrt{\varepsilon' + 1} - j\varepsilon''} = \beta_o \left( \bar{k}_{oc}' - j \bar{k}_{oc}'' \right) \]

The separation \( \lambda_x \) perpendicular to the surface of points of equal phase is:
\[ \lambda_x = \frac{2\pi}{k'} = \frac{2\pi}{\beta_o k'} \]

And the depth of penetration \( \chi_d \) is:
\[ \chi_d = \frac{1}{k''} = \frac{1}{\beta_o k''} \]

All the quantities of interest are evaluated from \((\varepsilon' - j\varepsilon'')\) for Ge. The values for \( \varepsilon \) are taken from Tables 8.7 - 1 and 2.
This does not take into account the topic of section 8.8.
However, the behaviour at the elevated temperature of interest is not likely to be unduly sensitive to the exact value of \( \varepsilon'' \) --- as will be seen.

The values obtained are shown in tables 8.13 - 1 to 3.

The most exciting, and most astounding feature is the constancy of the surface wavelength \( \lambda_x \). In particular, at and around the
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<th>δ'</th>
<th>δ''</th>
<th>β'</th>
<th>β''</th>
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<th>k_ge</th>
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<th>E_{x0}/E_z</th>
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**TABLE 8.13-2**
### TABLE 8.13-3

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$\lambda_o = 10.6 \mu m$

**FIG. 8.13-2** Surface wave is elliptically polarised.
M.P. temperature, the value of \( \beta = 1.0 \) giving a surface wavelength of \( \lambda_z = 10.6 \mu m \). Examining the expression for \( \beta \), it is seen that the magnitude of \(|\epsilon|\) is large compared to \( 1(=\epsilon\text{ for free space}) \), so that \( \beta'\approx 1 \) and \( \beta'' \) remains fairly small. This result leads to an exact value \( \lambda_z = 10.6\mu m \) for the author's Ge model. This is in accord with observation.

One may reasonably generalise this result. For any material for which \(|\epsilon|\gg 1\) at or near its M.P., the interface wavelength \( \lambda_z \) of a surface wave \( \approx \lambda_o \). This is probably true for a large number of semiconductors, and it is certainly true for metals.

This result is unexpected in this sense. It might be pondered "why does \( \lambda_z \) appear to depend predominantly on the properties of the free space side of the interface, and appear almost independent of the properties of the lossy dielectric?". In fact, it turns out to be exactly the reverse. The expression for \( \beta \) is symmetrical in \( \epsilon_1 \) and \( \epsilon_2 \) as would be expected: but the very large value of \(|\epsilon|\) for the lossy dielectric dominates \( \beta \), which in turn leads to \( \beta'\approx 1 \), and \( \lambda_z \approx \lambda_o \).

One other feature will be noted here. The ratio of \( E_x/E_z \) is important to this study, because \( E_z \) has to be substantial to support the proposition. Therefore, the closer \( E_x/E_z \) is to 1, the more effective will \( E_z \) be. If \( E_x/E_z \rightarrow \infty \), as in a metal, \( E_z \) could not produce substantial results.

It will be noted that the Ge model shows a value of \( E_x/E_z \) more favourable to our damage hypothesis at M.P. than at 300K.
Again because of the behaviour of metals, this result was unexpected, but very welcome. The ratio reaches its optimum value at \( \sim 1150K \), around the onset of plasticity, when the effect of \( E_z \) will be greatest.

The value of \( Ex/Ez \) is surprisingly constant over the full temperature range \( \ldots 4 \rightarrow 2.3 \rightarrow 2.7 \). This is due to the relative constancy of \( |\varepsilon| \) for Ge. As \( \varepsilon' \) reduces toward zero, \( \varepsilon'' \) increases to compensate, as it were. This property of \( |\varepsilon| \) ensures a substantial component of \( E_z \).

The results obtained in this section concerning the properties of surface waves over Ge are consistent with the proposition relating to the 10.6\( \mu \)m pattern observed.

8.14 Damage at the entrance face.

The damage studied here occurred almost entirely on the entrance face of the Ge mirror. This needs discussion. That laser damage nearly always occurred at the exit face of a transparent material was the subject of several papers (refs 17,18).

This aspect is difficult to deal with quantitatively with the data presently to hand. But even though the significance of the three proposals to be put forward cannot be adequately evaluated, they are nevertheless recorded.

When a component is external to the laser, the reflected and transmitted field are such that those at the exit face are larger than those at the entrance face (ref. 18).
When the component is active in the laser cavity, as is the Ge mirror, this is still true (see Fig. 3.10 - 1). The entrance face field in our laser was $\sim 1.5 \times 10^6 \text{ V/m}$, and the exit face field was $\sim 6.1 \times 10^6 \text{ V/m}$. Yet the damage was at the entrance.

Three suggestions are offered.

The first is that the damage does not start at the surface, but at the electric field antinode 0.625 μm below the surface (see Fig. 8.10 - 1). The damage might be expected then to spread forward toward the entrance face as the Ge becomes opaque. This suggestion begs the question. The field strength at the sub-surface antinode is $\sim 6 \times 10^6 \text{ V/m}$, as it is at all the other antinodes, including that at the exit face. One may sidestep it by arguing that as each antinode becomes more absorbing with rising temperature, the positive feedback mechanisms at work ensure that the leading antinode is rendered more absorbant, while deprived of illumination, the others fail to grow.

The second suggestion is to note that the incident field on the entrance surface is $\sim 10^7 \text{ V/m}$ (Fig. 8.10-1). This might be expected to penetrate at least the first few layers of Ge atoms before the reflected field is fully called into being. The absorption of energy in the surface layers would be larger, and because of the relative thermal isolation, vulnerability to damage would be consequently at the entrance face.

An extract from Moss (ref 9) is quoted here to support the point.

APPENDIX A

THEORY OF TRANSITION LAYER AT INTERFACE OF TWO DIELECTRICS
The experimental result that when plane parallel light is reflected from a dielectric at the Brewster angle it is elliptically polarized to a slight degree, can be explained by the presence on the surface of the dielectric of a thin transition layer, within which the dielectric constant changes continuously from its value in the first medium, \( \varepsilon_1 \), to that in the second medium, \( \varepsilon_2 \). It has been shown by Drude (1902) that the ellipticity at the Brewster angle (i.e., ratio of wave amplitudes) is given by

\[
\rho = \frac{\pi(\varepsilon_1 + \varepsilon_2)^{1/2}}{\lambda(\varepsilon_1 - \varepsilon_2)} \int_{x=0}^{x=l} \frac{(\varepsilon - \varepsilon_1)(\varepsilon - \varepsilon_2)}{\varepsilon} \, dx
\]

where \( l \) is the layer thickness.

Consider the case for heavy flint glass (for which \( \varepsilon_2 = 3 \)), with \( \varepsilon_1 = 1 \) for air as the first medium, where it is found experimentally that \( \rho = 0.03 \) in the visible region. It is reasonable to assume that the dielectric constant will vary monotonically in some sigmoid fashion, and we will assume for convenience that \( \varepsilon = 2 - \cos \pi x/l \). Evaluation of the integral gives \( \rho = 0.85/\lambda \) so that the observed value \( \rho = 0.03 \) corresponds to \( l/\lambda = 0.035 \) or a transition layer \(~\lambda/30\) thick.

