Laser induced damage in single crystal calcium fluoride

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LASER INDUCED DAMAGE IN
SINGLE CRYSTAL CALCIUM
FLUORIDE

by

IAN LAIDLER

A doctoral thesis

Submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy of the
Loughborough University of Technology

July 1988

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I would like to thank all the members of the Physics Department for their encouragement, and particularly my supervisor, Dr. David Emmony, for his guidance. Thanks also go to Stephen Wiseall and Stuart Clark who collaborated in much of the work. I would like to thank Barry Kinsman of B.D.H. Chemicals Limited for his help and co-operation and B.D.H. Chemicals Limited for their support.

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I would like to thank my parents and all those who helped in preparing the original manuscripts.
The thesis describes the establishment of a laser damage facility in the ultra violet. The laser is a pulsed excimer laser (25 n sec) capable of an output energy of 1 Joule at wavelengths of 193, 245, 308, 337 and 351 nm. The problems involved in making reliable damage threshold measurements are addressed, such as energy calibration, beam attenuation, damage detection and temporal and spatial beam profiling. A computer controlled frame store and video system enabling single shot spatial profiling and peak fluence measurements to be performed is described. Such a system is essential if reliable results are to be obtained from lasers whose spatial output cannot be described by a Gaussian.

Using the damage facility, work has been performed on single crystal CaF$_2$ laser windows ascertaining the bulk and surface damage thresholds as a function of crystal purity, surface finishing and polishing procedures. The results of a T.E.M. study give an insight into the fundamental damage mechanism of this material to be electron avalanche breakdown. The role of transient primary defects in the bulk breakdown of CaF$_2$ has been investigated using dye laser probe techniques, and indicate that the presence of U.V. generated self trapped excitons, acting as sinks for the conduction band electrons, greatly enhances the damage threshold.

Work on coatings using a LIMA (Laser-induced ion mass analyser) is reported and the potential of this machine as a laser damage diagnostic tool is explored.
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Perhaps an introduction to the field of laser induced damage in optical materials would do well to simply point the interested reader to a number of key papers in the field, review articles and to the conference proceedings of the annual "Laser Induced Damage" symposium held at Boulder, Colorado. I shall very briefly attempt to precis this material and to present the parts that I feel are relevant to this thesis. To begin with, however, I'd like to quote a few paragraphs from an introduction to the subject published in Applied Optics vol. 23 No. 21 pp 3741 written by A. Stewart and A. H. Guenther.

"Laser induced damage caused by the interaction of intense optical radiation with matter was the premiere field of study when the laser first appeared in 1960. In those days experiments might begin and end with only a single firing of a ruby laser. Operation of most lasers in 1984 however is no longer such a tenuous proposition, but laser applications in many fields such as materials processing, the pursuit of fusion and defense applications continue to stress the limits of optical materials. The motivation is always to increase the areal power or energy density in a device, to realize higher economy, efficiency and performance, frequently in a smaller, lighter weight package.

The study of laser induced damage is a very complex subject and the field has experienced its share of controversy while knowledge was gained. The large number of applications for lasers, in a wide variety of operating conditions, means that many processes dependant on laser characteristics such as wavelength, pulse duration, duty cycle, etc, as well as properties of the optical materials
or components themselves usually come into play. There are two other issues which also contribute to the confusion. First it has always been true that two ostensibly identical components may behave quite differently in a damage experiment. There is not much that can be done about this aspect until the operative mechanisms of laser damage are revealed and better understood and the salient features of the optical elements are identified and characterized. Second, the manner and environmental conditions in which an experiment is conducted and the definitions used for terms like damage, fluence and threshold can further prevent duplication of results or usage at another laboratory, i.e. an aspect of transferance. To an observer it is clear that this field cannot advance without some consensus on definitions, testing procedures, and analysis methods i.e. until adequate standardization takes place."

This was written one month after the work on this thesis began and accurately summed up the situation in the field at that time. Today the situation is a little improved although confusion among workers and lack of standardization is still present. Work has progressed in the tightening up of definitions and experimental methods and measurements have improved. Part of this thesis deals with our own endeavours in quantifying our damaging pulse in the plane of the target and in bringing a greater reproducability to our measurements as well as credence to our results.

The work of this thesis is concerned with transparent materials i.e. ideally pure inclusion free dielectrics. It has been pointed out that the word "pure" is a misnomer and a function of time. A damaging or sub-threshold damage pulse will introduce defects within a perfect crystal. The effect of bulk impurities and lattice defects require
careful attention as, too, will surface quality and contamina
tion. The material under investigation is syntheti
cally grown, single crystal calcium fluoride. Grateful
appreciation goes to B.D.H. Chemicals L.t.d. of Poole,
Dorset for supplying, growing and polishing all the
samples. In order to study experimentally any aspect of a
topic an understanding of the topic is initially
essential. This, as mentioned by A. Stewart and A. H.
Guenther in the above quotation, is particularly true of
laser induced damage in order that the experimentalist can
attempt to characterize his samples and bring some form of
control into his work. With this in mind a brief outline
of the theories on damage in dielectrics at the time of
initiation of this work will be given and the salient
features noted.

1:10 Avalanche Ionization

In transparent dielectric materials two physical
mechanisms capable of coupling the laser light into the
material and thereby generating an absorbing plasma and
lattice melting have been proposed. They are avalanche
ionization and multiphoton absorption.

In 1971 E. Yablonavitch [1] published some laser
induced breakdown threshold measurements indicating a
compatibility between breakdown measurements at d.c. and
infra-red optical frequencies. The d.c. theory of electric
breakdown in insulators was founded by von Hippel
[2], Frohlich [3], Callen [4] and Seitz [5]. The experi-
mental data was von Hippel's conducted on the alkali hal-
ides. Figure 1:10,1 shows this data for the sodium halides
at d.c. and optical frequencies up to $2.71 \times 10^{15}$ Hz.
D. W. Fradin and M. Bass [7] reported similar behaviour for the
potassium and rubidium halides. The mechanism for d.c.
breakdown has generally been accepted as avalanche ionization and since Yablonavitch's paper this theory received much attention as a laser induced damage process.

![Figure 1:10,1 Experimental Trend Of The Breakdown Threshold Electric Field Through The Na-Halides. [6]](image)

In semiconductors [8] and gases [9] avalanche ionization has been established whilst in the wide band gap insulators conclusive evidence and measurements have proved elusive. Some workers reported evidence consistent with such a theory [10], [11] whilst others remained unconvinced [12], [13]. In 1975 N. Klein and P. Solomon [14] reported avalanche ionization in SiO$_2$ films. Further work at optical frequencies confirmed the similarities at near infra-red wavelengths whilst in the shorter wavelength domain deviations began to appear from the d.c. case.

The process of avalanche ionization can be divided into three stages [15], [16].

i) initiating electron liberation

ii) avalanche ionization plasma production

iii) transfer of a damaging quantity of energy from the incident light wave to the material's lattice by the
dense absorbing plasma.
In stage (i) the first few electrons are raised to the material's conduction band. Generally these will be through non-linear optical processes depending upon the material parameters, purity, structural perfection, stoichiometric and chemical imperfections, as well as the laser photon energy. Once the electron is in the conduction band in the presence of an electric field $E$ and electron-phonon collisions it will drift in the direction of $E$ gaining energy $\Delta E$ as it goes. The rate of energy gain will be given by:

$$\left( \frac{dE}{dt} \right)_E = \frac{e^2 \tau_k E^2}{m(1+\omega^2 \tau_k^2)}$$

where $\omega$ = the frequency of the electric field
and $\tau_k$ = the electron relaxation frequency for large angle scattering

When the electron attains sufficient energy $E_f$ it can excite another valence electron across the electronic energy gap into the conduction band. Repetition of this multiplication process increases the number of conduction band electrons until breakdown occurs. All the early theories assumed that breakdown would occur when the conduction band electron density, $n_c$, was raised from an estimated initial value of $10^8$ to $10^{10}$ cm$^{-3}$ up to $10^{18}$ cm$^{-3}$. Seitz [5] in 1949 first estimated a criteria electron density for damage in which he defined a "40 generation" rule, i.e. an electron would need to undergo forty ionizing collisions to incur lattice damage. This corresponds to:

$$n_c/n_o = (2)^{40}$$

This figure was obtained loosely but has remained a guide for many workers since then. The $10^{18}$ cm$^{-3}$ criteria assumes:

$$n_c/n_o = (10)^9 = (2)^{30}$$

and this implies a "30 generation" process. Thus we have
an example of differing damage criteria. Note that these criteria imply that damage is purely as a result of joule heating as the plasma frequency at this electron density is well into the infra-red, and the material has a purely real refractive index.

M. Sparks [17] showed that the estimation of the initial electron density of between $10^8$ and $10^{10}$ cm$^{-3}$ in the conduction band was unreasonably large, and inconsistent with photoconductivity experiments. Furthermore, by considering the value of $\sigma$ (the d.c. conductivity) he derived an estimate of the initial electron concentration. $\sigma$ (ohm.cm$^{-1}$) for a good conductor is $10^6$, for a semiconductor between $10^2$ and $10^{-9}$ and for an insulator between $10^{-14}$ and $10^{-22}$ [18]. From this it can be shown that if $n_e$ is $10^8$ to $10^{10}$ then the material would be lying in the semiconductor category, and not be behaving as a wide band gap insulator. By considering the conductivity relation [18]:

$$n_e = \frac{m\sigma}{e^2\tau_k}$$

and taking $\sigma \leq 10^{-14}$ ohm.cm$^{-1}$
and $\tau_k \approx 9 \times 10^{-3}$ sec$^{-1}$
Sparks showed that $n_e = 2 \times 10^4$ cm$^{-3}$. When one multiplies this figure by the focal volume in a typical damage experiment e.g. $10^{-10}$ cm$^{-3}$, the probability of finding an electron to begin the avalanche with is about $10^{-6}$. A source of starting electrons is thus critical to the avalanche theory.

Returning to the basic framework of avalanche ionization. In the d.c. case electron-phonon collisions prevent the electron from accelerating very rapidly to high energies by changing its direction of travel every $\tau_k$ seconds (on average). If the electron were to go without suffering
a collision for a long time its energy would be increased more efficiently. Small angle collisions are obviously less effective at inhibiting the build up of energy, though all collisions, in imparting energy to the phonons will reduce the electron energy. The rate of loss of energy to the lattice phonons is:

\[
\frac{dE}{dt} = \frac{\hbar \omega_p}{\tau_L}
\]

where \(\hbar \omega_p\) = the average phonon energy and \(\tau_L\) = the time constant including large and small angle scattering.

Equating 1:10.1 and 1:10.3 gives:

\[
E = \left(\frac{m \hbar \omega_p}{e^2} \cdot \frac{1 + \omega^2 \tau_k^2}{\tau_k \tau_L}\right)^{1/2}
\]

at which the net rate of change of energy \(E\) of the electron is zero. We shall call this value \(E_{EL}\). For \(E > E_{EL}\) the electron gains energy on average and for \(E < E_{EL}\) it loses energy on average. This then forms another simple criteria for damage i.e. \(E > E_{EL}\).

We must now consider the value of \(\tau_k\) a little more earnestly for it plays an important part in the energy gained from the electric field. The energy gain will be small when the electron momentum is rapidly altered by large angle scattering from phonons i.e. with small \(\omega \tau_k\) the phonon collisions inhibit the acceleration of the electron by changing its momentum to the opposite direction imparted by the electric field. Equally as much, in the other limit of \(\omega \tau_k \gg 1\) i.e. slow momentum change the energy gain will again be small. Here the electron is accelerated and then decelerated by the oscillating field. This process will happen many times before the electron will undergo a momentum changing collision. The energy gained in one half cycle is lost during the next. The maximum energy gain, a function of the momentum relaxation time \(\tau_k\), occurs at.
Here on average the electron momentum is reversed every time the electric field is reversed.

The dependence of the breakdown field on the laser frequency as dictated by the avalanche theory has been discussed by a number of workers [17], and it has been found that although agreement between experiment and theory is present from d.c. up to about 10.6 μm this fell away as the frequency was further increased, giving no agreement at 694 nm and even less in the vacuum ultraviolet. The deviation of the frequency dependence from theoretical predictions can be seen in Figure 1:10,2 [17].

![Breakdown Field vs Laser Frequency](image)

Figure 1:10,2 Comparison Of Experimental And Theoretical Breakdown Thresholds As A Function Of The Laser Frequency.

The frequency dependence has been taken from:

\[ E_B \sim (1 + \omega^2 \tau^2)^{1/2} \]

1:10,5

This is a consequence of Equation 1:10,4. M. Sparks [17] showed that if the theory was to fit the experimental
results in the ranges between 10.6 to 0.694 μm the value of \( \tau_k \) would need be less than \( 2 \times 10^{-16} \) sec. and it is unlikely that \( \tau_k \) is this small. At the energetic end of the optical spectrum it would appear that the avalanche model certainly needs modifying.

The electron avalanche theory, providing a framework from which to operate, has its limitations. Its frequency dependence is unsure, it needs another mechanism capable of generating the initial seed electrons and as M. Sparks [17] pointed out the probability of finding an electron in the focal volume experiencing large angle phonon collisions in phase with the optical field is very small indeed. Since then other variations have been investigated, at least theoretically, looking at mechanisms for generating and sustaining an avalanche. These include such mechanisms as photon-electron-phonon processes and intraband transitions. [17].

1:20 Multiphoton Ionization Breakdown

The incentive to understand multiphoton processes increased with the arrival of the U.V. and V.U.V. lasers. For a good review on multiphoton processes see the paper by H. Mahr [19]. Early on in the days of the U.V. laser it was thought that NaCl would be an ideal window material. It was found, however, that working at the KrF wavelength of 248 nm (\( \hbar \omega = 5.0 \) eV) that 50% absorption due to two photon absorption was occurring. This could quickly lead to damage as the electrons generated by this process are numerous. As a result of this the interplay between avalanche ionization and multiphoton ionization has been considered and a number of discussions can be found in the literature [20], [21] and [22].
The absorption of light by a material is described by an exponential attenuation:

\[ \frac{dI}{dx} = -\alpha I \]  

\[ I(x) = I_0 \exp(-\alpha x) \]  

Here the attenuation is the result of multiple individual absorptions of single photons by the material's system. This is referred to as linear absorption as the differential attenuation rate is proportional to the first power of the light intensity i.e.

\[ \frac{dI}{dx} = -\alpha I \]  

To be more general however, the other attenuation terms should be written into the equation, especially when the light intensity reaches the \(10^8\) to \(10^9\) W.cm\(^{-2}\) regime. This is commonly achieved with laser applications. The differential attenuation relation of \(1:20,2\) then becomes:

\[ \frac{dI}{dx} = -\alpha I - \varphi I^2 - \gamma I^3 \]  

where \(\varphi\) is the 2PA (two photon absorption) coefficient and \(\gamma\) is the 3PA coefficient etc.

The nPA term will be proportional to \(I^n\). The occurrence of multiphoton processes is not only related to the light intensities but also to the energy conservation relations. In materials with the optical band gap greater than the energy of a single photon but less than the energy of two photons it is possible for transitions to occur by the simultaneous absorption of two photons from a sufficiently intense laser beam. Although the expression for the 2PA transition rate can be written down from second order perturbation theory it has proven difficult for workers to proceed further from the basic equation. A different approach was then developed by L. V. Keldysh [23] by directly modifying the wave functions to account for the strong
electric field. From his expressions values have been predicted for the breakdown thresholds of a number of crystals [24]. It has been observed [24] that the electric field strengths needed for breakdown caused solely by multiphoton processes of an order higher than four are much larger than measured experimental values, and this mechanism can be thought of playing only a secondary role. For cases where $E_g \approx 4\hbar \omega$ or less (where $E_g$ is the dielectric band gap) the damage field strengths predicted by the Keldysh formula are smaller than those obtained by the avalanche theories and in closer agreement with experiment. By assuming the two theories to be independant mechanisms, models combining the effects of both have been developed [25] and closer agreement with experiment has been achieved.

1:30 Summary

Two theories have thus been propounded and the uncertainty existing among the damage community outlined. The work of this thesis is concerned with laser induced damage to synthetic, single crystal substrates of calcium fluoride. The surface and bulk damage thresholds at 248 nm. (KrF wavelength) has been investigated. Surface damage has been concerned with the sample preparation i.e. the polishing procedures, with the intent on optimizing the surface damage resistance, as well as understanding the features of the damage morphology. The chapter on bulk damage looks at the formation of colour centers during 248 nm. excitation and tries to understand the role these transient defects play in the formation of bulk damage. Are F-centers for instance a viable source of seed electrons as is often claimed? Prior to this work, however, the establishment of a laser damage facility and damage diagnostics was needed and consequently the first portion of
the thesis deals with this aspect, the experimental side of the field. Then finally there is a further chapter on the use of a LIMA (laser induced mass analyser) as a diagnostic tool for laser damage studies.

1:40 Bibliography

18. C. Kittel, Introduction To Solid State Physics,


CHAPTER 2.00 A LASER DAMAGE FACILITY

2:10 Introduction

A minimum system for performing a laser damage test can be seen in the following figure. The basic essentials

![Diagram of a basic laser damage facility]

should consist of a well characterized laser focused via some optical system onto the target under test. Included in the system should be a means of beam attenuation in order to vary the incident energy, without altering the focal plane of the target. In the early days of laser damage testing the sample was moved along the axis of the beam waist thereby changing the energy density on the target. Since, however, a knowledge of the beam parameters along the axis of propagation of the beam were hard to obtain, and tedious (via pinhole scanning), results obtained using this method were unreliable and un reproducible. A means of beam attenuation is the more practical and reliable method.
A beam diagnostics package is needed capable of measuring the beam spatially, temporally and also monitoring the total beam energy. To this some form of on line damage detection technique must be added to signify the onset of damage. A Nomarski (differential phase contrast) microscope should be used for off line damage confirmation and to study the damage morphology. The whole system needs to be carefully calibrated. When one reads the literature relating to the early days of damage testing a wide range of damage thresholds can be seen for similar materials due mainly to the different laboratories in which the work was undertaken.

Before a damage test can be undertaken the criteria for damage should be clearly defined. This will depend upon the intended application of the sample under test. For instance V-type anti-reflection coatings on glass substrates [1] undergo very light pitting, discernible only under high magnification or as increased surface scatter, well prior to any catastrophic failure. This form of damage may be acceptable if the mirror is to be used as an external laser window, but not if it is to be used as a resonator mirror. The resultant losses due to the pitting would be unacceptable. Again the damage community seldom considers the fluences at which colour centers appear in their definition of damage. Yet the presence of these absorbing sites can seriously hinder the efficiency of a laser system, if not stop it working altogether. For the purpose of the work undertaken at Loughborough I have erred on the side of conservatism and considered any observable change as damage, however small. This I feel is justified as the work has been intended to further understanding rather than comply with a manufacturer's specification.
The damage threshold or damage fluence, should be for all practical purposes the value at which the substrate or coating would first fail, assuming total and uniform irradiation. Failure in substrates and coatings is generally defect initiated. In scaled damage tests, therefore, where the damaging fluences are obtained by focusing the radiation to small spot sizes, it must be ensured that the spot size at the target surface is at least an order of magnitude greater than the average defect separation, typically in a coating between 50 and 100 μm. This will increase favourably the probability that defects are being irradiated with each shot, hence removing any statistical trends in the damage threshold value.

In the sections that follow the damage facility that has been set up at Loughborough will be described along with the equipment that has been developed to make the laboratory a source of reliable damage data.

2:20 Experimental Arrangement

A schematic diagram of the facility at Loughborough can be seen in Figure 2:20,1. This represents the present system and is the result of five year's work. As mentioned in the introduction we have tried to use as large a beam area in the damage plane as possible to make the figures realistic. The laser is a Lambda Physik EMG 200 excimer laser quoted capable of one Joule at 249 nm, with a maximum repetition rate of 10 Hertz. With fresh gas we have managed a maximum output of around 800 mJ. The output is stable to within 5% on a shot to shot basis and does not deteriorate significantly during the day. We do not use it, however, on a repetitive mode very often which probably accounts for the observed stability in output energy.
Figure 2:20,1 Experimental Arrangement

2:21 The Temporal Profile

The pulse's temporal profile can be seen in Figure 2:21,1. This profile was measured with an I.T.L. 1850 vacuum photodiode and a Tektronix 466 oscilloscope. On a shot to shot basis no variation within the resolution of the
oscilloscope is seen in the profile, yet over a two week period as the gas gets progressively older the profile tends to narrow slightly from a width at half maximum intensity of 28 ns to about 20 ns. It has also been noted that the temporal profile at the edges of the beam is different from the profile at the center. Peak fluences do not occur concurrently at the edge and the middle of the beam, and whereas the middle has two peaks of maximum intensity with time, the edge usually has only one. If the gas is fresh and the laser working well the edge, too, will show two peaks. To quantitatively understand the temporal profile is not easy. The amplification in the discharge plasma is so large [2] and [3] that no resonator at all is required to produce laser emission. The excimer laser and other high gain systems are termed "superradiant". This is in fact a misnomer for the term superradiance was first used by R. H. Dicke [4] in 1954 to describe coherent radiating states in an active media. If a population inversion exists emission may take place by the emission of one atom influencing the emission of others. This leads to superradiance [4] and superfluorescence [5]. There are a couple of characteristics of these phenomena that excimer and other high gain laser systems cannot reproduce.

i) The length of the active media "l" must be smaller than some characteristic length whose value will depend upon the initial inversion.

ii) For a rod shaped active media with diameter "D", the light will be emitted in a solid angle corresponding to the diffraction angle :-

\[ \theta_d = \frac{\lambda}{2D} \]

The difference between superradiance and superfluorescence is small, and depends upon the nature of the initial inversion. If at t=0 the phases of the oscillating dipole moments are random the resulting coherent emission takes
finite time to be established. This is superfluorescence. If, however, at \( t=0 \) a phase correlation already exists between the dipole moments such that a macroscopic dipole moment is present then superradiance is the result. Although high gain lasers are often called superradiant theirs is basically just a case of amplified spontaneous emission, though they do have common features. I.e. the emission lifetime is much shorter than the characteristic spontaneous emission lifetime. In the excimer laser, when the inversion reaches a certain critical threshold an intense emission is observed even if no mirrors are used. This is similar to superfluorescence. The solid angle of emission is no longer derived from the diffraction angle but the cavity geometry as shown in Figure 2:21,2.

![Diagram of emission angle for amplified spontaneous emission](image)

**Figure 2:21,2 Emission Angle For Amplified Spontaneous Emission**

The emission angle for no back mirror in place (2:21,2a) is simply:

\[
\frac{\pi D^2 n^2}{16 \lambda^2}
\]

and for a back mirror in the cavity (2:21,2b) it is:

\[
\frac{\pi D^2 n^2}{16 \lambda^2}
\]

These give values similar to those quoted in the laser handbook for beam divergence. I.e. 4 mrad horizontally and 2 mrad vertically. A point to realise in the above is the
lack of any structure within these lasers that define modes. This means that "superradiant" lasers are not very coherent. Further reading on the subject of superradiance, superfluorescence and high gain lasers can be found in the texts by Yariv, Svelto and Shen.

If it were possible to create an instantaneous population inversion by pumping for a very short space of time with respect to the amplified spontaneous emission curve, the temporal profile would, as already mentioned form some form of bell shaped curve. See Figure 2:21,3 [6]. With a KrF mix $\tau_{sp}$ is of the order of $1.7 \times 10^{-8}$ s whilst

![Figure 2:21,3 Temporal Characteristic Of Superfluorescence Superradiance And Normal Fluorescence](image)

$\tau$ will be proportional to $\tau_{sp}/N$ [7], and in the nanosecond regime. The pumping for the EMG 200, however, lasts for approximately 30 ns and it is the duration of the pumping envelope that gives the profile its pulse width and the characteristic oscillations seen on the falling edge. A form of gain switching is thought to be the mechanism here. For a detailed treatment of gainswitching see [8]. Here I shall just outline the salient features. Gain
switching occurs when the population inversion builds up faster than the photon density within the cavity. This occurs in the excimer systems because of the high transmission of the output coupler, a CaF₂ disk, and the time required to establish the macroscopic dipole of a "superfluorescent" system. Once this dipole has been established, however, the photon population builds up very rapidly and soon depletes the population inversion. The photon density in the cavity will now fall rapidly and the dipole will tend to dephase itself. Pumping is still, however, continuing and the population inversion is re-established, followed by the dipole which re-aligns itself. When this occurs a second peak is seen on the profile as "superfluorescence" and takes over. This relaxation oscillation continues for as long as the pump energy can raise the population inversion over some critical threshold. It has been noticed that by removing the rear mirror so that the cavity simply consists of two 92% transmitting windows that the rise time of the emission is slowed by about 1.5 ns. The doubling of the losses in the cavity means that it takes longer for the "superfluorescent" state to be established, and hence the delay in emission.

2:22 Beam Attenuation

As mentioned in the introduction, a means of beam attenuation is needed in any damage test, and it is preferable to do this by varying the energy in a fixed plane rather than varying the position of the target with respect to the focus. Three techniques were proposed to do this, two were tried and one has been implemented successfully. The three possibilities were
i) using crossed polarizers
ii) using doped transmitting glasses
iii) using an absorbing liquid
The Los Alamos Laboratory in America had been using crossed polarisers to attenuate their excimer radiation and had had a marked degree of success reporting that with use the polarisers tended to become indiscriminate. Bearing this in mind and the price of U.V. polarisers it was thought to look for alternative methods.

A company of optical components and materials in England had just brought onto the market U.V. attenuators for use with ultra violet lamps though they knew nothing about its characteristics under intense laser radiation. Varying thickness samples of these were obtained and their attenuation monitored over a prolonged number of shots. It was found that they became progressively transparent with use and that it was possible actually to imprint through them the laser profile. This system, too, had to be abandoned.

The third method was to use an absorbing liquid and vary the path length of the beam in the liquid. The transmitted intensity would obey Lambert's Law:

\[ I = I_0 \exp(-\alpha x) \]

Where \( I_0 \) = the incident intensity  
\( \alpha \) = the extinction coefficient  
\( x \) = the path length

At first it was considered using a gas and rather than varying the mechanical size of the cell, vary the gas pressure within the cell. It can be shown, however, by an approximate calculation, that if an attenuation of 90% is desired of a 400 mJ beam in a path length of 5cm then one might reasonably expect a temperature rise in the gas of approaching 100°C. A rise of this magnitude could be catastrophic if the gas were flammable, and if not would
almost certainly cause beam deformation by generating refractive index gradients. It was because of this possibility that a liquid medium was chosen. It can easily be shown that in a liquid heating effects will be negligible. If we assume that the solution acts purely as the solvent and that the salts only provide a means of coupling the radiation into the liquid then we can perform a rough estimate using the properties of water only. We define a worst case where most of the energy is absorbed in the first cm of the cell, i.e. we deposit about 400 mJ (90% say). This, from Equation 2:22,1 implies that $\alpha$ is about 0.2. The same equation then implies that in the first mm traversed the media absorbs near on 100 mJ. If the beam dimensions are 2cm by 1cm then this energy is absorbed in a volume of 0.2 cm$^3$. With the S.H.C. of water at 4200 J.Kg$^{-1}$K$^{-1}$ a temperature rise of 1x$10^{-3}$ K can be expected. The effect of this will cause the refractive index of the water to drop by about 1x$10^{-7}$, [9]. There will be no significant change to the beam's spatial profile because of this. It may also be added that for water the temperature coefficient of the refractive index is negative. This means that rather than causing thermal self-focusing (if any effect could occur) it would cause self-defocusing. Such a mechanism would tend to regulate itself.

The mechanical construction of the attenuator can be seen in Figure 2:22,1. The solution chosen was a mixture of two organic salts. Nickelous and cobaltous sulphate. Both of these have a fairly high ultra violet transmission as seen in the diagram for the concentrations quoted. The nickelous sulphate has high transmission peaks at 570 and 900 nm whilst the cobaltous sulphate absorbs strongly in these regions. A combination of the two materials thus gives a solution absorbing strongly over the whole visible region, bar a little hump at 570 nm, yet about 50% trans-
missive between 240 and 320 nm. This is seen in Figure 2:22,3. [10]. The solution was found to retain its prop-
erties under prolonged excimer irradiation. Before its application in any damage test the cell was thoroughly tested and the solution calibrated. Different concentrations of the solution were used, Lambert's Law verified for this application and the extinction coefficient at 249nm was obtained experimentally. Equation 2:22,1 can be written as :

\[ I = I_0 \exp(-kcx) \]  

2:22,2
where \( k \) = extinction coefficient
and \( c \) = the concentration based on an arbitrary reference

The reflected intensity co-efficient is:

\[
r = \left( \frac{n_1 - n_0}{n_1 + n_0} \right)^2anumber{2:22,3}
\]

and hence:

\[
r(\text{air-quartz}) = r(\text{quartz-air}) = 0.04
\]

and similarly:

\[
r(\text{quartz-solution}) = r(\text{solution-quartz}) = 0.005
\]

We choose to neglect the 0.5% intensity loss due to the reflection from the solution-quartz interfaces and then apply the following analysis. With the solution in the

\[
\begin{align*}
\text{Air} & \quad \text{Quartz} & \quad \text{Liquid} & \quad \text{Quartz} & \quad \text{Air} \\
I_0 & \quad I_0(1-r_{AQ}) & \quad I_0(1-r_{AQ}) & \quad I_0(1-r_{AQ}) & \quad I_0(1-r_{AQ})e^{-kcx}
\end{align*}
\]

Figure 2:22,4 Reflection Losses Through The Quartz Cell

the loss through reflection will be of the order of 8% i.e. \((1 - r_{AQ})^2\). Then from:

\[
I = I_0 \exp(-kcx)(1-r_{AQ})^2
\]

we get:

\[
I = I_0 \exp(-kcx)(1-r_{AQ})^2
\]
\[
\ln \left( \frac{I}{I_0} \right) = -kcx + \ln \left( 1 - 2r_{AQ} + r_{AQ}^2 \right)
\]

and, hence, plotting \( \ln \frac{I}{I_0} \) against \( x \) gives a gradient of \(-kc\). The attenuation as a function of path length and the natural log of the attenuation as a function of path length for three different concentrations can be seen in Figures 2:22,5 and 2:22,6 respectively. The value of "k" was found to be 0.30 ± 0.03 for a unity concentration solution as defined by (1) on Figure 2:22,5.

It can be seen from Figure 2:22,4 that the contribution to the output intensity by the reflected components will be negligible. Taking the reflection from the exit surface, before it can add to the output intensity it must twice traverse the attenuator liquid as well as losing 96% transmitted through the back surface. Hence when it re-arrives at the front window its intensity will be sufficiently attenuated as to be of no consequence.

As a final consideration for the attenuator it can be shown that the insertion of a cube of material, about 5 cm long, with a higher refractive index, into the path of a slightly divergent beam, prior to a focusing lens, has little effect on the focus parameters. By using, for simplicity, geometrical optics and taking the object distance to be 200 cm (a typical figure for the situation at Loughborough), the addition of the cell (\( n = 1.33 \)) effectively moves the object 1.25 cm towards the lens. If the lens has a 10 cm focal length, the position of the focus will change by 0.004 cm. This is less than the accuracy to which we can position the target plane, and its effect will be overruled by greater errors elsewhere in the system. The above was experimentally verified by profiling the beam with the cell fully extended and then fully compressed. No change in beam dimensions were detected and...
Figure 2.22.5 Attenuation As A Function Of Path Length

<table>
<thead>
<tr>
<th>NiSO₄·6H₂O</th>
<th>CoSO₄·7H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>gms/200mls</td>
<td>gms/200mls</td>
</tr>
<tr>
<td>48.0</td>
<td>9.0</td>
</tr>
<tr>
<td>77.8</td>
<td>14.6</td>
</tr>
<tr>
<td>107.6</td>
<td>20.2</td>
</tr>
</tbody>
</table>

Path Length (cm.)
neither was there any change in the localised spatial non-uniformities.

The only note of caution with the attenuator is that care must be taken, after having moved the plunger, to re-align it against some reference position on the housing. It would appear that the windows are not perfectly parallel and so rotation of the plunger with respect to the housing causes a slight rotation of the focused beam. Prior to a damage test, therefore, during the alignment procedure, the position of the plunger should be noted. As it is moved during a series of measurements it must always be replaced to the same angular orientation. This will ensure a reproducibility of all the parameters.

