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Spin-Lattice Relaxation in Dysprosium Ethyl Sulphate

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Measurements of spin-lattice relaxation in dysprosium ethyl sulphate using magnetic fields along the symmetry axis of the crystal have shown that at temperatures in the helium range the predominant relaxation mechanism is the resonance relaxation process, in which the relaxation time T_1 varies exponentially with $1/T$. Application of crystalline field theory shows that in this substance the 'direct' one-phonon process may be expected to be important at low temperatures, but that the relaxation time for this process will depend strongly on the angle between the magnetic field and the crystal axis, and should be least when the angle is $\pi/4$. This has been confirmed experimentally. When the magnetic field is applied at $\pi/4$ to the axis the variation of the relaxation time with temperature and with field is quite changed, and at high fields it is possible to follow the transition from the resonance to the direct relaxation process, in which the relaxation time is inversely proportional to the temperature.

We have carried out spin-lattice relaxation measurements on dysprosium ethyl sulphate at temperatures in the liquid helium range. Measurements of the magnetic properties of this salt have been reported previously by Becquerel, de Haas and van den Handel[1)], and by Cooke, Edmonds, McKim and Wolf[2)]. Recently Powell and Orbach[3)] have applied the crystalline field theory of Elliott and Stevens[4)] to the optical absorption spectrum as measured by Gramberg[5)], and they have computed all the wave functions and splittings within the ground multiplet. We may summarize the properties important for the present work, as follows. In this salt, the ground multiplet of the free Dy^{3+} ion ($J=15/2$) is split by the crystalline electric field into eight separated time-conjugated doublets, the lowest being a mixture of $J_z=\pm 9/2, \mp 3/2, \mp 15/2$, with $g_{\parallel}=10.8$, $g_{\perp}=0$. The first excited state is a mixture of $J_z=\pm 7/2, \mp 5/2$, at an energy $\Delta=16.0\,\mathrm{cm}^{-1}(=23.1°\mathrm{K})$. The lowest excited state formed from the same mixture as the ground state lies at $58.9\,\mathrm{cm}^{-1}$.

As already briefly reported[6)], we have found that in the upper part of the helium range the relaxation time T_1 varies as $\exp(23/T)$, in agreement with the theory of Orbach[7)]. The relaxation mechanism is the resonance relaxation process introduced by Finn, Orbach and Wolf[8)] to explain the results of experiments on cerium magnesium nitrate. In this process, relaxation takes place through real transitions, accompanied by the emission or the absorption of a phonon, between the states of the ground doublet and an excited doublet at energy Δ. Thus because phonons of energy Δ are principally involved, their scarcity when $\Delta \gg kT$ leads to the exponential dependence of T_1 on $1/T$. As the temperature is lowered this process will be frozen out and according to the theory[9),10)] two others may become important. The first is the non-resonant two-phonon process, usually referred to as the Raman process, in which $T_1 \propto T^{-9}$. This is not expected to be important in this salt at low temperatures. The second is the direct process,' for which $T_1 \propto a(\theta)H^{-4}T^{-1}$, where $a(\theta)$ is a function depending on the angle the field H makes with the symmetry axis of the crystal. We have now found experimentally that the direct process is important in high fields at the lowest temperatures at which we could measure relaxation times.

The theory of the direct process in dysprosium ethyl sulphate predicts an enormous anisotropy in the dependence of the relaxation time on the field direction. This effect, which is related to the anisotoropy of the temperature-independent part of the susceptibillity, comes about as follows. The direct process is important in a Kramers salt (i.e. one with an odd number of magnetic electrons) because the magnetic field breaks the time-conjugated nature of the ground doublet by admixing excited states. Without these admixtures, relaxation transitions between the states of the ground doublet would be forbidden[10]. However, the lowest excited state with which a field parallel to the symmetry axis can connect the ground doublet is that at 58.9 cm^{-1}. Because the ground state is mainly $J_z=\pm 9/2$, while the excited state has only a small component of this value of J_z, the Zeeman matrix element between these two states is very small. On the other hand, a field perpendicular to the symmetry axis will admix the lowest excited level into the ground state. The energy of this level is only 16.0 cm^{-1}, and the Zeeman matrix element connecting it with the ground state is very large. Because both these factors enter as the square, we might expect that a field perpendicular to the symmetry axis will be much more effective in bringing about relaxation by the direct process than a field parallel to it. However, $g_\perp=0$ for the ground doublet, and we must strike a compromise because T_1 is inversely proportional to the square of the static field splitting of the ground doublet. In fact we find that for dysprosium ethyl sulphate the function $\alpha(\theta)=\sin^{-2}\theta\cos^{-2}\theta$, so that, at a given field and temperature, the time for relaxation by the direct process is least when $\theta=\pi/4$.