An indication of the effect of assuming different laws for the variation of \( \varepsilon \) with \( x \) is given by taking the maximum possible value of the integral for \( \rho \), which would occur if throughout the whole of the transition layer \( \varepsilon = (\varepsilon_1 \varepsilon_2)^{1/2} \). For the parameters used above this extreme case gives \( l/\lambda = 0.018 \) or \( l/\lambda = 4/35 \). As another example, a linear variation throughout the transition layer gives \( \rho = 1.1/\lambda \) or \( l/\lambda = 0.027 \).

The third point is to observe the fact that immediately preceding the radiation, the light from the T.E.A. discharge falls on the entrance face, generating photo-electron-hole pairs. If still present in appreciable concentration when the cavity gain reaches threshold, the absorbed energy from the beam must be greater at the entrance face than elsewhere. The positive feedback mechanisms would then easily ensure damage was at the entrance, and not at the exit.

The damage did occur at the entrance face. The material Ge is a semi-conductor. The author would further explore the last suggestion, preferably by quantifying the enhanced photo absorption experimentally if further resolution of the point were required.

8.15 Conclusion to Chapter 8.

The purpose of Chapter 8 has been to construct a model to represent the optical behaviour of Ge over the temperature range 300K-1200K. To achieve this, magnitudes have been
assigned to all the parameters of optical interest. The frequency of relevance is 28.3 THz (\( \lambda = 10.6 \mu m \)).

The assignments have been based on a combination of experimental data, and theoretical framework.

The main experimental data base was the conductivity \( \sigma_0 = \sigma(T) \) over the full temperature range. Behaviour of mobility \( \mu = \mu(T) \), \( n_i = n_i(T) \) and momentum relaxation time \( \tau' = \tau'(T) \) were also used. The Drude-Zener theory provided the required optical parameters.

Validation of this model was sought by using it to calculate \( R \) versus \( \lambda_0 \) for a heavily doped n-type Ge specimen. Very good agreement with published experimental data was obtained. The Drude-Zener description is very good for electrons in Ge.

To account for the hole absorption, published experimental and theoretical material was used. For holes, the Drude conductivity mechanism is swamped by induced transitions between the heavy and light hole bands. This was taken into account over the lower range of temperature 300K - 500K, by using an empirically based formula due to Bishop & Gibson, which provides a good description of \( \alpha \) for intrinsic Ge.

The situation above 500K is less certain. But for the modelling purposes of this study, it is thought that the solution sensitivity to \( \alpha \) will not be high in this range. It was shown that absorption of CO\(_2\) laser radiation in Ge at M.P. temperatures would be within a penetration depth of \(~ 1 \mu m\) using
model values. This is in accord with observation. It is believed that the model is adequate over the elevated temperature range for the intended purpose.

A calculated $R$ versus $T$ was displayed in Fig. 8.4 - 1, which was based on Drude. If the extra hole absorption is taken into account, the reflectivity dip is in all probability smeared out. The effect of this would be to make $R$ essentially constant over most of the temperature range, with a certain rise to 60-70% in the liquid phase. The constancy of $R$ means that the Ge model will be insensitive to $R = R(T)$ over all but the top end of the temperature range; for a radiation intensity near to that of damage threshold, the increase of $R$ in the molten state may well prevent enough energy being admitted to sustain a melt. An equilibrium may well be set up with the Ge maintained in a solid/liquid transition condition. This possibility could be crucial in the pattern formation mechanism.

A further detail of great importance is the phase relationship of radiation scattered by the linear melts to that of the main beam. The model suggests that the Ge around M.P. temperature is in a condition of plasma resonance. The co-incidence of the model predicted temperature (1190K) for $\omega_p = \omega_c$ with the M.P. (1210K) is so close that it is impossible to predict with certainty which side of the M.P. the resonance really occurs.

But Fig.8.6 - 1 shows how rapidly the phase of the total conductivity $\sigma$ changes over a few degrees K in the region of plasma resonance. For the setting up of stable interference
patterns of the type that could sculpture the Ge surface with the observed pattern, the temperature at which this phase change occurs is critical. The model places it precisely correctly – just below the melting point. An experimental confirmation would be very significant.

Finally, an exciting result concerning surface waves was obtained. The surface wave plays a vital role in the proposed hypothesis of surface pattern formation. But a necessary requirement was for the wavelength of the surface wave measured along the interface to be \( \lambda_0 \). With \( \varepsilon' \) for Ge dropping toward zero as \( T \rightarrow 1200K \), the fulfillment of this requirement seemed an unlikely prospect. But the full calculation using the model data showed that the surface wavelength at \( T=1200K \) was exactly \( \lambda_0 \). The experimental confirmation of this result would appear to be the patterns themselves.

This chapter (together with Chapter 6 and 7) now completes the data base describing the relevant physical behaviour of Ge over the temperature range 300K-1200K. All the elements required for the numerical solution of the partial differential equation 6.3 - 4 are now in place.
Section 9  Conclusions

This project has provided a wide range of experiences. To list them all would be too extensive, but one or two particular aspects will be remarked upon. The work to date is briefly reviewed, followed by indications of future directions in which investigation might continue to progress. But first, a general comment concerning the style of this thesis is made.

The text reflects some of the twists and turns that the work has taken. Because of the part-time character of the work, it became apparent that it was essential to produce the final record section by section at suitable intervals throughout the project period. The style at any point in the text reflects the state of development at the time of writing. References are given at the end of most chapters. To conform to usual practice, these are collected and presented again at the back of the thesis.

Looking back, some of the earlier material now appears rather primitive; the other side of that coin is that considerable conceptual development has taken place, and new skills have been acquired and developed. A contribution has been made to the scientific literature and to the understanding of laser interaction with matter. A brief review of the achievements and aspirations of the work is now presented.

The work is, of course, completely open-ended; there is no defineable "end", no point at which the investigation can be tidily closed. This is being written shortly after the opening
up of a whole new line of enquiry following directly on the results of the work so far completed. More of this later.

This opening up of avenues of enquiry has typified the project. At the outset, there was never any suspicion that considerable effort would be devoted to understanding the thermal dependence of the optical properties of materials, of semiconductors especially, of germanium in particular. No suspicion that the knowledge of radio engineers relating to antenna systems and e - m field propagation would be gleaned for assistance. (That this source was of value in solving an optical problem is a testimony to the power of Maxwells' work!). No suspicion that numerical methods for the solution of partial differential equations would be studied. Yet this is what has happened during work which at the outset was defined in terms of the design and development of one of the latest in the line of laser species, which at that time was a T.E.A. laser.

A major time element (2 years) was devoted to the design and construction of a T.E.A. laser capable of substantial pulse energy. The designs produced were at the time alongside the most advanced available. The first model was a pin-bar design, which was quickly superceded by two Rogowski profile designs developed in close collaboration with S.E.R.L.

As laser Mk III was run up and optimised, the damage patterns on the output mirror were first observed. They were to change the whole direction of the work. Even though very little diagnostic capital equipment was available, a detailed examination of the areas of damage enabled a time history of
the stages of damage development to be postulated. This was described in the attached publication of 1975. To achieve the hypothesis, a number of important deductions were made from the visual evidence, all of which have been borne out by subsequent work with many diverse materials over the last several years.