2:23 Beam Profiling

2:23,i

After the completion of a damage test and the energy needed to initiate damage has been determined the figure will only be meaningful if the laser pulse has been accurately measured in the target plane. There are various ways of expressing the damage threshold but they all derive from the following analysis.

In a target plane normal to the axis of propagation of the beam the instantaneous local intensity can be described by a spatial profile function \( g(x,y) \) and a temporal profile function \( h(t) \) such that:

\[
I(x,y,t) = I_o g(x,y) h(t)
\]

where \( I_o \) represents the peak axial intensity (W.cm\(^{-2}\)). In actual fact, to prevent back reflections into the laser cavity causing power fluctuations by increasing the energy
output of the cavity and extending h(t), the normal to the target surface is inclined at a small angle to the direction of propagation. This small angle, however, can be ignored. Integration over the duration of the pulse yields the axial fluence $F_0$ (J.cm$^{-2}$).

$$F_0 = \lim_{\substack{x \to 0 \\ y \to 0}} \int_{-\infty}^{\infty} I(x,y,t) dt = I_0 \int_{-\infty}^{\infty} h(t) dt = I_0 T_{eff} \quad 2:23,2$$

The integrated temporal profile function has units of time and represents an effective pulse duration $T_{eff}$. The peak power $P_0$ (W) is obtained by integrating over the target plane:

$$P_0 = \lim_{t \to 0} \iint_{-\infty}^{\infty} I(x,y,t) dx dy = I_0 \iint_{-\infty}^{\infty} g(x,y) dx dy = I_0 A_{eff} \quad 2:23,3$$

The integrated spatial profile represents an effective cross sectional area $A_{eff}$. Integrating the intensity over both time and space yields the total energy in joules:

$$E_T = I_0 A_{eff} T_{eff} \quad 2:23,4$$

For work undertaken on pulsed lasers, damage thresholds are usually quoted as J.cm$^{-2}$. Using the laser calorimeter a direct reading of the total output energy is obtained. I.e. the calorimeter measures $I_0 A_{eff} T_{eff}$. To convert this figure into an energy density we must divide by $A_{eff}$. This then gives J.cm$^{-2}$. The energy in the beam is given by:

$$E_T = \iiint_{-\infty}^{\infty} F(x,y) dx dy \quad 2:23,5$$

where $F(x,y)$ is the fluence distribution and is equivalent to:

$$F(x,y) = F_0 g(x,y) \quad 2:23,6$$
The peak fluence is then obtained by:

\[ F_0 = \frac{E_T}{\int g(x,y) \, dx \, dy} \]

This analysis assumes that the beam is centrosymmetric. It becomes obvious that there must be found a way of experimentally determining:

\[ \int g(x,y) \, dx \, dy \]

Virtually all the damage laboratories simplified this measurement by assuming that their beam profile at the target plane was equivalent to a circular or elliptical gaussian. They then chose the effective area to be the beam dimensions at the 1/e² point. This meant that the effective area was:

\[ A_{\text{eff}} = \prod c_1 c_2 \frac{1}{2} \]

and the beam needed only be profiled once in the horizontal and once in the vertical direction to obtain the values of \( c_1 \) and \( c_2 \). \( c_1 \) and \( c_2 \) being the gaussian widths at the 1/e² point. This method is all well and good if the assumptions can be met. I.e. if the profile is a good approximation to a gaussian. In many lasers, however, this is not the case and especially in regards to the excimer systems. In the absence, though, of quick, accurate profiling methods most measurements, including our own were based on the above. It is hardly surprising then to see such a range of damage data. Later in this section I shall return to the profiling system we now use to get an abso-
lute value of the peak fluence, but for the moment will briefly describe some of the other attempts we had at measuring the profile.

2:23, ii Burn Paper

There exists a number of ways of measuring the transverse beam intensity, the different methods being suited to the variety of lasers available. The methods may be classified as follows:-

i) Photographic techniques

ii) Beam scanning techniques

For a detailed introduction to the history, use and bibliography of the methods in use see [11]. Not mentioned in the above is the use of burn paper. Although this does not actually provide the user with knowledge of the spatial profile itself it does allow him to make a reasonable estimate of the energy density in the target plane. Since this is the aim of profiling techniques it should not be forgotten. Polaroid paper was for a long while the most popular burn paper even though its damage threshold was very ill defined and the beam dimensions were open to speculation. Kodak, however, have recently produced a burn paper specifically for laser diagnostics. This paper was investigated at Loughborough, and found useful if no alternative is available, though a little clumsy for regular use. It is a helpful guide in aligning the laser cavity as it provides a quick test of the approximate intensity distribution. The burn pattern highlights the beam symmetry. To measure energy densities with the material it must first be "calibrated" in the target plane. Again it is necessary to assume that the beam profile is some regular function and a gaussian is chosen. Defining the gaussian radius in the x-direction as \( \rho_1 \) and in the y-direction as \( \rho_2 \) the spatial intensity function becomes:-
The beam energy is given by:

\[ E = \int_{-\infty}^{\infty} e^{-\frac{x^2}{\sigma_1^2}} \int_{-\infty}^{\infty} e^{-\frac{y^2}{\sigma_2^2}} \, dx \, dy \]

Using the substitution \( t^2 = \frac{x^2}{\sigma_1^2} \) and \( t_1^2 = \frac{y^2}{\sigma_2^2} \) and performing the integration the energy is shown to be:

\[ E = \pi \sigma_1 \sigma_2 \]

Returning to equation 2:23,11 and taking the natural logs we have:

\[ \ln I = \ln I_0 + \frac{x^2}{\sigma_1^2} + \frac{y^2}{\sigma_2^2} \]

The burn paper, as mentioned, has a sharply defined threshold \( I = I_B \). At this threshold we shall define the beam parameters as \( x_B \) and \( y_B \). Then at the threshold:

\[ \ln I = \ln I_0 + \frac{x_B^2}{\sigma_1^2} + \frac{y_B^2}{\sigma_2^2} \]

And substituting from equation 2:23,3 we get:

\[ \ln E = \ln I + \frac{x_B^2}{\sigma_1^2} + \frac{y_B^2}{\sigma_2^2} \]

By measuring \( x_B \) and \( y_B \) for varying incident energies and plotting \( \ln E \) against \( x_B^2 \) and \( \ln E \) against \( y_B^2 \) a straight line graph results to which future measurements of the burn dimensions can be related and the energy densities immediately ascertained. Figures 2:23,1,2 and 3 show the calibration lines for three different target planes. Once these graphs have been obtained this method is a quick and
Figure 2:23.1 Burn Dimensions vs. Incident Energy

Damage Plane is 65mm Inside Focus Of 20 cm. Lens
Figure 2:23,2 Burn Dimensions vs. Incident Energy

Damage Plane Is At The Focus

\[ \text{Damage Plane Is At The Focus} \]

\[ \text{Energy (mJ)} \]

\[ \text{Energy (mJ)} \]

\[ d^2_2 \text{ (mm}^2) \]

\[ d^2_1 \text{ (mm}^2) \]

36
Figure 2.23.3 Burn Dimensions vs. Incident Energy

Damage Plane is 65 mm. Beyond the Lens Focus
easy way of obtaining the energy density on the sample. Due to poor burn patterns at the low fluences it is not really reliable for measurements below about 500 mJ.cm\(^{-2}\). It must also be remembered that it is a fairly inaccurate method because of the initial assumption of a gaussian profile. Its main use, we have found, is solely in aligning the laser cavity.

2:23,iii Photographic Techniques

Semi-quantitative intensity measurements are possible using standard photographic procedures. Photosensitive emulsions respond to optical energy in a characteristic manner that is defined by the "D-logE" curve. This represents a plot of the optical density of the film against the log\(_{10}\) of the exposure. Exposure being the intensity multiplied by the time. If the "D-logE" curve is available it is then possible to relate back to the intensity that was present at any point in the image plane by measuring the optical density at that point. For further details see [12] and [13]. None of the theory of photographic densitometry will be covered in this thesis for it is well documented in the literature, but a brief outline of the methods approached at Loughborough will be given. Two techniques were used:

i) Using Dylux 608 film

ii) Using standard black and white negative film.

The Dylux 608 film is produced by the Du Pont Corp. Photo Products Department as an instant image, dry process photographic proofing material for use in the graphic arts industry. Our attention was first brought to the film by M. W. Taylor [14] where the author reported using it for U.V. beam diagnostics. The material develops a blue image when exposed to radiation below 400 nm and can then be
fixed by an intense exposure to visible light. The blue dye formed on exposure has an absorption band that peaks at 625 nm with half width points at 660 and 570 nm. For the purposes of densitometry it can be read with a red filter or a He-Ne laser. The manufacturer's quoted spectral response can be seen in Figure 2:23,4. Before it could be used for laser beam diagnostics certain properties of the film needed to be investigated:—

i) The effect of reading the density with a He-Ne beam.

ii) The image stability.

iii) The dynamic range.

These are placed in order of experimental necessity.

To monitor the image density a He-Ne laser was used in the following arrangement. It was noticed that with the

Figure 2:23,4 Spectral Response Of Dylux 608 Film [15].

Figure 2:23,5 Densitometer Arrangement.
application of the laser beam the density began to fall fairly rapidly as the dye was thermally annealed. This effect can be seen in Figure 2:23,6. A safe operating level needed to be determined that would not alter the dye's density. For this reason the interference filter was placed in the path of the He-Ne laser and the chopper used. It was possible to attenuate the beam sufficiently using the filter but the signal out of the detector was then so small that unacceptable errors were being introduced. The chopper had a mark space ratio of about 1:140 and enabled the beam intensity to be considerably increased without bleaching the dye.

According to [14] a 7% decrease in optical density could be expected after five days storage in an unfixed state, in the dark. Fixing, as already mentioned, is achieved by exposure to intense visible light. This had been observed to give rise to a lower image density and a higher background density [14]. The degree to which these changes occurred depended upon the conditions of fixing and were found to be unreproducible. Couple this to the fact that the image density will still degrade after fixing and it appears best to read the material in the unfixed state, and store it in the dark. When operating, therefore, subdued room lighting is recommended and no fluorescent lighting must be present. The rate at which the image density degraded was investigated by exposing several samples to the focused, attenuated excimer beam, and then monitoring the optical density of the samples over a ten week period. The densitometer of Figure 2:23,5 was used for these measurements. The sample was scanned in the beam's horizontal plane. The results have been plotted in Figure 2:23,7. There would not appear to be any obvious trend for the optical density to decrease and any variations in density can be attributed to slightly differing
Figure 2: Bleaching of Absorption Band as a Function of Exposure Time.
Figure 2: Image Stability

- Film 1
- Film 2
- Film 3
- Film 4
- Film 5
scan lines over the duration of the experiment. Using a white light microdensitometer and a red filter produced the horizontal profile of Figure 2:23,8. Most of the structure can be attributed to detector noise as the red filter was greatly reducing the signal strength. The two
main spikes, however, can be put down to beam irregularities, i.e. "hot spots" occurring in the beam profile. This has proved to be the only method we have found capable of detecting these "hot spots". This example serves to illustrate the potential of the Dylux film. Given the availability of a scanning microdensitometer using Dylux could prove to be a much quicker way of beam profiling than conventional pin-holing techniques. If one is only concerned with measuring the $1/e^2$ parameters the calibration of the film is not a critical consideration as long as the operator is confident that he is working in the film's linear region, and is not above saturation.

The final experiment performed on the Dylux was to confirm the D-logE curve given in [14]. This can be seen in Figure 2:23,9. Initial experiments seemed to indicate

![Figure 2:23,9 D-logE Curve [14]](image)

that saturation was occurring at an optical density of 0.33. This is in contradiction to the curve of Figure 2:23,9. Four samples of Dylux were exposed to a "top hat" intensity profile of known dimensions and energy content.
Figure 2:23,10 Dylux D log E Curve

The error bars represent the region of overlap in the individual error bars of each four sample films.
and the density then measured. This was done over a range of energies and the D-logE curve of Figure 2:23,10 plotted. This curve represents the region of overlap of all four samples. The low energy portion could not be accurately obtained as we did not possess a calorimeter sensitive enough. The four samples of Dylux used here all came from the same batch.

It is seen that the dynamic range obtained at Loughborough is less than that of [14]. We would suggest from our readings that a safe operating range would be between 10 to 40 mJ.cm\(^{-2}\), whilst [14] could claim a range of 5 to 80 mJ.cm\(^{-2}\). This discrepancy may arise because of differences between production batches or because of shelf life effects. Whatever the cause, it would appear that the D-logE curve would need to be established prior to any quantitative evaluation, and must be considered to vary from sample to sample. This would, to some extent, hinder the usefulness of the material, though for quick measurements and for looking for intensity irregularities it is ideal.

2:23,iv Black And White Processing

Dylux film, though quick and simple to use was found to be unreliable for quantitative measurements. Its disadvantage was a lack of reproduceability between, perhaps, batch numbers or else the effect of the shelf life altering the material's U.V. response. In order to use it with confidence would require its calibration prior to every profile. To overcome this normal wet processing techniques were tried, using standard consumer film, i.e. Ilford's FP4. This material is well documented and standardized between batches. The negatives are very stable over long time periods and under normal lighting conditions. Handl-
ing care is therefore reduced to a minimum. The film does have two disadvantages for U.V. beam diagnostics. Namely the time taken to process it, but more importantly, its U.V. response cuts off at about 375 nm. This means that a method of converting the 249 nm radiation to the visible, without changing the spatial profile, is needed.

![Figure 2: Spectral Dependence Of Singlet Absorption And Emission For A Solution Of Rhodamine 6G](image)

To do this conversion the laser beam was shot into a solution of Rhodamine 6G. Rhodamine 6G is an efficient laser dye, often excimer pumped at 249 nm. The resulting emission is around 600 nm. The dye solution was weak, $10^{-4}$M.l$^{-1}$, yet strong enough to absorb completely the excimer radiation in a 6 cm path. It is assumed that the absorption follows Lambert's Law, and that the fluorescent
intensity would, over a certain range of input energy, linearly follow the absorption. This would imply that the fluorescence intensity would be directly proportional to the input intensity at any point on the spatial profile. We are also assuming that the solution is transparent to, and unaffected by its own emission. This is justifiable if we consider Figure 2:23,11 [16].

An SLR camera was used and the laser was synchronised to the camera shutter. The camera took side on photographs of the fluorescence as shown in Figure 2:23,12. Analysis

![Diagram]

Figure 2:23,12 Photographic Arrangement

of the negatives is not easy and one needs at least two negatives for each profile if any quantitative results are required. A microdensitometer scan across the surface of
the liquid can be seen in Figure 2:23,13. The scan has been performed in two directions so the profile can be
extracted from the detector noise. This profile does not represent a line scan of the beam. Consider Figure 2:23,14. Assuming that the photographic acceptance angle is negligible then a single point on the density scan represents the sum of a single line of emitting sources in the solution. As an aside it should be noted that the depth below the surface chosen for the scan is irrelevant as long as the Rhodamine solution is not being saturated and non-linear effects are present. This was shown to be true by scanning perpendicular to the surface, i.e. into the volume of the fluorescer, and using the film's D-logE curve to convert the scan into a graph of logE against depth. This can be seen in Figure 2:23,15. The graph produces a straight line.

If one could digitize the surface scan it would then be possible to produce a three dimensional intensity map of the input beam. If we assume for convenience sake, that the input beam is a perfectly symmetric gaussian as in Figure 2:23,16 it would give rise to the densitometer scan
Figure 2: 23, 15 Intensity Depth Profile

shown. Then, given that the 'I' values represent the areas shown in the figure and the 'e' values the emittance of all the point sources within the area governed by 'I' it can be seen that:

\[ I_1 \propto l_1 e_1 \]
\[ I_2 \propto 2l_2 e_1 + l_3 e_2 \]
\[ I_3 \propto 2l_4 e_1 + 2l_5 e_2 + l_6 e_3 \] and so on

\( I_1 \) is known from the film density and \( l_1 \) can be calculated, hence \( e_1 \) found. Using this value for \( e_1 \) we can now find \( e_2 \) and so on until the whole profile is plotted.

This analysis is fine for a perfectly symmetrical beam without irregularities. To overcome the effect of hot
spots and non symmetrical beams at least two photographs would be needed taken at right angles to each other. One

\begin{figure}
\centering
\includegraphics[width=\textwidth]{cross_section_densitometer_scan}
\caption{Cross Section Under Consideration Densitometer Scan}
\end{figure}

would then have to correlate the intensity patterns produced in each scan in the above analysis to localize the non-uniformities. This was never done as it was obvious that a simpler technique would be to photograph the beam end on rather than side on. This would side step the above procedure. The work of the next section describes the present profiling system.

2:23,v Beam Scanning

The principle behind this method is very simple. A photodetector, sampling only a small portion of the beam's intensity profile, is used to scan the beam in space. With pulsed laser systems many shots may be needed to build up an averaged profile, a truer representation being obtained the more repeatable the laser is in output energy. The EMG
200 has typically a 5% variation in energy, shot to shot, and in performing a "pinhole" scan we average each detector position over 16 shots. With a beam size on target ranging from two to three millimeters, a pinhole of 50 µm, and sampling every 100 µm, the process is a long one. A computer programme was developed by S. S. Wiseall to correct for the size of the pinhole on the final profile, but the error was generally so small that this was seldom used, the errors in calorimetry being much greater.

The main limitation to pinhole scanning is that it provides information along a single line only. The beam is therefore assumed to be a specific shape to which the scanned profile then fits the relevant parameters. As already mentioned we assume a gaussian distribution and use the $1/e^2$ dimensions to determine the effective area. This method, along with knife edge inversion techniques is still probably the most common in use today [11].

There are two points of caution in using pinhole scanning. With the pinhole located in the target plane, this often being very close to the focus of the beam, the energy of the radiation must be very much attenuated to prevent damage to the pinhole itself. One must remember that in a completed scan the pinhole will face many shots so one must work well below the multiple shot damage threshold. This will prevent the physical dimensions of the pinhole changing and thereby giving false readings. Secondly one must ensure that the energy incident on the detector is well below the damage threshold. This is not as obvious as it may seem for if the target plane is in front of the focus the radiation will be further focused on going through the pinhole, and the damage threshold may then be reached at the detector face. We use a pyro-electric detector with a photosensitive area of about 2mm x
2mm, and always try to ensure that at least 75% of the detector's surface area is being irradiated.

Using a Gould Biomation Transient Recorder, which has an automatic averaging facility, pinhole scanning is a simple technique, if tedious. All the methods described so far have only provided line scans of the beam. The photographic methods have all the information contained on the film to reconstruct a full three dimensional profile, and yet this information is hard to obtain. The Dylux film would offer the best method if it could be scanned by a densitometer across its whole surface. This however would take a lot of time. The following section describes our present profiling system which is capable of quickly providing all the relevant information, including values such as the peak on axis intensity and the average fluence.

2:23,vi The Image III Profiling System

The profiling system was developed at Loughborough in conjunction with Dr. M. J. Shaw and Mr. B. A. Omar of the Laser Division of the Rutherford Appleton Laboratories. It consists of a solid state camera and a video frame store controlled by an Apple IIe microcomputer. A block diagram of the profiling system can be seen in the Figure 2:23,1.

The camera has a U.V. spectral cut-off at around 400 nm. This is a consequence of the the charge transfer electrode structure, used to provide the read strobe, being deposited over the imaging area. This polysilicon layer absorbs the U.V. Thus, as with the wet processing method, a means of converting the U.V. to the visible was needed, and past experience had shown that it was desirable to photograph the beam end on. A material with a very large absorption was required. Dr. Shaw and Mr. Omar tried a
number of doped glasses before concluding that the best fluorescer was a borosilicate microscope coverslip. These coverslips are about 150 μm thick and have a U.V. penetration of around 1 μm, [17]. This ensures a good three dimensional representation of the profile and as it is transparent to its own fluorescence it can be viewed in reflection or transmission providing a little bit of experimental flexibility. It has a damage threshold between 1 and 2 J.cm\(^{-2}\). The dynamic range and linearity of the fluorescence was investigated at the Rutherford Appleton Laboratory using two calibrated photodiodes, one measuring the U.V. beam energy and the other the fluorescence emission. It was found that the linear range lay between 10 μJ.cm\(^{-2}\) and 10 mJ.cm\(^{-2}\). The camera is used to directly image the fluorescence. Its magnification is easily adjusted to suit different damage spot sizes. The camera in use at present is a Hitachi KP-120. This employs Hitachi's monochromatic imaging chip HE97211, a MOS device comprising a photodiode array of 320 (H) x 244 (V) pixels with a unit cell size of 27 μm x 27 μm. [18]. The picture elements are arranged to have the same pitch horizontally and
vertically and so no geometric distortion is produced. Such distortion is an unavoidable consequence of vidicon tubes. This camera, apart from very favourable size considerations, is ideal for profiling applications. The use of a solid state device prevents the picture from lag and sticking problems commonly associated with the conventional vidicon tube. Sticking occurs when the same object is viewed for a long time or when an extremely bright object is imaged. The image produced may never completely fade away. As we have used the camera to profile He-Ne beams directly we have on a number of occasions exceeded its operating range and saturated it. No permanent damage has yet been produced whereas it would almost certainly have damaged a vidicon camera.

A further advantage of the solid state device is that it may be used to image very fast events, in the ns regime, given enough light. With the use of lasers as the light source this becomes feasible. This capability arises from the manner in which the device images and is read. Each pixel, or photodiode, is turned on for an imaging period and then off for a read period. With CCDs (charge coupled devices) all the photodiodes are on simultaneously and off simultaneously. The HE97211 is different in that it sequentially reads the array, so that while some of the photodiodes are being read others are imaging, i.e. integrating all the light that falls upon them. During the field blanking period, however, [18], of 4 ms duration all the photodiodes are on and imaging. If, therefore, the event can be arranged to occur within this time slot and the camera is kept in the dark, then, however quick the event, it will be recorded and the information retained until the pixel is read and reset. The same principle applies to CCDs though the window of integration is longer, about 18 ms. With vidicon tubes this is not possible.
as the image must continually be refreshed. Fast events may have faded away before the image has been completely scanned. The fluorescence of the borosilicate glass is of the order of 100μs and so with the appropriate triggering it is easy to image it with the KP-120.

The Image III Frame Store, from which the system takes its name, is a TV picture store board developed by the British Telecom Research Centre as a cheap monochrome digital field store with hardware selectable resolution. Included on the board is a digital field store, a microprocessor interface, all the input/output analogue television circuitry and six bit A/D and D/A converters. The highest resolution obtainable is a single 512 x 512 pixel picture. Lower resolution, however, can be obtained to give multiple field stores on the one board. Two stores are available if a resolution of 512 x 256 is chosen and four if 256 x 256 pixels is adequate. Six planes of storage exist for each resolution giving rise to 64 grey levels.

The store board interfaces directly with any of the Motorola 6800 series of microprocessors and occupies a 1K block of the microprocessor memory. Individual pixels can be accessed by storing their x-y locations in address latches and then instructing the store to perform a read or write operation. This feature makes available a whole variety of user designed video processing operations. The Apple IIe microcomputer has been interfaced to our frame store. A field snatch may be requested either by the microprocessor controller causing the snatch control circuitry to respond to the start of the next full field, or by externally pulling an input on the snatch control circuitry to ground. This feature is very useful in synchronising the store to the laser and camera.
In the discussion on the camera it was noted that fast events shorter than the field blanking period could be captured if they were arranged to coincide with this part of the video waveform. The composition of a 625 line monochrome waveform can be seen in Figure 2:23,18.

![Figure 2:23,18 Composition of A Video Signal](image)

**Waveform Durations (between half-amplitude points):**

- Line period: 64 µs nominal.
- Line blanking: 12.05 ± 0.25 µs.
- Front porch: 1.55 ± 0.25 µs.
- Line-synchronize pulse: 4.7 ± 0.1 µs.
- Field-period: 20 ms.
- Field blanking: 25 lines + 12.05 µs.
- Equalising pulse: 2.33 ± 0.1 µs.
- Separation between fields: 4.7 ± 0.1 µs.

Figure 2:23,18 Composition of A Video Signal [19]
A frame constitutes two fields, each with a field blanking period of 1.612 ms. Each line of video information is separated by negative going line sync pulses of 4.7 µs duration. From Figure 2:23,18 it can be seen that the fields are also discerned by a series of negative going pulses of the same level but a longer duration (27 µs) than the line sync pulses. After the occurrence of the field sync pulses there still remains 1.28 ms of field blanking time. This is long compared to the 100 µs of fluorescence signal needing imaging. The triggering has therefore been based upon the field sync pulses.

The sequence of triggering is as follows. When the experiment is ready the operator manually presses a start button. This causes the trigger electronics, continually monitoring the video signal, to combine the manually formed pulse with the next field sync pulse. This pulls to ground the relevant input of the field store's snatch control. The field store is then initiated to snatch the next field that comes along. The trigger electronics waits for the next field sync pulse. When it detects it, it sends a trigger signal to the laser's external trigger socket and within 10 ns the laser fires and the 100 µs of fluorescence is initiated. This information is then contained in the field formed by the camera and captured by the frame store. A block diagram of the triggering and the timing can be seen in Figure 2:23,19.

The hardest part of the trigger circuit was separating the field sync from the line sync pulses. This was achieved as follows. The trigger electronics receives the video signal and inverts it. It then strips from it all the picture information leaving only the scan control pulses. I.e. line and field syncs. These need to be distinguished from each other and the line syncs removed. This
is done by integrating. Obviously
\[
\int_{0}^{4.7\mu s} A(t)\,dt < \int_{0}^{7\mu s} A(t)\,dt \quad 2:23,17
\]
and so a level detector may then be applied to the output to determine whether a field or line sync is present. Caution is needed in this process for changing the level of illumination on the camera shifts the d.c. level of the

![Triggering Arrangement For Profiler](image)

Figure 2:23,19 Triggering Arrangement For Profiler

signal and can significantly alter the setting needed on the level detector (comparator). Once the field sync pulses have been extracted from the video signal the logic to derive the trigger pulses is easy to construct. I shall not deal with that here for anyone wishing to construct such a system would need to design it for the laser to be triggered, each being different in operation. Suffice it to say it is not a difficult task.

It has been shown that the system is simply three sub-systems, i.e. a camera, a digital store and a micro-processor control, linked by a triggering system. It was necessary to determine whether any of these three sub-systems was likely to introduce any non-linearity into the recorded beam profile. The work of Dr. M. J. Shaw and
Mr. B. A. Omar, already referred to, ascertained the acceptable working fluences for the boro-silicate glass slide, to prevent any excursions into a non-linear regime. This left the camera and the field store to be investigated. The camera's linearity was checked using a source of known intensity and calibrated filters. The output video signal was monitored on an oscilloscope and the signal level plotted against the source intensity. The results proved to be linear over the camera's working range. The camera was also checked using a calibrated grey scale with a linear progression of reflectance. Again the output proved to be linear. The automatic gain control on the camera, though not disabled, is not significant to our profiling application as it does not adjust the level of the video signal's background instantaneously. The adjustment will begin a frame later and continue as the camera monitors the background over a number of frames. As we are only concerned with the first field to contain information the gain control is irrelevant.

The greyscale used to check the camera's linearity was also used to check the field store's A/D convertor. The graded scale was "snatched" by the store and then a programme written to profile the stored grey scale. It was found that the steps were again linear. Thus providing care was being taken to ensure that:

i) The fluorescer was not being excited beyond its linear response

ii) The fluorescer was not saturating the camera

confidence in the system's linearity was ensured. It was found that the fluorescer reached its non-linear range before it saturated the camera. To exploit this a video amplifier was built to amplify the video signal prior to the field store. The video signal was then adjusted to give $1v_{pk}$ to $pk$ corresponding to fluorescence right on
the edge of the glass's linear region. This meant that full use of the field store's 64 grey levels were made and also proved to be a useful guide to operating the glass slide in the correct range. With operating conditions changing every experiment the simplest way of judging whether a safe fluence was incident upon the fluorescer was by seeing if the 64th grey level (corresponding to the maximum intensity) was being reached. If so the energy was attenuated a little and a new profile taken. If only the 63rd grey level was reached we would know that the whole system was linear.

Data processing with the field store is easy as each pixel can be addressed individually by the Apple Computer and its grey level monitored. The routines initiating field snatches, read and write operations and data retrieval etc, i.e. all routines involving the field store directly must be performed in Assembly Language. This is because of speed considerations when one bears in mind the large number of points in a single frame of 512 x 256 pixels. Once the data has been accessed, however, arithmetic operations may be performed in Pascal or any language compatible with the Apple. At Loughborough we have only used the field store in its 512 x 256 mode giving us two stores. This is necessary for some of the routines developed require an updated picture and a reference picture. I.e. the act of writing a cursor over one store destroys the information under the cursor. This information must then be retrieved from the second store if the pixel values are required. The computer programmes for the routines will not be given in this thesis. Many of them were developed for commercial customers and are not relevant to the work for this degree. I am indebted to Mr. S. Clarke who performed the bulk of the programming. For all the programmes and the present scope of the system see [20].
Here I shall describe only the function of the routines used in profiling and damage testing experiments.

One of the first programmes to be written, labelled "Profile", enables the operator to place a cursor horizontally, vertically or at any angle over any portion of the screen and obtain an intensity profile of the line under the cursor. The cursor may be moved at the operator's will and will continually update the intensity profile accordingly. At the operator's request the area under the profile will be calculated as well as the $1/e^2$ values. These will be displayed upon the monitor screen or a hard copy of the profile, cursor position, area and $1/e^2$ values may be selected. This is very useful in quickly ascertaining the beam quality at the focus, searching for unwanted hot spots and generally characterising the beam spatially. It requires that the laser be fired only once, and so variations on a shot to shot basis can be monitored. It must be commented that the beam is very stable in its spatial output.

The programme most useful for damage testing is one entitled "Stats". This programme enables the operator to derive the following information:

i) Fluence per grey level
ii) Average fluence
iii) Standard deviation of the fluence
iv) Peak fluence

It is the value of the peak fluence that is the most relevant as it enables us to define damage thresholds realistically making no assumptions about the beam shape and effective area. A typical horizontal and vertical profile of our excimer laser can be seen in Figure 2:23,20. Horizontally the profile is flat, covering a substantial portion of the beam. The peak fluence figure measured at the
damage threshold can be taken with confidence to represent the true damage threshold of the sample. The beam is wide enough in this region to encompass a number of defect sites, removing the statistical dependance on defects.

When using the "Stats" programme the operator must first measure the geometric distortion introduced by the field store's digitization. This results in stored pixels being taller than they are wide, and the new area of these pixels must be found. No longer do they correspond to the camera's 27 x 27 \( \mu \)m. This is easily done by imaging and storing a grid of known dimensions located exactly in the damage plane. At the same time this gives us the magnification factors needed to work out the beam dimensions.
Having stored the grid the "profile" programme is used to measure the distance between the grid lines in units of pixels, both horizontally and vertically. From this information the pixel area in cm\(^{-2}\) can be calculated. One other measurement is necessary. The energy of the beam incident upon the fluorescor must be measured as the programme requires this figure to calculate the fluences. This must be given in joules.

The fluence per grey level and hence the peak fluence is calculated using the following algorithm, on the basis that the whole system is linear:-

We take any given pixel irradiated with an incident energy \(E_i\). Then:

\[
E_i = k'g
\]

where \(k'\) = energy per grey level
and \(g\) = grey level of pixel

The pixel fluence is given by:

\[
F_i = kg_i = E_i / \text{Pixel area}
\]

where \(k\) = fluence per grey level

The pixel area is:

\[
\frac{1}{N_xN_y}
\]

where \(N_x\) = number of pixels in the x-direction
and \(N_y\) = number of pixels in the y-direction

The energy \(E_i\) is thus:

\[
E_i = \frac{F_i}{N_xN_y}
\]

If we have \(n_i\) pixels with energy \(E_i\) upon them, then the
The total energy of the \( n_i \) pixels is simply \( n_iE_i \). The total energy \( E_T \) over the whole profile is the summation of \( n_iE_i \) over each quantized (by the field store's A/D convertor) energy:

\[
E_T = \frac{\sum n_iE_i}{N_xN_y} = \frac{\sum k_i g_i n_i}{N_xN_y} \tag{2:23,22}
\]

and hence:

\[
k = \frac{E_T N_x N_y}{\sum g_i n_i} \tag{2:23,23}
\]

In determining "\( k \)" no allowance has been made for background light levels adding to the profile's apparent intensity. This will arise from both background room lighting, though it is kept at a minimum, and the imaging device's dark current. We assume that the data does have an unacceptable level of d.c. background light. This is subtracted as follows:

Let

\[
g_i(\text{true}) = g_i - g_b \tag{2:23,24}
\]

where \( g_b \) = grey level due to background

Then:

\[
k = \frac{E_T N_x N_y}{\sum (g_i - g_b)} \tag{2:23,25}
\]

\[
k = \frac{E_T N_x N_y}{I_T - n g_b} \tag{2:23,26}
\]

where \( I_T = \sum g_i \) and \( n = \) total number of pixels over the TV screen.

