

the conductivity data were obtained was<sup>6,19</sup> 0.7 ohm-cm (before irradiation), as compared with the 5.4 ohm-cm specimen used for lifetime measurements. The results agree with the observation previously made that this annealing process is not dependent upon impurity concentration. NC As 5.4 had a pre-anneal treatment of one hour at 126°C. In the case of the conductivity samples with much higher impurity concentrations, the early lower-temperature anneal would probably have occurred in a relatively short time at room temperature and would not have been observed. The dose used for conductivity changes was very large compared with those used for lifetime changes. Their initial concentration of bombardment-induced defects was<sup>6</sup>  $\sim 10^{15}$  cm<sup>-3</sup>, while the value in the present case was  $\sim 2 \times 10^{13}$  cm<sup>-3</sup>. The agreement between the two types of data further substantiates the fact that this anneal is defect-concentration independent.

It seems unlikely that the agreement<sup>20</sup> of the two sets of data shown in Fig. 11 is fortuitous. On the basis

<sup>20</sup> One must not assume from these data that the recovery of lifetime and conductivity go together in the lower-temperature range or in antimony-doped material.

of this agreement, the center responsible for recombination in arsenic-doped material after the early anneal had occurred is felt to be the same center responsible for carrier removal. Therefore, it was possible to count the number of recombination levels on the basis of Hall measurements and, thus, determine the electron-capture probability for the recombination level. The value obtained is  $(2.0 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> sec<sup>-1</sup>. Any inaccuracy in the position of the recombination level would have a large effect on this value. However, the estimated error does not include any such uncertainty. The cross section is approximately equal to the capture probability divided by the mean-thermal velocity,  $\langle v \rangle$ . Using a value for the mean thermal velocity of electrons in germanium at 300°K of  $3.1 \times 10^7$  cm sec<sup>-1</sup>, the electron capture cross section was found to be approximately  $7 \times 10^{-19}$  cm<sup>2</sup>.

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### Spin-Lattice Relaxation Time of Samarium Ethyl Sulfate\*

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The spin-lattice relaxation time  $T_1$  of  $\text{Sm}^{3+}$  in the ethyl sulfate is computed. It is shown that  $T_1$  in the direct-process region should exhibit a large anisotropy with respect to the direction of the external magnetic field. The necessary Zeeman admixture of excited levels into the ground level is shown to be much smaller when the external field is parallel rather than perpendicular to the symmetry axis. This is because, on the one hand, the levels connected by a parallel field lie in the next  $J$  multiplet, some 1100 cm<sup>-1</sup> away. On the other hand, a perpendicular field can connect the ground state with a level within the ground multiplet, only 53.6 cm<sup>-1</sup> away. This is shown to be a general result for ions with small  $J$  values in crystals of moderately high symmetry.

THE theory of the spin-lattice relaxation time  $T_1$  for rare-earth salts has been given previously<sup>1</sup> but was restricted to orbit-lattice transitions solely between ground multiplet states. It was pointed out that  $T_1$  in the direct process region could vary markedly with the direction of the applied magnetic field, and a specific case, dysprosium ethyl sulfate, was examined at some length. In this paper we extend the theory to cover cases when intermultiplet transitions are important. Such a condition will arise, for example, for  $\text{Sm}^{3+}$  in the ethyl sulfate. Rather than treat an abstract case, we shall restrict our attention to samarium ethyl

sulfate, and indicate when necessary how to extend the treatment to other salts.

The configuration for  $\text{Sm}^{3+}$  is  $4f^5$  and the lowest term value is  $^6H$ . As Sm is in the first half of the rare-earth series,  $J = \frac{5}{2}$  for ground multiplet, and the first excited multiplet is a  $J = \frac{7}{2}$  level at about 1100 cm<sup>-1</sup>. The local symmetry in the ethyl sulfate is  $C_{3h}$  and, as Elliott and Stevens<sup>2</sup> have shown, this implies that an expansion of the static crystalline field in the spherical harmonics  $Y_n^m$  need only retain terms with  $n=2, 4$ , and 6 and  $m=0, \pm 6$ . Optical measurements<sup>3</sup> indicate the lowest level to be a  $|J = \frac{5}{2}, J_z = \pm \frac{1}{2}\rangle$  with a  $|J = \frac{5}{2}, J_z = \pm \frac{3}{2}\rangle$

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<sup>1</sup> R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

<sup>2</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952); **A218**, 553 (1953); **A219**, 387 (1953).