Incidently the level of interest in these damage patterns has greatly increased recently due to the desire to process semiconductors for device manufacture by laser annealing. The ripple patterning has been manifest as concentration variations of the dopant material - usually undesirable.

A few of the deductions made from the early photographic examinations will be recalled.

1. **Damage patterns** only occur in regions where the incident energy is at the **threshold** of material damage. This feature is now widely accepted.

2. The damage pattern results from optical interference.

3. The surface profile is the result of a cycle of melting and refreezing (fully described in enclosed publication). From the damage photographs it was predicted that germanium expands on freezing - later confirmed from published data.

4. The melt cycle permanently increases the local conductivity of the cycled material. Damage is able to build up cumulatively over $10^5$ pulses or so.

5. The pattern builds up in a step by step manner, each new
feature location influenced by its immediate neighbours. The result is an orderly pattern extending over very considerable areas. The pattern building process is rather like that of building a wall with bricks.

6. Beam polarisation had to be postulated as an essential feature of the damage scenario. This was a completely unexpected twist, as it was thought at the time that the laser output from the particular laser unit was unpolarised. The polarisation, and its relationship to the ripple damage has since been universally confirmed by authors discussing similar damage on other materials.

7. The transverse character of e-m radiation made matching of the proposed intensity hot spots with the direction of the melts impossible, until the presence of a surface wave was proposed. This proposal was the main burden of the 1975 publication.

8. The proposed surface wave allowed deductions to be made concerning the surface wavelength of the ripple pattern. This aspect is particularly interesting, because all our observations on patterns on germanium using normal incidence showed a surface wavelength marginally larger than the free space wavelength, with some variance. The 1975 publication offered an account of this feature.

Since then, other workers have observed a wide variety of surface wavelengths; usually close to the free space wavelength, on a variety of other materials.
but needing especial attention were those reporting surface wavelengths shorter, even considerably shorter, than the free space wavelength. A refinement of the earlier hypothesis was needed to deal with this. The required refinement has been produced as the climax of the present work. This is how it happened.

It was decided to attempt to model in some detail the heating processes in germanium as a function of time and depth into the material as the laser beam intensity grows and decays. The complexity of the interactions was recognised, and the necessity of simplifications accepted; yet a policy of retaining as many aspects of the model as far into the development as possible was operated. This was to allow elements which had to be simplified out at earlier stages to be picked up again later with maximum ease as the levels of sophistication of the modelling were increased.

The basic requirements for such a model were (a) detailed accounts of the behaviour of relevant material parameters as a function of temperature, and (b) suitable computer software. It was considered a good idea to deal first with the "more straightforward" parameters such as specific thermal capacity, thermal conductivity etc., and then to move into the assessment of the optical parameters as a function of temperature via conductivity data.

This was a long and painstaking process.

However, as a necessary part of this work, the parameters ε' and ε" for germanium were evaluated and tabulated over the temperature
range $300K - 1200K$.

Then the exciting part happened. The dependence of the surface wavelength of the ripple damage pattern was calculated, and found to correspond closely to the observations on germanium. This, of course, was very encouraging.

But there was a feature which had been disturbing right from the time of the earliest observations. The refractive index for free space is 1, that for germanium is 4, yet the patterns in the surface had a periodicity of $\sim \lambda_0$. Why, why, why did the free space side of the surface interface appear to "over-rule" the germanium side of the boundary when it came to determining the surface wavelength?

It was in contemplating this question through the relationship (see chapter 8),

$$\beta = \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$

that a breakthrough took place.

The answer is fascinating. As might be expected, the relationship for $\beta$ is symmetric in $\varepsilon_1$ and $\varepsilon_2$; that is, each dielectric has an equal "say" in determining the surface wavelength. If $\varepsilon_1 = 1$ (free space), and $\varepsilon_2 = \varepsilon' - j \varepsilon''$ (germanium), the expression becomes

$$\beta = \sqrt{\frac{\varepsilon' - j \varepsilon''}{(\varepsilon' + 1) - j \varepsilon''}}$$
in which clearly the germanium becomes the "heavy weight". As a consequence \( \beta \rightarrow 1 \), and the surface wavelength \( \rightarrow \lambda_0 \); that is, as a consequence of germanium dominating the relationship, the surface wavelength becomes \( \lambda_0 \)!!!!!!

This led on to a general examination of the surface wavelength as a function of \( \epsilon' \) and \( \epsilon'' \). It was realised that as the temperature of any material approached that of melting point (the condition appropriate to pattern formation), a variety of combinations of \( \epsilon' \) and \( \epsilon'' \) are possible. A feedback mechanism could be postulated that would tend to ensure that under laser irradiance, the value of \( \epsilon' \) would stabilise such that \( \epsilon' \approx 0 \) or slightly negative. According as to \( \epsilon' > 0 \) or \( \approx -0.1 \), so the surface wavelength \( \lambda_z > 0 \approx \lambda_0 \). By how much depends primarily on the value of \( \epsilon'' \); if \( \epsilon'' \) is large, \( \lambda_z \rightarrow \lambda_z \).

It became possible to provide a reasonable account of those cases where the surface wavelength \( \lambda_z < \lambda_0 \), as well as for those cases where \( \lambda_z > \lambda_0 \). In particular, the initially unexpected look of Isenor's results with Ni\(_x\)P\(_{1-x}\) fall into place. (Fig. 9-1)

What still needs to be done?

Clearly, an accumulation of detailed data for \( \epsilon' \) and \( \epsilon'' \) for the materials on which the ripple patterning has already been observed and recorded needs to be obtained, particularly values pertinent near the M.P. temperatures. A wide range of data here to consolidate the prediction of surface wavelength would indeed be welcome.
The factor $\sqrt{\frac{1}{\beta}}$ plotted versus $\epsilon'$, with $\epsilon''$ as parameter.

$$\lambda_z = \frac{1}{\sqrt{\beta}}, \lambda_o$$
A great deal of work still needs to be done to achieve a run of the model of germanium under irradiation. The basic requirements of a numerical solution are presently available. Detailed computer software needs to be completed.

A new line of investigation recently opened up has been mentioned already. It is presently much too early to have anything resembling a conclusion. But the proposition under consideration is recorded.

It is well known that the reflectivity of a metal reduces under intense laser irradiation. Ready quotes the energy coefficient for silver dropping as low as 5%. The reflectivity minimum occurs before melting, in which case the metal fully recovers its reflectivity after cessation of radiation.

One way of describing the situation might be that for the irradiated metal $\varepsilon'$ drops to near zero, and $\varepsilon''$ has a low value around unity. This might occur if the relevant surface concentrations of electrons were reduced to sufficiently low values ($N \approx 10^{25} \text{m}^{-3}$) from the normal levels ($N \approx 10^{28} \text{m}^{-3}$).

Some investigation of this proposition has been carried out with findings which are somewhat discouraging. However, the reflectivity does fall drastically! And the Loughborough Physics Staff confirm that they are not aware of a satisfactory explanation of this phenomenon at the present time.