Having thus found "\( k \)" the fluence per grey level, it is simply a matter of multiplying this figure by the peak grey level in the profile. The Apple IIe can easily be taught how to search out this value yielding the peak
fluence.

To enable the operator to decide what the background level is the programme will first display a histogram of all the grey levels. This is shown in Figure 2:23,21. Note that this figure has been normalized for the Apple Graphics system and the higher grey levels occurring only a few times cannot be seen. It does not mean they do not exist. From the histogram it is obvious that levels 1 and 2 are the most common, indicating that these are due to background noise and not the laser profile. The operator, as shown by Equations 2:23,25 and 26 is given the option to subtract these.

The Average Fluence, $\bar{F}$, is calculated as follows:

$$\bar{F} = k\bar{G} = \frac{k \sum n_i(g_i - g_b)}{\sum n_i}$$  \hspace{1cm} 2:23,27

where $\bar{G}$ = average values per grey level

Hence:

$$F = \frac{E_T N_x N_y \sum n_i(g_i - g_b)}{\sum n_i (g_i - g_b) \sum n_i}$$  \hspace{1cm} 2:23,28

$$\bar{F} = \frac{E_T N_x N_y}{\sum n_i}$$  \hspace{1cm} 2:23,29

The standard deviation of the fluence is given by:

$$\sigma = k \sqrt{\frac{1}{\sum n_i} \left[ \frac{\sum n_i (g_i - g_b)^2}{\sum n_i} - \left( \frac{\sum n_i (g_i - g_b)}{\sum n_i} \right)^2 \right]}$$  \hspace{1cm} 2:23,30

$$\sigma = \frac{E_T N_x N_y}{\sum n_i (g_i - g_b) \sqrt{\sum n_i (g_i - g_b)^2}} \sqrt{\frac{1}{\sum n_i} \left[ \frac{\sum n_i (g_i - g_b)^2}{\sum n_i} - \left( \frac{\sum n_i (g_i - g_b)}{\sum n_i} \right)^2 \right]}$$  \hspace{1cm} 2:23,31

Thus:
Figure 2:23,21 Unprocessed And Processed Histograms
Showing The Effect Of Background Noise

Sampling Started At Level 5
Background Level Subtracted = 5
Fluence Per Grey Level = 1,60860 J/sq.cm
Average Fluence = 2,13154E1J/sq.cm
Standard Deviation Of Fluence = 2,40314E1 J/sq.cm
Highest Fluence = 8,36470E1 J/sq.cm
Most Frequent Fluence = 8,40298 J/sq.cm
\[ \sigma = \sqrt{\frac{\sum n_i (g_i - g_b)^2 (\sum n_i) - 1}{\sum n_i (g_i - g_b)^2}} \]

Once these values have been calculated the results are displayed on the Apple monitor and the option of a hard copy is available. The programme then goes on to produce a second histogram minus the subtracted background levels. This brings the less frequent high grey levels into view. The "Stats" programme uses the whole picture, i.e. it counts every pixel in the store. If this is not required and the operator would prefer to perform the analysis over a selected portion of the screen only this is available through another routine. The algorithms are identical, only the user is given control over a cursor with which to mark the boundaries of integration. The programmes described form the backbone of the profiling system. The system is also used for damage detection and relevant features of it will later be described in that section.

2:24 On-Line Damage Detection

At first damage detection was performed by the operator looking down a x10 telescope, with a 16 cm working distance, during the duration of the laser pulse. The appearance of a plasma above the surface was the criteria for damage. Not all materials damage accompanied by this phenomena, i.e. calcium flouride may damage by cleaving as it cools down, having never lost any material to the production of a plasma. The reader will be able to sympathise with the operator who was supposed to be simultaneously monitoring the laser energy via the calorimeter. The method was obviously unsatisfactory.
To update it a video system was purchased, based on a Hitachi KP4 Vidicon camera and a Grundig 2000 video recorder. The camera was used to image the target plane and via a suitable lens magnifications of up to x500 were easily produced. It must be remembered that the system has a built in electronic magnification of around x30. That is the transfer of the image from the camera's photosensitive screen to the video monitor. Large magnifications were therefore easily produced. Target illumination was achieved using a bright, white light source or an expanded 5 mW He-Ne laser beam and imaging the scattered laser light. A sample area would first have to be damaged to enable optimum illumination to be found. With many samples, especially coatings with little or no contrast the final image quality would be poor and damage sites hard to see. The system however was a vast improvement on the previous method, the operator being free to concentrate on the laser energy and then able to study the irradiated area at leisure.

With the purchase of the Image III field store using a video system became very versatile. Pictures could now be stored on floppy disk, pre and post damage fields captured and then subtracted from each other and computer generated image enhancements applied. Thus we could look for small changes at the onset of damage and where contrast was poor apply the necessary routines to accentuate these changes. It is hoped that in the near future we will be able to expand the system with the aid of a 16 bit computer and a Winchester storage facility. At present a lot of analysis time is spent in transferring the data pixel by pixel to and from the field store. This is because the Apple IIe does not possess sufficient memory to contain a whole field at a time and hence analyses a field point by point. It may take up to a minute to subtract two
fields from each other. The subtraction time is negligible compared to the read and writing time with the field store. The programmes that perform the subtraction and the image enhancement routines can be found in [20].

The system had two main disadvantages both arising from the use of the vidicon camera. As previously mentioned such cameras are subject to lag and sticking. This became a serious problem for the image brightness was liable to change dramatically for some instances of damage and the ghost of the image would remain for minutes. The other problem lay with the physical size of the camera. Vidicon tubes are fairly bulky devices and the camera took up a lot of space on the experimental table. At high magnifications it was hard to keep the camera steady due to its size. The obvious solution was to use a solid state camera, and although the present camera is only monochrome this has proven no disadvantage.

Having developed the mechanical, hardware and software side of the detection system attention was turned to the image quality and the optical possibilities. Most often the size of the target to be imaged was about 3 mm x 1 mm. This meant that with the Hitachi KP120 camera a maximum resolution of 10 μm was possible. In most cases this is adequate as damage features are of this order and above. For features smaller than this, for instance light pitting or scrubbing of the surface, detection is achieved by monitoring the increase in scattered light from the surface. Although the camera will not resolve these features it will show an increase in image brightness. Thus when considering an optical system the criteria would be:

i) sensitivity to small changes in scattered light.

ii) the ability to image poor contrast objects

The second point is imperative for on good quality surf-
aces defects and relief can be impossible to see. Schlieren methods would appear to fulfil these requirements. Having been developed to image refractive index changes, the Schlieren technique enables the viewer to see phase objects as opposed to amplitude objects. A typical schlieren system using lenses can be seen in the Figure 2:24,1.

![Schlieren System Diagram](image)

**Figure 2:24,1 A Lens Schlieren Combination**

Schlieren systems are well documented and explained in the literature. For some good reviews see [21] and [22]. I shall give no more than a brief explanation of their theory. Figure 2:24,2 shows an arrangement for viewing Fraunhofer diffraction.

![Fraunhofer Diffraction Diagram](image)

**Figure 2:24,2 Fraunhofer Diffraction**
If the diffracting aperture in the diagram were to be replaced by a phase object a Fraunhofer pattern would still be produced at $\Sigma_t$, and if $\Sigma_t$ were to be followed by the objective lens of a camera an image would be formed. The image would be that of any amplitude objects on the plane $\Sigma$. If a knife edge were to be introduced at $\Sigma_t$ until it obstructed (perhaps only partially) the zeroth order and all higher orders on the lower side, then phase objects will become visible. A Schlieren system is an adaptation of spatial filtering. Flaws in the lenses will also become visible and for this reason many systems are designed around mirrors. This is not a problem for our application and space considerations dictated that we use lenses. The flaws they introduce can always be subtracted if not desired. We do not usually worry. The system has proved ideal for our purposes as it enables us to visualize coating defects, transparent grooves etc. that normally would be invisible, and slight changes in film thickness due to the passage of the laser beam. Note the Schlieren method still enables one to image amplitude objects. The knife edge passes light that is scattered by the amplitude objects and this can then be imaged along with the diffracted light. Choosing the correct magnification is simply a matter of geometrical optics and a quick adjustment of the knife edge gives the operator the best possible contrast.

The light source in the Schlieren system is a 5mW He-Ne laser. The problem arising from using a laser in a conventional knife edge system can be seen in the photographs of Figure 2:24,3. In regions of strong contrast diffraction patterns become visible and at times can seriously hinder the interpretation of the visual image. Figure 2:24,3 (a) and (b) show this to a minor extent as well as indicating the nature of the image produced. Fig-
Figures 2:24,3 (a), (b) and (c) Schlieren Images Of Laser-induced Damage On Optical Coatings

Figure 2:24,3 (c) is the same surface as (b) but more seriously damaged. The camera's automatic gain control has forced the background level down to compensate for the high intensity regions. As mentioned before, such an image could damage a vidicon tube and remain burnt in to the photo-sensitive device for the rest of its life. No detrimental effects have been recorded using a solid state camera. It is experimentally difficult to avoid the effect shown in (c) as it must be the undamaged surface that defines the criteria for illumination. The diffraction patterns on (a), (b) and (c) exist because the knife edge
at the focus of the transform lens is interacting with the fringes of a diffraction spot rather than with a geometrical point of light. There is a number of ways around this problem, and though they have not yet been implemented, can be used as suggestions for further work. They are:

i) using a neutral density wedge

ii) using a prism polaroid combination

These devices would replace the knife edge, effectively removing a straight edge from the system which is serving to strengthen the diffraction patterns.

A prism of quartz or any other suitable material, which rotates the plane of polarization, will produce a final polarization dependant on the distance traversed within the prism, and hence on the position of the incident beam. For instance plane polarized light rays of wavelength 650 nm entering a 30° quartz prism 1 cm apart will emerge with their planes of polarization almost perpendicular. By placing the prism at the knife edge position and following it with a sheet of polaroid, variations from extinction to transmission will result for any angle of deflection $\theta$ in the sample, given by:

$$\theta = \frac{p}{f}$$

where $p$ = the distance along the prism in which the angle of polarization changes by 90° and $f$ = the focal length of the transform lens. The problem of diffraction would still exist if we used a white light source, though it would be less pronounced until high sensitivities were reached. The geometrical theory of Schlieren systems [24] neglects diffraction and it is under the conditions of high sensitivities that this omission becomes a limitation.
A similar technique to the Schlieren method was also investigated as a means of detection of optical damage. The technique uses the physical mechanism of scattering to monitor the surface quality of the target. Changes in the scattered signal indicate changes in the surface. If one considers scattering as the mechanism behind the phenomena of reflection, refraction and diffraction, then perhaps the technique is just another version of the described Schlieren arrangement. Scattering off a smooth surface gives rise to specular reflection where the incident light is reflected into a single angle. Off a rough surface, however, the light will be scattered into a wide variety of angles. For a randomly rough surface the light will be scattered into a continuum of angles whilst for a periodically rough surface it will be distributed through a set of maxima, i.e. a diffraction grating.

Light scattered by optical components arises from several sources:-

i) scratches and digs larger than the wavelength of the viewing light.

ii) isolated irregularities which are comparable in size or smaller than the wavelength of the viewing light.

iii) correlated irregularities which have heights small relative to the wavelength.

The third cause generally dominates the scattered signal. These micro irregularities cover the entire surface with a gaussian statistical dependance, and the light scattered into directions other than the specular angle is found from scalar scattering theory based on the Kirchhoff diffraction integral. For normal incident light the dependance of the total integrated scattered light (TIS) on wavelength is given by:-

\[
TIS = 1 - \frac{R}{R_s} = 1 - \exp \left[ - \left( \frac{4 \pi \delta}{\lambda} \right)^2 \right] \approx \left( \frac{4 \pi \delta}{\lambda} \right)^2
\]
where $R_0 =$ the fraction of the incident light reflected including specular reflection 
$R =$ the specular reflection  
$\delta =$ the rms height of the surface microrifts  

This theory is so established that the rms roughness of a surface is often measured using this relationship.

At the onset of laser induced damage deterioration of the surface takes place. Melting, fracture, ripple formation and scrubbing of the surface resulting in light pitting can occur. This inevitably leads to a change in the scattering characteristics of the surface which can be monitored. Some sample photographs of the early stages of damage can be seen in Figure 2:24,5, indicating the small changes at the onset of damage. These changes give rise to an increase in the forward scattered signal. The light will be back scattered under two conditions. Firstly if the conductivity of the scattering body is high. This is not the case in our experiments. Secondly if the geometry of the scattering body is large compared to the wavelength of light and normal geometric optics can be applied to the reflections off the surface. Again this should not be the case. Figure 2:24,4 shows the polar diagrams for the scat-
Figure 2.24,5 Onset Of Surface Damage
ttered intensities from a gold sphere as a function of its radius. The diagram [25] details three cases and shows that:

i) the scattering from a vanishingly small sphere is symmetrical about the plane through the center of the sphere and at right angles to the direction of propagation of the light.

ii) that as the radius of the sphere is increased the polar diagram loses its symmetry and more light is scattered in the forward direction. This is shown in (b) and (c).

As already mentioned if the sphere were to get too big geometrical optics would apply.

Individual damage features are generally no larger than the 10 to 100 μm size and thus we can expect most of the scattered light to be in the forward direction. The experimental arrangement shown in Figure 2:24,6 looks at

![Figure 2:24,6 Dark Ground Scatter Detection System](image)

the intensity of the forward scattered light. The probe beam to be scattered was a 5 mW He-Ne laser with a spot
size of 0.85 mm as measured using the Image III profiling system. The beam was expanded by the use of a Galilean telescope configuration to a 3 mm diameter in order to interrogate the entire surface. A beam stop was placed at the focus for parallel light of the lens to remove completely the zeroth order. It is clearly seen then that if the sample surface were perfectly flat the stop would block out the entire He-Ne beam, and the resulting "image" would be completely dark. This gives rise to the name of "dark ground". The lens focuses the scattered or diffracted light onto photodetector, protected from ambient room light by a He-Ne band pass filter. In this system we have not attempted to image the scattered light but rather de-magnify the source of scatter onto the photodetector. Thus the target plane is imaged on the detector's photosensitive area. The detector was an RCA solid state device, model number C30816, with a typical rise time of 35 ns.

Immediately it should be apparent that this system should be more sensitive than the Schlieren set up for monitoring small changes in scatter for two reasons. i) we are demagnifying the image so the photon density at the detector will be greater and will be seen on a background of near zero. ii) We are collecting all the scattered light through a 360° cone whilst the Schlieren arrangement looks only at the light escaping past the knife edge. By running both systems concurrently during damage testing, however, we found that the onset of damage was detected simultaneously, i.e. the first sign of damage was always severe enough to be monitored by either method. This work was performed with L. A. Mahmood and further details and results can be found in [26].

To conclude therefore it should be noted that the
Schlieren system was maintained at the expense of the dark ground method as it enables the operator to visualize the form of damage, the cleanliness of the surface and the quality of the optical element under test. This concludes the chapter on the experimental facility and it is hoped that the reader is now a little familiar with the equipment and approach to making laser-induced damage measurements at Loughborough University.

2:30 Bibliography

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CHAPTER 3:00 SURFACE STUDIES TO CALCIUM FLUORIDE

3:10 Introduction

Introducing a chapter on surface laser-induced breakdown to calcium fluoride windows is not easy. The literature is well endowed with references, phenomenological and theoretical, covering the various aspects of damage, and each year at the damage symposium in Boulder, (Colorado) a little more is said on the matter. U.V. damage thresholds have been measured for the fluoride glasses and crystals [1], the mechanical properties and their effect on the damage morphology considered in [2] and the effects of surface finish on a variety of materials has been studied by many. All the reports cover a range of materials, wavelengths, pulse shapes and times, and have come from a wide range of laboratories. The samples under test have been grown by different companies and subjected to different surface finishes. It might therefore appear that this chapter represents another damage laboratory's observations on a well studied topic. I hope it will be a little more than that, if not to everybody, to those who sponsored the work. The work was performed in conjunction with B.D.H. Chemicals who grew the crystals of calcium fluoride, and in whose shop the samples were polished. I am indebted to Mr. P. Henwood and Mr. J. Church for their insights into crystal growing and polishing respectively. The aim of the work was to study their production techniques for U.V. quality optics with the emphasis on improving the U.V. laser-induced damage thresholds within the confines of their existing facilities. Bulk and surface damage was investigated, Chapter 4 addressing the phenomena of bulk damage. The bulk breakdown is concerned primarily with the crystal's purity and defect behaviour under conditions of high irradiation and thus considers the
first stage of production, the crystal growth. This chapter, being concerned with surface damage, looks at the company's polishing techniques and monitors the change in surface thresholds for a variety of surface finishes.

Section 3:20 will describe the crystal production and surface preparation. Section 3:30 deals with the surface characterisation and section 3:40 will comment upon the experimental method and present the results. It will be left to Section 3:50 to discuss the findings, present Nomarski and T.E.M. photomicrographs of the damage morphologies and to comment upon the fundamental aspects of surface damage.

3:20 Crystal Production And Polishing

All the crystals were grown using the Bridgman-Stockbarger method. The crystal melt, contained in a graphite crucible, is held in a temperature gradient as shown in Figure 3:20,1 and cooling begins from the base upwards.
as the crystal is slowly lowered through the gradient. This is perhaps the most commonly used furnace technique. The development of the Bridgman-Stockbarger process and a useful insight into crystal growing may be found in [3]. Two sources of material for conversion into fluorite crystals were used. One was an as mined fluorspar from Mexico and the other a highly pure source of calcium fluoride from evaporated stock. These shall henceforth be referred to as Mexican (abbreviated as Mex) and Optipur (abbreviated as Op) respectively. According to the intended application of the crystals B.D.H. would use either source. When growing the Mexican material a scavenging agent of lead fluoride (PbF₂) would be added to the stock, one part in fifty. This was to prevent hydrolysis occurring during growth. Naturally occurring fluorspar has small quantities of water in it and hot calcium fluoride is very sensitive to water vapour. Hydrolysis would occur resulting in small negative crystals within the crystal. These would appear as little light scattering hollows with (111) crystallographic planes [3]. The Optipur material, being free of water had no need for a scavenging agent.

Natural cleavage of single crystal calcium fluoride occurs along the (111) crystallographic planes. Lenses and windows are usually produced with a random orientation as the crystal is not seeded in any specific manner and cutting is performed perpendicular to the boule axis. In order to standardise as many parameters as possible all the boules were orientated such that the polished surfaces were (111) planes, unless otherwise stated.

The (111) plane would be located in the grown boules and then a diamond blade would cut the discs as required. The rest of the preparation was the domain of the polishing shop. The polishing procedure followed by B.D.H. for
standard quality optical surfaces is outlined below:-

Stage 1:—Roughing and trueing. The diamond cut discs are placed upon a polishing tool or block, a flat circular metal disc capable of holding a number of similar thickness flats. Adhesion is obtained using an empirically designed mixture of beeswax, the light of experience. Trueing and roughing seeks to ensure that the entire surface area of each optical flat is in contact with the polishing lap and that the surface created by the diamond blade has been removed before polishing begins. The circular metal disc to which the samples are attached is assumed perfectly flat and if the operator is careful he can seek to ensure that the two disc faces are polished parallel to each other, as opposed to polishing them into a wedge. Generally the roughing process removes 8 µm of the surface. The emery powder employed is a carborundum (silicon carbide).

Stage 2:—Lapping and Pre-polishing. The polishing block is washed in running water to remove all traces of the emery powder and then mounted on the polishing lap. At B.D.H. this is a felt lap. The mechanical arrangement of the polishing machine can be seen in Figure 3:20,2. The

![Figure 3:20,2 Mechanical Polishing Arrangement](image-url)
polishing lap rotates about 1 to 2 revolutions a second. The sample holder, resting upon the lap, rotates with it and weights above the holder apply the pressure required for calcium fluoride polishing. The sample holder is given a horizontal motion across the polishing lap by a separate driving arm. Diamond abrasive is used as the polishing paste, and water as the wetting agent. For standard quality optics an 8 μm paste is used. This has a mean particle size of 8 μm ranging between 4 and 12 μms.

Stage 3:– Polishing. This process is as in stage 2 but the polishing abrasive is finer. The diamond abrasives will go down to 0.1 μm.

Stage 4:– For high quality surfaces a final polish is applied using a wax lap and alumina abrasive. The particle size is now down to 0.075 μm. By this stage all surface scratches will have been removed and the surface is covered by a mass of little pits. This can be seen in the photographs of the next section. The wetting agent used in stage 4 is no longer water but an alcohol. If a further finish is required a velvet lap is used without any abrasive. This stage is entirely manual.

At the time of this work the polishing shop at B.D.H. did not apply any chemical etches to their polished work. After polishing the discs would simply be removed from the sample holder and cleaned in 1.1.1. trichloro-ethane. For the work at Loughborough, however, a half of every sample underwent a chemical etch. The chemical etch was developed in America specifically for calcium fluoride and is prepared as follows:-

Three parts of concentrated sulphuric acid (95% \( H_2SO_4 \) S.G.1.84) is slowly added to two parts of glacial acetic acid (99.7% \( CH_3COOH \)). The calcium fluoride was held in the
etch for a period of five minutes. After fifteen minutes of immersion a severe etching becomes noticeable and the U.V. transmission is degraded. After the five minute period, however, no visible effect could be seen despite attempts with electron microscopy. The damage threshold was significantly increased by this process. See section 3:40. Two samples were also prepared using diamond turning machines. The samples were not polished in any way so the surfaces were uncontaminated by any polishing compounds. The sample surfaces had a cloudy appearance due to the rough finish and gave rise to diffraction orders when a He-Ne laser was shone through them. In fact the diamond turning pitch could be calculated from the diffraction maxima.

The physical processes involved in polishing are still little understood. The nature of the damage it creates, the system of sub-surface micro-cracks and stresses that it leaves in the surface and the effect these play in the role of laser-induced damage is uncertain. P. Temple [4] showed a substantial increase in the surface damage threshold of mechanically polished fused silica after subjecting the surface to carbon dioxide laser polishing. This involves scanning the surface with a c.w. CO\textsubscript{2} laser and heating it to just below its melting point. Two possible explanations of this effect were given:-

i) the laser polishing evaporated the absorbing impurities which were trapped in the surface as a result of the mechanical polishing.

ii) the laser polishing healed the surface and sub-surface micro-fractures resulting from the mechanical grinding and polishing processes.

silica. In this process, though physically similar to mechanical polishing, material removal is by a chemical reaction. It is thus possible to produce scratch free surfaces without the system of micro-fractures. The damage figures showed a very marginal increase in threshold over sapphire (0.3 μm) polished surfaces and an equivalent threshold to cerium oxide polished surfaces. This would imply that the micro-fractures are not important in laser-induced surface damage, at least to fused silica samples, and that it is the trapped impurities initiating damage. Calcium fluoride is, however, a very brittle material, strong in compression and weak in tension, and any increases in surface stresses could reduce the damage threshold.

Figure 3:20,3 shows the typical action of polishing abrasive during mechanical polishing. The loose abrasive

![Image](Polished_Surface)

Figure 3:20,3 Abrasive Polishing Action

tumbles across the grinding tool between the substrate and the work piece causing impact fracture and material removal. Figure 3:20,4 shows the effects of an impact fracture to the surface and sub-surface regions.

Here
- $d =$ the grinding particle size
- $h =$ the depth of the fracture
- $\Phi =$ the angle of the fracture
- $D =$ the diameter of the fracture
Figure 3:20,4 An Impact Fracture [6]

It has been suggested that the fracture depth will be a factor of 3 to 4 times the depth of the surface pit created [7]. It can be seen from Figure 3:20,4 that the polished surface will appear to expand. This expansion has been experimentally verified [7].

The following figure represents the surface finishes applied to the calcium fluoride discs prepared at B.D.H. and damage tested at Loughborough. The vendors of the diamond turning machines will not be indentified.

Surfaces G and H had twice the normal depth of material removed during the roughing and trueing stage. This was done to determine whether the diamond cutting of the boules was having a detrimental effect on the damage threshold. Of the stages involved in surface preparation this is thought to be the most traumatic and the extent of the sub-surface damage that this incurs is unknown. Calcium fluoride, as the polishing shop will tell, is liable to cleave as it cools. In surface damage cleavage is often noticed and attributed to the cooling stage of the damage cycle. Plastic deformation is thought to occur as the surface heats up. The material constraints being into and along the surface, the material is forced to expand outwards and deform. As it cools this plastically deformed
Figure 3:20,5 Prepared Samples.

region will result in increased tension between the bonds and the material cleaves. Obviously the crystal can handle a certain degree of surface strain which may be incurred during the growth and polishing processes but the greater this "intrinsic strain" the more susceptible the crystal will be to cleave as its environment is altered. The diamond cutting stage was suspected of producing the most "intrinsic stress", which would decrease with depth from
the surface.

3:30 Surface Characterisation

No attempt has been made to quantify the surface roughness of each sample. This may be considered an omission though it would probably provide information of little value. There was no equipment readily available for making T.I.S. measurements (total integrated scatter) and the only other option before us was a Talysurf Surface Profiler. The Talysurf machine available to us had a minimum tip size of 12 μm and as the sample's surface features will be this size or less all results taken on such a system will represent the convolution of the surface and the tip radius. Meaningful figures would take a lot of extracting. Instead the surface quality has been visually characterised via Nomarski photo-micrographs. These have provided excellent visual comparisons between surface finishes and give a good idea as to the quality of the surface under test. Representative portions of the photomicrographs can be seen in Figures 3:30,1 through to 3:30,6. These six photographs characterise the various categories of surface finish detailed in the previous

Figure 3:30,1 Sample A
Figure 3:30,2 Sample A.c.e.
section. Every sample mentioned in Figure 3:20,5 will have a surface finish corresponding to one of the photographs. There was no significant variation from any of these. Figure 3:30,1 and 3:30,2 are taken from the same disc and represent the un-etched and etched portions of the disc. At this magnification there is no discernible difference. The surfaces were also investigated using electron microscopy. The dielectric nature of CaF$_2$ meant that the S.E.M. (scanning electron microscope) facility could not be used though it would have been the most practical. This is because the surface of the sample would have charged up under the influence of the electron beam. Instead the
T.E.M. microscope (transmission electron microscope) had to be used and this involved taking replicas of the surface. This was only partially successful as the replica material tended to tear at any sharp feature in the surface. Inspection of the surface up to x20 000 revealed no secrets from the effect of the chemical etch. There was no point in taking the magnification any further as interpretation of the visual image was becoming speculative.

Figures 3:30,3 and 3:30,4 compare a final polish using a wax lap and particle size of 0,075 pm with a final polish on a velvet lap and no abrasive on a surface as in 3:30,3. Again there does not seem to be any major difference in the two surface finishes, and again electron microscopy could reveal no changes.

Figure 3:30,5 and 3:30,6 show the two diamond turned surfaces. That of 3:30,5 is a much coarser grained surface than 3:30,6. A feature that can be seen on both the photographs is that the machines appear to have a "wobble" in the cutting head. This has, in both cases, produced a periodic pattern in the grid lines left by the diamond head. This is more pronounced in the first of the two photographs.

As a guide to the rms roughness of the surfaces, two, those of Figures 3:30,1 and 3:30,4, were profiled on the "Wycko II Surface Profiler", using the demonstration machine of Dr. Gibson. I would like to thank Dr. Gibson for running the profiles for me. The Wycko II Surface Profiler uses direct phase detection to build up a three dimensional image of the surface. It employs a Michelson Interferometer to mix a reference beam with a beam reflected from off the surface under test. The surface is divided into a number of pixel points, the phase of each
point monitored and then the surface moved by a p.z.t. before a second set of points is taken. For a detailed analysis of such interferometric systems see [8]. It cannot be said to give a true representation of the surface as each pixel point is effectively looking at the average phase shift over its area. Thus very sharp discontinuities in the sample could lead to ambiguities. The results of the scans can be seen in the following figures. Figure 3:30,7 shows a three dimensional map of a small portion of

**Time**: 08:20  **Date**: 03/19/86
**RMS**: 4.60 nm  **SURFACE**: P-V: 39.1 nm
**RA**: 3.65 nm

![3D Surface Profile](image)

**Figure 3:30,7 3-D Surface Profile Of Sample A.**

the surface, from which has been derived the rms surface roughness and the maximum peak to valley swing. This represents a standard polish with 8 μm. paste as the final finish. Figure 3:30,8 represents a line scan taken on this portion of the surface. The black square at the side of the scan can be ignored. Officially it represents a grey scale contour map of the individual pixel heights of Fig-
Figure 3:30,8 Line Scan Taken From Figure 3:30,7. The printer, however, was not capable of such refinements.

Similar scans were performed on the velvet lapped surface of Figure 3:30,4. These can be seen in Figures 3:30,9 and 3:30,10. The final figure, 3:30,11, for demonstration purposes only has reproduced Figure 3:30,9 but ignored all the values below 1.8 nm. This is shown on the scale beside it. This plot has just served to emphasise the peaks in the surface.

A summary of the numbers produced by the Wycko profiler is given in the following table:-
Figure 3:30,9 3-D Profile Of Sample F

Figure 3:30,10 Line Scan From Figure 3:30,9
Figure 3:30,11 Emphasized 3-D Profile Of Figure 3:30,9

<table>
<thead>
<tr>
<th>Description</th>
<th>8 μm Finish</th>
<th>Velvet Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>rms roughness taken over the area of the profile.</td>
<td>4,60 nm</td>
<td>2,23 nm</td>
</tr>
<tr>
<td>Peak to valley height taken over the area of the profile.</td>
<td>39,1 nm</td>
<td>30,0 nm</td>
</tr>
<tr>
<td>rms roughness taken from a single line scan.</td>
<td>3,50 nm</td>
<td>1,94 nm</td>
</tr>
<tr>
<td>Peak to valley height taken from a single line scan.</td>
<td>18,0 nm</td>
<td>17,5 nm</td>
</tr>
</tbody>
</table>

RMS: 2,23nm  SURFACE P-V: 30,0nm
RA: 1,72nm
These numbers would indicate that the extra hours spent on polishing and working the abrasive size down from 8 \( \mu \text{m} \) to 0.075 \( \mu \text{m} \) has improved the quality, as intended, but perhaps not to the degree expected. The improvement doesn't even appear to be by a factor of two. Using these numbers for the surface finish and [7] we can predict surface micro-fractures down to depths of 120 nm for the 8 \( \mu \text{m} \) polish and 90 nm for the velvet finish. The effect this may have on the surface damage threshold needs to be determined.

3:40 Experimental Considerations And Results

The experimental facility used to damage test the samples has been detailed in Chapter 2. Figure 3:40,1 shows the apparatus. Prior to experimentation the beam's spatial profile was obtained using the Image III profiling system. Ideally we would have liked to have profiled each shot or damage pulse. This would have enabled us to build
up an excellent data base for analysis. Experimentally, however, we were unable to arrange such a facility. The problem this wish imposes is how to monitor the profile in the damage plane without interfering with the sample under test. A commercial company, who simultaneously developed a video profiling package, claims that this can be done by introducing a wedged beam splitter into the path of the focused beam as shown in Figure 3:40,2. Given a sufficient wedge angle three separate foci would be produced. This is shown in the Figure. The wedge, however, will result in distortion of the transmitted beam. This is especially apparent when one considers that the input beam is being focused by a lens and so is no longer parallel. This distortion can be quite appreciable. The distortion for any given set of conditions can be calculated, though the problem is not as obvious as it may appear, and is dependent upon many parameters. This is shown by Figure 3:40,3. The parameters in the diagram that will affect the degree of distortion are:-

i) \( f \) - the focal length of the lens.

ii) \( D \) - the beam's dimensions at the input to the lens (assuming a parallel beam).
iii) $x$ - the distance from the center of the lens to the wedge, i.e., the length of the axial ray prior to the wedge and after the lens.

iv) $w$ - the distance from the wedge apex to the intersection of the axial ray and the first surface of the wedge.

v) $\alpha$ - the wedge angle.

vi) $l$ - the position of the target plane with respect to the focus.