<sup>3</sup> H. Lammerman, Z. Physik **150**, 551 (1958).

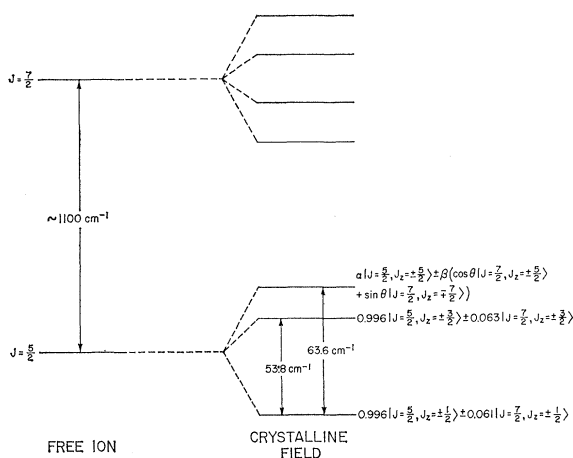


FIG. 1. A schematic energy level diagram for  $\text{Sm}^{3+}$  in the ethyl sulfate (not to scale). The left-hand side represents the free-ion splitting between the ground ( $J = \frac{5}{2}$ ) multiplet and the first-excited ( $J = \frac{7}{2}$ ) multiplet. The right side shows the splitting of the multiplets in the presence of the ethyl sulfate crystalline field.

level at  $53.8 \text{ cm}^{-1}$  and a  $|J = \frac{5}{2}, J_z = \pm \frac{5}{2}\rangle$  level at  $63.6 \text{ cm}^{-1}$ . In fact, the crystalline field is large enough to cause appreciable admixture of the  $J = \frac{7}{2}$  level into the ground multiplet and the first order admixtures, as computed using the extrapolated values of  $V_n^m$  given by Powell and Orbach,<sup>4</sup> are given in Fig. 1.

The formula for the direct process relaxation time for a Kramers salt is<sup>1</sup>

$$\frac{1}{T_1} = \frac{3(g\beta H)^3 4\beta^2}{2\pi\rho v^5 \hbar^4 \Delta_q^2} |\mathbf{H} \cdot \langle -\frac{1}{2}q | \mathbf{L} + 2\mathbf{S} | -\frac{1}{2}p \rangle|^2 \times |\langle -\frac{1}{2}p | \sum_{nm} V_n^m | \frac{1}{2}q \rangle|^2 \coth(g\beta H / 2kT), \quad (1)$$

where  $g$  refers to the ground doublet,

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta,$$

$\theta$  is the angle  $\mathbf{H}$  makes with the symmetry axis. We have used  $(\mathbf{L} + 2\mathbf{S})$  for the Zeeman interaction, instead of  $\Lambda\mathbf{J}$ , where  $\Lambda$  is the Landé  $g$  factor. The state  $|\pm \frac{1}{2}q\rangle$  designates an excited Kramers doublet at energy  $\Delta_q$  away from the ground doublet, the latter to be designated by  $|\pm \frac{1}{2}q\rangle$ . The presence of the matrix element of the Zeeman interaction  $\mathbf{H} \cdot \langle \frac{1}{2}q | \mathbf{L} + 2\mathbf{S} | -\frac{1}{2}p \rangle$  is necessary in order to break the time conjugate nature of the ground doublet.