So alongside the solid achievement to date, there remains plenty to challenge for the future.
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Laser Induced Surface Structure


Fig. A 1.
Germanium output mirror, showing damage.

Fig. A 2.
"Streaks" of \( \lambda \) -pattern damage viewed under dark field illumination.
Fig. A3.
The $\lambda$-pattern extending over a range of many wavelengths.

Fig. A4.
S.E.M. of $\lambda$-pattern.
Note fault running obliquely across the pattern.
Fig. A 5
S.E.M. of \( \lambda \)-pattern.
Showing the boundary of the region of damage.
The region contains the view shown in Fig. A4.

\[ 50 \mu m \]

Fig. A 6
S.E.M. showing a boundary region similar to that depicted above.
The \( \lambda \)-pattern is clearly shown to be thickness and height variations of the fine pattern at the damage region edge.
Fig. A 7
Optical micrograph of the $\lambda$-pattern.
Note the loss of strength to centre right of picture, where pattern gets "out of step".
This feature supports the interpretation that the pattern is built up (as bricks lay together to form a wall); as distinct from a surface wave (originated somewhere off picture) sweeping over the area generating the pattern.
Further, as the pattern builds up over about $10^5$ laser pulses, it is unlikely that the oscillator is as consistent as the pattern, which is evidently stable in space, would suggest.
The evidence suggests that the pattern location is determined by the condition of the material near the surface.

\[ \text{50} \mu\text{m} \]

Fig. A 8
Kundt's famous dust experiment for sound reproduced here for electro-magnetic waves!!
The "dust" is material removed from adjacent regions of heavy damage. A picture of the debris is available in the attached publication (Willis and Emmony).
Fig. A 9
Melting and material removal at intervals of $\lambda_0 (= 10.6 \, \mu m)$.

Fig. A 10
The same region, showing detail of melting.
Observe at the edge of the damage the typical "spearhead" of the fine pattern.
Fig. A 11
T.E.M. of the fine pattern. Formation of the "spearhead" features is discussed in attached paper.

About actual size

Fig. A 12
The fine pattern reproduced on a macroscopic scale in ice. A hot blade of steel is plunged into the ice to rapidly melt a trough. The melt is rapidly refrozen, leaving the characteristic surface profile. Both water and Germanium expand on freezing.
Fig. A 13.

Showing fine pattern extending over some 100 μm. 
Note fault (scratch) passing through fine pattern at oblique angle indicating that direction of pattern is independent of surface features.
In the centre of the picture, the \( \lambda \)-pattern is seen at an early stage of development.
Laser mirror damage in germanium at 10.6 \( \mu \text{m} \)

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Damage in the germanium output mirror of a TEA CO\(_2\) laser shows a periodicity of 10.6 \( \mu \text{m} \), the laser wavelength. A mechanism is proposed in which scattered and cavity radiation interfere. An interference mechanism is confirmed by experiments outside of the laser cavity. Periodic damage is obtained in thin films irradiated at angles other than the normal where the fringe spacing is modified.

An important limiting factor in the high-power operation of lasers is the damage threshold of the optical components of the laser system.\(^1\) The development of transversely excited atmospheric pressure (TEA) lasers has demanded the development of infrared materials capable of withstanding peak powers above 10 MW cm\(^{-2}\). High-thermal-conductivity high-reflectivity gold-coated copper alloys are widely used for high-reflectance surfaces and single-crystal dielectrics are used as partially transmitting mirrors. Uncoated germanium in particular is often used as the output coupling reflector because of its simplicity and cost, as well as possessing a satisfactory dielectric reflectance (78% at 10.6 \( \mu \text{m} \)).

We have built and operated a TEA CO\(_2\) laser and observed damage in the uncoated germanium surfaces of the output mirror. The laser was similar in design to that described by Lamberton and Pearson\(^2\) but featured some simplifications, such as simple radiussed electrodes and slow gas flow rates (one complete change every 2 min). One end of the laser cavity was a gold-coated zirconium-copper concave mirror with a radius of curvature of 10 m. Output coupling was achieved by a 5-mm-thick uncoated germanium etalon. No polarizing elements or mode selecting apertures were in the laser optical cavity.

The laser consistently gave an output with a total energy of 2–4 J depending upon the input energy, with a pulse repetition rate of 1 Hz. The output pulse was measured with a Ge photon drag detector\(^5\) and was similar to those observed by other workers,\(^2,4\) that is a pulse 80 ns long at FWHM followed by a long tail lasting up to 600 ns. It was estimated that 90% of the laser energy was contained in the initial high-power pulse. The output pattern was observed on a graphite block and showed some bar structure parallel to the plane of the electrodes.

Damage was observed on the inside surface of the germanium etalon after approximately \(10^5\) discharges. At the stage in the development of the surface damage at which this could be seen the output energy of the laser remained approximately constant. The damage covered approximately 10% of the mirror surface (Fig. 1). Similar damage has also been produced on four other germanium etalons and shows similar features. The horizontal bars in Fig. 1 correspond to those in the near-field pattern of the laser output and, as might be expected, correspond to the most intense region in the laser output.

Figure 2 shows one area with regular bars which are approximately at right angles to the coarse bars visible in Fig. 1. The spacing is 10.6 \( \mu \text{m} \), the wavelength of the laser radiation.

The depth of the damage was measured with a Taly-
step\textsuperscript{3} and was approximately 0.5 \( \mu \text{m} \).

In the laser cavity, radiation only propagates normally to the output mirror of the laser. For damage to occur with a periodicity corresponding to the laser wavelength a mechanism must be invoked in which radiation propagates with a component velocity along the surface and hence normal to the laser beam. One such mechanism may be scattering from dust or other particles on the mirror surface. In the laser used in these experiments the mirror was 10 cm from the discharge region and therefore liable to be contaminated by metal particles generated when an occasional arc is formed. If it is assumed that a scattering centre is formed on the mirror surface then wavefronts may propagate radially as shown in Fig. 3. Interference between the scattered and cavity radiation can now proceed and interference fringes will occur with a spacing corresponding to the wavelength of the laser at 10.6 \( \mu \text{m} \).

We have made further preliminary experiments outside the laser cavity to verify the suggested damage mechanism. A thin film of germanium, 0.1 \( \mu \text{m} \) thick, on a glass substrate was inserted in the near field of the laser output and the parallel damage structure was reproduced. Damage could be more easily produced if the film was first scored and damage fringes were produced parallel to the scratch. Further proof of surface scattering and interference was obtained by tilting the germanium film about the axis of the scratch in the film and to the axis of the laser beam, Fig. 4.

Interference will occur when \( OX = 1X \), \( OY = 2Y \), etc., in forward scattering directions and \( OA = 1A \), \( OB = 2B \), etc., in the backward direction; in which case the spacing of the fringes is given by

\[
d = \frac{\lambda}{(1 \pm \sin \theta)},
\]

corresponding to the two cases where the scattered radiation has a component of velocity towards or away from the incident laser beam. Figure 5 is a photomicrograph of a germanium film tilted by an angle of 30° from the normal to the laser beam. The right-hand edge of the film was towards the laser. Damage bars can be seen on both sides of the scratch, with spacings of 7.3 and 19.9 \( \mu \text{m} \). These values are in good agreement with those predicted by the above equation.