To test these ideas, we have made experiments on a single crystal of dysprosium ethyl sulphate in magnetic fields parallel to the symmetry axis and at $\pi/4$ to it. The measurements have been made by the low frequency bridge method[11], in which the in-phase and out-of-phase components of the susceptibility were measured in alternating fields, of frequencies from 25 c/s to 900 c/s, superposed on static magnetic fields up to 1,100 oersted. The sensitivity of the method is strongly dependent on the static field used; in fields of 1,000 oersted it was possible to measure relaxation times in the range between approximately 1 sec and 10^{-4} sec, but in fields of 300 oersted the measurements extended only to approximately 0.1 sec. Because of the very rapid variation of the relaxation time with temperature in this salt, the temperature range covered is small and lies entirely in the helium range. Fig. 1 shows the dependence of T_1 on $1/T$ when the field is applied parallel to the axis. The experimental points in a field of 1,110 oersted can best be fitted by the relationship $1/T_1=1.1\times 10^8\exp(-23/T)$ in agreement with Orbach's estimate[10]. The relaxation time is found to

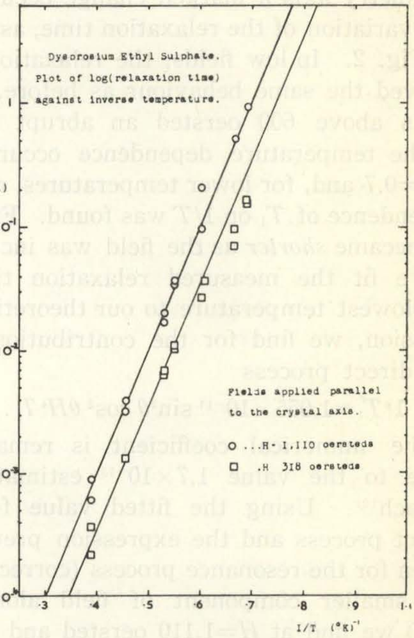

Fig. 1, Variation of relaxation time with temperature when a magnetic field is applied parallel to the crystal axis.

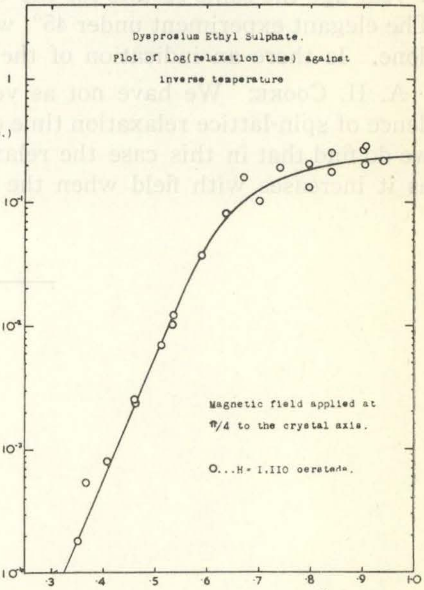

Figure 2. Variation of relaxation time with temperature when a magnetic field is applied at $\pi/4$ to the crystal axis.

increase with increasing magnetic field, as is to be expected for the two-phonon process. There is no evidence that the direct process is contributing appreciably in this case.

When the field was rotated by $\pi/4$ from the symmetry axis a marked change occurred in the variation of the relaxation time, as shown in Fig. 2. In low fields, the relaxation time showed the same behaviour as before, but in fields above 600 oersted an abrupt change in the temperature dependence occurred at $1/T=0.7$ and, for lower temperatures, a linear dependence of T_1 on $1/T$ was found. Further, T_1 became *shorter* as the field was increased. If we fit the measured relaxation time at the lowest temperature to our theoretical expression, we find for the contribution from the direct process

$$1/T_1=1.055\times10^{-11}\sin^2\theta\cos^2\theta H^4 T\,.$$

The numerical coefficient is remarkably close to the value 1.7×10^{-11} estimated by Orbach[10)]. Using the fitted value for the direct process and the expression previously given for the resonance process (corrected for the smaller component of field along the axis) we find at $H=1{,}110$ oersted and $\theta=\pi/4$,

$$1/T_1=1.8\times10^8\exp(-23/T)+4.25T\,.$$

This expression, which is shown as the continuous line in Fig. 2, fits the experimental points extremely well. We believe that this is an unequivocal experimental observation of the direct process.

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DISCUSSION

C. J. GORTER: van den Broek and van der Marel found in Leiden already more than a year ago the same results for the direction of the axis of dysprosium ethyl sulphate. The elegant experiment under 45°, which confirms Orbach's ideas so well, had not been done. Is there an indication of the experimental H^{-4} dependence of T_1 in large fields?

A. H. COOKE: We have not as yet made a quantitative investigation of the dependence of spin-lattice relaxation time on magnetic field for the direct process. However we do find that in this case the relaxation time diminishes as the field increases, whereas it increases with field when the Orbach process is dominant.