For the case of  $\text{Sm}^{3+}$  in the ethyl sulfate, one can see immediately an important consequence of (1) from Fig. 1. The Zeeman interaction,  $\mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S})$ , for a magnetic field parallel to the  $z$  axis, cannot connect the ground doublet with any other state in the ground ( $J = \frac{5}{2}$ ) multiplet. The symmetry is high enough so that  $|\pm \frac{1}{2}q\rangle$  can at best be a state in the first excited multiplet ( $J = \frac{7}{2}$ ). Hence,  $\Delta_q \sim 1100 \text{ cm}^{-1}$ . This is to be

compared with the case of a magnetic field perpendicular to the  $z$  axis. In such a case,  $\mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S})$  can connect ground doublet with the first excited doublet (within the ground  $J = \frac{5}{2}$  multiplet) which is only at  $\Delta_q = 53.8 \text{ cm}^{-1}$ . Thus, the energy denominator in (1) increases by a factor of  $(1100/53.8)^2 = 418$  if we rotate the field from a direction perpendicular to a direction parallel to the  $z$  axis. This is a general result for salts of small  $J$  values in crystals of moderately high symmetry. It presents in more extreme cases the possibility of enormous anisotropies in relaxation times as a function of the direction of the magnetic field, when the predominant relaxation mechanism is the direct process. At the lowest temperatures it is entirely possible that a "heat switch" could be constructed which could be regulated by merely rotating the direction of the external field. Because the thermal resistance of a paramagnetic salt is proportional to  $1/T_1$ ,<sup>5</sup> such a device would not require the sudden application of an external field, but would need only a field rotation to shut off the heat current. This effect is expected to be important only at the lowest of temperatures, but it is just in this region where such a device may be useful. The anisotropy in  $T_1$  may also be useful in adiabatic demagnetization experiments. The spins could be used to cool the pill with an external magnetic field in the direction for which  $T_1$  was shortest. After the demagnetization, the magnetic field could be reapplied and the pill would not warm up if in the interim the magnetic field direction had been rotated to the position for which  $T_1$  was very long, as the spins would be decoupled from the lattice. This would be somewhat analogous to a technique introduced by Wheatley,<sup>6</sup> but would not be limited to salts whose  $g$  value in a certain direction was zero.

We now compute  $T_1$  for samarium ethyl sulfate. The only additional computations which must be carried out over what was done in reference 1 concern the matrix elements of  $V_n^m$  between states of different  $J$ , and the estimates of the magnitude of the  $A_n^m \langle r^n \rangle$ . The former is accomplished utilizing the general formation of Elliott, Judd, and Runciman.<sup>7</sup> They have computed, in general terms, the matrix elements of the crystalline field operators for rare-earth ions when expressed in an expansion in spherical harmonics. Their general formula is

$$(f^n \tau U_j S L J J_z | U_q^k | f^n \tau' U' j' S' L' J' J_z') = (-1)^{J+J_z+k+q} (2k+1)^{-\frac{1}{2}} (J J' - J_z J_z' | J J' k - q) \times (f^n \tau U_j S L J | U^k | f^n \tau' U' j' S' L' J'),$$

and they give formulas for the double bar matrix

<sup>5</sup> R. Orbach, *Phil. Mag.* **5**, 1303 (1960).

<sup>6</sup> J. C. Wheatley and T. L. Estle, *Phys. Rev.* **104**, 264 (1956); T. L. Estle, H. R. Hart, Jr., and J. C. Wheatley, *ibid.* **112**, 1576 (1958).

<sup>7</sup> J. P. Elliott, B. R. Judd, and W. A. Runciman, *Proc. Roy. Soc. (London)* **A240**, 509 (1957).

<sup>4</sup> M. J. D. Powell and R. Orbach, *Proc. Phys. Soc. (London)* (to be published).

element. The  $U_q^k$  are  $[4\pi/(2k+1)]^{1/2} Y_k^q(\theta, \phi)$  where  $q$  is the azimuthal quantum number,  $k$  is the orbital quantum number, and  $Y_k^q(\theta, \phi)$  is a spherical harmonic. We obtain for  $\text{Sm}^{3+}$ ,

$$\begin{aligned} \langle \psi_{7/2} || U^2 || \psi_{5/2} \rangle &= -[13(5)^{1/2}/63]; \\ \langle \psi_{7/2} || U^4 || \psi_{5/2} \rangle &= 10(6)^{1/2}/693; \\ \langle \psi_{7/2} || U^6 || \psi_{5/2} \rangle &= 34(35)^{1/2}/693. \end{aligned}$$