The most interesting feature in the surface damage is the predominantly parallel nature of the damage bars with a spacing which may be explained by the interference mechanism. If the radiation is scattered isotropically at centres (whatever these may be) on the surface of the laser mirror, then a circular interference pattern might be expected and not a series of parallel lines. A possible explanation of this effect may be obtained by considering the part played by the bar structure which is clearly visible in the laser near-field pattern. This shows that the intensity is not uniform across the laser beam. If isotropic scattering commences at a point of

---

**FIG. 3.** Formation of interference fringes by interference of scattered and incident laser radiation.

**FIG. 4.** 1, 2, 3, etc., are wavefronts in the incident laser beam. For radiation scattered to the right, with a component towards the laser \( OA = A1 \), \( OB = B2 \), \( OC = C3 \), etc., and for radiation to the left \( OX = X1 \), \( OY = Y2 \), \( OZ = Z3 \), etc. The resulting interference pattern is shown at the bottom of the diagram corresponding to Fig. 5.

**FIG. 5.** 0.1-\( \mu \text{m} \)-thick germanium film on glass substrate. The film has been scored and irradiated with one pulse of laser radiation.
high intensity, interference will occur symmetrically around the centre. However, if the radiation intensity falls rapidly in all directions except along the direction parallel to the surface of the laser electrodes, then high radiation intensities will only occur in the interference fringes along this direction. A mechanism is therefore envisaged which will generate damage at the laser wavelength along the large bars in the laser output pattern. The damage marks which will initially be in line, along the centre of the high-intensity regions, may then act as a diffraction grating with a spacing corresponding to that of the laser radiation. The first-order diffracted beam will therefore lie in the surface of the mirror and consequently a high proportion of the scattered radiation will be in this plane. The damage then grows along the normals to the row of initial damage points.

5Rank Taylor Hobson Limited, Leicester, U. K.
Conclusions
Structured damage patterns have been observed on germanium mirrors used in TEA CO₂ lasers. Two regular pattern intervals occur orthogonally. The patterns result from melting of the germanium following the formation of avalanche currents in response to the electric field of the incident laser radiation. The orientation of the linear current tracks follows the predominant polarization of the laser radiation. The proposed sequence of pattern growth is avalanche formation, linear melting, constructive interference between the incident radiation and the field of the induced current doublet, followed by initiation of new avalanches conforming to a regular array. The near field within the germanium gives rise to broadside pattern growth (~1.7 μm spacing), whilst a surface wave produces new avalanches and/or increased damage at a spacing close to the free space wavelength (λ₀ = 10.6 μm).

Similar effects have been observed in germanium thin films on a glass substrate external to the laser cavity. It has been demonstrated that the fine pattern orientation follows the plane of polarization of the incident radiation in this case. Patterns have also been observed on silicon. These were produced external to the laser cavity by a focused beam, and showed similar features to those on the germanium etalon.

Acknowledgements
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Fig.22 Lines of constant phase and constant amplitude for a surface wave

Fig.23 SEM showing propagation of avalanche doublets

The electron micrographs were taken by Mr M. Hayles to whom thanks are also due for many helpful discussions. One of us (L. J. Willis) would like to thank the Principal of the Derby College of Art and Technology for leave to carry out this work.

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The electric field components radiated by a doublet in free space. The in-phase $|E_p|$ and quadrature $|E_q|$ components are shown with reference to the oscillating electric current.

Fig. 18 The electric field components radiated by a doublet in free space. The in-phase $|E_p|$ and quadrature $|E_q|$ components are shown with reference to the oscillating electric current.

The length of the current track, and the associated melt in the germanium surface, increases with each laser pulse. Over regions where the irradiating laser intensity is just below breakdown threshold, the electric field enhancement at 0.7 $\lambda_{Ge}$ provided by the near field of the linear current is likely to produce a new avalanche current parallel to the first. This represents pattern growth in a "broadside" direction (Figs 19 and 23). Since a progressive wave with an electric field component in the plane of the interface cannot be sustained due to the boundary conditions, only the near field of a doublet is significant in new broadside avalanche formation. Consequently, in the broadside direction only the adjacent current influences the growth path of a fresh avalanche.

Surface wave effects

The fine pattern represents an array of co-phased currents oscillating at the frequency of, and in phase with, the incident laser field. In accord with electro-magnetic field theory, a surface wave will be launched in the dielectric interface formed by the mirror and gas. The direction of maximum intensity is along the axis of the current track. The polar diagram for a doublet is shown in Fig. 20a. An array of such doublets will modify the polar diagram so as to increase the electric intensity of the surface wave in the direction of the current axis (Fig. 20b). A surface wave has an electric vector $E_N$ perpendicular to the interface and a component $E_L$ in the direction of propagation (Fig. 21). A surface wave is an inhomogenous electromagnetic wave guided along the interface. The lines of constant phase and of constant amplitude are shown in Fig. 22.

For a surface wave travelling over germanium the angle of tilt $\theta$ is $\approx 14^\circ$, and the longitudinal component of the electric field in the direction of propagation, $E_L$, has a magnitude of 0.25 $E_N$. Consequently $E_L$ has a significant magnitude, and is correctly oriented to influence the current magnitude in the avalanche tracks. The phase of the incident laser radiation relative to that of the surface wave is important. The phase will enhance at intervals of $\approx \lambda_0$, the free space wavelength, across the surface. At these locations an existing current may be increased (Fig. 12), or a new avalanche may be created as the field strength is raised over threshold (Fig. 23). In either case, surface damage due to melting will be greater and display a periodic interval of $\approx \lambda_0$. This is the $\lambda$ pattern, which is observed in regions of moderate damage.

The exact interval for the $\lambda$ pattern will be the distance $AB$ in Fig. 22 which will be given by $\lambda_0$ sec $\theta$. For a germanium interface, the pattern interval is:

$$x = 10.6 \mu m \times \sec 14^\circ$$

$\geq 10.9 \mu m$.

Fig. 19 The formation of a new avalanche event in the region of constructive interference between the incident laser beam and the near field of the induced doublet.

Fig. 20 Polar diagram of radiation for: a doublet; b - an array of doublets in a dielectric interface. The plane of the diagram corresponds to that of the dielectric interface.

Fig. 21 The components of electric field of a surface wave propagating in a dielectric interface. There is a field component in the direction of propagation.
Various mechanisms have been proposed for the initiation of damage following absorption around defects in the crystal structure. The mechanism relevant to the growth of periodic damage of the type discussed above is the formation of electron avalanches. This involves the existence of low ionization energy centres such as scratches, dislocations, etc in the germanium surface. A defect acts as a source of carriers which enables the avalanche current to form and grow in the direction of the exciting electric vector of the radiation field.

