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Spin-lattice relaxation in gadolinium-doped calcium tungstate

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The spin-lattice relaxation of the S-state ion Gd^{3+} in a calcium tungstate host lattice has been examined at 37.5 GHz over the temperature range 1.5 to 30 K. The gadolinium concentrations in the doped single crystals used were about 50 ppm. Single exponential recovery was observed and the spin-lattice relaxation time (T_1) varied from about 14 msec at 1.5 K to 0.03 msec at 30 K, measured with $\theta = 90°$ and $\phi = 8°$. It was found that T_1 varied with temperature (T) as $T_1 \propto T^{-1}$ below 8 K and as $T_1 \propto T^{-3}$ between 8 and 30 K. The experimental data was fitted by the expressions $T_1^{-1} = 35\,T + 0.5\,T^3$ and $T_1^{-1} = 35\,T + 0.1\,T^{3.6}$ for crystals of nominal gadolinium concentrations 0.005 wt % and 0.05 wt % respectively. The difference between the observed dependence and the T^{-5} variation predicted in the Raman region for an S-state ion in a perfect lattice is attributed to defects. Measurements in the ϕ-plane at 4.2 K showed that T_1 was anisotropic with a maximum value at $\phi = 25°$ about three times greater than the minimum value obtained at $\phi = 55°$. The angular positions at which these features occur show a remarkable coincidence with the "acoustic axes of symmetry" of the crystal, which have recently been determined by ultrasonic methods.

1. Introduction

Calcium tungstate has been used fairly extensively as a host lattice in electron spin resonance studies. The crystallographic features [1], which offer the possibility of paramagnetic ion substitution [2] at either calcium or tungsten sites, are well established; single crystals can be grown relatively easily at temperatures about 1600° C and a number of physical parameters of the lattice, including the elastic properties [3], have been determined. Consequently, it forms a useful medium for studies on relaxation mechanisms and several paramagnetic ions, including neodymium [4, 5] and some other rare earth ions, have been examined as doped calcium tungstate single crystals. It is noteworthy that whereas many of the rare earths in calcium tungstate have very short spin lattice relaxation times, which result in their esr spectra being visible only at temperatures in the liquid helium range, the spectrum of gadolinium-doped calcium tungstate is well defined at room temperature. Some preliminary 37.5 GHz relaxation data on $Gd/CaWO_4$ was reported by this group recently [6] and in this it was shown that there was a region of direct relaxation below about 8 K, the spin lattice relaxation time T_1 being 6.5 msec at 4.2 K, with $\phi = 10°$. In the work described in this paper the previous 37.5 GHz measurements have been extended to 30 K to allow study of the Raman region and the angular variation of T_1 has also been investigated.

2. Experimental

The single crystals used in these experiments were obtained from boules supplied by I.R.D. Co Ltd (Newcastle-upon-Tyne). Three nominal concentrations of gadolinium were used, 0.005, 0.01 and 0.05 wt% respectively. Analysis undertaken by the Analytical Services Laboratory Imperial College, London, showed, however, that the gadolinium concentrations in the three boules were not markedly dissimilar and that all were near 50 ppm; it was possible to use estimates of the esr line intensities to arrange the crystals in qualitative concentration order although the chemical analysis was unable to make a quantitative differentiation.

The pulse-saturation method used in the previous work [6, 7] was again adopted. To allow measurements to be made over a wide temperature range above 4.2 K an araldite block (Type AT1) was inserted over the waveguide section containing the specimen and inside the tail of the cryostat. The specific heat of this araldite was given by Parkinson and Quarrington [8], and due to its high thermal capacity at low temperatures it seemed to be a suitable material. With this arrargement the warming-up time was sufficiently slow to permit measurements at intermediate temperatures between 4.2 K and 30 K to be made without any additional temperature stabilization equipment. Copper–copper/constanton thermocouples were used for temperature measurements.

The amplifier system used to detect the recovery to thermal equilibrium had a dead-time of 10 μsec; this dead-time determined the upper temperature limit for measurements since it was found that T_1 decreased to the same order as the dead-time at about 30 K. The spin lattice relaxation times were derived from the slopes of the log plots obtained by analysis of the photographs of the recovery traces. The example in Fig. 1 shows that a linear log plot was obtained indicating, as previously observed [6], that the recovery could adequately be described by a single exponential; this was true for all the recovery traces observed over the whole temperature range examined. To enable the present data to be compared directly with the earlier results measurements were made with the magnetic field perpendicular to the c-axis, i.e. in the ϕ-plane. When studying the temperature variation of T_1 an angle of $\phi = 8°$ was used as at this angle clean single lines were observed at room temperature and at lower temperatures the components of the line could be resolved. At 4.2 K the angular variation of T_1 in the ϕ-plane was also examined. The overall experimental accuracy of the relaxation time measurements was ± 10%.