By considering the two external rays $R_1$ and $R_2$ the problem can be solved by calculating their vertical displacements with the wedge in position with respect to their positions prior to the wedge's influence. The vertical displacement is given by the following expression:

$$P_{1,2} = \left[ f - x \left( \frac{D(f - x) \cos \theta_1 \sin \theta_t}{f \cos(\theta_t \pm \theta_1)} \right) - \left( w \frac{D(f - x) \cos \theta_1}{f \cos(\theta_t \pm \theta_1)} \right) \right] \left( \frac{\sin \theta_{1,2} - \theta_t - \theta_1}{\cos(\delta_{1,2} \pm \theta_t) \cos \theta_t} \right)$$

Figure 3:40.3 Geometry Of Transparent Wedge In The Path Of A Focused Beam
where $\delta_{1,2}$ is the angle of deviation introduced as the ray traverses the prism. This is given by:

$$\delta_{1,2} = \theta_{i,2} \sin^{-1} \left[ \frac{\sin \alpha (n^2 - \sin^2 \theta_{i,2})^{1/2}}{\sin \theta_{i,2} \cos \alpha} \right]$$

and $\theta_i$ can be found from Snell's law. The derivation of Equation 3.40.1 can be found in Appendix 3.

From Equation 3.40.1 it can be shown that with a typical arrangement used at Loughborough in which the relevant parameters would be: $f = 100$ mm, $D = 5$ mm, $x = 45$ mm, $w = 80$ mm, $\alpha = 3^\circ$ and $l = 5$ mm, a 0.5 mm spot will distort in the vertical direction to 1.165 mm. This will have a catastrophic effect on the measured damage threshold if the operator is not aware of it.

Reducing the wedge angle improves the situation but as long as the input beam is non-parallel distortion will always result even for a wedge angle of zero. As the wedge angle is reduced the two foci will merge together and the measured profile will be confused by their superposition. An infinitely thin parallel slab is obviously required for the purpose, but hard to manufacture. In this case the two reflections would be directly on top of each other. We considered using a very thin slab of CaF$_2$ but were unable to produce one thin enough without cleaving it during polishing. No manufacturers of fused silica would sell us a large enough and thin enough slab of the material. Anti-reflection coating one side would be a further improvement. Unfortunately we had neither the time nor the money to pursue these possibilities. Alternatively we could have had a matched set of lenses made and beam split
the excimer radiation while it was still near parallel, i.e. prior to the lens. Again we would have required one side of the beam splitter to be anti-reflection coated. Inserting a lens in both of the arms we could have attempted to produce in each identical foci. This system would take time to establish and a fair amount of calibration before it could be used with confidence. Thus we continue to profile in the damage plane prior to performing the experiment.

The arrangement for measuring the profile is shown in Figure 3:40,4. The camera viewed the borosilicate cover-slip from the same side as the input beam and slightly off axis. We were close enough to the axis of the system, however, not to cause distortion in the photographic image. It was found necessary to go this side of the cover slip rather than viewing it in transmission and on axis. This would at first seem the better option but we found too much background light was entering the camera in this mode. A mechanical positioner had been devised that enabled the sample holder and coverslip holder to be interchanged yet maintain the front surface of the sample and

![Diagram](image)
Figure 3: 30,5 Beam Profile Used To Damage Test CaF$_2$ Samples
cover slip in the same plane. The beam was profiled over ten shots and the average figures relevant to the damage test obtained. One of these profiles can be seen in Figure 3:30,5. The figures quoted for the average fluence, peak fluence, fluence per grey level etc. have been obtained by assuming an input energy of 1 joule. This is purely a choice of convenience. To derive these figures a calibration grid had first been processed to calculate the system's magnification. From this we ascertained that in the frame store 83 pixels or divisions corresponded to 1 mm in the horizontal direction and 51 in the vertical direction. This difference is a consequence of the camera and field store having a different pixel count in the horizontal and vertical directions. The spot size from these figures, at the 1/e^2 values is 1.83 x 0.39 mm. As can be seen from Figures 3:30,1 to 3:30,6 this is ample to sample a representative area of the surface. The average peak fluence was 304 J.cm^-2 (normalized to one joule) and so the actual peak fluence is this figure multiplied by the measured energy. The value of the peak fluence over the ten profiles was found to vary by 2%. This highlights the laser's stability on a shot to shot basis. It is known that the laser output energy falls as a function of the time at which the laser is left charged and in a ready condition for firing. If the energy were to fall too much the laser emission would be affected and the profile altered. To ensure that this was not happening, we would always fire two shots close on each other. The first shot would be shuttered off from the experiment and served only to recharge the laser for the experimental pulse that would follow. To be able to quote the peak fluence to within 2% is especially good when one considers the irregular shape of the beam profile. Had we been using conventional profiling systems or applying gaussian fits to the pulse shape our error figure would have been in the
teens. No attempt has been made in calculating the peak fluences to subtract or even measure the energy contained in the wings of the profile, as seen in Figure 3:40,5. This energy can represent up to 20% of the total on target energy and yet play no role in any damage process. The "stats" programme, however considers the entire profile and this energy is accounted for exactly as it occurs in the profile. Adjustments for the wings are therefore unnecessary.

The energy measurements made by the calorimeter are assumed to be absolute. At low levels of incident energy, however, the calorimeter is very sensitive to thermal sources within the room and cannot be effectively zeroed prior to making a measurement. This obviously increases the error as readings must be made before and after the pulse. A reasonable figure for measurement and human error has been set at 5%. From the measured energy the energy incident on the sample is calculated. Figure 3:40,6 shows

![Diagram showing energy measurement setup]

Figure 3:40,6 Reflections Suffered By The Excimer Radiation Prior To The Sample Surface

the reflective losses to be considered in this calculation. The normal to the beam splitter surface is at 30% to
the direction of propagation of the excimer beam. The polarization characteristics of the excimer are not well enough known to enable the use of the Fresnel equations for reflections from dielectric surfaces to be used with confidence. Instead the reflectance was measured experimentally. Two energy meters were employed. The calorimeter was used to calibrate a large surface "Gentec" energy monitor and then the energy of the transmitted and reflected beam from the beam splitter simultaneously monitored over a number of fluences. The energy meters were then interchanged and the experiment repeated. It was found that the beam splitter was reflecting 7.9% of the total beam energy. This would indicate a polarization of the excimer radiation with a bias towards the parallel component. Reflection losses were calculated for the lens by assuming that all the radiation was normal to the lens surface. This approximation is valid for the small angles involved as the reflection coefficients remain almost constant until around 20° is reached. This is true for the parallel component. The reflectance from a single surface is given by:

\[ R = \left( \frac{n_t - n_i}{n_t + n_i} \right)^2 = 4\% \]

and with \( n = 1.5 \) the total reflective losses from the lens can be assumed to be 8%. Thus the measured energy can now be converted into an on sample energy and the figure fed into the Apple IIe and the peak on axis fluence obtained.

The error in the calculated damage threshold is thus composed of:

Profile error + Calorimeter error + Random losses from the lens and beam splitter. This has been assigned at 5%. The quoted damage thresholds are therefore to 12%. All the damage figures quoted in this chapter represent the value
for single shot damage and are the thresholds for the 50% probability of damage. This is achieved by monitoring at each fluence the number of times the sample does or does not damage. Sample graphs of this process can be seen in Figures 3:40,7 and 3:30,8. Each surface detailed in Figure

![Figure 3:40,7 Threshold Determination Of Sample G](image_url)

Figure 3:40,7 Threshold Determination Of Sample G

![Figure 3:40,8 Threshold Determination Of Sample L](image_url)

Figure 3:40,8 Threshold Determination Of Sample L

3:20,5 was damage tested under identical conditions and with the same profile. The damage plane was beyond the focus to prevent the exit surface damaging first. The
laser energy was never high enough to cause beam deformation or to create a plasma at the lens focus. A 20 cm lens was used.

Figure 3:40.9 is a graphical representation of the damage thresholds of all the surfaces prepared and ment-

Figure 3:40.9 Damage Thresholds Of Sample Surfaces
Discussion And Observations Of Damage

Considering the results directly from the last graph of the previous section and bearing in mind the surface finish applied to each test sample we can make a number of immediate observations.

i) A chemical etch has virtually doubled the damage resistance attained by each surface. Remember that the un-etched and etched surfaces were tested within minutes of each other and without changing the physical layout of the experiment in any way.

ii) There is no increase in the damage threshold for the samples that underwent the most thorough polishing procedures. In fact the wax lapped and velvet finished sample had the lowest damage resistance of all those tested. This was surface H.

iii) The least worked samples i.e. the least handled, which were the diamond turned samples, manifest easily the highest, pre-chemical etch damage thresholds. This was despite the fact that they had the roughest surface finish.

iv) The surfaces which had the greatest depth of material removed during the roughing and trueing stage showed no favourable increase in the damage threshold and were amongst the lowest thresholds. This may or may not be of consequence. It should be commented that these two samples, G and H, despite different final finishes showed the same characteristic damage morphology, which was not seen in the other samples. These two samples showed damage
morphologies that indicated the cause of damage to be absorbing inclusions lying on or just below the surface. An example of this can be seen in the Nomarski photomicrograph of Figure 3:50,1. It is possible that the

![Image](image_url)

Figure 3:50,1 Inclusion Damage In Sample G

discs of G and H were cut from the end of the boule that solidified last. This end will have the highest concentration of inclusions as these tend to get swept along, during growth, with the advance of the solid/liquid interface.

v) Samples C and D which were polished simultaneously on the same sample polishing block, but which were grown from different source material, have almost identical damage thresholds. It would seem true to say that the purity of the source material is not a factor that significantly
contributes to the surface damage threshold.

vi) The (110) polished surfaces showed no change in damage threshold when compared with the (111) surfaces.

From these we might say that the quality of surface finish has played no role in defining the damage threshold and the differing depths of the sub-surface microfractures has had no obvious impact on either the threshold or the resultant damage morphology. The chemical etch on the other hand has proved to be a very beneficial process, nearly doubling the thresholds in all but the case of the diamond turned samples. The damage thresholds of all the etched surfaces lie approximately within each other's error bars and can perhaps be taken as identical. No trends as regards surface finish can therefore be extracted.

In the discussion that follows Nomarski photomicrographs of the surface damage will be shown and features of note pointed out. Figures 3:50,2,3 and 4 show typical examples of the three observed forms of surface damage. They are:—

i) plasma etching, Figure 3:50,2.

ii) surface melting, Figure 3:50,3.

iii) surface cleavage, Figure 3:50,4.

These have been listed according to their order of occurrence in the damage process. Note that at 248 nm. plasma shielding of the surface by a plasma generated above the surface by the laser pulse is unlikely. This phenomenon has been observed at the longer wavelengths and serves to protect the surface from further damage as the laser generated plasma can become dense enough to absorb any further radiation. At 248 nm. however the electron density to attain this cut off is higher than is physically possible. The first sign of damage is plasma etching where surface
Figure 3:50,2 Plasma Etching

Figure 3:50,3 Surface Melting At The Onset Of Damage
Figure 3:50,4 Surface Cleavage

material, perhaps foreign material is evaporated and forms a plasma above the surface. As this plasma expands it will press back against the surface and cause a "scrubbing effect". This is clearly shown in Figure 3:50,2, which was taken on a T.E.M. facility.

Surface melting has been placed second in the order of damage as opposed to cleavage, as it is believed that cleavage is always a secondary effect incurred as a result of the surface having been melted. The reason for this belief comes from microscopic examination of all the damage sites. All the cleaved surfaces show evidence of having been melted, i.e. the polishing marks have been removed from the surface leaving it perfectly smooth. This was further justified using T.E.M. microscopy under high magnification. Figure 3:50,5 shows a cleaved portion of the surface and the "perfect polish" applied as the mat-
material has frozen. Cleavage of calcium fluoride comes as the material is placed in tension. It is a material very strong in compression [9]. A hot expanding crystal represents a system in compression but a cool contracting crystal represents a crystal in tension. It seems that when cleavage occurs the crystal has always been taken up to melting point. These points will be discussed in more detail later.

A. A. Manekov [10] showed that the electron avalanche theory has a temperature dependence. This is perhaps intuitive. He derived expressions to predict the value of the critical field strengths for breakdown as a function of the initial temperature of the crystal, and showed that the temperature dependence was a monotonically decreasing function as the temperature increased. See Figure 3:30,6, [10]. This was the case for the condition $\mu \gg e_{\text{eff}}$.
where:

\[ \text{eff} = \text{the electron-phonon collision frequency.} \]

and \( \omega = \text{the laser frequency.} \)

From Chapter 1 it was mentioned that the critical field for breakdown occurred at the field strength sufficient to enable the conduction electron to, on average, gain energy from the field at the same rate at which it lost it to electron-phonon collisions. At 248 nm, we are well in the region of \( \omega \gg \text{eff}. \)

Surface impurities and layers of polishing compound or perhaps organic cleaning agents, capable of absorbing the incident radiation, will effectively heat up the top few layers of calcium fluoride upon which they reside. Thus certain portions of the crystal will have a higher "initial temperature" than others. This hot layer will give rise to the predicted lower critical field strengths. This would possibly account for the low, and yet similar damage thresholds across the range of surface finishes experienced prior to the chemical etch. At 248 nm, multi-photon initiated processes might have been considered the primary cause of damage, yet it would seem more probable
that the actual damage is a mixture of the two. The chemical etch, though not long enough in time to cause etching of the calcium fluoride, would act as a very thorough cleaning agent, removing the sources of localized heating. The chemical etch acts on calcium fluoride in preferential crystal planes and thus an etched crystal reveals the crystal structure. It is fairly easy to determine when etching has modified the crystal surface. After the etch the damage sites tended to be more uniformly distributed across the beam profile, whereas prior to the etch they seemed more random in nature.

After the chemical etch had been applied and the damage threshold raised the surfaces still showed a consistent value for the breakdown threshold despite the differing surface finishes. The previous section showed that although the surfaces had been worked to differing degrees there was not too vast a difference in the actual rms surface roughness. N. Bloembergen [11] predicted the changes or decrease in damage threshold with increasing surface roughness and from his analysis it can be seen that in CaF$_2$, taking $n = 1.48$ and $\varepsilon = 2.19$ where:

$$n = \text{the refractive index}$$
$$\varepsilon = \text{the dielectric permittivity}$$

a typical scratch would reduce the damage threshold by a factor of five. Perhaps all the surfaces tested were sufficiently scratched to fall into this category. On the other hand if the thresholds attained were to be multiplied by five they would then be a lot higher than the theoretical thresholds quoted, [12]. A set of graded surfaces and a final finish of higher quality than could be attained at B.D.H. would be needed to see if the surface quality really was playing a principle role in the damage process.
Let us now consider the damage morphology and try and gain a little clearer insight into the damage sequence. Figures 3:50, 7, 8 and 9 bring to light a number of interesting points. Firstly Figure 3:50, 9 shows that damage, or more precisely, cleavage is severest around scratches. Remember, though, that cleavage was always secondary in nature. Even around scratches T.E.M. examination showed that the surface had first melted. All the cleavage sites on the (111) surfaces are triangular and the apexes of the triangles are all located in the same direction. Cleavage would appear to begin at one apex and in all the triangles on a damage site it would be the same apex. This can be seen in Figure 3:50, 7 and 8. Figure 3:50, 7 shows the cleavage pattern of damage well above threshold. One can see that even the wings of the damage profile shown in the

Figure 3:50, 7 Large Area Damage
Figure 3:50.8 Severe Cleavage

Figure 3:50.9 Cleavage Around A Surface Scratch
previous section (Figure 3:30,5) contained sufficient energy to damage the surface. The size of the cleavage triangles is interesting and perhaps can be more clearly seen in Figure, 3:50,8 and 3:50,10, shown below. At the edges of the pulse, where the fluence was least and only just sufficient to cause damage the average size of the triangles are smaller than in the center of the pulse where the energy input was greatest. This would indicate that cleavage occurs well after the pulse has been and gone.

If we divide the crystal surface into unit areas each unit area will experience a total energy flow through it as the radiation is transmitted by the crystal. The value of this total will depend upon the unit area's position

Figure 3:50,10 A Further Example Of Surface Cleavage
with respect to the excimer's spatial profile. If the fluence was high enough to set in motion some form of damage process then a portion of the surface will become molten, and the melt will have a spatial temperature profile in some way similar to that of the laser's spatial profile. The exact relationship between these two profiles will depend upon the mechanisms of energy deposition to the crystal lattice. After the pulse of laser radiation has been and gone the liquid solid interface will tend to advance into the crystal as the heat diffuses away. The rate of advance will be greatest where the surface to liquid/solid interface temperature gradient is a maximum. This can be seen in Figure 3:50,11, and will occur where

![Temperature Gradient Across The Melt Pool](image)

Figure 3:50,11 Temperature Gradient Across The Melt Pool

the peak fluence was experienced. The liquid solid interface will penetrate to a certain depth after which it will start to retreat. This can be seen from Figure 3:50,12. Note that this figure is not true but is used merely to aid the text. T1 represents the surface temperature immediately on cessation of the laser pulse. With the progression of time and the process of diffusion T1 falls, pushing the liquid solid interface away from the surface.
As can be seen from the figure, however, a time is inevitable when the advance is halted and the interface recedes. T2, T3, T4 etc. show later and later times in this process. Each unit area of the surface would have its own set of cooling curves, characterised by the initial surface temperature. One would expect the extremities of the surface to freeze up first.

Let us now consider what happens in the crystal as the liquid solid interface advances and then retreats. As it advances the crystal will tend to expand as the influence of the heat penetrates the lattice. Consequently forces will be experienced along certain crystal planes, which if they are large enough will cause the planes to slip. This will result in plastic deformation. By considering a surface of calcium fluoride orientated in the (111) plane and the system of "sub-cells" formed by the remaining (111) planes we will be able to understand the first aspect of the damage morphology. Remember that the CaF₂ crystal structure has the least bonds per unit area.

Figure 3: 50, 12 Depth Temperature Profiles With Time
in the (111) plane and so preferentially cleaves and slips in this plane. Figure 3:50,13 shows the system under con-

Figure 3:50,13 (111) Planes In CaF₂

sideration. From the figure we can see that as the crystal expands there will be a tendency for volume A to be squeezed out of the surface, whilst volumes B, C and D will remain seated. Figure 3:50,14 shows the resultant force

Figure 3:50,14 Forces On The (111) Slip Plane

F \cos \theta \text{ along the (111) planes within the crystal. The}
tendency will be for the atoms at the boundaries of "A" to slip over those for instance of "B". The only thing that restrains the slip is the bond strengths between the planes. This restraining force we shall call $F_B$ and when $F \cos \theta = F_B$ the plane will slip upwards and the volume of "A" will plastically deform. It would now be constructive to review briefly the mechanism of slipping and plastic deformation in crystals. Where dislocations and crystal imperfections are present $F \cos \theta$ does not have to be large to cause slipping.

In the theories of the equilibrium of crystal lattices an atom is supposed to sit in a position of minimum energy in relation to its neighbours, [13]. Heat motion will agitate the atom so that it moves about in this position, but until a certain temperature is reached the chance that the atom will escape across this potential barrier is very small. Let us consider, for the sake of simplicity, a perfect cubic crystal and the potential along a line CD placed midway between two regularly spaced lines of atoms $A_0$, $A_1$, $A_2$, etc. and $B_0$, $B_1$, $B_2$, etc. This is represented diagramatically in Figure 3:50,15. If the

![Diagram of a perfect crystal with potential along CD](image)

Figure 3:50,15 Arrangement Of Atoms In A Perfect Crystal
positions of minimum potential due to the lines $A_a$ and $B_b$, considered separately were to occur at points $C_0$, $C_1$, $C_2$, etc., where $C_0$ is midway between $A_0$ and $B_0$, atoms placed at these points would then be in equilibrium with the surrounding structure. We may assume that the potential along row $CD$ due to either of the rows $A_a$ or $B_b$ may be given by:-

$$-A \cos \left( \frac{2 \pi x}{\lambda} \right)$$

where $\lambda$ is the lattice spacing.
and $x$ is measured from position $C_0$.
This is an obvious approximation and a more realistic expression would be one governing the force exerted on an atom by another as a function of their separation. This, however, would not be quite as convenient to work with.
The total potential due to both rows then becomes:-

$$P = -2A \cos \left( \frac{2 \pi x}{\lambda} \right)$$

The height of the potential hill or barrier which must be climbed by any atom in order to escape from this position is thus $4A$. This is shown graphically by the sine wave of Figure 3:50,15.

Let us now advance the above model and consider the situation in the presence of a positive dislocation. A positive dislocation is shown in Figure 3:50,16. Here the atoms above the center of the dislocation are compressed in the direction of the slip while those in the plane below are extended. At some distance from the center the spacings along lines of atoms above and below the dislocation become regular and equal to the normal spacings for the crystal. If the number of atoms in a length $L$ of a line of atoms, which passes below the center of a unit
Figure 3:50,16 A Positive Dislocation

dislocation, is \( N \), then the number in the same length \( L \), passing above the center will be \( N+1 \). To calculate the distribution of potential along the line of atoms on which the actual center of dislocation passes would be complex, involving finding the equilibrium positions of all the surrounding atoms. The basic nature of this potential may, however, be inferred by calculating the potential along

![Diagram of dislocation](image)

Figure 3:50,17 Conditions At A Dislocation When No External Stress Is Applied
the line of dislocation using a system with \(N+1\) atoms above it and \(N\) atoms below it. The simplest arrangement of this kind has \(N+2\) atoms in the upper row, evenly spaced over a length \((N+\frac{1}{2})\) whilst the \(N+1\) atoms of the lower row are evenly spaced over the same length. This situation may be seen in Figure 3:50.17. Here \(N = 3\). Outside this range we may assume that the atoms have the spacing equal to that of the unstrained crystal. Making the same approximations as for the regular lattice the potential along CD is given by:

\[
P = -A\cos 2\pi \frac{X}{\lambda} \left( \frac{N+1}{N+1/2} \right) - A\cos 2\pi \frac{X}{\lambda} \left( \frac{N}{N+1/2} \right)
\]

The nature of this expression is shown in the figure of 3:50.17. In the length of \((N+\frac{1}{2})\) it has \(N+2\) minima, including those at the two ends of the range. The heights of the potential hills and depths of the potential valleys decrease from each end to the center of the range. If we now imagine that each potential valley with the exception of the center one is filled by an atom, we have a rough picture of a possible equilibrium distribution of atoms in the neighborhood of a center of dislocation, the center being at 0 in the figure.

It has been mentioned that in perfect crystals an atom will remain in its potential well until a certain temperature is reached and it is able to jump the barrier. At this temperature atom \(C_0\) in Figure 3:50.17 might jump into the position belonging to \(C_1\). At lower temperatures this would not be feasible, though it might be possible for an atom to jump one of the lower barriers nearer the center of the dislocation. The lowest temperature at which a jump can be made is thus that permitting either \(C_1\) or \(C_2\) to jump into the central hollow. This temperature will be called \(T_0\). When one of these atoms has jumped into the
central hollow, the potential hollow which is left vacant becomes the new center of dislocation and all the surrounding atoms will re-adjust themselves into new positions of equilibrium. Hence we can see that there is a temperature above which a dislocation within the crystal is free to move in either direction along a slip plane.

In conditions of laser damage, however, we need to know what happens in the above situation when an external shear stress is applied to the crystal. This can be seen in Figure 3:50,18. The shear stress is applied in the direction indicated by the arrow. This gives the row of atoms \( A \) a small displacement to the right with respect to the row \( B \). If we define this small displacement as \( \delta \) the potential along the line \( CD \) now becomes:

\[
\begin{align*}
\text{Potential along line } CD & = \text{Vacant Potential Hollow} \\
& = \text{Small Displacement to the Right}
\end{align*}
\]

Figure 3:50,18 Conditions At A Dislocation Subject To A Shear Stress

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This expression is also shown in the figure. It can clearly be seen that it has lowered the height of the barrier over which the atom to the right of the central hollow needs to jump in order to enter the hollow. The barrier over which the atom on the left must jump has been correspondingly raised. At low temperatures therefore, there will be a tendency for the dislocation to move to the right and though at high temperatures it is permitted to move in any direction there will be a preference for it to go towards the right. Thus for positive dislocations there will be a tendency for a dislocation to move in the direction of the applied shear stress. A negative dislocation will tend to move contrary to the applied stress, a negative dislocation being a mirror image of the positive.

Returning to the (111) slip plane in calcium fluoride under the effect of thermal expansion and hence a shear stress we can see, as shown in Figure 3:50,19, that we have a dislocation forming. Volumes B, C, and D of Figure

![Figure 3:50,19 Formation Of Dislocation In CaF2 Surface](image)

3:50,13 will have rows of atoms adjacent to the slip plane.
with \( N+x \) atoms whilst \( A \) will have \( N-x \) atoms. The force producing the displacement will increase exponentially towards the surface, in accordance with the temperature/depth profile. Where defects already exist in the crystal, these will start to migrate before intrinsic defects are created, and consequently certain planes, those containing defects will go first. This will relieve the forces on the perfect portions of the lattice, and the defects will tend to migrate downwards into the crystal. As the force producing the displacement of atoms from their equilibrium position is increased, then obviously, their displacement will increase. Thus we will have the situation up the slip plane where the atoms on either side of the dislocation line are in and out of phase with their positions in a perfect structure. Every so often the atoms of \( A_a \) and \( B_b \) will coincide with each other and the perfect lattice configuration, only to go out of phase again, and so on up the slip plane. Where \( \beta \) is small, i.e. the applied shear force is small, the number of atoms in a dislocation line lying between perfect lattice points will be large. As \( \beta \) becomes larger the number of atoms before the dislocation is in phase again will decrease. This is shown in Figure 3:50,20. As \( N \) decreases the internal stress upon the bonds

![Internal Stress vs Distance](image)

Figure 3:50,20 Displacement From Perfect Lattice Points As \( N \) Decreases Towards The Surface
will increase, and the planes will have a greater tendency to slip and the dislocation will migrate downwards. Thus the material can be said to have been plastically deformed, though no cleavage has yet taken place.

The material will now begin to cool down, the final stage of the damage process. Cooling to ambient surroundings will occur from the depth of the crystal first. As the forces of the thermal expansion are removed the crystal will try to regain its perfect lattice configuration. The plastic deformation experienced as it heated up has meant, however, that it has been irreversibly changed. In the depths of the crystal where $\delta$ was very small the re-arrangement on cooling may be possible but this will further stress the atoms higher up the slip plane, where the tensions are already severe. Couple this to the removal of the forces that initially caused the change and the fact that calcium fluoride is a very brittle material, and the material begins to cleave. The threshold for cleavage can be related to the severity of a dislocation line, i.e. the number of atoms in a range between perfect lattice points. For argument's sake let this be 10000. At the hottest part of the crystal this dislocation range will occur deep down, whilst on the cooler edges it will be nearer the surface. When cleavage is initiated much of the crystal's internal stress will be relieved. This will explain the fact that the cleavage triangles i) always point the same way and ii) the cleaved triangles at the center of the damage profile are larger than those at the edge. As we progress into the depth of the crystal we could define the deformation of the crystal into three separate regions. This is shown in Figure 3:50,21. The surface temperature will dictate the extent of these three regions and hence the crystalite size.
Figure 3:50,21 Deformation Of Crystal With Depth Showing The Three Deformed Regions

From the photographs in Figures 3:50,8 and 3:50,10 it can be seen that the crystals have cleaved parallel to the surface resulting in the appearance of Newton's rings. This is because the cleaved volume looks as follows:

Figure 3:50,22 Deformed Volume Giving Rise To Newton's Rings

As the volume plastically deformed and elongated the dis-
tortion from the equilibrium position would be greatest directly adjacent to the slip plane. The bonds of the (111) plane parallel to the surface plane will consequently be stretched, yet the degree of stretching will fall off as one proceeds horizontally away from the slip plane. The crystal will be able to withstand a certain maximum tension in the planes parallel to the surface, but when this is exceeded, they too will cleave. This tension will build up from the depth outwards as the material cools. After cleavage the layers above them will tend to relax and their stresses be relieved, though they will tend to pull the remaining surface layers upwards. Hence the Newton's rings.

Any stresses within the crystal due to the growing procedure or the polishing operation will tend to aggravate the situation already described. It was noted that cleavage was always more severe around deep scratches. The stress distribution around scratches will always be higher than the perfect crystal because of the effect of dangling bonds and an unterminated surface. Thus all stresses will be summative on top of that introduced by the temperature rise of the damage process, and will tend to make the damage appear more severe than is perhaps necessary.

3:60 Summary

To summarize this chapter on surface damage at 248 nm. we may conclude by saying:-

i) Damage at low fluences is initiated by surface impurities, polishing agents, human contamination etc.

ii) A chemical etch, without changing the nature of the polished surface will greatly enhance the damage resist-
ance of the crystal.

iii) High threshold damage appears irrespective of the surface finish, within the bounds of the polishing quality attainable at B.D.H.

iv) Surface finish, though not affecting the damage threshold appears to affect the damage morphology, i.e. the more scratched a surface the more severe will the damage appear as it will exhibit a greater degree of cleavage.

The best surface is thus the cleanest surface.

3:70 Bibliography


Chapter 4:00 DEFECT PROCESSES IN LASER DAMAGE

4:10 Introduction

The study of laser induced damage should not only be confined to the mechanical failure of the component due to intense laser irradiation. This may be the main failure route in optical coatings and on surfaces and one of the problems within the bulk of the material but it by no means represents the complete picture. Single crystal CaF$_2$ for instance is used as the material for excimer laser windows. It is almost ideal for the task. It is resistant to the fluorine atmosphere within the cavity and transparent below 193 nm (the ArF wavelength). CaF$_2$ does have a disadvantage, however, in that it has a tendency to form colour centers. Indeed, one laboratory has reported such severe window colouration within the first few minutes of operation that the laser was rendered inoperable. This was a rare case. Generally the colouration is a long term effect, slowly degrading the laser output with many hours of operation, and eventually necessitating a window change. The formation of colour centers is usually accompanied by a degree of fluorescence which may or may not be acceptable and may become more acute with time.

Defect centers have been widely studied in the alkali-halide family of insulating crystals, and to a lesser extent in the alkaline-earth halides. Virtually no work, however, has been reported on the role that these defects may play in laser induced damage, nor to the colouration processes occurring when excited by intense, short pulse optical fields. At the Boulder Damage Symposium (Colorado, U.S.A.) in 1980 the problem was addressed for almost the first and last time. P. Braunlich, G. Brost, A. Schmid and P. Kelly presented a paper [1] hypothesising
the role of laser induced primary defects in the optical breakdown of NaCl. They admitted that as very little was known about the various parameters of primary defect formation no hard and fast conclusions could be drawn. They at best could point out some of the possible consequences of defect formation. Since then little has been done in this field.

In the 1970's M. N. Kabler, R. T. Williams, W. L. Faust and J. N. Bradford [2] and also Y. Suzuki and J. Hirai [3] showed that primary defects such as $V_K$, F and H centers, as well as self-trapped excitons are produced extremely rapidly and efficiently from multiphoton and impact ionization generated excitons in the alkali and alkaline-earth halides [4]. The formation of primary defects, all of which are strong absorbers in the ultra violet through to the infra-red region of the electromagnetic spectrum, were suspected by M. N. Kabler and R. T. Williams to effect seriously the mechanisms whereby energy from an intense photon beam is coupled to the lattice causing breakdown. They noted that:

i) As well as free carrier (polaron absorption), new channels of energy deposition to the lattice are created by the generated defects and these could drastically reduce the theoretical laser induced damage thresholds predicted by either the electron-avalanche or multiphoton model.

ii) The efficient removal of electron-hole pairs by the rapid process of primary defect formation reduces the multiphoton/electron-avalanche generated free carrier concentration and as a consequence affects the free carrier absorption mechanism of joule-lattice heating. This would increase the theoretical damage threshold.

