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Low-Temperature Thermal Expansion of γ-Irradiated Ruby

I. J. Brown and M. A. Brown

Department of Physics, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, United Kingdom

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Measurements of the low-temperature thermal expansion of γ-irradiated rubies have been made with use of a three-terminal capacitance dilatometer. The data exhibit a positive Schottky-type anomaly at \(\sim 3.9\) K, not present in the data obtained for a pure Al\(_2\)O\(_3\) sample, and this contribution to the thermal expansion has been tentatively attributed to the presence of Cr\(^{2+}\) (produced by γ irradiation) exhibiting a large positive magnetic Grüneisen coefficient as predicted by a dynamic Jahn-Teller model.

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A great deal of experimental and theoretical work, over several years, has been done on the properties of various paramagnetic ions in several host lattices (see Bates\(^4\) for an extensive bibliography). Of particular interest are ions which, with use of static field theory, have \(E\) orbitals in an octahedral environment, such as Cr\(^{3+}\)(3\(d^4\), 5\(D\)) in MgO, when it is thought that the orbit-lattice interaction is so strong that a simple description using static crystal theory is inadequate. In this situation, the electronic states couple to the vibrations of the neighboring atoms producing a dynamic Jahn-Teller system\(^2\) which has been calculated in some detail for this particular case.\(^3\)

Experimentally, the quantitative measurement, or even the detection, of small quantities of impurity ion is extremely difficult. The energy-level splittings of such ions are typically in the range \(\sim 1-10\) cm\(^{-1}\) and are difficult to measure by resonance techniques which use electromagnetic or acoustic radiation. Sheard\(^6\) suggested, however, that thermodynamic quantities may provide useful information. Specific-heat measurements give useful information on energy-level splittings and ionic concentrations but are experimentally difficult measurements to perform and lack the absolute precision of spectroscopic techniques. Thermal expansion provides additional information (since it also depends on the pressure dependence of the splittings), such as the magnetic Grüneisen coefficient \(\gamma_s\) which, when determined, would point in a more direct way to the existence of a tunnelling splitting and provide a clear test for a dynamic Jahn-Teller model.

The standard Grüneisen theory\(^2\) may be generalized to include the effect of two-level impurity ions, with level splitting \(E_s\). The volume expansion coefficient \(\beta\) is then given by

\[
\beta/\chi_T = (\gamma_L C_L + \gamma_s C_s)/V,
\]

where \(C_L\) and \(C_s\) are the heat capacities at constant volume \(V\) of the lattice and ions, respectively, \(\chi_T\) is the isothermal compressibility, and \(\gamma_L\) and \(\gamma_s\) are the magnetic Grüneisen coefficients, respectively. This theory can be readily generalized to a many-level system. There will be an observable effect in the thermal expansion when \(\gamma_L C_L - \gamma_s C_s\), and the theoretical work of Sheard\(^6\) indicated that this condition should be readily satisfied for strongly coupled magnetic ions at low temperatures. Recently, experimental observations of the thermal expansion of natural crystals of ZnS containing Fe impurities\(^7\) have been made and the experimental results were shown to be consistent with the predictions of a static crystal-field model (suggesting a magnetic Grüneisen parameter of \(-2/3\)), although the presence of a weak Jahn-Teller effect was not precluded.

With the success of the three-terminal capacitance dilatometers in resolving the magnetic contribution to the thermal expansion,\(^4\) it seemed appropriate to apply the technique to a known strongly coupled ion which was thought to produce a dynamic Jahn-Teller system. The system of Cr\(^{2+}\) in Al\(_2\)O\(_3\) was chosen for several reasons: (a) The Debye temperature of Al\(_2\)O\(_3\) is 1034 K (Ref. 9) so that at low temperatures the lattice thermal expansion is small and should not dominate any magnetic contributions; (b) the amount of Cr\(^{2+}\) present in Al\(_2\)O\(_3\) can be changed by γ irradiation and uv treatment\(^10\); (c) large single crystals of ruby were available; (d) although Cr substitutes for Al, which experiences essentially a trigonally distorted cubic field, there is evidence\(^11,12\) that Cr\(^{2+}\) produces an almost pure cubic field environment for itself; and (e) the static cubic-field model does not explain the behavior of Cr\(^{2+}\) in Al\(_2\)O\(_3\),\(^13\) and consequently the dynamic Jahn-Teller model has been recently developed\(^12\) for this system.