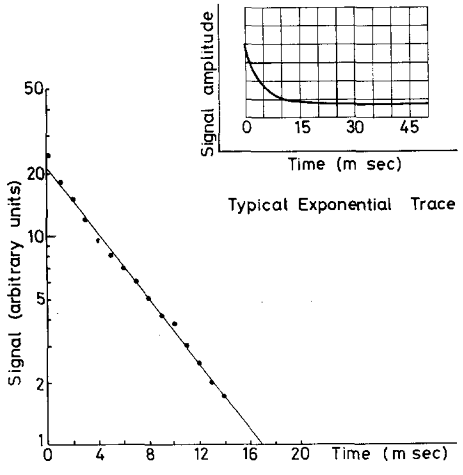

Figure 1 A semilogarithmic plot of the exponential recovery trace at $T = 4.2$ K, $\phi = 8°$, 37.5 GHz.

3. Results

The form of the temperature variation of T_1 for the crystal containing 0.005 wt% gadolinium is shown in Fig. 2 which, for completeness, includes the earlier results obtained in the 1.5 to 8 K region. The figure shows the occurrence of two distinct regimes indicative of direct and Raman relaxation. At temperatures below about 8 K the variation follows, to within experimental error, a $T_1 \propto T^{-1}$ law; in this temperature range the magnitudes of T_1 were found to be 5.8 msec at 4.2 K and 2.8 msec at 8 K, in close agreement with the earlier measurements. The transition temperature is near 8 K and above this temperature the spin lattice relaxation time varies as $T_1 \propto T^{-3}$; at

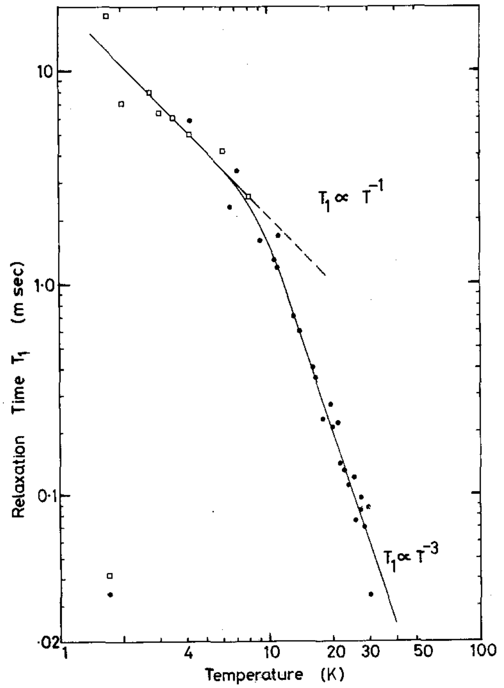

Figure 2 Temperature dependence of T_1; Gd/CaWO$_4$ (0.005%), $\phi = 8°$, frequency 37.5 GHz. □ previous data; ● present data.

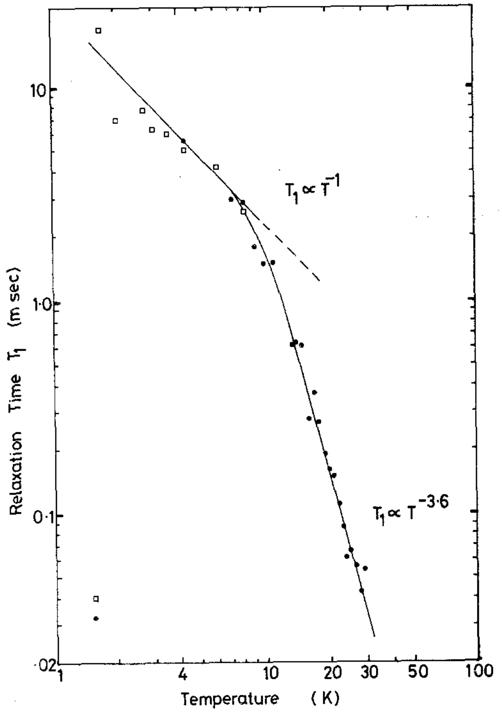

Figure 3 Temperature dependence of T_1; Gd/CaWO$_4$ (0.05%), $\phi = 8°$, frequency 37.5 GHz. □ previous data; • present data.