The net effect of these two processes is hard to assess without a detailed study of the dynamics involved.
in the damage process and a knowledge of the reaction cross sections and lifetimes of the transient defect stages produced during irradiation.

4:20 Nomenclature, Defect Processes And Defect Types

In this section the classes of radiation damage, the nomenclature and the characteristics of the defects will be defined. The section is intended to produce familiarity with the aspects of radiation damage relevant to intense, short pulse ultra violet irradiation. There are three accepted classes of radiation damage defined as:-

i) electronic processes in which an electronic state is changed or charge is transferred by the absorption of radiant energy but in which no ionic or atomic defect is produced. An example might be the raising of the valency state of an impurity ion from +2 to +3.

ii) elastic collisions in which atoms or ions are displaced due to momentum or energy transfer from irradiating particles. This class will not be considered further.

iii) radiolysis whereby atomic or ionic defects are produced by a series of reactions initiated by an electronic excitation.

Processes which lead to electronic damage include photon absorption as in the photo-electric effect and the Compton effect. Energy absorbed in the crystal appears as electrons in a normally empty conduction band and holes in a normally full valence band, or else as excitons at lattice ions, impurity ions or defects in the crystal. In electronic processes the excitation is the first step leading to an observable electronic state. The reaction may include the separation of electrons and holes and the subsequent trapping of the separated charges. It should be noted that these defects will occur in pairs and will not
change the overall charge neutrality of the crystal.

In highly ionic polar crystals, radiolysis is a common form of damage as seen by the creation of Frenkel pairs on irradiation with ultra violet light. For radiolysis to occur a three stage sequence must be accomplished. Firstly an electronic excitation must result in the creation of a polarized or charged electronic defect. The energy of this defect must then be converted to kinetic energy in a lattice ion in such a way as to cause the ion to move. Finally the ion must be stabilized. It is both radiolysis and electronic defect formation that is the concern of this chapter, and may be amalgamated under the heading of photochemical phenomena. Photochemical effects are certainly no new area, though the production of vacancies and interstitials by mere bandgap excitation alone is not common. There are a number of reasons for this. To begin with the energy supplied by the photon must exceed the sum of the formation energy of the defects and any intermediate stage required en route. Then there needs to be some reaction after excitation to prevent total recombination. In the alkali and alkali-earth halides for instance the exothermic reaction \( X^- + X \rightarrow X_2^- \) is sufficient. The oxides on the other hand have \( O^2^- + O^- \rightarrow O^3^- \) as endothermic and consequently do not naturally exhibit photochemical behaviour. Often when vacancies and interstitials form they exist for only a brief period and are considered inconsequential. With respect to a 30 nsec laser pulse, however, they are long lived and need to be considered for any role they may play. Recombination can be inhibited, for instance by a local barrier or by thermal migration.

There is general agreement throughout the literature that the primary products of radiolysis in the alkali and alkali-earth halides are the F center and complementary H
center. Initially the ionizing radiation produces "free electrons" and holes. The electrons may be trapped within the band gap by impurities and require further photon absorption before being liberated into the conduction band. The electrons in the conduction band thermalize rapidly through phonon emission, heating the lattice. The holes in these halide crystals are believed to self-trap very rapidly within a time period of 0.1 to 1.0 psec. Fast pulse optical studies have indicated that F centers may form in their ground state within 10 psec of the band gap excitation [4]. This is short compared with the radiative lifetime of the excited F center which is about 600 μsec. Experiments have also indicated that V_K centers have a capture cross section for electrons in the region of 10^{-14} cm^{-2}.

Once a free exciton has been created by optical absorption the next stage is the self trapping of the hole resulting in what is termed a "self trapped exciton". This exciton will be in one of three states:

i) e^*h^* - electron and hole excited.

ii) e^*h - electron only excited.

iii) eh^* - hole only excited.

After this, depending on the nature of the lattice and the ambient conditions within the lattice a series of complex processes will occur resulting in either a perfect crystal or a radiation damaged crystal containing F and H centers.

To try and clarify the last few paragraphs a description of the relevant defect types will be given. First, however, it will be necessary to give a brief introduction to the spectroscopic notation used for diatomic molecules. It will be assumed though that the reader is familiar with the quantum theory of atomic orbitals.
4:21 Spectroscopic Notation For Diatomic Molecules

The motion of the electrons in an atom takes place in a spherically symmetric field of force. Thus the electronic orbital angular momentum $\mathbf{L}$ is a constant of the motion, assuming the effect of the electron spin is small. In a diatomic molecule, however, the symmetry of the field is reduced to axial symmetry about the internuclear axis. For the purposes of this introduction the axis will be taken as fixed. This means that only the component of the orbital angular momentum of the electrons about the axis is a constant of the motion. The situation is analogous to the atom in a strong electric field, where the field is the electrostatic field of the two nuclei. $\mathbf{L}$ precesses about the internuclear axis with a constant component $M_L(h/2\pi)$, where $M_L$ can take the values:

$$M_L = \pm L, \pm (L-1), \pm (L-2), \ldots, \pm L$$

This is illustrated in Figure 4:21,1. In an electric field reversing the directions of motion of all the electrons does not change the energy of the system, though it will change $M_L$ into $-M_L$. Thus in diatomic molecules states that differ only in the sign of $M_L$ will be degenerate. On the other hand states with differing $|M_L|$ will have differing energies as the field that causes the splitting is
very strong. As the strength of the field increases \( L \) will precess faster and faster and the significance of its angular momentum will be lost. \( M_L \), however, will remain unchanged and therefore the electronic states of a diatomic molecule are classified according to the value of \(|M_L|\). By convention, therefore:

\[
\Lambda = |M_L|
\]

4:21,2

The corresponding angular momentum vector \( \Lambda \) represents the component of the electronic orbital angular momentum along the internuclear axis.

From Eq. 4:21,1, for a given value of \( L \), the quantum number \( \Lambda \) can take the values:

\[
\Lambda = 0, 1, \ldots, L
\]

4:21,3

Hence in a molecule, for each value of \( L \) there are \( L + 1 \) distinct states with different energy. Depending on whether \( \Lambda = 0, 1, 2, 3, \ldots \) the corresponding molecular state is designated as a \( \Sigma, \Pi, \Delta, \Phi, \ldots \) state, analogous again to the notation for atoms. Greek letters are used throughout in the designation of molecular quantities and refer to the components of the electronic angular momenta whilst the italic letters used for atoms refer to the electronic angular momenta themselves. As already mentioned the \( \Pi, \Delta, \Phi, \ldots \) states are doubly degenerate as \( M_L \) can have the two values \( +\Lambda \) and \( -\Lambda \). \( \Sigma \) states on the other hand are non-degenerate.

The fine structure of electronic bands in diatomic molecules often show multiplet levels, which, as for atoms is due to the electron spins. The spins of the individual electrons form a resultant vector \( \mathbf{S} \), the corresponding
quantum number being either integral or half integral according to whether the total number of electrons in the molecule is even or odd. In $\Sigma$ states, similar to the $S$ states of atoms, the resultant spin $S$, as it is unaffected by an electric field, is fixed in space providing the molecule does not rotate and there is no external magnetic field. When $\Lambda \neq 0$ however, i.e. for the $\Pi$, $\Delta$, ... states, there is an internal magnetic field in the direction of the internuclear axis as a result of the orbital motions of the electrons. This magnetic field causes a precession of $S$ about the field direction with a constant component $M_s(h/2\pi)$. For molecules $M_s$ is denoted by $\Sigma$. This should not be confused with the quantum number $\Sigma$ when $\Lambda = 0$. This, it may be noted, is no more confusing than the atomic case where $S$ is used both to denote the spin quantum number and as a symbol for the term with $L = 0$. The values of $\Sigma$ allowed by quantum theory are:

$$\Sigma = S, S-1, S-2, \ldots, -S$$  \hspace{1cm} 4:21,4

The total electronic angular momentum about the internuclear axis, denoted by $\Omega$ is obtained by adding $\Lambda$ and $\Sigma$. This is similar to the atomic case where $J = L + S$. Note that for molecules an algebraic summation suffices as both vectors lie along the internuclear axis. Thus the quantum number of the resultant electronic angular momentum about the axis is:

$$\Omega = |\Lambda + \Sigma|$$  \hspace{1cm} 4:21,5

If $\Lambda$ is not equal to zero, then according to Eq. 4:21,4, there are $2S + 1$ different values of $\Lambda + \Sigma$ for a given value of $\Lambda$. Because of the interaction of $S$ with the magnetic field produced by $\Lambda$, the different values of $\Lambda$
+ Σ correspond to the different energies of the resulting molecular states. An electronic term with a given \( \Lambda = 0 \) splits into a multiplet of \( 2S + 1 \) components. When \( \Lambda = 0 \) there is no magnetic field in the direction of the internuclear axis ( \( \Sigma \) is not defined) and no splitting occurs. \( \Sigma \) states are single as long as the molecule does not rotate. Figure 4:21,2 shows the orientation of the vectors \( \Lambda \) and \( S \) for a term with \( \Lambda = 2 \) and \( S = 1 \).

![Figure 4:21,2 Vector Diagrams And Energy Level Diagrams For A \( ^3\Delta \) State](image)

According to standard nomenclature the multiplicity is added as a left superscript whilst the value \( \Lambda + \Sigma \) is added as a subscript. As \( \Lambda = 2 \) we are dealing with a \( \Delta \) term whose components are \( ^3\Delta_3 \), \( ^3\Delta_2 \) and \( ^3\Delta_1 \).

To summarize. For singlet terms (\( S = 0 \)) \( \Omega = \Lambda \) e.g. \( ^1\Pi_1 \), for doublet terms (\( S = \frac{1}{2} \)) \( \Omega = \Lambda \pm \frac{1}{2} \) e.g. \( ^2\Pi_{1/2} \), \( ^2\Pi_{3/2} \) and for triplet terms (\( S = 1 \)) \( \Omega = \Lambda \pm 1 \) e.g. \( ^3\Pi_0 \), \( ^3\Pi_1 \) etc. As with atoms there is an alternation with multiplicities. Molecules with an even number of electrons have odd multiplicities i.e. singlets and triplets, whilst those with an odd number of electrons have even multiplicities, i.e. doublets and quartets.

Also to be considered are the symmetry properties of the electronic eigenfunctions as these are of great importance, and depend upon the symmetry properties of the
field in which the electrons move. In diatomic molecules any plane through the internuclear axis is a plane of symmetry. Thus the electronic eigenfunction of a non-degenerate state (Σ state) remains unchanged or changes sign upon reflection about any plane passing through both nuclei. In the first instance the state is termed a Σ⁺ state and in the second a Σ⁻ state. In the case of states with \( \Omega = 0, \Lambda \approx 0 \) a slight splitting exists and again the eigenfunctions of one of the components remains unchanged whilst the other changes sign upon reflection about any plane through the two nuclei. An example of this would be the \( ^3\Pi_0 \) state being distinguished as \( ^3\Pi_{0^+} \) and \( ^3\Pi_{0^-} \).

If the two nuclei have the same charge, as in the case of the \( V_k \) center, the field in which the electrons move has, as well as a symmetry axis, a center of symmetry (this will be equidistant between the two nuclei). This means that the field remains unchanged by reflection of the two nuclei at this center of symmetry. This means that the eigenfunctions remain unchanged or only change sign when reflected about this center. In the case of the unaltered eigenfunctions the states to which they belong are known as even states, whilst in the second case where they change sign, odd states. Wigner and Witmer [5] showed that this property applied to degenerate as well as non-degenerate states and that for degenerate states both components always have the same symmetry with respect to reflection at the center. This symmetry property, even or odd, is indicated by adding a subscript \( g \) or \( u \) respectively to the term symbol. Thus diatomic molecules with like nuclei have \( ^3\Sigma_g^+ , ^1\Sigma_u^+ , ^1\Pi_g , \ldots \) states. The electron spin has no influence on this symmetry property and hence the components of a given multiplet are either all odd or all even.

If we were to construct a model of a \( V_k \) center we
would need to construct 9 orbitals for the 18 electrons of the fluorine atoms. 10 of these would be the p orbital electrons. To see what occurs when we linearly add atomic orbitals to construct molecular orbitals we shall combine the \( p_x \), \( p_y \) and \( p_z \) orbitals. The \( p_z \) orbitals lie along the internuclear axis and can combine in either a symmetric or an anti-symmetric mode yielding \( \sigma_g \ 2p \) and \( \sigma_u \ 2p \) orbitals respectively. This combination can be seen in Figure 4:21,3. The \( p_x \) and \( p_y \) orbitals, on the other hand will combine to form orbitals non cylindrically symmetric with

![Figure 4:21,3 Linear Combination Of Two \( p_z \) Orbitals](image)

\[ \lambda = 1. \] Analogous to the atomic case these are denoted \( \pi \) orbitals. Here, note that the symmetric combination, having the lowest energy, is antisymmetric with respect to inversion through a center of symmetry and vice versa. Hence the orbitals are designated \( \pi_u \ 2p \) and \( \pi_g \ 2p \) respectively. This is best illustrated in Figure 4:21,4.

To summarize the orbital picture, then, there are \( \sigma \), \( \pi \), \( \delta \), \( \varphi \), ... one electron molecular orbitals for which the angular momentum eigenvalues are \( \lambda = 0, 1, 2, 3, ... \). For molecules with like nuclei there are \( u \) and \( g \) orbitals
Figure 4:21,4 Addition Of $p_x$ and $p_y$ Orbitals corresponding to antisymmetric and symmetric combinations of atomic orbitals.

It is hoped that this section has served its purpose in providing a brief introduction to the notation of the spectroscopy of diatomic molecules. For further reading [7] and [9] can be recommended.

4:22 The $V_K$ Center

The $V_K$ center can be thought of as a hole localized between two adjacent halide ions and to a good approximation is simply an $X^-_2$ molecule where $X^-$ is a halide ion. It is thus the addition of two $X^-$ ions and a hole, and is a good example of a "molecule-in-a-crystal" defect where the host lattice only weakly perturbs the molecular ion. A molecular orbital picture of the $V_K$ center may be constructed based on the valence orbitals of the relevant halogen ion, 2$p$ for fluorine. The model is derived from the LCAO approximation (linear combination of atomic orbitals).
als), and ignoring the departure from axial symmetry of the \( V_k \) center in the crystal the derived energy level diagram will be as shown in Figure 4:22,1. Before the hole is trapped the twelve 2p electrons of the two \( F^- \) ions completely fill the molecular orbitals giving no net bonding. When, however, a hole is trapped in the \( \sigma_u^- \) orbital, its lowest energy state, an antibonding electron is lost giving a stable \( X_2^- \) ion with the ground state configuration of:

\[
\sigma_g^2 \, \tau_u^6 \, \tau_g^4 \, \sigma_u^- \quad \left( ^2\Sigma_u^- \right)
\]
The hole may be excited to the $\pi_g$, $\pi_u$ or $\alpha_u$ orbitals resulting in the excited states $^2\Pi_g$, $^2\Pi_u$ and $^2\Sigma_g^+$ respectively. The transition $^2\Sigma_g^+ \rightarrow ^2\Sigma_g^+$ is electric dipole allowed and gives rise to an intense broad absorption band in the ultra violet polarized parallel to the molecular axis. The infra-red transition $^2\Sigma_u^+ \rightarrow ^2\Pi_g$ has a dipole polarization normal to the molecular axis whilst the transition $^2\Sigma_u^+ \rightarrow ^2\Pi_u$ is parity forbidden. Note that no luminescence due to the $V_k$ center has yet been reported although the exact mechanism of non-radiative recovery is not yet certain.

As a final comment on the "molecule-in-a-crystal" model of the $V_k$ center, calculations show that the internuclear spacing of the molecule in its ground state in the lattice is less than 5% greater than the free $X_2^-$ molecule. This would tend to justify the use of such a model.

4:23 The Self Trapped Exciton

The self trapped exciton in the halide crystals is essentially a self trapped hole to which an electron is bound i.e. ($V_k$.e) or (h.e). As already mentioned there are three types of excited state of the self trapped exciton, electron excited, hole excited, and both components excited. Non-radiative transitions can take the center from one type of state into another. The hole excitations can be considered as those of the $V_k$ center as it is only very weakly perturbed by the presence of the electron. The electron excitations have the electron moving in a field of localised positive charge and resemble those of the hydrogen atom bar the axial perturbation that splits the $p$ states into axial $\sigma^-$ and equitorial $\Pi$ states. Also singlet and triplet excitations can occur depending on whether the electron and hole have antiparallel or parallel spins.
The triplet form can recombine only by a spin forbidden transition, the lowest triplet state having a lifetime of \(10^{-3}\) sec. Many transitions have been observed or inferred to the self trapped exciton, the principle luminescence transitions giving the \(\pi\) and \(\sigma\) bands. There is also a variety of non-radiative possibilities involving self trapped excitons:-

i) the normal multiphonon processes between levels of the self trapped exciton leading to electron hole recombination. It is believed that the \(\sigma\) band is missing in some hosts because of the rapid recombination of the excited singlet states. It is also possible to combine multiphonon transitions with Auger transitions induced by electron-electron interactions transferring energy from electron excited to hole excited states.

ii) the formation of F centers and H centers from the non-radiative decay of self trapped excitons.

4:24 The F Center

This is perhaps the best understood and most widely studied of centers in ionic crystals, especially in the alkali halides. It consists of an electron localised at a halide ion vacancy and is often modelled along the lines of a hydrogen atom, being given the same atomic orbitals. Figure 4:24,1 shows a number of defect sites in an alkali halide host lattice. The electron is held in the vicinity of the halide ion vacancy by the electrostatic forces of the remainder of the crystal. Chemically it is a little hard to describe for it can be thought of as a valence electron without a nucleus. The center has a number of electronic states and optical absorption produces a transition from the ground state to its first excited state. Each host crystal produces a characteristic absorption band for the F center that often falls in the visible part
of the electromagnetic spectrum causing the crystal to appear coloured. Once in the excited state the F center may return to the ground level via the emission of radiation or through radiationless transitions. Although there is a similarity between the hydrogen atom and the F center the spectra of defects in ionic solids is never characteristically similar to that of an atom in a gas. The F center spectra is never a line even at low temperatures and exhibits a large shift in energy between the absorption band and the emission band. This shift, known as a Stokes Shift, is characteristic of optical centers in ionic crystals. The "configuration co-ordinate model" used to describe the Stokes Shift can be seen in Figure 4:24,2.

Figure 4:24,2 can be explained simply as follows. The lowest energy state of the defect center corresponds to
the lower parabola. The energy of this state varies as the configuration co-ordinate is altered. In a general sense the co-ordinate represents the positions of all the ions in the solid that interact with the center and to some degree may be thought of as the distance from the defect center to its nearest neighbours. As this distance changes there is a lowest energy for the state (point A), the equilibrium position for that state. If the forces acting on the center were to be proportional with displacement from A, then the curve would be a parabola. Because of thermal vibrations there will always be displacements from A which will increase as the temperature is raised.

If the system were now to absorb light an electronic transition would occur to raise the center to an excited state, the upper parabola shown in the Figure. The electronic properties of the center will now be different and so too will its interaction with its neighbours. This means that the equilibrium displacement of the center in
its excited state has now moved to C, corresponding to a
different value of the configuration co-ordinate (or a
different distance from its nearest neighbours). When a
transition occurs, as from A to B, it will, to all intents
and purposes, be vertical. The positions of the nuclei of
the lattice do not change significantly during the nearly
instantaneous transition. This is known as the Frank-
Condon principle. If the center were displaced from A by
lattice vibrations when the transition occurred it would be
equally displaced from B. The curve at B, however, varies
rapidly with displacement from B and hence lattice
vibrations at A lead to a spread in energies due to the
steepness of the curve near B. This is manifest
experimentally by a broad absorption band with a
considerable spread in energies.

Once the center has reached its excited state about B
it will proceed to its new equilibrium point at C. This
will be accomplished by having the neighbouring lattice
ions change position with the center giving off its excess
energy to these lattice vibrations. At C the center will
again experience thermal vibrations and after some time
may make another transition back to the ground state with
the emission of light. This is shown in the Figure as the
transition C to D. As before, D is on a steeply varying
portion of the ground state's energy curve and the emiss-
ion is seen as a broad band. At D the center will relax
back to A by giving off its excess energy as heat. This
illustrates the origin of the Stokes Shift and also shows
that the difference in energy (A to B) — (C to D) appears
in the host lattice as heat.

Alone this might indicate that as the temperature was
to approach absolute zero and the lattice vibrations cease
we could then expect to see line spectra. This is not so.
The quantum mechanical treatment of a simple harmonic oscillator shows that it has a series of equally spaced energy levels with a separation $\hbar \nu$, $\hbar$ being Planck's constant and $\nu$ the frequency of the vibrator. The lowest of these levels is $\hbar \nu / 2$ above the minimum of the classical parabola. These levels can be seen in Figure 4:24,2. At high temperatures many of these levels are populated and the quantum mechanical approach merges into the classical situation. At low temperatures the lowest energy level alone may be populated. This is termed "zero point vibration"; and the probability of the center being at the different values of the co-ordinate is shown in the figure by the dashed curve which is gaussian. As the temperature is raised this will remain gaussian though its half width will increase as already noted. Thus even at temperatures approaching absolute zero, the spectral line though it narrows will never become a line as for atomic gases. An exactly similar situation applies to the emission of light.

In some cases the curves overlap such that the lowest energy level of the excited state can be accessed directly from the lowest energy level of the ground state and vice versa. This results in electronic transitions without the production of heat and the absorption and emission spectra both have a sharp line, called the zero phonon line, at the same wavelength. This, too, is shown in Figure 4:24,2.

It should be noted that the widths of the absorption and emission bands at some temperature $T$, denoted $H(T)$, can be related to the width of the band at absolute zero, $H(0)$, by the equation :-

$$\frac{H^2(T)}{H^2(0)} = \coth (\hbar \nu / 2kT)$$

4:24,1
where $H(0)$ is easy to measure as it is virtually constant below about 40 K. Using Eq. 4:24,1 by plotting $\coth[H^2(T)/H^2(0)]$ against $1/T$ W. Gebhardt and H. Kuhnert [10] were able to derive the effective vibrational frequencies which interact with the F center for a variety of hosts, and to show that there is indeed an appreciable interaction between the F center and the lattice, and that the distribution of the lattice modes of vibration near the F center are of a lower frequency than those of the undamaged lattice.

Measurements of the absorption spectra of F centers show, apart from the gaussian lineshape, an oscillator strength near unity. This, together with electron spin resonance results showing the ground state to be isotropic confirm the hydrogen like nature of the center and indicate that the single allowed transition is equivalent to a $1s$ to $2p$ transition. Difficulties, though, arise in the interpretation of the luminescence lifetimes. The strong F center absorption transition would indicate a similar emission transition with a lifetime in the region of $10^{-8}$ sec. Measured lifetimes of F center decay however, are all in the $10^{-6}$ sec regime. Suitable explanations are still being sought after, though a number have been submitted [11].

Aggregate F centers have also been observed and are stable in ionic solids in units of two (M centers), three (R centers) and four (N centers). F centers themselves are electrically neutral though they may lose their electron to form an empty anion vacancy (α center) or gain an electron to form a charged center, the F' center. This center is stable only at low temperatures and will not concern us. The α center on the other hand generally has a broad absorption band in the ultra violet, close to the
first exciton peak. In fact it is accepted that the absorption is due to the creation of a perturbed exciton near the ionized F center. For a more detailed discussion of F centers and their properties the reader is referred to [11], chapter 5.

4:25 The H Center

The H center is a neutral anion interstitial and in some respects is similar to the $V_k$ center in that it too resembles an $X_2$ molecule. The analogy is particularly strong in the alkali halides where both the $V_k$ center and the H center have (110) symmetry. In CaF$_2$ however, the difference is more pronounced for the $V_k$ center has a (100) molecular axis involving the two nearest neighbour ions on a cube edge whilst the H center has a (111) molecular axis with one fluorine atom almost correctly placed whilst the other sits near the center of the normally empty cube characteristic of the fluorite structure. This can be seen in Figure 4:25,1. This molecular species in

![Figure 4:25,1 The $V_k$ And H Center In CaF$_2$](image-url)
fluorite consequently has a pronounced asymmetry between its two components. The ion near the cube center can be thought of as F$^{-1/3}$ and that near the correct site as F$^{-2/3}$.

4:26 Rare Earth Impurities

The most important family of impurities found in the alkali earth halides are the rare earths. V. M. Goldschmidt [12] noted that the trivalent rare earths have radii comparable to that of the Ca ion in CaF$_2$ (1.06 Å). K. Przibram et al [13] concluded that the colouration of the fluorites when found naturally was due to the rare earth ions that had been reduced to the divalent state by radioactive radiations. W. J. Scouler and A. Smakula [14] and J. R. O'Conner and J. H. Chen [15] concluded that Y$^{3+}$ ions were responsible for the Smakula type absorption in irradiated CaF$_2$ crystals of high purity. Indeed Y$^{3+}$ with an atomic radius of 1.06 Å has a great affinity for CaF$_2$ and is exceptionally hard to cleanse. Trace quantities of trivalent rare earth ions are generally charge compensated by F$^-$ interstitials or by O$^{2-}$ ions incorporated into the lattice during growth by the hydrolysis of the CaF$_2$. In order to overcome this hydrolysis when CaF$_2$ is grown synthetically a scavenging agent is added in the form of lead fluoride. Oxygen in the crystals gives rise to scattering centers and the crystals may have a milky appearance. The concentration of lead in the final crystals is less than 1 ppm in 75% of all the samples tested. All the crystals grown for these experiments were by B.D.H. Limited in Poole, Dorset. This low level does not appear to have any detrimental effect on the crystal's spectral qualities. It does mean, however, that there are plenty of excess fluorine atoms present which may be incorporated into the crystal, destroying its stoiochemistry.
There are two series of elements comprising the rare
earths. These are:-
i) the lanthanides, obtained by filling up the 4f shell.
ii) the actinides, by filling up the 5f shell.
With the lanthanides especially the tri-positive oxidation
state usually prevails when the impurity is incorporated
into the lattice. Reduction may occur and the divalent
rare earths may give rise to a diffuse fluorescent band
when irradiated with ultra violet light. An example would
be divalent europium (Eu) in CaF$_2$ which has a fluorescence
peaking around 400 nm, whilst divalent samarium (Sm) gives
a fluorescence at 690 nm.

It is possible with these impurities to have absorp-
tion AND emission bands resulting solely from the impurity
alone. Transitions such as:-
4f to 5d
4f to 6s
4f to 4f
are feasible. The external shells of the divalent impurity
ion are largely perturbed by the host environment and as a
result transitions involving these shells are diffuse. The
internal 4f shells, on the other hand are protected from
the crystal fields and show transitions that are narrow
and line-like in character. These 4f to 4f transitions are
forbidden and therefore are very weak. In all the crystals
grown by B.D.H. the level of impurities has been kept as
low as possible and are no more than in the ppm bracket
and so colouration by this method will not be a problem.
That does not mean that the impurities themselves can be
tolerated in the lattice for it is their ability to act as
electron traps that most concerns the field of laser dam-
age. In the trivalent state they provide a trap just above
the valence band and in the divalent condition they can be
found lying below the conduction band, ready to be photo-
ionized, liberating an electron to the conduction band and becoming accessible once more as a vacant electron trap. Such systems were studied in the search for photo-chromic materials. Consider Figure 4:26,1 based on a system of Sm

![Diagram of absorption spectra and energy level diagram](image)

Figure 4:26,1 Schematic Absorption Spectra And Energy Level Diagram Of An Ideal Photochromic Material

and Eu in CaF₂ [16]. The absorption spectra shown is not genuine but merely useful to illustrate the possible charge transfer mechanism. With the crystal in state A absorption is a result of the "write band" overlapping the conduction band whilst the "read band" is left below the conduction band. Once the write light has caused the Sm²⁺ ion to lose its electron to the conduction band this electron becomes available for trapping, in this case by the Eu³⁺ ion. In state A the system was of an Sm²⁺ ion and an Eu³⁺ ion whereas now in state B it comprises an Sm³⁺ ion and an Eu²⁺ ion. If erase light were to be absorbed by the Eu²⁺ ion it would re-excite the electron back to the conduction band to be re-trapped by the Sm³⁺ ion and state A would have been returned. Crystals for such systems
would be carefully doped and then one of the impurity centers reduced in the relevant atmosphere. Lanthanum (La), cerium (Ce), gadolinium (Gd) and terbium (Tb), all with a 5d ground state, have been shown to exhibit this photochromic behaviour at room temperature. Under normal conditions of growth, in for instance a Stockbarger furnace, all these crystals would appear in the 3+ oxidation state, having no electron of their own to give to the conduction band. They do provide traps for photo excitation of electrons out of the valence band by 248 nm photons. Thus they become stepping stones enabling the electrons to cross the crystal band gap prior to the onset of mechanisms such as multiphoton absorption and electron avalanche processes.

It has been noted that F center colouration in CaF$_2$ can occur in concentrations far in excess of the impurity concentrations and yet experiments have also shown that impurities play an important role in the formation of "intrinsic" defect centers, [8, pp311], [17].

Prior to any experimentation being performed on the crystals mass spectrographic analysis was performed on both sources of raw material, called Mexican and Optipur. Optipur is an evaporated source that is highly pure. A summary of the study is given in Figure 4:26,2. The full details can be found in Appendix 4.

<table>
<thead>
<tr>
<th>Lanthanides</th>
<th>Source Material</th>
<th>Actinides</th>
<th>Source Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>3.0</td>
<td>&lt;0.1</td>
<td>Th</td>
</tr>
<tr>
<td>Pr</td>
<td>3.0</td>
<td>&lt;0.1</td>
<td>Pa</td>
</tr>
<tr>
<td>Nd</td>
<td>3.0</td>
<td>&lt;0.4</td>
<td>U</td>
</tr>
<tr>
<td>Pm</td>
<td>-</td>
<td>-</td>
<td>Np</td>
</tr>
</tbody>
</table>

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### Table: Main Impurities and Their Concentrations

<table>
<thead>
<tr>
<th>Lanthanides Source Material</th>
<th>Actinides Source Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Eu</td>
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</tr>
<tr>
<td>Gd</td>
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</tr>
<tr>
<td>Tm</td>
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</tr>
<tr>
<td>Yb</td>
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</tr>
<tr>
<td>Lu</td>
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</tr>
<tr>
<td>La</td>
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</tr>
<tr>
<td>Y</td>
<td>30.0</td>
</tr>
</tbody>
</table>

**Figure 4:26:2 Main Impurities and Their Concentrations In ppm Found By Mass Spectrographic Analysis Of The Crystal Source Material**

Where the "<" sign occurs it means that the element was detected but no reliable figure could be given to its concentration. A "-" indicates that no trace was found. The main impurities would appear to be La, Y, Ba, Ce, Pr, Nd, Gd, Eu, Tb, Dy, Ho and Er. These all occur in the Mexican stock material whilst the Optipur seems fairly free of contaminants. With this knowledge of the differences in the impurity concentrations between the crystals the growth of defects can be monitored and comparisons made.

It is hoped that from section 4:22 onwards the scenario for defect damage in CaF$_2$ has been set and the defect
possibilities described. Reference will now be made to the work of M. N. Kabler and R. T. Williams [18], [19] and [20], in which they studied the photochemistry of CaF$_2$.