The laser radiation was partially plane polarized with the maximum electric field intensity perpendicular to the cavity electrode surfaces. This was due to the existence of whisper modes (Fig.17) which involved reflections from the electrode surfaces and a consequent enhancement of $E_1$ (the electric intensity normal to the plane of the incidence) over $E_r$. The reflectivity for $E_1$ is greater than for $E_r$ for glancing angles at a metal surface. The interaction of the whisper modes with the main cavity beam gave rise to a beam intensity which was not uniform over its cross-section. This is indicated by the damage structure (Fig.1). It follows that particular areas, somewhere between maximum damage and no damage, were irradiated with an intensity just at the threshold level for avalanche formation. In these areas only the maximum field intensity occurring during a laser pulse will be sufficient to generate an avalanche. The maximum field strength will occur in the direction of $E_1$. The avalanche currents are therefore in the direction of $E_1$, which is parallel to the laser electrode surfaces. The periodic damage has been observed in such threshold regions, where the damage is slight.

The avalanche current excited by the laser radiation re-radiates energy at $\sim 10^{13}$ Hz. The most usual case dealt with in the radio antenna literature is that of an oscillating doublet radiating into free space. Here the situation is that of a radiating doublet in the interface separating two semi-infinite dielectrics (considering the dimensions of the germanium mirror as very large in comparison to a radiation wavelength of $10.6/n \mu m$ in the germanium, where $n = 4$ is the refractive index). The radiation from the oscillating doublet interferes with the laser radiation, and in regions of constructive interference the probability of forming a new avalanche current is increased.

The constructive interference patterns which give rise to a regular array of avalanche currents, and therefore to surface damage with structured appearance, will be discussed in some detail. The doublet near field inside the germanium gives rise to the fine pattern, whilst the surface wave in the interface causes the $\lambda$ pattern.

Near field effects

The fine pattern has a spacing of approximately $1.7 \mu m$ with some variation about this value, (spacings from $1.4 \mu m$ to about $2.1 \mu m$ have been observed). Since there is a self-reinforcing pattern, the individual currents must be in phase, and therefore maintain a consistent phase relationship with the incident laser radiation (in this case the reactive component of the current element impedance only influences the phase slightly). The simplest condition for this to occur for a row of short doublets is with a spacing of $0.7 \lambda$. At this distance the near field of a doublet (Fig.18) would induce an in-phase current in a resistive element.

Nickel electrodes

Fig.15 SEM showing fissures in mirror surface

Fig.16 SEM of debris on mirror surface around regions of severe damage

Fig.17 Formation of whisper modes between electrode surfaces and laser cavity mirrors
Fig.11  SEM showing orthogonal orientation of \( \lambda \) and fine patterns

Fig.12  \( \lambda \) pattern as coordinated thickness variations of the fine pattern

Fig.13  SEM showing formation of \( \lambda \) pattern by melting and dispersion of fine pattern ridges

Fig.14  SEM showing \( \lambda \) and fine pattern in more severely damaged region

The onset of damage in the germanium surface must result from the absorption of laser radiation in that surface.

**Damage mechanisms**

**Avalanche formation**

The fissures are due to cleavage along the crystal planes to relieve thermal stresses in the surface following absorption of laser radiation. There is no relationship between the orientation of the \( \lambda \) pattern and the cleavage cracks. The edges of the cracks are rounded, suggesting melting. A grey powder collects on the surface on and around the severely damaged areas. Individual particles are re-solidified droplets of germanium (Fig.16). There is just a hint of facets on some of them.
The cross-section which is shown in Fig.9 results from a process of melting and refreezing (Fig.10). The germanium within the boundary of the mark is melted by the laser flux, and because of the higher density of the liquid occupies a smaller volume (Fig.10a). Re-solidification begins at the perimeter, locking a depression into the surface contour (Fig.10b).

As re-solidification is completed, a central ridge is formed enabling the former volume of solid to be regained. The central ridge is then above the original surface level. The density of germanium at 25°C is 5 323 kg m⁻³ (solid) and at 960°C is 5 571 kg m⁻³ (liquid).⁴

Some areas of the damage clearly show the λ pattern and the fine pattern in co-existence (Fig.11). The two patterns are orthogonal. The fine pattern is not necessarily con-
The damage structure

It will be seen in Fig.1 that the damage occurs with regions of heavy damage and of less severe damage, and that a tendency to form in bars is apparent. The bar structure is parallel to the laser electrode surface and is not a function of crystal orientation.

Magnification reveals the \( \lambda \) pattern bars extending some hundreds of wavelengths (several millimetres), the bar pattern direction being perpendicular to the laser electrode surface (Figs 2 and 3). The \( \lambda \) pattern is seen in moderately damaged regions and becomes increasingly difficult to distinguish in severely damaged regions where melting and thermal stresses disrupt the regular surface pattern (Fig.5).

The fine pattern is most easily observed in regions where damage is very slight. It takes the form of lines separated by \( \sim 1.7 \mu \text{m} \), parallel to each other, and extending up to a few tens of micrometres (Fig.6). They are sometimes in association with a surface mark (for example, a shallow scratch) on the mirror surface (Fig.7). The direction of the fine pattern on the laser mirror was parallel to the laser electrode surfaces and largely independent of the direction of the surface mark. A surface scratch nearly parallel to the fine pattern direction may 'capture' and deflect a line of the fine pattern (Fig.7). A feature of interest is the fine pattern line termination where it merges into the undamaged surface.

Fig.8 is an electron micrograph of the tips of the fine pattern lines. The central region is raised above the mirror surface level, while the adjacent regions are slightly depressed. The appearance is similar to that of a 'spearhead'.

---

**Fig.2** Extensive \( \lambda \) pattern

**Fig.3** \( \lambda \) and 'fine' patterns

**Fig.4** Scanning electron micrograph (SEM) of area showing fine damage with a spacing of \( \sim 1.7 \mu \text{m} \)

**Fig.5** SEM of region where melting and thermal stresses have disrupted the regular \( \lambda \) pattern
Laser damage in germanium

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We present a photographic study of areas of damage which occurred on a number of germanium etalons used as output mirrors of a pulsed CO\textsubscript{2} TEA laser. A search of the damage revealed certain characteristics which appeared at many locations on any particular etalon face, and on each of the several etalons used. The damage on the inside cavity face was always greater, both in extent and in depth, than that on the outside or exit face of the etalon. However, the patterns observed showed similar characteristics on both faces.

A detailed description of the topographical features of the damage is given followed by an account of the proposed damage mechanisms.

A simple explanation of the periodic damage which occurs on a single crystal germanium TEA CO\textsubscript{2} laser window has been given previously. Interference between the cavity radiation and scattered radiation was considered to be the damage mechanism. A more detailed study of the surface damage in its different stages confirms this.

The damage processes described below have been observed in single crystal near intrinsic germanium output mirrors. The mirrors were plane parallel crystal slices 6 mm thick, flat to \( \lambda/4 \) of Hg green light, and parallel to 5 seconds of arc. Fig.1 is a photograph of a damaged germanium laser mirror. The laser has been described previously. The main features are: quasi-Rogowski nickel plated steel electrodes, and an active volume of 2 cm x 2 cm x 60 cm. The laser resonator cavity comprised the germanium mirror and a 10 m radius of curvature gold coated zirconium-copper total reflector. The laser was operated with a slowly flowing atmospheric pressure gas mixture consisting of He: CO\textsubscript{2}: N\textsubscript{2} in the ratio 4:1:1, and the electrical input energy was varied between 20-40 J with a corresponding output energy range of 2-4 J. The output pulse profile was measured with a germanium photon drag detector and was similar to those observed by other workers, that is a pulse 80 ns long at fwhh followed by a tail lasting ~600 ns.