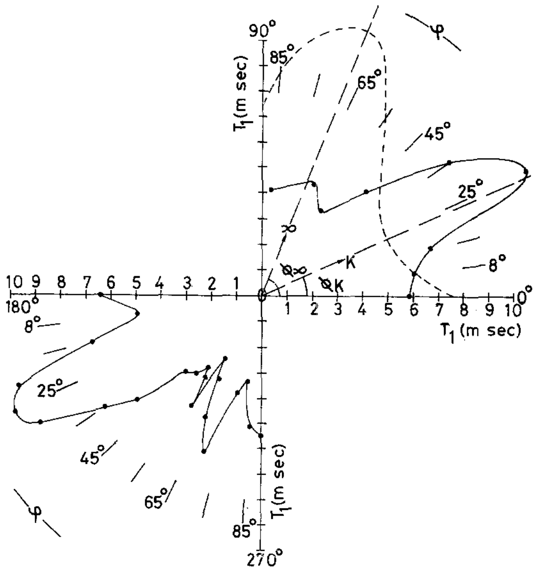

Figure 4 Angular variation of T_1 in the ϕ-plane; Gd/CaWO$_4$ (0.005%), temperature 4.2 K, frequency 37.5 GHz. (– – –) previous measurements of Young's modulus in the same plane [20].

10 K, T_1 = 1.6 msec and falls only to 0.07 msec at 28 K. The corresponding temperature variation for the higher gadolinium concentration (0.05 wt%) is given in Fig. 3. The exponents of T in the direct and Raman regions are (−1) and (−3.6) respectively which agree closely with those obtained from Fig. 2. The actual magnitudes of T_1 at corresponding temperatures, e.g. 5.8 msec for 0.005 wt%Gd and 5.6 msec for 0.05 wt%Gd at 4.2 K suggest that at these gadolinium levels T_1 is not strongly dependent on concentration.

The variation of T_1 with angle in the ϕ-plane is illustrated by Fig. 4 in which all the data was obtained at 4.2 K. It was found that T_1 was anisotropic. In the first quadrant there is a fairly broad but distinct minimum between $\phi = 45°$ and $\phi = 65°$. T_1 varies from a maximum of 11.6 msec at $\phi = 25°$ to a minimum of 4.1 msec at $\phi = 55°$; at this angle T_1 is reduced by a factor of about three. Rotation of the crystal through 180° in order to examine the range $180° < \phi < 270°$ revealed a similar variation with another minimum near $\phi = 235°$ and a maximum at $\phi = 205°$.

4. Discussion

When dealing with the relaxation of a single ion to the lattice two processes were initially involved; the direct and Raman processes, Kronig [9] and Van Vleck [10]. A third process, the Orbach or resonance relaxation mechanism, was proposed by Finn *et al.* [11]. The spin-lattice relaxation time T_1 may thus be expressed in terms of temperature T as

$$T_1^{-1} = AT^m + BT^n + C\exp(-\Delta/kT) \qquad (1)$$

where A, B and C are constants. In the first term, corresponding to the direct process, $m = 1$; in the second term, corresponding to the Raman process, $n = 7$ for a non-Kramers ion or $n = 9$ for a Kramers ion, and in the last term, representing the Orbach mechanism, Δ is the energy splitting of the excited state above the ground level. The processes outlined above do not involve any co-operative mechanisms such as cross-relaxation or exchange interactions between clusters of ions. Usually Equation 1 is applicable only to salts where the paramagnetic ion concentration is low so that the experimental conditions approximate to the assumptions of single ion theory; moreover, the derivation rests on the postulate of coupling between lattice phonons and the orbital angular momentum of the paramagnetic ion and consequently would not be expected to hold for S-state ions in which $L = 0$. Orbach and Blume [12] proposed a further Raman type relaxation mechanism which would occur with S-state ions having multilevel systems of Kramers doublets.

They concluded that a T^5 term may dominate the relaxation rate, at least in the lower region of the Raman temperature range, when the intermediate states $|i>$ are ground level states (rather than orbital states) and

$$\Delta i < \hbar \omega_p \sim kT$$

where Δi is the energy separation between the intermediate state and the ground state and $\hbar \omega_p$ is the phonon energy. There is, in fact, experimental evidence for the T^5 Raman behaviour in several S-state ions. For example, Bierig et al. [13] found this kind of temperature dependence for Gd^{3+}/CaF_2; Chao-Yuan Huang [14] also observed it in Eu^{2+}/CaF_2 and Horak and Nolle [15] reported T^5 behaviour in Eu^{2+}/CaF_2, Mn^{2+}/BaF_2 and Mn^{2+}/SrF_2.