4:30 The Photochemistry of CaF$_2$

This section will describe the photochemistry of defect formation in CaF$_2$ specifically with the aim of establishing the possible decay mechanisms available to the defect after it has been created, initially via the 3+ impurity traps and later via the mechanisms of multiphoton absorption and electron avalanche excitation. Pure fluorite crystals have been observed to luminesce strongly under band gap excitation and the nature of this fluorescence is similar to that obtained by intense ultra violet irradiation. One is led to believe that the mechanism responsible for this luminescence is the same in both cases and is characteristic of the intrinsic crystal. The luminescence comprises a broad band peaking just beyond 300 nm. This manifests an extraordinarily large Stokes Shift. Remember that the band gap for CaF$_2$ is 10.6 eV, so that the Stokes Shift is in the order of 7 eV. The luminescence lies between the first exciton absorption peak and the intrinsic emission band and is suggestive of exciton self trapping. Hole self trapping in the fluorite crystals is well established [21]. The connection between the intrinsic emission in the fluorites to the recombination of electrons and self trapped holes was first achieved by Beaumont, Hayes, Kirk and Summers [22]. They doped crystals with thulium to provide electron traps and then created self trapped holes by irradiation. The self trapped holes were aligned by optical bleaching. The luminescence produced upon annihilation of the aligned $V_k$ centers with electrons photo-excited from the traps, matched the spectrum of X-ray excited intrinsic luminescence, and was
polarized in the direction of the $V_k$ centers. Since then further evidence has increased the belief that the intrinsic emission of the fluorites is associated with the S.T.E's (self trapped excitons).

One should be aware that in CaF$_2$ there is very little, if any, distinction between the self trapped exciton and the close F-H pair. The close F-H pair is simply an F center and a nearest neighbour H center, or more correctly an H center that is close enough to the F center such that its stability is governed by the lifetime of the recombination of the F-H pair. Both the close F-H pair and the S.T.E. can be considered isomers of the electron hole pair in the host lattice. This comes about as follows. Figure 4:30,1 illustrates F center formation in a CaF$_2$ crystal.

![Diagram of F center formation in CaF$_2$](image)

**Figure 4:30,1 F Center Formation In CaF$_2$ [19]**
In CaF$_2$ a triplet state of the electron hole pair is observed in which the two fluoride ions forming the F$_2$ core are not at equivalent sites. Evidence suggests that their nuclear axis is approximately $<111>$. This is the morphology of the H center and hence the ambiguity. Figure 4:30,1a shows the perfect lattice whilst Figure 4:30,1b shows the self trapped hole or $V_k$ center. This center in CaF$_2$ is known to have a $<100>$ orientation [23], yet it does not appear to be stable in the presence of an electron and thus moves to the $<111>$ orientation of the F-H pair configuration. The F-H pair separation at the F-H$_{nn}$ (nearest neighbour) configuration is still small enough for the system to be considered as a modified S.T.E. This is shown in Figure 4:30,1c. Radiative recombination may occur from this position in times of 5 to 10 msec restoring the perfect lattice.

Part (d) of the figure is a conceptual drawing of the energy curves for the modes of the exciton or F-H pair. $Q_1$ is the symmetric stretching mode appropriate to the F$_2$ molecule and the unstable $<010>$ self trapped exciton. $Q_2$ represents a generalized rotation and translation taking the $<010>$ S.T.E. to the F-H$_{nn}$ position. The arrows represent the optical absorption and emission transitions of the metastable F-H pair. $Q_3$ corresponds to the separation of the F-H pair to distances where its stability is not dependent upon the electron hole recombination probability. In fluorites the production of $Q_3$ is small despite the fact that under normal conditions nearly every electron hole pair attains the F-H$_{nn}$ configuration. $Q_3$, if attained, represents a stable separated pair of defects that may colour the crystal.

It should be noted in the diagram that no absorption or emission bands are indicated from the $<100>$ S.T.E.
configuration. None have been experimentally detected. This indicates that there is no significant minimum on this potential surface to stabilize the center against relaxation into the <111> nuclear axis [20].

As can be seen from Figure 4.30,1 there are various routes open to the S.T.E. under the continuing presence of radiation. As mentioned in [4] the \( V_k \) center in the <100> position is thought to form within 0.1 psec and the F-Hnn configuration within 10 psec. The energy of formation released on the realisation of the <100> \( V_k \) center is thought to be about 1 eV and on the formation of the <111> S.T.E. about 2 eV. This energy is believed to be immediately available to the lattice. Hole self trapping and electron capture is a fast and efficient process. The following diagram is a summary of the decay routes and excitation possibilities open to the <111> S.T.E. in CaF\(_2\) under conditions of excimer irradiation.

Absorb photon to dissociate to unrelaxed hole

\[ \text{Trapeed } \text{<100> Hole} \]

\[ \text{Migrate To Form Stable Defects} \]

\[ \text{In Presence Of Electron Becomes Isomer Of S.T.E.} \]

\[ \text{With <111> Configuration} \]

\[ \text{Emits Photon To Give Recombination Luminescence} \]
\[ \text{i.e. Forms } F^+ - H^- \text{ and Relaxes To Perfect Crystal} \]

\[ \text{Absorb Photon To Become S.T.E. } \text{i.e. May Exist Either As i) Hole Excited ii) Electron Excited. Phonon Transitions Lead To e In C.B. and Lattice Heating} \]
The presence of the holes and consequently the F-H isomer of the S.T.E. is important in laser damage as the hole centers may be the dominant mechanism in depleting the free carrier concentration of the conduction band. A set of rate equations for the defect system in CaF$_2$ may look as follows:

\[
\dot{V}_{K_{100}} = p \tau_{V_{K}}^{-1} - \sigma_{V_{K}} V_{K} F - \sigma_{n_{c}V_{K}} V_{K} \quad 4:30,1
\]

for \(<100>\) \(V_{K}\) centers and:

\[
\tau_{S.T.E._{111}} = \sigma_{n_{c}V_{K}} V_{K} - \tau_{S.T.E._{111}}^{-1} - \sigma_{S.T.E._{111}}^{-1} F - \tau_{S.T.E._{111}}^{-1} C^{-1} \quad 4:30,2
\]

for \(<111>\) S.T.E. centers where

- \(V_{K_{100}}\) = concentration of \(<100>\) orientated \(V_{K}\) centers.
- \(p\) = hole concentration.
- \(\tau_{V_{K}}\) = lifetime of a free hole.
- \(\sigma_{V_{K}}\) = cross section for photon absorption by and dissociation of a \(V_{K}\) center.
- \(F\) = photon fluence.
- \(\sigma_{e}\) = cross section for electron capture by \(<100>\) \(V_{K}\) center and rotation to \(F(1s)\)-\(H(\sigma)\) state of \(<111>\) S.T.E.
- \(n_{c}\) = concentration of conduction band electrons.
- \(v\) = average thermal velocity of free electrons.
- \(S.T.E._{111}\) = concentration of S.T.E.s in the ground state \(F(1s)\)-\(H(\sigma)\) configuration.
- \(\tau_{S.T.E}\) = lifetime of \(F(1s)\)-\(H(\sigma)\) state in transition to \(F^{+}\)-\(H^{-}\) state (Recombination luminescence to perfect crystal).
- \(\sigma_{S.T.E}\) = cross section for photon absorption of \(F(1s)\)-\(H(\sigma)\) exciton state.
- \(\tau_{F-H}\) = lifetime of \(F(1s)\)-\(H(\sigma)\) state in transition to separate defect configuration.
To derive a similar equation for the free carrier concentration we must consider the possible processes available to deplete and replenish the species. The replenishing mechanisms are those intrinsic to laser damage processes as well as photon absorption by the excited S.T.E. which results in dissociation of this defect. This may be detrimental to the damage threshold in two ways.

i) it places a "hot" electron in the conduction band which will relax down to the lower edge of the band giving its excess energy to the lattice.

ii) on dissociation it will yield to the lattice the binding energy of the S.T.E.

The depleting mechanisms of the free carrier concentration are the capture of the electron via a \(<100> V_k\) center and the trapping of electrons by impurity 3+ ions. This last method can be ignored for the impurity ions should not be present in such quantities to provide a sufficient drain on \(n_c\). Thus the rate equation may be written as:

\[
\dot{n}_c = \sigma_{\text{STE}} n_v - \sigma_{\text{STE}} v V_k + \sigma_{\text{STE}} \dot{F}
\]

where \(\text{STE}^+\) = concentration of excited S.T.E.'s.

\[
\sigma_{\text{STE}} = \text{cross section for photon absorption of excited S.T.E. leading to dissociation of the S.T.E.}
\]

\(n_v\) = the concentration of the valence band electrons.

These rate equations, without knowledge of their parameters, cannot usefully be solved. It is of interest, therefore, to try and obtain information experimentally that will lead to an insight to the situation described. We can assume that well below damage levels the effect of multiphoton generated electrons can be ignored, whilst approaching damage and temperatures near melting point we might expect thermal re-orientation of the defects to increase, leading to a greater number of stable defects.
The experiment to be described aims at monitoring the transient population of the $\text{F}(1s)-\text{H}(\sigma^-)$ S.T.E's during the irradiating laser pulse as a function of the incident intensity, and to a lesser extent, time during the period of the laser pulse. This was done by monitoring the absorption strength of the $\text{F}(1s)-\text{H}(\sigma^-)$ to $\text{F}(2p)-\text{H}(\sigma^-)$ transition.

4:40 Experimental Procedure

The concentration of the $<1\text{11}>$ S.T.E. isomer is to be monitored during transient excitation by the excimer laser pulse. The characteristics of this pulse can be found in Chapter 2. The concentration is monitored by assuming some function linking the absorption strength to the population of defects. The absorption measurements are made using a synchronously pumped dye laser tuned to the relevant wavelength for peak absorption by the $<1\text{11}>$ S.T.E. This is at 3.88 eV [11 pp.342]. The experimental arrangement finally adopted can be seen in Figure 4:40,1. This was built upon the light of experience, and represents a number of modifications. Essentially the apparatus comprises a typical laser damage facility as described in Chapter 2 less the Schlieren detection facility. The incident energy of the pump beam can be attenuated and measured. Prior to the aperture and attenuator is an 8% beam splitter, the reflected light being diverted to a dye laser, a Lambda Physik FL2000. The dye laser has a temporal profile similar to, yet shorter than its pumping source, the excimer laser. Typical pulse durations for the width at half maximum are 25 nsec for the excimer and 18 nsec for the dye laser. This is to be expected as the temporal extremities of the excimer laser are not energetic enough to cause the dye laser to lase. The output from the dye laser is beam split into two arms, again in the approximate ratio of 92 : 8.
Figure 4:40.1. Experimental arrangement for monitoring transient absorption.
The reflected arm, or the "probe arm" interrogates the crystal perpendicular to and co-incident with the axis of excitation by the excimer laser. The path length of the probe arm is arranged such that temporally it traverses the crystal centrally within the period of irradiation. It thus arrives at the crystal after about 4 nsec of excitation. Assuming [4] to be correct an equilibrium level of defects will have been established and variations upon this level will arise according to changes in the environment in the crystal. Any changes will be brought about by the energy and temporal profile of the pump beam. On emerging from the crystal the probe pulse is terminated on a vacuum photodiode (ITT 2L) connected to a fast oscilloscope, a Tektronix 466. This system is capable of the temporal resolution required. The trace on the oscilloscope can thus be thought of as the temporal evolution of the photon population within the cross section of the probe arm.

The other arm of the dye pulse, termed the "reference arm" is sent along a delay line, three reflections each off two parallel mirrors, introducing a 35 nsec delay. It, too, is then terminated on the vacuum photodiode. The oscilloscope trace thus displays two identical profiles in time but not necessarily in intensity, separated by about 15 nsec. The reference arm is critical to the experiment as the excimer laser varies in output intensity by about 5%. This variation is consequently manifest in the dye pulse. The absorption changes that we are concerned with are smaller than 5%. By monitoring the probe pulse with respect to the reference pulse absolute changes in intensity of the probe pulse due to the absorption in the crystal can be detected.

To consider Figure 4:40,1 in greater detail there is
a Gallilean telescope at the output of the dye laser. This initially was not the case and the reference arm was allowed to follow its natural divergence over the 35 nsec delay line. On reaching the vacuum photodiode its diameter was about 1 cm. This was approaching the size of the photodiode's light sensitive cathode. In principle this would not matter. The probe arm was diverged by a lens such that its cross sectional area at the vacuum photodiode matched that of the reference beam. Thus the detection system looked as shown in Figure 4:40,2. Provided that the beams

![Figure 4:40,2 Probe And Reference Beam Overlap Upon The Vacuum Photodiode](image)

were co-incident upon the detector, the fact that the detector was sampling only a portion of the beam was irrelevant. It had only to be the same portion for each arm. This was, should have been, easy to arrange. A He-Ne laser was interlaced to the axis of the dye pulse prior to the beam splitter, and used for alignment purposes. With the He-Ne laser turned off and operating the dye laser, however, it was found that, even with no sample in place, the two traces on the oscilloscope were varying greatly from each other, shot to shot. This variation was not only in intensity, but also in temporal shape. The reference arm showed the greatest fluctuations, though neither was the
probe arm consistent. No measurements were possible with this system. The reasons for the variation became apparent by noting the positions of the two pulses upon the detector face. Their positions were constantly changing. This was due to the pump in the dye laser that circulates the dye. This pump is housed in the laser body and its rotary action was causing it to vibrate. These vibrations were being transferred to the laser body from which the optical axis of the cavity received its rigidity. The vibration was causing the beam to wander through an angle of about a mrad, which was amplified by the length of the reference arm's delay line. At the detector face displacements of a cm were being experienced. As can be seen from Figure 4:40.2 this would represent a significant change in intensity. The figure is approximately to scale. By monitoring the temporal profile as we swept the beam's cross section across the face of the detector it was found that the temporal profile at the edges of the dye pulse was considerably different from that at the middle. This would probably be a consequence of the variation in pumping intensity across the focus of the excimer laser in the dye cell. By removing the dye laser motor from the housing the readings stabilized, though they were still subject to table and room vibrations. At this stage we had only wooden tables which were far from satisfactory.

To try and overcome this problem of unwanted variations it was decided to focus the whole of the dye pulse upon the detector's cathode such that the focused spot size was considerably smaller than the cathode. Error due to beam displacement would then be a result of non-uniform cathode response, assumed to be small. The focusing was achieved by the Galilean telescope. The two lenses used are as shown in Figure 4:40.3.
The output beam from the dye laser can be characterised as shown in Figure 4:40.4. For gaussian beams the formula relating the beam dimensions to a distance \( z \) from the waist along the axis of propagation is:

\[
W(z) = W_0 \left[ 1 + \left( \frac{\lambda z}{\pi W_0^2} \right)^2 \right]^{1/2}
\]  

Figure 4:40.4 Dye Laser Beam Parameters

(where all the symbols are as shown in Figure 4:40.4) which for large values of \( z \) approaches:

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\[ w(z) = \frac{\lambda z}{\pi w_*} \]

The irradiance \(1/e^2\) contour is then defined by a cone of angular radius:

\[ \theta = \frac{\lambda}{\pi w_*} \]

From the dimensions given in Figure 4:40,4 the beam radius at a distance of 10 m from the waist (the length of the delay line) will be:

\[ w(z) = z\theta = 4.3 \text{mm} \]

Using the Galilean telescope the divergence of the beam is reduced and consequently the spot size for large values of \(z\) is smaller. The telescope has an angular magnification of 5.33 and is focused so as to form a waist at its output lens. The size of the waist is:

\[ 5.33 w_* = 1.33 \text{ mm} \]

Using Eq.4:40,1 the new beam radius at \(z = 10 \text{ m}\) is shown to be 1.5 mm. Thus the spot size is 3 mm. This is more acceptable when aligned centrally on the photocathode as displacements due to vibration never move it beyond the cathode. In fact with the purchase of a vibration isolation optical table the movement of the spot on the detector was eliminated.

The second lens combination appears in the probe arm and focuses the dye beam through the region of excitation in the crystal. The dye pulse is brought to a much tighter focus than the excimer pulse and is aligned to probe a region central to the excimer's area of influence. The
lenses used here are two 75 mm, 0.05 N.A. flat mounted refracting microscope objectives with a broad band anti-reflection coating. The first lens is the focusing lens whilst the second acts only to re-collimate the beam. Figure 4:40,5 is a schematic of the probe arm and shows the dimensions needed in deriving the position of the crystal relative to the lens. It is required that the probe beam waist from the output of lens L3 is situated at the center of the crystal as it is along this axis that the excimer laser is aligned. The crystal is a cube of sides 2 cm. In air it is relatively simple to locate the position of the probe beam's best focus, but with the crystal in place this cannot be done and consequently has to be calculated. Thus the distance "$l" in Figure 4:40,5 needs to be determined. This can then be experimentally measured. The probe beam is TEM$_{00}$ and so the problem must be considered from the stand of gaussian optics. If the spot size is to be a minimum at the center of the crystal then the beam's radius of curvature at the distance $z = u + v$ (Figure 4:40,5) must be infinite. The solution is found by matrix multiplication having adopted a gauss-
Using matrices for geometrical ray tracing is a common technique and may be briefly introduced by considering Figure 4:40,6. In a given plane \( z = z_1 \), a light ray can be specified by giving:

i) \( y_1 \) = its distance from the optical axis.

and ii) \( \alpha_1 \) = the angle it makes with the axis.

Tracing a ray through an optical system then consists of finding \( y_2 \) and \( \alpha_2 \) at a plane \( z_2 \) starting from \( y_1, \alpha_1 \) at \( z_1 \).

The transformation matrices for elements in a system are derived depending on whether the element alters terms in \( y \) or terms in \( \alpha \) or both. Thus:

\[
\begin{pmatrix}
  y_2 \\
  \alpha_2
\end{pmatrix} =
\begin{pmatrix}
  A & B \\
  C & D
\end{pmatrix}
\begin{pmatrix}
  y_1 \\
  \alpha_1
\end{pmatrix}
\]

where \( \begin{pmatrix} A & B \\ C & D \end{pmatrix} \) represents the transformation matrix of the system.

The method needs to be adapted for the focusing or transmission of gaussian beams. This is done as follows.
Figure 4:40,7 A Spherical Wavefront

Consider Figure 4:40,7. A spherical wave travelling away from a center at $-z_1$ has a radius of curvature $\mathcal{C} = z + z_1$. The amplitude,

$$u = U e^{i(k\mathcal{C} - \omega t)}$$

is an exact solution of the scalar wave equation. If we take a paraxial approximation $(x, y \ll \mathcal{C})$ then:

$$u = U e^{i(k\mathcal{C} - \omega t)} \frac{exp ikr^2/2\mathcal{C}}{\mathcal{C}}$$

This expression is a solution to the wave equation provided that $r^2$ is restricted to $x^2 + y^2 \ll \mathcal{C}^2$. If we substituted $U$ into the wave equation with $\mathcal{C}(z)$ left unspecified a differential equation would result for $\mathcal{C}$, i.e.

$$\frac{d\mathcal{C}}{dz} = 1$$

which has a solution $\mathcal{C} = z + z_1$ where $z_1$ is a constant of integration. As a differential equation yields no inform-
ation regarding its constants an imagery or complex value may be used for $z_1$ and the result will still be a solution to the wave equation. $z_1$ is thus chosen to be complex, i.e.:

$$z_1 = -z_2 - ib$$

and we define a "complex radius" $q$ where:

$$q = z + z_1$$

$$= z - z_2 - ib$$

Hence:

$$U = U_\exp i(kz - \omega t) \cdot \frac{\exp ikr^2/2q}{q}$$

where:

$$q = z - z_2 - ib$$

Thus "q" is basically a scaled radius of curvature and the matrix method for gaussian beams involves finding "q". By referring to Figure 4.40,5 the matrix formulation of the probe system can be written down as follows:

$$\begin{pmatrix} q_2 / n \\ 1 \end{pmatrix} = \begin{pmatrix} 1 & m/n \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -p_e & 1 \end{pmatrix} \begin{pmatrix} 1 & u \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

The matrices in this equation, (4.40,14), represent the following:

$A = $ Gaussian representation of the input beam.

$B = $ The translation of the beam from its waist to the lens.

$C = $ The matrix representing the effect of the lens on
the gaussian beam.

D = The translation of the gaussian beam from the lens to the front face of the crystal.

E = The matrix representing the effect of the crystal on the beam. The crystal is taken to be a lens of infinite radius or zero power.

F = The translation from the front surface of the crystal to the center of the crystal.

G = The matrix detailing the final radius of curvature of the gaussian beam.

Note that the last element or translation is represented by the first matrix etc.

$P_l$ = the power of the lens = 1/f.

$P_c$ = the power of the crystal = 0.

By matrix multiplication (right to left) we arrive at:

$$q/n = \frac{(1-(P_l-mP/n)q+u+1+m/n-P_lu-Pmu/n}{-P_lq-Pu+1} \quad 4:40,15$$

From Figure 4:40,5 we have by definition:

$$u = f + X \quad 4:40,16$$

$$l + m/n = f + Y \quad 4:40,17$$

and so Eq.4:40,15 becomes:

$$q_z/n = \frac{(XY-f^2) + Yq_1}{4:40,18}$$

Now $q_1 = z - z_1 - ib \quad 4:40,19$

but $z = 0$ from Figure 4:40,5 and at the waist, $z_1 = 0$. The similar applies to the output side of the lens and so we have:

$$q_1 = -ib \quad 4:40,20$$
\[ q_2 = -ib_2 \]

Substituting these into 4:40,18 we get:-

\[
b_2 = \frac{f^2 - XY}{b_1} \quad \text{and} \quad b_1 = \frac{b_2 X}{Y}
\]

We now have all we need to calculate the relevant distances in order to ensure that the probe is focused centrally in the crystal. From the experimental geometry we know:-

i) \( u = 2 \, m \)

and ii) \( m = 10 \, mm \)

but \( u = f + X \) (Equation 4:40,16)

hence \( X = 1.925 \, m \).

'It can be shown that:-

\[
w_2^2 = 2b/k = b\lambda/n\pi
\]

Where \( k = \omega n/c \)

The waist at \( z = 0 \) was derived by considering the beam expander configuration (L1 and L2) and we can use these figures then to obtain \( b_1 \):

Thus \( b_1 = w_2^2 n A = 16.4 \, m \)

Eq.4:40,22 implies that:-

\[
Y = \frac{f^2}{X(1 + b_1^2/X^2)}
\]

and so \( Y = 4 \times 10^{-5} \, m \).

But \( l = f + Y - m/n = 6.81 \, cm \).

The value of \( n \) was taken to be 1.448 at 20°C at 334 nm [24]. To calculate the spot size we use again Equation 4:40,23, where \( b_2 \) is obtained from Eq.4:40,22. \( w \) is found
to be 5 µm.

To summarize this last section then it has been shown that for a distance of:

\[ u = 2 \, \text{m} \]

The probe arm will have its beam waist centrally located in the crystal, using the lens specified, if the distance from the lens to the face of the crystal, \( l \), is:

\[ l = 6.81 \, \text{cm} \]

It has also been shown that the value of \( b_i \), the confocal parameter, gives rise to a waist radius within the crystal of:

\[ w_c = 5 \, \mu\text{m} \]

and this corresponds to a waist diameter of 10 µm.

The next adjustment to make to the probe arm is its height in order to ensure that it probes centrally within the excimer waist. This is simply done. The crystal is removed and a vertical card is mounted at the excimer focus and at 45° to both excimer and probe beam. The excimer laser is then allowed to make a hole in the card, which will correspond to the most intense portion of the beam. The probe arm can be adjusted vertically to pass through this hole. The hole dimensions are generally of the order of half a millimeter and the probe adjustment is on a calibrated thread with 10 µm resolution. The probe is set to just touch the top of the hole and its position noted and similarly for the bottom of the hole. The readings are then averaged to locate the center of the hole and the probe beam set in this position. All that remains to ensure is that the probe waist is crossing the path of the excimer waist. Thus we need to be concerned with the excimer's focus within the crystal.

It was noted in Chapter 2 that the excimer laser
being a superradiant system has very limited coherence and this is notably demonstrated by the spatial profile at the focus of a lens. See Figure 4:40,8. The figure shows the

focused spot size of an incoherent light source (extended source) compared with that of a truly coherent source. The extended source produces an extended image, which is very similar to that which is obtained when the excimer laser is focused. The size of the focused region is governed by the geometrical formula for magnification by a lens i.e. $M = v/u$, and in the case of the Lambda Physik laser the focused spot is comparable with this formula. It does not represent the whole picture, however, as the laser cavity is approximately a meter long with a high reflector at one end, effectively doubling its length. In the experimental damage facility the focusing lens is 1 m from the laser's output window. For this experiment a 10 cm focal length lens was used. This means that superradiant emission coming directly from the output end of the laser will be focused 11.1 cm beyond the lens whilst the light that is emitted after having made a round trip of the cavity will

Figure 4:40,8 Comparison Of The Focused Spot Size Of An Extended Source And A Laser
be focused 10.3 cm beyond the lens. When a beam profile is performed anywhere within the "focal region" of the lens it represents a summation of:-

i) a plane of emitting sources whose focus lies on the plane of the profile.

ii) out of focus light from planes of emitting sources on either side of the plane in (i).

This tends to give the beam a characteristic waist that is similar in shape to that of a gaussian beam. This can be seen in Figure 4:40,10, a and b. These measurements were obtained using the Image III profiling system and the graphs represent the 1/e^2 dimensions of the beam at each plane. The planes are taken through the region of focus and are separated by a mm as progression is made along the axis of the excimer. Figure 4:40,10 enables us to determine the position of tightest focus and the beam dimensions at this point. Admittedly they are the values for the focus in air, yet the dimensions can be scaled by the refractive index to allow for the effect of the crystal.

It is the region of tightest focus that is to be probed by the dye laser. The excimer laser is positioned centrally on the crystal face. See Figure 4:40,9. Vert-

---

Figure 4:40,9 Interaction Geometry
Figure 4: Excimer Beam Waist

Distance From Lens (mm)

1/2 Beam Dimensions
ical alignment has already been achieved. To avoid entrance surface damage terminating the experiment prematurely the crystals were cut as 2 cm cubes. The excimer's region of tightest focus was then arranged to fall about two thirds of the way into the crystal. This ensures a fairly low energy density on the front surface. A crystal showing a reasonable strength fluorescence signal was chosen for alignment purposes. The Image III profiler was used to take a side-on picture of the fluorescence as the excimer excited the crystal. The fluorescence followed the beam contour shown in Figure 4:40,10 and by using the cursor facility of the profiler the position of the waist was located and measured as a distance from the front of the crystal. The probe beam was then adjusted to this distance and alignment of the interaction region was completed.

Almost as an aside at this point it should be noted that the lens in the probe arm on the exit side of the crystal desensitises the system against thermal defocusing. Calcium fluoride has a negative dn/dT. This means that absorption within the crystal, leading to a localised temperature rise, will create a diverging lens effect. If the detection system had remained as in Figure 4:40,2 then it would have been sensitive to the small changes in intensity as the beam diverged. The lens L4, however, has an aperture an order of magnitude larger than the spot size upon it and focuses the probe beam onto the detector face. It thus collects all the light, despite any slight spreading of the beam due to thermal effects within the crystal. This means that any decrease in signal measured by the detector can confidently be taken as loss of light by absorption within the crystal.

The samples, as previously mentioned were cut into 2 cm cubes, with two of the faces being (111) planes. The
material was always calcium fluoride and the final surface finish was with a wax lap and Al₂O₃ powder, of particle size 0.075 μm. A number of calcium fluoride boules were grown, as in Chapter 3, using the Bridgman-Stockbarger furnace, and each boule contained varying portions of the two stock materials, i.e. Mexican and the purer Optipur material. Appendix 4 contrasts the differing purities of the sources. The following table details the crystals grown, their composition, i.e. the percentages of each stock material in the mix, and their nomenclature with regard to this chapter.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>S.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEXICAN%</td>
<td>---</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>OPTIPUR%</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>---</td>
<td>100</td>
</tr>
<tr>
<td>10ppm Ce</td>
<td>---</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>---</td>
<td>xxx</td>
</tr>
</tbody>
</table>

Table 4:40,1 Crystal Nomenclature and Composition.

One reference crystal was grown using 100% Optipur material but doped with 10ppm of cerium. Cerium is a very active impurity in calcium fluoride and the reference crystal was to enable us to determine which, if any, effects were cerium initiated. The crystal called S.A. was a strain annealed crystal, the annealing having been performed by holding the crystal in a furnace below melting point for 30 days.

The experiments were performed in the following sequence:-

1) The excimer energy density at the probe interaction region was set to the desired level. The profile at the interaction region had previously been determined using the Image III Profiling system and scaled according to the

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refractive index of CaF$_2$.

ii) The crystal was located in the region of interaction. A mount was made to enable the crystal to be removed and then replaced in exactly the same position. This was done to ensure consistency within the experiment.

iii) The excimer pulse was terminated before reaching the crystal. The dye beam, however, was allowed to pass through the crystal, and also traverse the delay line. The vacuum photodioide then recorded its temporal profile, the area under the curve being proportional to the energy in the pulse, and consequently the height at any point proportional to the photon fluence at that time. The trace on the oscilloscope would appear as in Figure 4:40,11. The two pulses have been labelled P (probe) and R (reference),

\[ \text{Figure 4:40,11 Oscilloscope Trace Of The Dye Laser's Probe And Reference Beams} \]

and each peak as shown in the diagram $p_1$, $p_2$, $r_1$, and $r_2$.

iv) Ten readings were taken at thirty second intervals
with this configuration. Each reading consisted of recording the height (in mV) of each peak in Figure 4.40,11 i.e. \( p_1', p_2', r_1 \) and \( r_2' \). At this stage the excimer radiation was not traversing the crystal.

v) The excimer pulse was then allowed to irradiate the crystal concurrently with the dye pulse. This was done ten times at one minute intervals. The one minute intervals would enable the crystal to reach a stable state after excitation, prior to the next pulse. Again the height of each peak was recorded along with the excimer's beam energy.

vi) The excimer pulse was again terminated prior to the crystal and as in (iv) ten readings were taken at thirty second intervals. Thus the dye laser was again interrogating the crystal without the influence of the excimer laser.

vii) The whole process would then be repeated for another crystal and eventually at another energy density.

4:50 Method Of Analysis

For each energy density, as seen by the above procedure, there were three stages to the measurement:
Stage 1........prior to irradiation.
Stage 2........during irradiation.
Stage 3........after irradiation.

Analysis of the results at each energy density was then performed in the following manner. A graph would be plotted of time versus \( r_1/p_1 \) and similarly for \( r_2/p_2 \). Time would start at 0 seconds for Stage 1 and progress in thirty second intervals to 270 seconds. For Stage 2 each point would be separated by sixty seconds and then event-
ually Stage 3 would revert back to the thirty second spacing. The total experimental time was thus twenty minutes. For Stage 1 \( r_1/p_1 \) and \( r_2/p_2 \) provide a figure of reference for the background level of absorption. By itself the figure is meaningless as it represents the difference in losses between the two arms of the dye laser. These losses however remain fixed throughout the experiment with one exception to be discussed later.

The ten values obtained in Stage 1 would be plotted, a least squares line put through them, an average value obtained, a standard deviation (\( \sigma \)) and the standard error (s.e.) calculated. The standard error is given by the formula:

\[
\text{s.e.} = \frac{\sigma}{\sqrt{n}}
\]

where \( n \) = the number of samples.