Several germanium mirrors have been damaged, and all the mirrors examined show similar features. Electron microscope examination of the germanium surfaces shows evidence of melting and large thermal stresses. Where the damage was not so severe as to cause obliteration, two periodic patterns were visible. The period of the larger pattern is ~10.6 \( \mu \text{m} \) (Fig.2). (The laser free space wavelength is 10.6 \( \mu \text{m} \).) This pattern will be referred to here as the '\( \lambda \) pattern'. The smaller pattern, which will be termed the 'fine pattern', occurs perpendicular to the \( \lambda \) pattern when the two are in association (Fig.3), although the \( \lambda \) pattern is not always in evidence (Fig.4). The period of

![Fig.1 Damaged germanium mirror](image)

the fine pattern is not constant even over distances as short as 10 \( \mu \text{m} \), but is in the range 1.4 \( \mu \text{m} \) to 2.1 \( \mu \text{m} \) with a usual value ~1.7 \( \mu \text{m} \).

The observed dimensions of the periodicities show good agreement with those predicted by the field theory for radio antennae, when the dimensions are expressed in terms of wavelengths. The use of antenna theory is justified if the marks in the mirror surface are interpreted as indicating the paths of alternating electric currents induced in the germanium mirror surface region by the laser cavity radiation fields. The frequency of the induced currents is \( 2.8 \times 10^{13} \) Hz, the CO\textsubscript{2} laser output frequency. A description of the damage is followed by an analysis of the field interactions resulting from the presence of the induced currents.
has been developed for calculating strains from displacement fringe patterns and includes compensation for out of plane motion and rotation of the object.

**Contouring of three-dimensional objects**

The white-light speckle technique is not restricted to measuring deformation; it can also be used to determine the absolute shape of an object. A double exposure is made during which a small rotation of either the camera about the object or the object itself has taken place. Contour fringes appear in the spatially filtered image generated from the processed negative (Fig. 9). They define almost perfect planes parallel to the axis of rotation. The planes appear to recede in the direction of the slots when projected onto the contour fringe map. A rotation of the slots about the axis of the lens produces a corresponding change in the orientation of the sectioning.

The contour sections become finer as the rotation angle of the object is increased but eventually correlation of the speckles is lost at positions furthest away from the axis of rotation. In order to recover good contrast fringes over different regions of the object it is necessary to adopt the single exposure superimposition technique when reconstructing the image.

It should be noted that the displacement or contour information would be present even if the object were re-entrant, since the illumination is located close to the camera and thus illuminates nearly all parts of the object seen by the camera. This feature is also possessed by some two-wavelength laser contouring techniques but the equipment required is much more elaborate.

**Vibration**

The white light speckle technique has also been applied to out-of-plane vibration analysis of a car door. The inner panel was subjected to large amplitude vibration at 165 Hz using an electro-magnetic transducer. At this frequency the mode pattern shown in Fig. 10 was recorded from an oblique direction by the modified camera. In this instance the duration of the flash was long enough to cover at least one cycle of vibration.

**Conclusion**

White light speckle photography using a masked aperture camera offers a new method for assessing both the deformation and the absolute shape of the surfaces. This method offers a controllable sensitivity and is applicable to a variety of objects. It is particularly suitable for large objects when other techniques may fail due to lack of illumination or to the foreshortening of the applied grid pattern. Where the object is subjected to tests over long periods an historical comparison of deformation states is possible using the single exposure superimposition technique.

The author would like to thank his colleague, Dr J. M. Burch, for the many useful discussions during this work.

**References**

3. 'Codil' reflective liquid, 3M Company, Traffic Control Products Division
4. Stock solutions: A - ammonium dichromate 20 g, concentrated sulphuric acid 14 ml, water to 1 l; B - sodium chloride 45 g, water to 1 l. For use: 1 part A, 1 part B, 10 parts water
5. Patent application no 21631/75
example, a spherical case can be solved by the same approach. Results of studies in wax and other materials are to be published elsewhere.

5. Conclusions

A simple model of melting and resolidification has been used to explain the damage contours on germanium in the region where damage is indenting into the germanium surface. The model only assumes matter conservation and resolidification at the solid–liquid boundary. A single computation has predicted the shapes of the surface contours, which are in good qualitative agreement with those shown by electron microscopy. It is clear that the surface recontouring following melting and resolidification is a fundamental process applicable to many different solids where $\eta$ is not necessarily less than unity.

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The position of the crossing zero of the function is given by $\xi = 1/3$, showing that the positive-going part of the function is cramped to lie near the origin.

In this section we have demonstrated that with certain stringent but plainly sensible assumptions a simple theoretical curve shape for the resolidified surface results. The normalized deviation of the original surface has been computed as a function of the normalized width $\xi$ for a circular-section melted zone on a germanium surface corresponding to figure 4(b).

The surface contour has been plotted for ten different values of $\Delta$ the incremental solidification layer thickness. The procedure for computation was as follows:

The quantity $\xi^*$ was first computed from the relation

$$\frac{\Delta}{h_0} (3\eta - 1)/2\eta = 1 - \xi^*(3\eta - 1)$$

where $\xi^*$ is the position at which the surface makes the transition from solid to liquid. The left-hand side was given ten incremental values between 0 and 1. The surface of the liquid part was then computed from the relation

$$f_1(\xi) = \xi^*2 - \frac{2\eta}{(3\eta - 1)} \xi^*(3\eta - 1) + \frac{2\eta}{(3\eta + 1)} + (\xi^2 - \xi^*2) (1 - \eta\xi^{3(\eta - 1)})$$

for values of $\xi$ between 0 and $\xi^*$.

Finally, the complete surface shape was evaluated by continuing $f_1(\xi) / h_0$ into $\chi(\xi)$ in the range $\xi^* \leq \xi \leq 1$, thus giving the total solution.

Note that the theoretical maximum height of the final solid surface is given by equation (17) setting $\xi = 0$ and we have

$$\chi_{\text{max}} = 2\eta/(3\eta - 1)$$

so that the bump in the middle deviates from the original surface by the amount

$$p = h_0(1 - \eta)/(3\eta - 1).$$

Although it may seem eminently sensible to use this feature as a diagnostic tool, measurement of this deviation is in practice very difficult. All we can really do at this stage is to offer a qualitative view based upon a theory which clearly fits the facts.

3.1. Computed surface contours

The normalized deviation from the original surface $[f_1(\xi)/h_0 - 1]$ is a function of the normalized width $x/h_0$ for a circular-section melted surface corresponding to figure 4(b). The surface contour is plotted in figure 5. Curve A represents the initial circular B-J have liquid and solid components and represent intermedia is the completely resolidified surface.

4. Discussion

The theory and experimental observations presented in this paper, minimum of theoretical hypotheses, the problem of melting and example, germanium can be solved in a simple and compact form. this theoretical treatment, are however worthy of further discu...
solution in which we also assume that \( r_L \gg t, f_5(t) \) etc. This immediately yields the result

\[
r_L \approx \frac{t}{(d f_5 / dt)}
\]

from equation (6).