The experimental details will be published later.
but essentially a “standard” three-terminal capacitance method was used, the sample being compared with a H.C.O.F. copper cell, corrected with use of the thermal-expansion data of Kroeger and Swenson. The three monocrystalline samples were cylindrical in form (the c axis being ~60° to the specimen axis), one being a “pure” Al₂O₃ sample, another being doped with ~800 ppm Cr (manufacturer’s quoted value), and the third sample containing 8100 ± 200 ppm Cr (value obtained by optical measurements—the manufacturer’s estimate having been ~1.0% Cr). The dimensions of the cylindrical samples were diameters 12, 10, and 5 mm and lengths 100, 100, and 50 mm for the pure, 800-ppm Cr-doped and 8100-ppm Cr-doped samples, respectively. The change in specimen length as a function of temperature was monitored with use of a General Radio precision capacitance bridge from 3.2 to 300 K, although only the temperature range of immediate interest is presented in this Letter.

The results obtained for the pure Al₂O₃ sample and the ruby samples after γ irradiation are shown in Fig. 1 and the Cr-doped samples show clear step anomalies not present in the data for the pure sample. Indeed, recent measurements on V-doped Al₂O₃ samples also show no such structure. The lines drawn through the data in Fig. 1 were obtained by fitting β-cubic spline functions to the data with use of Loughborough University of Technology’s Prime system so that, by numerical differentiation, the thermal expansion of the specimens could be obtained. The results of this exercise are shown in Fig. 2. Clearly, peaked anomalies are produced with a peak at ~3.9 K and this is tentatively ascribed to the presence of Cr²⁺ (produced from Cr³⁺ by γ irradiation). Obviously, the height and position of the peaks in Fig. 2, depending on the point of inflection in the fitted curve, will be sensitive to the exact computer fit, but we estimate that the peaks in the thermal-expansion curves are correct to ~20% and that the temperature at which the peaks occur is ~3.9 ± 0.2 K. The fact that the anomalous peaks apparently occur at slightly different temperatures is not thought to be physically significant; the smaller peak, in particular, is near the present limit of the sensitivity of the measurement technique and unfortunately measurements could not be made below 3.5 K, making the identification of the point of inflection in this curve very difficult.

We also note that Fig. 2 shows the “pure” Al₂O₃ sample to have a small negative linear thermal-expansion coefficient up to ~6 K. This may be an “apparatus effect,” perhaps partially caused by the H.C.O.F. copper of the expansion cell expanding in a slightly different way than that of Kroeger and Swenson, or it could be a “real effect,” perhaps due to the presence of other impurity ions in this sample (and possibly all three samples) and with negative magnetic Grüneisen coefficients. However, this small effect in the “pure” Al₂O₃ thermal-expansion “baseline” should not affect the interpretation of the impurity results significantly.

If one takes the recently published energy levels of Cr²⁺ in Al₂O₃, the Schottky specific-heat anomaly can be computed, the result peaking at

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**FIG. 1.** Change in specimen length as a function of temperature after γ irradiation for: open triangles, “pure” Al₂O₃; closed circles, Al₂O₃ doped with ~800 ppm Cr; and closed squares, Al₂O₃ doped with 8100 ppm Cr. The solid lines are computer fits with use of β-cubic spline functions.

**FIG. 2.** Thermal expansion of the three samples as a function of temperature, derived from the computer fits shown in Fig. 1.
a temperature of 2.6 K to a value of $20 \times 10^{-24}$ J K$^{-1}$ per ion. One only expects the specific-heat anomaly and the thermal-expansion anomaly to peak at exactly the same temperature if the Grüneisen coefficients for each level are the same. Unfortunately, although estimates of the magnetic Grüneisen coefficients $\gamma_4$ have been made for MgO:Cr$^{3+}$, no such detailed work has yet been done for Al$_2$O$_3$:Cr$^{2+}$. However, it is anticipated that the system will be qualitatively similar and in particular that a small negative value of $\gamma_4$ will be predicted by the static field model whereas a large positive value ($\sim 30$ for MgO:Cr$^{2+}$) will be predicted by the dynamic Jahn-Teller model.\textsuperscript{6} Clearly, from Fig. 2, a positive contribution to the thermal expansion is obtained; and by using the theoretical Schottky specific-heat values, a value for the isothermal compressibility\textsuperscript{10} of Al$_2$O$_3$ of $3.78 \times 10^{-12}$ Pa$^{-1}$, the estimated total chromium concentration, and an estimate of 5% for the number of Cr$^{2+}$ ions converted to Cr$^{3+}$ ions by $\gamma$ irradiation (based on low-temperature thermal-conductivity measurements and earlier work\textsuperscript{17}), we obtained an admittedly crude estimate for $\gamma_4$ of $\sim 80 (\pm 40)$. 

In conclusion, although we clearly have to do a great deal of further work, we have observed an anomaly in the thermal expansion of $\gamma$-irradiated Al$_2$O$_3$:Cr which has been interpreted in terms of a Schottky anomaly due to Cr$^{2+}$. The anomaly is positive and large and is consistent with a dynamic Jahn-Teller model.

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