Exactly the same procedure would be carried out on the results of Stage 2 and 3. If during Stage 2 transient absorbing centers were produced at the 339 nm. the peak \( p_1 \) would decrease with respect to \( r_1 \) and similarly for \( p_2 \). The ratio \( r_1/p_1 \) would thus increase and the change would be related to the density of defects. Since \( p_1 \) and \( p_2 \) probe the crystal at different times after the onset of the excimer pulse a degree of temporal resolution is introduced into the experiment. Although it was not done, careful experimentation would enable one to alter the position of the time window of the probe pulse with respect to the excimer pulse and obtain a complete temporal profile of the defect population. This would simply be a matter of increasing the delay in the dye beam by increasing the distance between the Galilean telescope (L1 and L2) and the first beam splitter, (BS1).
Above it was mentioned that the losses in the probe and reference arm remained fixed, with one exception, throughout the experiment. It is the exception that necessitated the need to plot these graphs and perform a least squares analysis. It was noticed that at times there was a d.c. shift in the absorption between stages 1 and 3 of the experiment. This shift was always manifest as a slight decrease in absorption towards the latter end of the thirty readings. An example of a typical shift can be seen in Figure 4:50.1. The occurrence of the shift seemed random and not prone to any specific crystal or any specific fluence. A point to note in Figure 4:50.1 is the gradients of the least squares fit. For stages 1 and 2 the gradients are very similar though slightly less steep for stage 2. Stage 3 is then a little less again. The slopes of the gradients are taken to represent an increase in the number of photons in the probe arm, the increase tailing off as the experiment progressed. As this change is immediately apparent in Stage 1 it has nothing to do with any changes that the excimer radiation is producing. Its cause lies with the dye pulse, and it is suggested that the dye pulse is cleaning the entrance and exit surface of the crystal. From the previous discussions it can be seen that at least twenty minutes is needed to complete one set of readings. At each energy density at least four and initially seven crystals were being tested. Thus in a day one might expect to perform two complete runs where a run would be each crystal at a given energy density. Because of the long time span over which the entire experiment was performed it was felt wise to clean the surfaces of the crystals prior to each test. It is thought that some cleaning residue or grease may have been left upon the surface and that this may have either been absorbing or perhaps scattering the probe beam. Although readings were being taken every thirty, sixty and then thirty seconds,
Figure 4.50.1 Error Analysis

Prior Excitation

\[ x = 0.59457 \]
\[ s = 0.005 \]
\[ se = 0.002 \]

\[ \text{Gradient} = -1.0930 \times 10^{-5} \]

During Excitation

\[ x = 0.61713 \]
\[ s = 0.006 \]
\[ se = 0.002 \]

\[ \text{Gradient} = -8.2462 \times 10^{-6} \]

After Excitation

\[ x = 0.58788 \]
\[ s = 0.007 \]
\[ se = 0.002 \]

\[ \text{Gradient} = -2.544 \times 10^{-6} \]
the excimer laser, and consequently the dye laser, was being fired by the internal trigger every 3 seconds. This was necessary to stabilise the excimer output energy. If the excimer is to be left charged i.e. at 36 kV for any period of time there is unavoidably a reverse current leakage through the holding diode in the pulse charging circuit. This leakage results in a decrease in the output energy of the laser. The decrease is not particularly reproduceable. To overcome this the excimer is fired regularly at a repetition rate of 0.2 to 0.5 Hz and the beam shuttered before reaching the target area. It is not shuttered before the beam splitter to the dye laser. In twenty minutes, at a pulse every three seconds, some four hundred dye pulses traverse the crystal. If each pulse slightly cleans the surface then with time this d.c. shift in "absorption" would be seen. One would also expect the effect to get less as the number of pulses the surface experiences rises, and this can be seen in the gradients of Figure 4:50,1 i.e. for stages 1, 2 and 3 the gradients are respectively:-

-1.09 x 10^{-5}
-8.25 x 10^{-6}
-2.54 x 10^{-6}

By plotting the graphs as described this d.c. shift is immediately seen and can be accounted for in the subsequent analysis.

From the graphs produced the relative change in absorption due to irradiation needs to be extracted. This is a simple matter. The mean ratios for stages 1 and 3 are added and halved to provide a mean background level. This is defined as unity absorption. i.e. :-

if \( \bar{x}_{i} \) is the mean ratio of stage 1
and \( \bar{x}_{ii} \) is the mean ratio of stage 3
then \( \frac{\bar{x}_{i} + \bar{x}_{ii}}{2} \) is the average background absorption,
and this divided by itself gives 1.

Given $\bar{x}_{i}$ to be the calculated mean for stage 2 then the relative change in absorption is defined as:

$$\frac{\bar{x}_{i}/(\bar{x}_{i} + \bar{x}_{i} + \bar{x}_{i})}{2}$$

As absorption increases, the percentage increase above the background is then the non-integer portion of the above expression multiplied by 100.

Error bars for each absorption value are obtained from the calculated standard errors. The combined standard error for stages 1 and 3 is calculated and converted to a percentage and then added to the percentage representation of the standard error incurred in stage 2. The final figure is then turned again into absolute terms. The quoted error bars thus contain two effects:

i) an error due to the experimental resolution, calculated from stages 1 and 3. This error was found to be consistent throughout, across every energy density and sample, and was approximately 0.3%.

ii) an error due to the fluctuation of the defect population from shot to shot. For all the samples at low fluences this error was consistent at 0.2 to 0.3%. At high fluences, however, in the less pure samples these fluctuations became huge and the error bars completely dominated the readings. This can be seen in the graphs that follow.

Graphs have been plotted of the change in absorption against the energy density within the interaction region for both ratios $r_1/p_1$ and $r_2/p_2$. These graphs, Figures 4:50,2 to 8, can be seen on the following pages. (They have all been drawn against the same scale for ease of comparison). Figures 4:50,9 and 10 super-impose each graph for the individual crystals, again for the sake of comp-
Figure 4:50.2 Transient Absorption. Sample A
Figure 4: Transient Absorption, Sample B
Figure 4:50.4 Transient Absorption. Sample C
Figure 4: Transient Absorption. Sample D
Figure 4:50.6 Transient Absorption. Sample E
Figure 4: Transient Absorption. Sample F
Figure 4: 50.8 Transient Absorption, Sample S.A.
Figure 4: Comparison of Transient Absorption, Peak 1
Figure 4:50,10 Comparison Of Transient Absorption, Peak 2
arison. Whilst performing these experiments the bulk damage thresholds were also measured, where possible. The results can be seen in the following table which re-emphasises the crystal composition.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>S.A</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEXICAN%</td>
<td>---</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>OPTIPUR%</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>---</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>10ppm Ce</td>
<td>---</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>---</td>
<td>xxx</td>
<td>---</td>
</tr>
<tr>
<td>Dam. Thr.</td>
<td>72</td>
<td>6.8</td>
<td>--</td>
<td>--</td>
<td>---</td>
<td>4.2</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 4:50,2 Bulk Damage Thresholds

With the experimental configuration described and the 10 cm focal length lens breakdown in samples C, D and E was unobtainable.

4:60 Discussion of Results

Along with the transient absorption measurements detailed in the previous section spectrophotometer absorption scans were made, at room temperature, on all the samples. These scans were performed in the wavelength ranges 210-360nm and 340-640nm prior to any irradiation and experimentation on the crystal. Scans were also performed at every intermediate stage in the transient absorption experiment i.e. after U.V. irradiation at each energy density. Figure 4:60,1 shows the relevant scans for each sample, basically prior irradiation and then after the completion of the experiment. The unirradiated spectra show a fair degree of absorption in the U.V. for samples B, C, D, E and F. These were, with the exception of F, all grown with a percentage of the Mexican stock material. The spectra for samples C, D and E can be considered identical whilst B and F's spectra, although showing the same trends
Figure 4: Absorption Scans
as C, D and E differ towards the high energy portion of the scans. Common to B, C, D, E and F is a considerable absorption peak at 307nm which can be attributed to the presence of Ce$^{3+}$ impurity ions. The spectra of the rareearths in calcium fluoride have been extensively studied by E. Loh [25] and [26]. He has placed the Ce$^{3+}$ 4f - 5d transition in a CaF$_2$ host at 307nm. The analogous absorption bands in the remaining rare-earths are at shorter wavelengths, the next nearest being Pr$^{3+}$, lying at 219nm. This band can also be seen in samples B through to E. Between the peaks at 219 and 307nm there is also absorption, peaking at 243nm. This band was put down to clustered Ce$^{3+}$ ions. Note that this absorption lies very close to the exciting KrF excimer wavelength. E. Loh performed experiments based on the concentrations of Ce$^{3+}$ in CaF$_2$ and determined that as the concentration of the Ce$^{3+}$ ion increased the 307nm peak decreased and the band shape of the Ce$^{3+}$ clustered ions altered and increased. This was taken to mean that Ce$^{3+}$ would prefer to exist in CaF$_2$ in clusters as opposed to isolated impurities. The spectra of B and F show this phenomenon, B apparently having become Ce contaminated during growth. C, D and E should contain no more than 3ppm of Ce$^{3+}$ according to the mass spectrographic analysis whilst F contains at least 10ppm. B would also appear to contain somewhere in this region of Ce$^{3+}$ ions.

Also notable on the spectra are small absorption bands, most prominent on samples F and B at 338nm. This absorption results from the presence of an oxygen O$^{2-}$ ion substituting for one of the monovalent nearest neighbours of the Ce$^{3+}$ ion i.e. for a lattice fluoride ion. This arrangement can be seen in Figure 4:60,2.
Comparison of the before and after irradiation scans of each crystal shows us the permanent colouration damage introduced as a result of excimer transmission. To summarize the differences:

Samples A, F and SA had identical spectra before and after irradiation. These crystals were all grown entirely from Optipur material with very few impurities. Sample F, despite the presence of 10 pm of Ce$^{3+}$ showed no change.

Samples B, C, D and E all have new absorption bands created in them at 264, 277 and 368nm. These bands would appear to be very small in comparison with the 307nm and 219 nm bands of the Ce$^{3+}$ and Pr$^{3+}$. This, however, is not the case and arises from the spectrophotometer optics. The spectrophotometer has a slit through which it views the sample, of variable width and 5mm high. To perform these measurements the slit width was 0.5mm, the maximum width as sensitivity around 200nm was low. Thus, the geometry of the measurements can be seen in Figure 4:60,3.
The whole crystal gives the background spectra of the unirradiated condition whilst only the small portion representing where the excimer beam had traversed would show the newly created defect bands. Thus we could expect to multiply the 264, 277 and 368nm bands by a factor of 10 at least to get a better idea of their relative strengths with respect to the Ce$^{3+}$ and Pr$^{3+}$ absorption bands.

The band at 368nm can be attributed to F centers [11 pp332] whilst the 264 and 277nm bands are unknown. It is most probable however that they have arisen from the rare-earth impurities, present in the crystal before irradiation as 3+ ions. Now, as a result of the radiation they have captured a photo-excited electron and are now a 2+ ion. Photochromic behaviour of this type is common with rare-earth doped halides and alkali-halides.

One cannot categorically claim that samples A, F and SA have not developed the stable absorption peaks. It shall be shown later on that the peak transient defect population is linearly proportional to the impurity concentration. Samples B, C, D and E all have about 30 - 60ppm
of rare-earth impurities. Samples A, F and SA have approximately 1ppm of impurity except for F which has approximately 10ppm of Ce$^{3+}$. Assuming the absorption bands are created in proportion to the impurity A, SA and F would have bands very hard to detect and beyond the capabilities of the machine. Since, however, A and SA showed no transient defect absorption it would probably be reasonable to assume that no permanent absorption bands have been established.

It can be seen from the Table 4:50,2 that samples B and F have exceptionally low bulk damage thresholds. Sample F is the Optipur crystal doped with cerium and sample B is a 25% Mexican 75% Optipur mix but with an absorption spectra similar to F. It seems reasonable to assume that the presence of cerium is having an adverse affect on the damage threshold. Samples B and F also show the greatest O$^{2-}$ absorption band. This band is virtually invisible in the remaining crystals. Samples C, D and E all have a greater level of rare-earth impurities than both B and F. The lowering of the damage threshold may thus be put down to either the presence of the O$^{2-}$ ion being stripped of an electron and initiating an avalanche or the fact that the charge transfer process of F$^{-}$ (2p$^6$) to Ce$^{3+}$ (6s) is more accessible to the U.V. photons than the remaining rare-earth sequence. The effect of crystal purity on the damage threshold will be discussed later.

From Graphs 4:51, 2 to 7 we can try and understand a little of the processes taking place within the crystals during irradiation. Firstly the Optipur only material, sample A and the Optovac crystal, showed no traces of transient defect absorption throughout the experiment, even up to bulk damage fluences. Sample B, contaminated by cerium, damaged too early in the experiment to be included
seriously in the discussion, yet by comparison it would probably have followed the trends set by samples C, D and E. The graphs probing the \( V_k \) population at 12nsec. show that these samples attain a peak transient absorbing population at fluences between 10 and 15 \( \text{Jcm}^{-2} \). This would appear to represent the maximum possible defect population attainable by each crystal. As the incident fluences increase above this value the \( V_k \) population appears to fall, before rising again and finally getting lost in the erratic nature of the readings at high fluences. As already mentioned in the previous section the large error bars on the readings at high fluences are a consequence of the physical processes occurring within the crystal as a result of the exciting radiation and not a limitation of the experimental facility. The graphs showing the \( V_k \)

![Figure 4:60,4 Peak Defect Population Plotted As A Function Of Crystal Impurity.](image-url)
concentration 20nsec. into the excimer pulse follow much the same trend except they rise a little more quickly, peaking at a lower fluence, and the second peak is not visible on them. The error bars become exceptionally large for these measurements as the fluence is raised.

Figure 4:60,4 shows the maximum change in absorption for each crystal plotted against the percentage increase in rare-earth impurity content, with respect to the Optipur material, for each crystal. This graph is linear, indicating the nature of the dependence of transient absorbing centers on rare-earth contaminants.

To consider Figures 4:50,2 to 8 in more detail a reminder of the possible relaxation routes available to the intrinsic F-H (<111> S.T.E.) center defect would not be amiss.

\[
\begin{align*}
\text{U.V. Radiation} \\
\text{electron excited out of valence band} \\
<111> V_k (\text{Self Trapped Hole}) \\
<111> V_k \text{ and F Center}
\end{align*}
\]
Close F-H pair recombination exhibiting luminescence 

Separates to become metastable defects i.e. an F center and H center

Absorbs 248nm photon to become excited S.T.E.

From the experiment we are probing the <111> V_k center or <111> S.T.E. center. No absorption or emission bands have ever been observed from the <100> V_k alignment. We are thus looking at the concentration of a defect state that has already trapped an electron. The material that we are considering, CaF_2, is a wide band gap insulator and consequently the density of electrons in the conduction band can be considered negligible. Photoconductivity experiments verify this. The crystals grown with a percentage of Mexican stock can all be considered as having an excess of electron traps i.e. 3+ rare-earth impurities although charge neutrality may be maintained during growth by F-interstitials. Defects arise as the interstitials are caused to migrate, perhaps to surfaces or grain boundaries. Generally it can be taken that prior to irradiation there are few free electrons available for trapping by excimer produced <100> V_k centers.

The <111> V_k concentrations peak between 10 and 15 Jcm^{-2}, reaching a value determined by the rare-earth contaminants. To be able to detect <111> V_k centers means that the following sequence has been enacted.

U.V. radiation
Assuming there are electrons available for trapping, the left hand side of this sequence can happen within 10 psec. The electrons, whose presence gives rise to the \(<111> V_k \) \(<111> S.T.E.\) state, however, must have originated at the onset of excitation from the valence band itself, first being excited to the 3+ impurity, and then either relaxing back down to the hole \(<100> V_k \) center or being further excited from the now 2+ impurity to the conduction band. Either way the 3+ impurity is again ready to receive a further valence band electron. How does one therefore manage to explain the fall in defects that follows at higher energy densities? There are three processes whereby the \(<111> V_k \) population can be decreased. They are:

i) photon absorption and dissociation
ii) recombination via luminescence
iii) separation to stable defects

At the fluence energy densities involved in which the peak defect concentrations begin to fall, no indications, despite spectrophotometer scans, of stable F and H center formation could be seen. Suggestion (iii) above can thus be discounted as a means of defect center depletion. We know
as a result of observation and using a monochromator and sensitive photodiode that recombination via the F$^+$ and H$^{-}$nn route, resulting in the intrinsic luminescence of CaF$_2$, is occurring. This is one possible depletion route. By monitoring the strength of the luminescence signal, however, it was found at all times to be linearly proportional to the measured $<111>$ $V_K$ center density. Neither could this then be the mechanism causing the fall in defect density. The radiative recombination rate is given by:

$$<111> V_K \tau^{(-1)} <111> S.T.E.$$  

and is independent of the irradiating photon flux, as far, of course, as $<111>$ $V_K$ can be assumed independent of the photon flux.

Photon absorption is the final decay route and this is governed by:

$$<111> S.T.E. \tau^{(-1)} S.T.E. <111> F$$

Here we have the fluence dependence. As the incident fluence is raised the photon absorption decay rate will increase and it is suggested that there comes a point at which this mechanism begins to dominate. The $<111>$ $V_K$ formation rate, is also, to an extent, fluence dependent but ultimately is limited by the time taken to free electrons for capture by the $<100>$ $V_K$ centers. The eventual consequence of photon absorption is a 'hot' electron in the conduction band. If damage is imminent this electron may become part of an absorbing plasma in the conduction band, and further absorb photons, or else if damage is not as imminent, it will relax down to the conduction band edge releasing its extra energy to lattice phonons as it
As the experiment progressed it was noted that the \(<111> V_k\) concentration began to rise again. This may be due to one of two causes:

i) for some reason photon absorption has decreased.

ii) a further method of \(<111> V_k\) generation has been introduced.

The second is the most likely explanation remembering that the photon fluence is still on the increase. It is believed that at this stage multiphoton absorption processes are beginning to occur. With CaF$_2$, having a band gap of 10.6 eV it only requires 2 photon absorption at 248nm to bridge the forbidden gap. This would create the necessary self trapped hole (\(<100> V_k\) center) in the valence band and a free electron in the conduction band for production of the \(<111> V_k\) (<111> S.T.E.) defect state. As the energy density continues to rise, however, and the damage threshold is approached the electrons raised to the conduction band tend to stay there, becoming a hot absorbing plasma, and few find their way back down to combine with the \(<100> V_k\) defects. Thus at the highest fluences the \(<111> V_k\) centers decrease in population and damage encroaches. The \(<100> V_k\) defects are invisible to the dye laser probe, having no absorption or emission bands.

It was as the incident energy density approached the damage thresholds for bulk material that the spectrophotometer traces began to indicate stable colouration occurring within the crystals i.e. samples C, D and E. Thus we can assume that conditions within the focal volume are, as damage is approached, beginning to aid thermal reorientation. In a hot energetic lattice the cohesive force
between the F-H pair will be overcome by the lattice vibrations. At high fluences just before damage when multiphoton processes occur and many holes are created it would be reasonable to expect a certain proportion of the defects to separate and become stable.

Returning to Table 4:50,2 and considering the bulk damage thresholds as a function of crystal impurity we see, almost surprisingly, that the purest crystals damaged earliest with the exception of the cerium doped sample. The effect of cerium has already been discussed. Most damage theories tend to be a mixture of avalanche and multiphoton theories, the multiphoton mechanism providing seed electrons to begin an avalanche process. With a pure crystal, once the seed electrons are in the conduction band, there is little, assuming correct conditions, to hinder the sequence of ionizing collisions needed to sustain damage. With the rare-earth doped material the host lattice comprises a series of electron traps in the form of \(<100> V_k\) centers, which are highly efficient at trapping electrons, or else 3+ impurity ions. The chances are that the few conduction band electrons are likely to be held by these traps hence preventing the build up of a suitable avalanche. Thus although the impurities mean that electrons can be excited out of the valence band prior to multiphoton processes it also means that there is a fairly efficient sink for those electrons in the conduction band hindering an effective avalanche. A strong crystal would therefore represent a compromise. Make it free of impurities and it is not as likely to colour except on the verge of damage, yet put up with intrinsic luminescence and the possibility of permanent colour centers and you may have a more damage resistant crystal.
Bibliography

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Chapter 5:00 THE LIMA

The following chapter investigates the use of a LIMA (Laser-induced Ion Mass Analyser) as a diagnostic damage facility. The samples studied are thin film coatings and multilayer stacks, not the calcium fluoride substrates as dealt with in the bulk of this thesis. Initially the calcium fluoride substrates were considered but the damage spectra for both the Mexican and Optipur material showed consistently only Ca⁺, F⁺ and [CaF]⁺, along with small quantities of hydrogen and carbon. A typical spectra can be seen in the following diagram.

![LIMA Spectra OF Calcium Fluoride Substrate](image)

CaF₂

Figure 5:00,1 LIMA Spectra OF Calcium Fluoride Substrate

It was thus decided to investigate other optical materials to assess the viability of the machine as a damage diagnostic technique.
Chapter 5:00 THE LIMA AS A DAMAGE FACILITY AND DIAGNOSTIC TOOL

5:10 Introduction

The LIMA (laser-induced ion mass analyser) was designed primarily for the surface science fraternity and analyses the plume of vapour produced by a damaging laser pulse. It has, without doubt, fulfilled its expected role as a qualitative light element analyser (including the ability to detect hydrogen) and the purpose of this chapter is to investigate the potential of the LIMA as applied to laser induced damage studies. The machine used for this work is owned by Loughborough Consultants Limited and I would particularly like to thank Dr. Edge for many hours of unexciting work. It should be noted that the LIMA is expected to pay for its existence and is thus used by the company on a commercial basis and not as an experimental facility. Thus although many obvious improvements could be made to it from the viewpoint of a person wishing to study laser-induced damage these could not be done. Furthermore, it would have been good to have delved more deeply into the machine's capabilities yet time factors made this impossible. The LIMA seems to be fully booked in its present form. Thus the work undertaken had to lie within the realms of the machine as it stood. A number of parameters are immediately noticeable by their absence, the laser's spatial profile at the target surface and beam dimensions and also the pulse energy. A photodiode has been built into the system to measure the laser energy, but seeing as this is not relevant to its normal mode of operation this has not been calibrated. All energy readings have hence been taken on a relative scale of mV.
**System Description**

The two principal elements of the LIMA are a pulsed laser and a time-of-flight mass spectrometer. The laser produces a pulse which is focused onto the surface of the target, placed within an ultra high vacuum chamber. The intense pulse evaporates and ionizes a small volume of the sample. The mass of the sample ions is then determined by their time of flight in the spectrometer. This whole process takes less than a msec. The laser is a Q-switched Nd:YAG that has been frequency quadrupled to give 266nm in a pulse time between 4 and 5nsec. The machine may work in two modes, reflection or transmission. Throughout these

![Figure 5:20,1 Schematic Diagram Of The LIMA](image_url)
experiments it was operating in the reflection mode. This means that the ions are emitted from the same side of the sample as the laser is incident. The spatial resolution at the target is the diffraction limited spot size which in the reflection mode is between 1 and 3\,\mu m. This may not be considered ideal by a damage fraternity hoping to eradicate statistical spot size effects. The sample stage however can be accurately aligned with the aid of a He-Ne spotting laser so the operator can choose the areas he desires to irradiate.

The mass spectrometer employs a folded flight path with an electrostatic mirror at the end to compensate for the differing energies of similar ions. The ions formed at the surface of the sample are accelerated towards the grid (see Figure 5:20,1) through a potential difference $V$, typically of the order of 1.5\,kV. After this they drift down a field free flight tube with a constant velocity $v$. The kinetic energy imparted to the ions is "$eV$" where "$e$" is the charge on the ion. Thus:

$$eV = \frac{1}{2} \cdot m \cdot v^2$$ \hspace{1cm} 5:20,1

and for any singly ionized species $eV$ will be constant. Thus:

$$v = \left( \frac{2eV}{m} \right)^{1/2}$$ \hspace{1cm} 5:20,2

or

$$v \propto \frac{1}{\sqrt{m}}$$ \hspace{1cm} 5:20,3

It can be seen immediately from Eq.5:20,2 that if the species has been doubly ionized then, to all intents and
purposes, its mass has been halved. The mass is characteristic of each ion species or molecular fragment and thus the ions are separated according to their mass. The heavier ones travel more slowly than the light ones. Equivalent ions travel in groups in which there exists a spread of energies. This spread arises mainly from the Maxwell-Boltzmann type thermal energy distribution caused by the laser energy absorption, but also to a lesser degree on factors such as space charge effects and small solid take off angles. As already mentioned, at the end of the flight tube they are reflected through nearly $180^\circ$ by an electrostatic mirror before entering the detector. For a given group of ions entering the mirror (consisting of a series of equipotential plates and grids) the ions with the greater velocities will penetrate further than those with the norm, whilst those travelling more slowly will be reflected sooner. By careful adjustment of the mirror voltages and accelerating grid the ions at the upper limit of the energy spread can be made to arrive at the detector simultaneously with the ions at the lower limit. The mirror thus provides greater mass resolution in two ways:

i) by compensating for the spread in energies.

ii) by almost doubling the length of the drift region.

The ions are detected by a 17 dynode electron multiplier, across which the voltage can be continuously varied. This enables the operator to select the required sensitivity. The signal is then amplified and sent into a "Biomation 8100" fast transient recorder. The data is then displayed immediately on a storage oscilloscope for quick reference, from which it can be output to a chart recorder to give the time of flight spectrum. The "Biomation 8100" also sends the information to a desk top computer for further analysis and storage, the computer processing results in a mass spectrum. For further details of the electronics see [1].

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The optics employed in the reflection mode uses a cassegrain system as shown in Figure 5:20,2. This enables the ions to be extracted through the center of the focusing optics and along the optical axis. Note that this axis is normal to the sample surface. An advantage of using the system of reflecting lenses is that chromatic aberrations are eliminated and hence frequency doubled 532 nm light can be used with equal facility.
Data Interpretation

In the manufacturer's data sensitivity is claimed to be 1ppm atomic or better for most elements. This is no doubt true if the element is present in the vapour plume as an ion. Much however, depends upon the bonding of the material to its host, the different ionization potentials of the elements and the different energy absorption mechanisms working in the various materials. A metallic impurity for instance of less than 1pm in a fused silica host will completely dominate the mass spectrum that results. This cannot be taken to mean that there is more metal impurity in the host than host itself, but rather that the photon absorption mechanisms at 266nm is vastly different for these two materials. A lot of caution and a little hindsight are advised when trying to make definitive statements about LIMA spectra, and quantitatively, at present, little can be deduced with certainty. Figure 5:30,1 shows a typical mass spectrum of an A.R. coating of alumina/cryolite (Al₂O₃/Na₃AlF₆) on a Spectrosil B substrate. Certain features have been marked on the spectrum such as the presence of doubly ionized fluorine, oxygen and carbon, all occupying positions at half their true mass. Peaks occurring at non integer values can often be assigned to doubly ionized species.

An aid to spectra recognition is the ability of the LIMA to resolve isotopes. For instance in Figure 5:30,1 three peaks have been assigned to silicon. One is at mass number 28, one at 29 and the other at 30. The relative abundancies of the naturally occuring silicon isotopes are 92.2% at a mass of 28, 4.2% at a mass of 29 and 3.1% at a mass of 30. Figure 5:30,1 shows these peaks in approximately this order of size. If enough silicon has been ionized these three peaks should always be seen.
The next figure (5:30,2) shows another spectrum from a different site on the same coating. Note the three silicon peaks are visible, though the last two only barely. The point of interest here though is the peak with a mass number of 65 A.M.U., Copper, has an isotope at 65 with a natural occurrence of 30.9%. Its other isotope occurs at 63 with an occurrence of 69.1%. As there is no peak on this spectrum at 63 that at 65 cannot be attributed to copper. Instead, remembering that the coating contains cryolite (cryolite being Na$_3$AlF$_6$) the peak at 65 is best assigned to the fragment Na(NaF).

It can be seen on both Figure 5:30,1 and 2 that a negative shift in the dc level is encountered after a
particularly large signal. In performing the experiments we hoped to see low levels of trace impurities present at the damage sites and hence needed the sensitivity as high as possible. The coating material, however, then proceeds to dominate the spectrum and send the detector off scale. Figure 5:30,2 shows that with respect to the time of flight of the ions the time constant of the dc shift is quite large. This can obviously be a disadvantage for small signals may never be seen if the detector has been forced too far negative. For instance, in Figure 5:30,1, if the oxygen signal had been a little larger the water peak would probably never have been seen. This problem is
more or less acute depending on the nature of the coating for all the elements in the periodic table with masses lighter than the coating materials will be recorded at the highest sensitivity without hindrance from the effect of the coating elements. This can be seen clearly from Figure 5:30,3. Here the spectrum is dominated by the zirconium isotopes at 90, 91, 92, 94 and 96, and although the signals go off scale all the elements present with lower masses have been recorded without interference.

5:40 The Lima In Damage Tests

The aim of this work was to use the LIMA as a damage
facility, assess its potential and see if, in its present form, it could give useful insights to the cause of damage specific to the coatings under investigation. The criteria of damage would have to be the presence of ions at the detector. This would appear to be a reasonable way of monitoring damage to coatings as in virtually all instances of damage we would expect the emission of ions from the surface. This is especially true when we consider that the sample is under the conditions of ultra high vacuum ($10^{-7}$ torr or less). The requirement of high vacuum places the only real restriction on the sample in that its vapour pressure must be low. The laser is capable of 80mJ in about 5nsec and as mentioned, focused to the diffraction limited spot size. Thus energy densities capable of producing non-linear absorption mechanisms are easily obtainable. The energy is continuously variable from 0 to 80mJ with the aid of filters and was found to be very reproduceable. Thus apart from the necessary measurements of spot size and energy, the LIMA contains all that is needed to measure damage thresholds.

5:41 Lima Diagnostics On A H.R. At 266nm.

The first coating to be investigated was a high reflector at 45° and 266nm. It consisted, according to the vendor, of a $\lambda/4 \ ZrO_2/\text{SiO}_2$ multilayer stack over which there was a $\lambda/2 \ \text{SiO}_2$ overcoat. First the damage threshold was located. The voltage output on the photodetector was monitored for each shot and the transition at which the 50% damage probability occurred was noted. At 160mV the damage probability was 75% whilst at 155mV it was 17%. The damage threshold was taken to fall between these two values. The energy output of the laser could not be adjusted between 155 and 160mV. Just how close in energy density these two values are, is unfortunately, unknown.
Having found where the damage threshold lay we irradiated the sample above threshold at a number of sites and then below threshold at a number of sites. Every time we caused damage we recorded and saved the data. The spectra were then compared for differences, seeking changes between above and below threshold damage.

5:42 Results

It would be impractical to present all the mass spectra here so Table 5:42,1 and Figures 5:42,1,2,3 and 4 shall be all that is used to discuss the results. The table represents the elements found in each damage spectrum. As can be seen from it zirconium dominated the data. This is despite the presence of the \( \lambda/2 \) SiO\(_2\) overcoat which must have been destroyed every time a zirconium signal was detected. This indicates the difficulties involved in trying to put quantitative values to the elements detected. Zirconium is more easily ionized than silicon as shown:

\[
\begin{align*}
Zr & \rightarrow Zr^+ + e = 6.84 \text{ eV} \\
Zr & \rightarrow Zr^{++} + 2e = 13.13 \text{ eV} \\
Si & \rightarrow Si^+ + e = 8.15 \text{ eV}
\end{align*}
\]

Yet this difference in ionization energy alone is a very poor guide to quantifying the results. Frequently the doubly charged zirconium signal was larger than the silicon.

The legend in the table is as follows:

- X = WEAK SIGNAL
- XX = MEDIUM SIGNAL
- XXX = STRONG SIGNAL
<table>
<thead>
<tr>
<th>Site</th>
<th>Zr/ZrO</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>Hf</th>
<th>O</th>
<th>H</th>
<th>Al/Al₂O</th>
</tr>
</thead>
<tbody>
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</tbody>
</table>

**Above Threshold Irradiation**

1. XXX XX X X X X
2. X
3. XX
4. XXX X X
5. XXX X X X
6. XXX X X X
7. X
8. XX
9. XXX X X X X
10. XX
11. XXX XXX X X X XX
12. XX
13. XXX XXX X X X XX
14. XXX X X X X X X
15. XXX X X X X X X
16. XX XX X X X X X

**Below Threshold Irradiation**

28. XXX XX XXX XXX X X
34. XXX X XXX XXX X
46. XX
47. X
52. X X X
64. XXX X XXX XXX X
73. XXX XX XX X
76. X
81. XXX XXX XXX XXX X
85. X
86. XXX XX XXX XXX X X
87. XX XX XX X
93. X

Table 5:42,1 Breakdown of the Spectra for the ZrO₂/SiO₂ H.R. Coating
From the table certain observations can be made, bearing in mind the following two points:-

i) the presence of hydrogen and oxygen can be taken to infer the presence of water in the sample.

ii) The detection of sodium and potassium in similar proportions is indicative of human contamination.

The observations are:-

1) When the irradiating fluence was above the damage threshold and a large zirconium signal was observed it was always accompanied by peaks of sodium and potassium. These peaks, though small compared to the zirconium were always of approximately the same size. If the spectra showed no sodium or potassium then the zirconium signal was considerably smaller. This can be seen by comparing the two spectra in Figure 5:42.1 (a and b).

Figure 5:42.1a Intrinsic Damage Of Uncontaminated Surface
Although damage was inevitable in both cases it is certainly more severe if there are flakes of human debris resting on the surface.