Substitution of equation (11) into equation (10) and the use of the large \( r_L \) approximation then gives us the equation

\[
M_0 = 2 \rho_5 \int_0^t f_5(x) \, dx - 3 \rho_5 t^9/3r_0 - 2 (\rho_5 - \rho_L) t^9/3r_0 + 2 \rho_5 f_5(t) - \frac{3}{2} t^2 \rho_L (d f_5 / dt)
\]

which by differentiation, leads to the equation

\[
\frac{1}{r_L} \frac{d^2 f_5}{dr_L^2} + \left( \frac{4}{3} \rho_L - \rho_5 \right) \frac{df_5}{dr_L} + (\rho_5 - \rho_L) \frac{t}{r_0} = 0.
\]

Now scaling the variables and writing \( \eta = \rho_5 / \rho_L \), \( \xi = t / t_0 \) and \( \chi = f_5 / h_0 \), we have

\[
\xi \frac{d^2 \chi}{d \xi^2} + (\frac{4}{3} \rho_L - \rho_5) \frac{d \chi}{d \xi} - 2 (1 - \eta) = 0.
\]

The boundary condition to be applied is that when \( t \to t_0 \), \( d f_5 / dt \to \) (slope of the initial liquid curve). This easily produces the result

\[
\left( \frac{d \chi}{d \xi} \right)_{\xi=1} = 2 (1 - \eta).
\]

Returning now to the integration of equation (14) we then obtain the solution

\[
\frac{d \chi}{d \xi} = 2 \xi - 2 \eta \xi^{3 \sigma - 2}
\]

which can then be integrated once more to give the final solution in the form

\[
\chi = \xi^2 - 2 \eta \xi^{3 \sigma - 1}/(3 \eta - 1) + 2 \eta/(3 \eta - 1).
\]

As a further check of theory, note that if we write \( \chi_1 = \chi - 1 \),

\[
\int_0^1 \chi_1 d \xi = \int_0^1 \left| \xi^2 - 2 \eta \xi^{3 \sigma - 1}/(3 \eta - 1) + (1 - \eta)/(3 \eta - 1) \right| d \xi = 0
\]

showing that, to this order of approximation, matter conservation is satisfied.

Some comment on the shape of the above curve is relevant to the experimental section. Firstly, note that the curves all exhibit stationarity at \( \xi = 0 \). Secondly, the position of the other stationary point is given by

\[
(\xi)_{\chi_{\text{stable}}} = (1/\eta)^{1/3(\sigma - 1)}.
\]

Note also that the solution becomes unstable if \( \eta < \frac{2}{3} \) as \( d \chi / d \xi \to \infty \) under these conditions. This does not infer an actual instability, but merely that the approximation breaks down. In practice, \( \eta \) is very close to unity so these sorts of instability do not arise. If we write \( \eta = 1 - \delta \), we then have the solution of the form

\[
(\xi)_{\chi_{\text{stable}}} = \left( 1/(1 - \delta) \right)^{(-1/3\delta)} \approx 2/3
\]

which is independent of \( \delta \). The other characteristic feature of the curves is the point at which the solution crosses the horizontal axis. The point is only found analytically in the special case \( \eta = 2/3 \) for which the solution is

\[
(\chi_1)_{\eta=2/3} = \xi^2 - 4 \xi^3/3 + 1/3.
\]
always be instantaneously spherical so as to minimize the free energy. In what follows
the solid will be considered as an isotropic continuum and thermal losses will be assumed
to be dominated by conduction into the solid base.

We consider an initial situation when an area of the germanium surface region has
been melted to form a pool with liquid–solid interfacial radius \( r_0 \). The liquid–vacuo
interface is then regarded as circular with radius \( r_1 \), because of the influence of surface
tension. The liquid–vacuo surface may be concave or convex. In germanium at its
melting point the densities of the liquid and the solid are \( \rho_L = 5.57 \times 10^3 \) kg m\(^{-3}\) and
\( \rho_S = 5.21 \times 10^3 \) kg m\(^{-3}\) (Shaskov 1961) respectively. Therefore, the volume of molten
germanium is less than that of the same mass of material in the solid phase. The surface
of the liquid will fall below that of the original solid as shown in figure 4(a). The central
depths of the solid–liquid and liquid–vacuo interfaces are \( h_0 \) and \( h_1 \) respectively. Here
\( t_0 \) is the initial distance from the centre of symmetry to the edge of the pool.

![Figure 4](image)

Figure 4. (a) Section through initial molten pool. (b) Section through partially resolidified
system.

It may be easily shown that when \( h_0, h_1 \ll r_0, r_1 \),
\[
r_0/r_1 \approx 1 - \rho_S/\rho_L
\]
(1)
as is required by matter conservation, where \( \rho_S \) is the density of the solid and \( \rho_L \) the
density of the liquid. Under the same shallow conditions
\[
t_0 \approx (2r_0h_0)^{1/2} \approx (2r_1h_1)^{1/2}.
\]
(2)
Figure 1. Antenna-like damage along a surface imperfection in germanium (Magnification $\sim \times 4000$, reduced by $\times \frac{1}{2}$ in printing).

Figure 2. Transmission electron microscope of melted and resolidified areas on germanium (Magnification $\sim \times 2000$, reduced by $\times \frac{3}{4}$ in printing).
The topography of laser-irradiated germanium

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Abstract. Considerable interest centres around the use of germanium as a reflector material in high-power carbon-dioxide lasers. An important problem is the damage caused to the mirror surface as the result of the dynamic development of imperfections. This damage may be caused by an interference process which has been described previously. A characteristic of the damage which occurs is the melting of the germanium followed by resolidification. This paper describes a certain type of melting pattern which depends upon density differences between the liquid and solid phases. The experimental phenomenon is first described with reference to germanium laser mirror damage and this is followed by a theoretical model of the resolidification process. The results of this model are generally applicable to resolidification of molten regions where a density difference occurs between the solid and liquid phases, as in paraffin wax for example.

1. Introduction

It is now well known (Emmony et al 1973, Willis and Emmony 1975) that one of the major causes of deterioration of a high-powered carbon-dioxide laser is damage to the surface of the commonly used germanium reflector by the intense 10.6 μm radiation. In essence, as soon as the reflecting surface becomes slightly inhomogeneous in its surface structure, the process of damage develops as a catastrophe in well defined patterns created by the interference of incident and diffracted waves.

Close examination of the surface damage shows two spatially periodic structures. A coarse pattern with a periodicity approximately equal to the wavelength of the incident laser radiation and a fine pattern with a separation of approximately 1.7 μm. The coarse pattern is generally distributed on the surface where heavy damage has occurred. The fine pattern is only seen in lightly damaged areas and at the extreme edge of heavily damaged regions. This fine pattern appears to be associated with areas in which damage is growing.

The purpose of this paper is to describe and interpret the topography of the germanium following the formation of molten zones on the surface. A model is proposed which describes what happens when the germanium is caused to melt and then allowed to resolidify after the source of heat is switched off. The theoretical ideas apply to some degree of approximation to all liquid–solid systems, but can be regarded as particularly pertinent to germanium for reasons outlined in the text.

All solid materials which melt when heated above a given temperature will, during the cooling process, be subject to a redistribution of the solid so that potentially at least a new surface contour may be formed.