When considering the present results on $Gd^{3+}/CaWO_4$ we may note first that the Orbach process is only important if the splitting Δ is less than the Debye energy, $k\theta_D$, which is that of the highest energy phonon in the lattice phonon spectrum, i.e. if

$$\Delta < k\theta_D$$

where θ_D is the Debye temperature. For the gadolinium-doped crystals used we may (in the absence of a direct determination) reasonably take θ_D as the value for pure $CaWO_4$ since the gadolinium concentration is low; Farley [16] using ultrasonic techniques for elastic constant determinations, reported that $\theta_D = 155$ K for pure $CaWO_4$. From spectroscopic data the value of Δ is about 30 000 cm^{-1}, Dieke [17] and so $k\theta_D$ is much less than Δ, ($k = 0.695$ cm^{-1} K^{-1}). We conclude that the Orbach process is not a possible mechanism. (If defect centres are present in the crystals the effective Debye temperature may be less than θ_D for a perfect lattice; hence the conclusion that the Orbach process is not possible remains valid for imperfect crystals.) Reference back to the general Equation 1 suggested therefore, that for $Gd^{3+}/CaWO_4$ a variation of the form

$$T_1^{-1} = AT^m + BT^n \tag{2}$$

may apply with $m = 1$ and $n = 5$. The absence of the Orbach term is confirmed by the experimental data because, when plotting log T_1^{-1} versus T^{-1} we do not get a straight line as would be expected if the recovery followed an Orbach mechanism. This absence of an Orbach type contribution was also found in the results obtained with the doped fluorides mentioned earlier.

The experimental results, however, show that although there is a good fit to a $T^{1.0}$ variation at low temperatures, the variation above about 8 K is much less rapid than T^5. The experimental variations can be expressed as

$$T_1^{-1} = 35T + 0.5T^3 \tag{3}$$

for the 0.005% Gd crystal, and

$$T_1^{-1} = 35T + 0.1T^{3.6} \tag{4}$$

for the 0.05% Gd crystal so that, on average, we can take the variation as nearly T^3 in the Raman region. Inspection of these equations shows that the contributions of the direct and Raman processes become equal at about 9 K above which temperature the Raman process is dominant.

The explanation of the observed T^3 variation appears to lie in the presence of defects in the crystals. The theories mentioned above deal with paramagnetic ions in crystallographically perfect diamagnetic lattices. The assumption of a perfect lattice is unlikely to be true for a doped single crystal because the paramagnetic ions substituting at lattice points usually differ in both mass and net electric charge from the ions they replace. A modification to spin-lattice relaxation theory which allows for defect sites was made by Castle *et al.* [18]; this predicted a T^{-3} variation of T_1 in the Raman region and fitted the observed behaviour of irradiation centres in quartz.

In the gadolinium-doped tungstate used here we may note that with the entry of Gd^{3+} into a Ca^{2+} site the formation of one calcium vacancy for every two Gd^{3+} ions occurs, which amounts to a calcium vacancy density of about 10^{18} cm^{-3} to be present. Besides, calcium and oxygen vacancies are also formed as Schottky defects even in pure $CaWO_4$ in air at the melting point. This is given by $\phi_{Ca} = \phi_0 = 0.054$ at.%, where ϕ indicates a vacancy and the subscripts indicate the crystal lattice site [19]. For $CaWO_4$, calculations of Schottky defects give the same order of magnitude mentioned above for calcium vacancy density, and hence for oxygen vacancy density. Furthermore, etching studies, Farley [16], showed that the dislocation density in calcium tungstate single crystals, grown by the same Czochralski technique as that used here, was about 10^5 cm^{-3}. The temperature required for growth of calcium tungstate is about 1600° C; that is considerably higher than that required for the fluorides in which, (although data was not specifically given in the references quoted), a much lower dislocation density might be expected. Consequently, there are substantial grounds for attributing the observed T^3 variation to defects although their exact nature is not yet fully resolved.

The main features of the variation of T_1 with angle in the ϕ-plane were the occurrence of marked maxima and rather less well defined minima. The angular positions at which these features occur show a remarkable coincidence with the "acoustic axes of symmetry" of the crystal whose positions have recently been determined by Farley *et al* [20], using ultrasonic methods. These authors investigated the elastic properties of scheelite structure molybdates and tungstates and found that, in the ϕ-plane of calcium tungstate the Young's modulus was anisotropic. Two features were noted, a maximum at $\phi = 68.6°$ and a minimum at $\phi = 23.6°$, and these were identified with the "axes of acoustic symmetry" which correspond to extrema in the ultrasound velocities and are the acoustic pure mode directions for which the acoustic energy flux direction is collinear with the propagation vector. The ultrasonic and relaxation data are compared in Fig. 4. It can be seen that there is a close fit between the direction of the minimum of T_1 and the acoustic γ-axis and also of the maximum of T_1 with the acoustic k-axis. The ratio of Young's modulus along the γ- and k-axis was given as 2.1 at 295 K and thus may be compared with the ratio of about 2.1 at 4.2 K for the spin-lattice relaxation rates in these directions. It appears that the maximum relaxation rate, (i.e. minimum T_1) occurs when the ultrasound velocity is greatest and vice versa. The acoustic axes have $4/mmm$ symmetry in calcium tungstate and this accounts, on the same basis, for the maxima and minima of T_1 found between $\phi = 180°$ and $\phi = 270°$.

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