Using Stevens' convention<sup>8</sup> of dropping normalization factors from the crystalline field operators and including them in the  $A_n^m \langle r^n \rangle$ , we find, for  $\text{Sm}^{3+}$

$$\begin{aligned} \langle J = \frac{7}{2}, J_z | V_n^m | J = \frac{5}{2}, J_z' \rangle &= (N_n^m)^{-1} (-1)^{J_z + \frac{1}{2}} \\ &\times \begin{pmatrix} \frac{5}{2} & \frac{7}{2} & n \\ -J_z' & J_z & m \end{pmatrix} \langle \psi_{7/2} || U^n || \psi_{5/2} \rangle, \end{aligned}$$

where we have used a  $3j$  symbol instead of the Wigner coefficient for compactness. The normalization coefficients  $N_n^m$  for the operators we need are,

$$\begin{aligned} N_2^1 &= (3)^{1/2}; & N_4^1 &= (10)^{1/2}/4; & N_6^1 &= (21)^{1/2}/8; \\ N_2^2 &= (3)^{1/2}/2; & N_4^2 &= (5)^{1/2}/4. \end{aligned}$$

We must now estimate the magnitudes of the  $A_n^m \langle r^n \rangle$ . Using a very approximate rule,<sup>1</sup> we find

$$\begin{aligned} A_2^1 \langle r^2 \rangle &\sim A_2^2 \langle r^2 \rangle \sim 77 \text{ cm}^{-1}, \\ A_4^1 \langle r^4 \rangle &\sim A_4^2 \langle r^4 \rangle \sim 48 \text{ cm}^{-1}, & A_6^1 \langle r^6 \rangle &\sim 61 \text{ cm}^{-1}. \end{aligned}$$

Using these values, neglecting possibilities of sign cancellation, and letting  $\rho = 2 \text{ g/cm}^3$ ,  $v = 2.3 \times 10^5 \text{ cm/sec}$ , we obtain

<sup>8</sup> K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

$$1/T_1 \cong 1.0 \times 10^{-17} H^4 T, \quad H \perp z \text{ axis};$$

$$1/T_1 \cong 1.8 \times 10^{-18} H^4 T, \quad H \parallel z \text{ axis}.$$

The relaxation time thus varies by a factor of  $\sim$ ten in rotating the field from a direction perpendicular to a direction parallel to the  $z$  axis. This is less than the factor of  $\sim$ 400 we would have guessed from a consideration of the energy denominators alone and is simply a consequence of the matrix elements being smaller for a field in the perpendicular direction than for a field in the parallel direction. Much also depends on the magnitudes of the  $A_n^m \langle r^n \rangle$ , which we have had to estimate very roughly.

Anisotropy in  $T_1$  should occur for a wide variety of salts. In particular, it should also be true of ytterbium ethyl sulfate which possesses a  $|J = \frac{7}{2}, J_z = \pm \frac{3}{2}\rangle$  ground doublet and where the next level connected by a field *parallel* to the  $z$  axis lies in the  $J = \frac{5}{2}$  excited multiplet at  $\Delta_q = 10\,300 \text{ cm}^{-1}$ . The excited state to which a perpendicular field has matrix elements is expected to be  $\Delta_q \sim 45 \text{ cm}^{-1}$  away,<sup>9</sup> so that at first glance a parallel-perpendicular anisotropy of  $T_1$  of order  $(10\,300/45)^2 = 5.2 \times 10^4$  might be expected. However, the ground doublet has  $g_1 = 0$ , so that  $T_1$  will be shortest when  $\mathbf{H}$  makes an angle of  $45^\circ$  with the  $z$  axis. The anisotropy should still remain large however. This case is somewhat analogous to the case of dysprosium ethyl sulfate.<sup>1</sup>

We do not expect any anisotropy in  $T_1$  for two-phonon processes, which will only be important at higher temperatures and which are discussed at length in reference 1.

<sup>9</sup> H. Meyer and P. L. Smith, J. Phys. Chem. Solids, **9**, 285 (1959); A. H. Cooke, C. B. P. Finn, and R. Orbach, Bull. Ampère **9**, 111 (1960).