2) Similarly for below threshold fluences a large zirconium signal was observed only in the presence of a large sodium and potassium signal. This effect is more pronounced with the spectra of damage sites irradiated below threshold as the quantity of coating material evaporated off is significantly smaller than in the above threshold damage. The effect of sodium and potassium for below threshold irradiation is shown in Figure 5:42,2.
3) The size of the silicon peak was always small except in the presence of hydrogen and oxygen, indicative of water. This was true of both above threshold fluences and below threshold fluences and can be seen by comparing Figure 5:42,3 with Figures 5:42,1 and 2. The cause of the increase in the silicon signal may only be surmised at present but it is likely that it indicates that damage has penetrated the substrate. SiO$_2$ is notoriously difficult to ionize as shown by its relatively high damage threshold. A large silicon peak is therefore a sign of an abundance of silicon and this is true of the substrate more than the coating. One could assume then that the water present at
4) Hafnium was found in many of the damage sites though only in small quantities. The size of the hafnium signal seemed directly proportional to the size of the zirconium signal. Hafnium is thought to be a common impurity of zirconium and it is likely that it has been incorporated into the coating as an atomic impurity through the raw material. The source materials used for this coating were 99.99% pure and it is unlikely that the damage threshold
has been seriously reduced by the inclusion of the hafnium. Certainly it cannot be blamed for the sub-threshold damage, and if it has had any effect it will be to have reduced the threshold for "intrinsic damage".

5) There were three occurrences of a spectrum showing only aluminium and aluminium oxide, and one occurrence of aluminium oxide accompanied by a small zirconium signal. Three of the four spectra were obtained at sites irradiated above threshold, and two were on consecutive sites. These would appear to be flakes of Al₂O₃ from previous coating runs, and judging by their appearance on consecutive sites would perhaps have a size of 10 to 30µm. According to the vendor the coating chamber used for this sample was also used to deposit Al₂O₃ and SiO₂ as well as ZrO₂. As no coating material appears in these spectra it would be reasonable to assume that the flakes lie on the surface and shield the coating from the effects of the damaging laser pulse. It should be noted that the size of the Al and Al₂O peaks were very small compared with the usual damage spectra.

6) As a final comment the substrate was polished by the vendor in the following sequence:-
   i) using diamond paste
   ii) using Al₂O₃ abrasive
   iii) using a barnsite (SrO₂) slurry
The barnsite slurry was progressively watered down to achieve a "super polish". None of the damage spectra contained any of the polishing abrasive although the barnsite slurry was probably the source of the substrate water causing severe damage.

If the vendor were to try to improve his coating bearing in mind the above observations, his first criteria
would be to improve handling and to ensure that his customers were aware of the possible catastrophic effect human contamination can have. The packing material could also be investigated. According to Dr. Edge, who operates the LIMA, lens tissue is a common source of sodium and potassium. The samples came wrapped in this tissue. The vendor would also be advised to give his substrates a long bake prior to coating to remove any water that may have been absorbed into the substrate during polishing. The last suggestion might be to grow another coating using purer zirconium and then have it re-tested to see if the removal of hafnium has in any way increased the intrinsic laser induced breakdown threshold of the coating.

5:43 LIMA Diagnostics On An A.R. Coating

The second and more detailed investigation was performed on an anti-reflection coating at 248nm. The coating was a multilayer alumina/cryolite stack on a Spectrosil B substrate. The chemical composition of cryolite is Na₃AlF₆.

A preliminary investigation in the manner of Section 5:41 was performed first, locating the damage threshold and recording the spectra of each damage site. A Table summarizing the collected data, similar to that of Table 5:42,1 can be found in Appendix 5A. From the information obtained the following points could be noted:-

1) The coating contained a greater number of metallic impurities than the previous high reflector. The elements detected were titanium, calcium, iron, molybdenum, cerium and its oxide as well as the inevitable potassium, no doubt in conjunction with sodium though this was masked by the sodium in the coating. The impurities were always
found in spectra dominated by the coating material and were probably grown into the coating as opposed to residing on top of it. Two consecutive sites revealed a large presence of titanium indicating a fairly large particle. Molybdenum was found in many of the spectra, though only in very small quantities, and has no doubt arisen from the source boat.

2) Potassium and calcium always occurred together, though generally in small quantities. Unfortunately the detector had often gone off scale due to large sodium, aluminium and silicon signals, and so the true occurrence of potassium and calcium could not be obtained.

3) Damage caused by above threshold fluences would have a typical spectrum as shown in Figure 5:43,1. This shows the

![Figure 5:43,1 A Typical Above Threshold Damage Spectrum For The Alumina/Cryolite Coating.](image)
size of the silicon peak. The silicon is indicative of the substrate being damaged. The silicon peak was increased, however, by one of two effects:-

i) the presence of water, shown by hydrogen and oxygen, see Figure 5:43,2.

ii) the presence of cerium and its oxide, see Figure 5:43,3.

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Figure 5:43,2 Typical Damage Spectrum Containing Water

4) The cerium contamination needs to be considered in more detail. In the damage sites caused by above threshold fluences cerium was found 73% of the time. Below threshold sites showed cerium only 50% of the time. The cerium could have come from two possible sources:-

i) as an atomic impurity in the cryolite where it
would be incorporated as a Ce\(^{3+}\) ion in place of the aluminium. If this was the case we would not expect to see its oxide in the spectrum.

ii) Ce\(_2\)O\(_3\) is a common polishing abrasive. Unfortunately we do not know how this substrate was polished as it came from a different vendor.

Figure 5:43,3 shows the presence of cerium in very large proportions. Larger, in fact, than would be expected if it were only distributed throughout the coating as an atomic impurity. When encountered in such proportions it was usually accompanied by its oxide. In some cases the
cerium spectra rivalled the size of the aluminium spectra. See Figure 5:43,4:

Figure 5:43,4 Severe Coating Damage Initiated By Cerium Impurities.

The points mentioned above and Figure 5:43,4 seem to indicate that cerium is a polishing residue. These spectra showed large substrate damage. On the other hand cerium often was seen without its oxide and in very small quantities, barely detectable. In such circumstances the substrate may not have been damaged and the damage spectra itself would not have been too severe. This can be seen in Figure 5:43,5, and would imply that the cerium here is an atomic impurity. Interpretation of the data can be further confused by considering Figure 5:43,6. Here we see the
Figure 5:43,5 Cerium as an Atomic Impurity?

spectra of the same site after the first shot and then after the third. In the first shot the damage was very small and showed no cerium. By the third shot however the damage was catastrophic and the cerium signal had become very evident. It may thus require more than a single shot to identify the cause of damage. Certainly, here, the first indication of damage suggested no impurity effects, whilst the third shot showed a large cerium contamination under the surface.

To try and clarify the interpretation of the spectra a more detailed investigation was performed. The sample was damage tested in three separate regions, labelled A, B and C in Figure 5:43,7. In each region twenty above
Figure 5.43.6 Damage Spectra For The First And Third Test On The Same Site.
threshold damage shots were performed in order to characterize the area. Then displaced to the side of these the sample was irradiated below the damaging fluence to look for sites going at sub-threshold levels.

If we were to consider the volume of material probed by the laser pulse, assuming that the laser is reproducible, we would expect a limit to the maximum possible sodium, aluminium and fluorine signal. Silicon and oxygen however would have no such bounds as the substrate represents an infinite source of such material. The tables summarizing the data taken from areas A, B and C may be found in Appendix 5B, 5C and 5D respectively, and do indeed show that sodium, aluminium and fluorine tend to a maximum that is fairly reproducible. This is encouraging for anyone attempting to quantify the damage process as it shows signs of consistency. The points to be considered from the new data are as follows:-

1) The damage caused by above threshold fluences always show silicon in their spectra indicating that the substrate has been affected. This is in accordance with the theories on damage to A.R. and H.R. coatings. The below threshold damage, however, was consistently free from
silicon, indicating that the substrate was not involved, and that damage was being initiated by sources other than the exceptionally high electric field found at the substrate coating interface of an A.R. coating.

2) Water was the cause of particularly severe above threshold damage, and seemed to occur fairly consistently across the sample. Virtually every instance of the Si signal overloading the detector was caused by a large water signal.

3) Potassium and calcium were found in nearly every above threshold damage yet in quantities so small as to perhaps be irrelevant. In only one sub-threshold damage site was the potassium and calcium signal particularly large. This spectrum can be seen in Figure 5:43,8. The spectrum is

![Figure 5:43,8 The Effect Of Potassium And Calcium?](image-url)
severe for sub-threshold irradiation and also shows a fair quantity of water present. It is unlikely though that the water has caused the damage. As already pointed out, water seems to be abundantly present throughout the substrate, not being localized at all. The few sub-threshold spectra obtained were after at least 100 sites in each area had been irradiated, and most were found to have contained water, though they didn't damage.

5) No new information could be shed on the source of the cerium and some further testing would be needed. For instance a substrate would need to be tested by the LIMA prior to coating to look for Ce$_2$O$_3$. In the sub-threshold region cerium was detected only three times in twenty three damage sites. Sub-threshold damage, however, seemed to take in only the top few layers of coating and may have been caused as already shown by cerium oxide particles lying below the surface.

6) Sub-threshold damage spectra were always small, except in one instance when titanium was detected, and often showed only sodium and aluminium. Consider Figure 5:43,9.

![Diagram](image)

Figure 5:43,9 Schematic of the Al$_2$O$_3$/Na$_3$AlF$_6$ Coating
Cryolite is the surface layer. If only the surface layer was damaged, and assuming all things equal, we would anticipate a larger sodium signal than aluminium remembering the chemical composition of cryolite. If more than the top layer was damaged then we might expect equal sized signals of sodium and aluminium. This would appear to be the case. For the sub-threshold damage spectra, the smallest spectra showed a larger sodium than aluminium signal. As the signals increased in size the aluminium signal overtook the sodium signal. This trend was consistent in all but three of the twenty three damage sites below threshold and can be seen in Figure 5:43,10a and b. This is again encouraging for those hoping to quantify the data and also gives

Figure 5:43,10a Spectra Showing The Relative Abundances Of Sodium And Aluminium.
the operator an insight into the extent of the damage. We can say almost certainly here whether damage has affected only the top layer or has penetrated through to the lower layers.

Comparing the data gathered according to the areas tested on the substrate we see that in:-

Area A

For above threshold fluences water occurred in 65% of the sites damaged and there is a direct correlation between the size of the hydrogen peak and the severity of the damage spectrum. Cerium was seen in 80% of the damage
sites yet the correlation between the cerium signal and the damage spectra was not as strong as for hydrogen.

For sub-threshold fluences only coating components were seen in the damage spectra. Damage probability at this fluence was 10%.

AREA B
For the above threshold fluences water occurred in 80% of the sites and the correlation mentioned above remained. Cerium was found in 55% of the sites.

Sub-threshold damage had a probability of 6%. 50% of the damaged sites showed the presence of potassium whilst the remaining 50% were spectra containing only the coating components.

AREA C
In this area water showed a 90% probability of being found in the above threshold sites whilst cerium remained at the level in B i.e. 55%. The correlations mentioned in A still hold true.

The probability of sub-threshold damage was 13%. Again potassium occurred in 50% of the sites. One site showed a cerium peak and one site which had damaged catastrophically had a large titanium spectrum.

Probability of sub-threshold damage was least in the center of the sample and it would appear from the tabulated data in the Appendices that the center of the sample was marginally cleaner than its edges. The vendor would have to be encouraged to clean up his production facilities as to see regular traces of molybdenum, iron, cerium, potassium, calcium and water cannot do his coating's res-
istance to damage much good.

5:50 Discussion

The LIMA was used in these experiments to detect atomic impurities. By changing the grid potential negative ions may be detected. This gives chemical information of the anion species present in the plasma i.e. enables one to look for sulphates etc, which could be useful depending upon the nature of the coating. Defect damage initiated by pinholes and coating imperfections might be used to explain the presence of sub-threshold damage sites with no impurity spectra. The LIMA’s ability to detect and help identify the cause of damage has been established. For instance, though the presence of water in optical coatings is no new discovery [2], [3], [4] and [5], and has been detected using laser desorption techniques, [5], and a quadrapole mass analyser, it would appear that every coating has its differences. That reported in [5] showed very localized water apparently absorbed at coating defects. In these samples the water seems to be general, originating in the substrate.

Models have been developed, [6] and [7], to derive parameters for the damage characterization of defect dominated samples. These models claim to be able to infer the nature of the defect and predict the absolute onset of damage from damage frequency measurements. No model, however, is going to be able to span the variety of variables arising from different vendors, production processes, cleanliness and the host of possibilities influencing the damage sensitivity of coatings. The LIMA however, has the potential of doing just this and would enable the buyer to test thoroughly and characterize the performance of a coating very quickly and efficiently. It would also give
the vendor insight into ways of improving his quality.

5:60 Bibliography

Chapter 6:00 SUGGESTIONS FOR FURTHER WORK

This chapter will consider each previous chapter in turn and comment on where it is felt that further work, either experimental or in terms of development would be beneficial. Chapter 1, the introduction, needs no comment.

6:10 The Damage Facility.

There exists plenty of opportunity for improving the damage facility. Some laboratories in America now run almost totally automated facilities. This, though, is more of a service to those requiring operational estimates on samples rather than as an experimental facility and as such lacks flexibility. To be able to change our facility is to us advantageous. Aspects of our damage laboratory, however, could certainly be altered. Beam attenuation is an area for improvement. If we were to remain with the present liquid absorbing system then a search could be made for a cleaner solution. Although the present mixture of nickelous and cobalteous sulphate works well it has a tendency to come out of solution and crystallize whenever in contact with air. This becomes a nuisance when switching solutions. Dilute solutions of Rhodomine 6G were tried for a while and proved to be a good solution, easily handled, etc., yet it had one severe drawback. When using the video camera to monitor damage or the spatial profile the Rhodomine 6G's fluorescence signal tended to be picked up as noise and make interpretation of the video image subject to uncertainty.

A completely new approach to attenuation could be adopted, as mentioned in Chapter 2, such as U.V. transmitting glasses, crossed polarizers or Brewster angle reflection techniques. Crossed polarizers are expensive and
don't have too high a damage threshold. One set of U.V. glasses was tried but over a period of exposure became more transparent where the incident beam was most intense. This is a typical problem in the U.V. i.e. the interaction of the U.V. with matter has a tendency to rearrange chemical bonds. Polarizers, too, are likely to degrade with time and exposure. Whatever technique was employed long term stability studies would be needed to ensure that the attenuator itself did not start to alter the beam's spatial characteristics. At least using a liquid the solution can be easily, and in the case of nickelous and cobalteous sulphate, cheaply replaced.

The beam profiling system can also undergo improvements, although it in itself is a great improvement on all the previous techniques. A discussion of the main drawback with the Image III video processing system can be found in Section 3:40 pp100-104 and details the inability of the system to actually profile the pulse that is performing the damage. Instead it is necessary to assume the reproducability of the laser. It would be a help in understanding surface damage if we could correlate the damage to the spatial profile of the damaging pulse. As mentioned in Section 3:40 this would entail producing a replica of the beam's spatial profile in the damage plane elsewhere in the system, without distorting that profile. A very thin parallel beam splitter with an A.R. coating on one side might be one solution, matched lenses might be another. A third possibility would be to work out how each pixel point in the damage plane distorts when an optical element such as a beam splitter or a wedge is introduced and let the Apple IIe build up the new spatial profile. To do this however would perhaps be impractical as it would limit the versatility of the damage facility as so many parameters i.e. lens focal length, damage plane, beam
size, beam splitter's angle to normal incidence, which at present are variables, would have to become fixed. These possibilities all need looking into; and if the problem could be surmounted the image III profiling system would allow us to build up a useful data base of damage morphologies and associated damaging pulse.

As mentioned in Chapter 2. The Image III profiler is also used for on line damage detection and diagnosis and here, too, there is plenty of scope for development. Chapter 2 section 2.13 dealt with the Schlieren technique as a means of monitoring the onset of damage. This method proves valuable as it monitors phase as well as amplitude objects. It, at high sensitivities however, is subject to diffraction or edge effects which introduce unwanted noise into the system and confuse interpretation. Work could be performed with the intention of improving picture quality. As already suggested replacing the knife edge by an alternative system might improve matters, a prism polaroid combination or neutral density wedge being possibilities.

The Image III system has the ability to snatch and store individual frames and to be triggered externally. One can thus store pictures of a sample surface before damage, during damage and after damage. Subtraction routines can be written to try and isolate differences and detect sites likely to damage. This aspect of damage detection needs to be more thoroughly studied. We can assume that surface damage in substrates and especially thin films occurs around impurity inclusions and at localized sites. These areas absorb the incident radiation to a greater degree than the pure substrate or film and thus the impurity and its surrounds will be hotter than the major portion of the surface. This thermal effect will not last much longer than the laser pulse itself as the heat
will soon diffuse away. This effect will occur whether the surface catastrophically damages or not, and if it could be monitored would give insight as to the weak areas of a coating, perhaps for further analysis for instance via the LIMA (Chapter 5). The Schlieren technique could be developed for this purpose if it could be made sensitive enough to monitor these small transient "hot spots". At present the damage detection uses the He-Ne laser as a source of illumination. Thus the camera is being continually illuminated and each pixel per frame receives 20ms of illumination. The thermal effects may last for periods as short as 100ns, remembering we are using a 30ns pulse, by which time the surface may have returned to its unexcited state. The relevant information concerning the hot spot is likely to have been overcome by the signal received from the unexcited surface. It is hard to pick out small changes on a bright surface. It would thus seem a reasonable idea to use a pulsed illumination source with a duration similar to the exciting pulse. This could be arranged using the dye laser which is excimer pumped. The Image III could look at the surface before irradiation and then during irradiation. Thus the camera will only be imaging during the period of the thermal transient and any effects should become visible. A subtraction routine could be used to highlight any changes that have occurred. The surface could then be damaged and positional correlation between the hot spots and damage sites investigated.

6:20 Surface Damage

Surface damage was investigated from the point of view of surface finish, within the bounds of the sponsoring company's equipment and standard polishing procedures. Such a study could be taken a lot further if a greater degree of surface finish could be applied and if the exp-
erimenter had access to a reliable means of quantifying the surface roughness. Access, for instance, to a machine like the Wycko Surface Profiler could prove very beneficial in aiding an understanding of the role of r.m.s. surface roughness on the damage thresholds. Before, however, such work could be undertaken a standard means of surface preparation and cleaning would need to be devised. A lot of surface breakdown would appear to be initiated by polishing residue and perhaps handling impurities i.e. human contamination. Until a person could confidently assert that as regards cleanliness each surface was identical, surface damage studies are always going to be open to debate. In this respect an indepth study of the effect of the chemical etch would be worthwhile. Monitoring the damage threshold as a function of time within the etch and the physical effect of the etch upon the surface would be advantageous. Such an investigation would involve easy access to a T.E.M. facility. With good microscopy facilities available a good study of surface finish would be possible. The damage thresholds for mechanical, mechano-chemical, chemical and laser polishing should be investigated and optimum polishing techniques could be developed. This, from the optical producer's viewpoint, would yield valuable insights into producing damage resistant optics.

As mentioned in Chapter 3 the act of polishing introduces a stored surface stress into the crystals. Polishing can be a traumatic experience. In CaF$_2$ cleavage is often a sign of damage. Surface stress induced by polishing will lower the threshold for cleavage. An optics user may be able to withstand a little surface melting but cleavage of the surface would be most unacceptable. It may be that surface stress induced by polishing could to a degree, be reduced by annealing. One firm sells strain
annealed crystals, where the crystals have sat in a hot oven for a month. The actual effect of this strain annealing has not in any way been quantified and might prove a useful study.

6:30 Colouration Processes

Reviewing this work it would appear to have hardly begun. Its aim was to unravel, experimentally, some of the possible decay rates open to the S.T.E. in CaF$_2$ once it had been created by U.V. photon absorption. The basic possibilities for this defect center are radiative recombination, absorption of a photon, separation to metastable defects. With this in mind an experiment was devised to monitor the transient $<111>$ $V_k$ population as a function of the incident photon fluence. This has been done, yet to get a clear picture of events a lot more work needs to be undertaken. Other defect states could be probed. If one considers again the series of rate equations for such a system we have,

$$
\dot{n}_c = \sigma^{(2)}_n n_v - \sigma n_c V_{k100}^* S F
$$

$$
\dot{V}_{k110} = pV_{k110}^{-1} - \sigma V_{k110} F - \sigma n_c V_{k110}
$$

$$
\dot{S^{TE}}_{<111>} = \sigma \gamma V_k - \sigma S^{TE} F - S^{TE} F^{-1}
$$

$$
\dot{S^{TE}} = \sigma S F - \sigma S F
$$

Symbols are as on Page 167

$S = S^{TE}_{<111>}$

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where we have been involved in examining the "S" concentration i.e. S.T.E., which in CaF$_2$ is analogous to the $<111>$ $V_k$ - F centre or close F-H pair. The complexity of these equations is apparent and it would be no mean task trying to unravel them. Thus instead one tries to look at each defect as appropriate. The $V_k$ state i.e. $<100>$ $V_k$ exhibits no absorption or emission bands and hence using an optical probe technique remains invisible. The hole concentration can be taken to follow the $<111>$ $V_k$ population as the holes self trap, it is thought, within pico-seconds. "S" ($<111>$ $V_k$ center) we've probed and it would be instructive to look at the population of excited S.T.E.'s and also the formation of stable F and H centers. Combine this with luminescence measurements from the recombination of the close F-H pair and perform this study at all energy densities up to damage levels and a picture would begin to emerge of the fluence dependent behaviour of the defects and their role in damage.

Ideally one would like to be able to replace the dye laser with a pico-second system and use this to build up a temporal picture of the defect population within the period of the exciting pulse. It would be easy enough to build an accurate and adjustable delay line in the probe arm of the system. The present dye laser, with a pulse that temporally mimics the excimer's pulse is a little cumbersome to achieve the temporal information that is desired. The two beams have to be separated by 30ns at least. This, as detailed in Chapter 4, was achieved using mirrors and a number of passes back and forth. There might be easier ways than this, for instance, sending the reference beam around a coil of fibre optics, yet the wavelengths at which the work is to be performed might hinder this idea. With a pico-second system the delay line would be much shorter, and consequently easier to handle.
Ideally I would like to see developed a damage facility in conjunction with a laser spectroscopic facility. This I feel would help a lot in understanding the fundamental nature of bulk damage in ionic solids. Such a facility has yet to appear. Luminescence and absorption spectra can hold a lot of information as to the events and conditions exciting them, yet it is an aspect the damage fraternity seems to have left untouched. A lot of literature exists concerning \( \text{CaF}_2 \) and its various defect centers, yet how these defects behave under the influence of high fields where non-linear effects play a role is completely unknown.

6:40 The LIMA

It is hoped that Chapter 5 emphasised that the LIMA has the possibilities of becoming a powerful damage facility if further developed. In its present role it can provide useful information as to the quality of laser optics and to the likely causes of damage. A little work on the machine to spatially profile the beam in the damage plane and to quantify the energy meter would provide an almost complete damage facility.

The main limitation of the LIMA at present is quantification of the spectra and a lot of work will be needed in this respect before the spectra can be fully understood. A full understanding of laser interactions with surfaces and the resultant plasma that is produced would help. Such an understanding is not available at present. Relating ionization potentials to elements in different bonding situations and understanding the formation of elemental fragments of ionic compounds would help. Since the LIMA is a relatively new machine much work remains to be done on quantifying spectra, work that will perhaps aid
the damage researcher as the LIMA is basically a laser induced damage technique.
APPENDIX 3

The appendix derives the expression quoted for the beam displacement and subsequent distortion when a quartz wedge is placed in the path of a converging beam. The expression is derived purely from geometric optics.

The situation to be considered is as shown in the Figure.

Figure 1 Geometry Of Transparent Wedge In The Path Of A Focused Beam

The parameters used to define the situation are shown on the Figure where:

\[ f = \text{focal length of the lens}. \]
\( \theta \) = vertical diameter of the input parallel wavefront.
\( x \) = the horizontal position of the wedge measured axially from the lens to the first surface of the wedge.
\( w \) = distance from apex of wedge to intersection of axial ray and first face of the crystal.
\( \alpha \) = the wedge angle.
\( l \) = distance from damage plane to focus. Is positive when damage plane is in front of focus and negative when behind.
\( \theta_i \) = angle of incidence of axial ray with first surface of wedge.
\( \theta_t \) = angle of approach i.e. angle subtended by axial ray with the external ray.

The problem is basically that of finding a value for \( P_1 \) and \( P_2 \) where \( P_1 \) is the displacement of \( P_i \) and similarly for \( P_2 \).

Let \( \delta_{1,2} \) be the prism deviation i.e. the angle through which the prism deviates a ray. Thus from the sine rule we know:

\[
\frac{P_{1,2}}{\sin \delta_{1,2}} = \frac{z_{1,2}}{\sin(90 \pm \theta_t)}
\]

But \( z_{1,2} \) is given by

\[
z_{1,2} = \frac{(f - x + x' - x'' - l)}{\cos(\delta_{1,2} \pm \theta_t)}
\]

where \( x' \) and \( x'' \) are as defined in the following diagram.
Figure 2

\[ P_{1,2} = \frac{(f-x-x'-x''-1) \sin \delta_{1,2}}{\cos(\delta_{1,2} \pm \theta_t) \sin(90 \pm \theta_t)} \]

We need to find values of \( x' \) and \( x'' \). These will be different depending upon which external ray is being considered.

\( x' \) is given by:

\[ x' = h \sin \theta_f \]

But \[ \frac{h}{\sin(90 \pm \theta_t)} = \frac{y}{\sin(90 \pm \theta_f \pm \theta_t)} \]

And \[ y = \frac{D(f-x)}{f} \]

\[ x' = \frac{D(f-x) \sin(90 \pm \theta_t) \sin \theta_f}{f \sin(90 \pm \theta_f \pm \theta_t)} \]

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$x''$ is not as obvious:

We know: $\cos \theta_t = \frac{x''}{z}$

But

$$z = \frac{\sin(\delta_{1,2} - \theta_i + \theta_r) \sin \alpha}{\sin(90 - \alpha + \theta_r) \sin(180 - \delta_{1,2})}$$

This is obtained by applying the sine rule to $\Delta$'s $ABC$, $BCD$, $CDE$ in turn.

$$a = w + h$$

And so

$$z = \frac{w - D(f - x) \sin(90 - \theta_t)}{f \sin(90 + \theta_t + \theta_t)} \cdot \frac{\sin(\delta_{1,2} - \theta_i + \theta_r) \sin \alpha}{\sin(90 - \alpha + \theta_r) \sin(180 - \delta_{1,2})}$$

Hence:

$$x'' = \frac{w - D(f - x) \sin(90 - \theta_t)}{f \sin(90 + \theta_t + \theta_t)} \cdot \frac{\sin(\delta_{1,2} - \theta_i + \theta_r) \sin \alpha \cos \theta_t}{\sin(90 - \alpha + \theta_r) \sin(180 - \delta_{1,2})}$$

$$\therefore P_{1,2} = \frac{f - x - \left(D(f - x) \cos \theta_t \sin \theta_t\right)}{f \cos(\theta_t + \theta_t)} - \frac{w - D(f - x) \cos \theta_t}{f \cos(\theta_t + \theta_t)} \sin(\delta_{1,2} - \theta_i + \theta_r) \cos(-\alpha + \theta_r)$$

$$\frac{\sin \alpha \cos \theta_t \cdot \sin(180 - \delta_{1,2})}{\cos(\delta_{1,2} + \theta_t) \cos \theta_t}$$

The spot size is then given by:

$$P_1 + P_2 - \frac{2Df}{l}$$
APPENDIX 4

Mass Spectrographic Results

The following table represents the mass spectrographic analysis of the stock materials used in the crystals investigated in this thesis. Two sources of stock material are represented, Mexican (as mined), and a purified calcium fluoride called Optipur. The analysis was carried out on the material prior to growth and after growth in a Bridgman/Stockbarger Furnace.

M1 = Mexican Raw Material
M2 = Mexican Grown Material
O1 = Optipur Raw Material
O2 = Optipur Grown Material

Figures represent ppm.

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<th>M2</th>
<th>O1</th>
<th>O2</th>
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<td>&lt;0.03</td>
<td>&lt;0.03</td>
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<tr>
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APPENDIX 5A

In Appendix 5A, B, C and D will be found the tabulated results taken from the LIMA spectra for the A.R. alumina/cryolite coating (248nm, normal incidence). Appendix 5A details the results of the preliminary investigation, whilst 5B, 5C and 5D show the results taken from areas A, B and C of the coating as shown in Figure 5:43, 5.

The abbreviations used in the Tables can be understood with reference to the following diagram.

Figure 5A Key To Abbreviations Used In The Tables.

Note "O" = Out of scale.
Site Na Al F Si O H Ce CeOK Ca Ti Fe Mo C

Above Threshold

1  M  M+  M  S-  S--S--
2  S-  S  D
2/3  M+  M+  L  S  M+  M+
4  M+  M+  M  S  S--  S--S-  S-
5  M+  M+  S  S  S  S  L  0  0  0  0
5  M+  M+  S  M  S  M+  M  0  0  0  0  S-
7  M+  M+  M  M+  M  S-  M  0  0  0  0
8  L  L  M+  L  M+  M+  0  0  0  0  S-
11  S  S  S  S
14  M+  M+  S  S  M  M  0  0  0  0
15  M  M  D  S  S  S--S-
19  S  S
24  M  M+  M+  M  S  M  S-
25  S-  S-  S-  S-
27  S-  S-  S-
29  S-  S-  S-  S-
30  M  M  S  M  S-  S--S--

Below Threshold

34  S--
42  M  S  S  S  S  M+
43  S-  S-  S-  S-  S-
44  S-  S-  S-
45  S  M  S--S
51  M  M
75  M  M  S-  S--
77  M  M  S--S
83  M  M  S-
85  M  M
113  S-  S-
128  S  S  S-
# APPENDIX 5B

## Investigation Of Site A

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<td>2   M+ M+ M M+ M M-- S--</td>
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<tr>
<td>3   M++L M+ L M+ M S--</td>
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<td>6   M+ M+ M M-- M-- S-- S--</td>
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<td>7   M+ M+ M M+ M M--</td>
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<tr>
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<td>S--S-- S--S--S--</td>
</tr>
<tr>
<td>9   M+ M+ S--S-- S-- S--</td>
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<td>20  M-- M S S-- S-- S--</td>
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## Below Threshold

| 254  S+ M-- |
| 288  S-- S-- |
| 299  S--S-- |
| 309  S+ S-- | S-- |
APPENDIX 5C

Investigation of Site B

Site Na Al F Si O H Ce CeOK Ca Ti Fe Mo C Sc

Above Threshold

21 M- M- M L L M 0 0 0 0 0 0 S 0
22 M- M M L L M 0 0 0 0 0 0 S+ 0
23 M- M M+ L L M 0 0 0 0 0 0 S+ 0
24 M M+ S+ M M S+ S- 0 0 S--S--S
25 M M S- M+ S+ S- S-- S--S-- S--S-
26 M+ L M- L L M- 0 0 0 0 0 S 0
27 M- M- M+ L L M- 0 0 0 0 0 S+ 0
28 M+ L M+ L M+ M- 0 0 0 0 0 M- 0
29 M- M S- S-
30 M M L+ L+ L+ M+ M-
31 S- S-
32 M M S- S S S- S- S--S--
33 M- M+ S--M M- S--S- S--S--S--S--S--
34 M M+ M- M+ M+ M- 0 0 0 0 0 S 0
35 M M+ S--M S+ S--S S--S--S--S--S--S--S--S--
36 M M+ S- M- M- M- S-- S--S--S--S--S-- S--
37 M M+ S M M- S- S- S--S--S--S--S--S--S--S--
38 S S+ S- S-
39 M- M S- M- S- S- S- S- S--S-- S--
40 M- M S- S- S--

Below Threshold

152 S--S--
161 S--S--
168 S S-- S-- S--
181 S S+ S-
185 S S-
192 S+ S-- S-- S--S--

269
APPENDIX 5D

Investigation of Site C

Site Na Al F Si O H Ce CeOκ Ca Ti Fe Mo C Sc

Above Threshold

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