The shapes of the fluorescent and absorption lines in Fig. 2 are determined by acoustic phonons; optical phonons chiefly cause a repetition of the basic pattern as shown in Fig. 1. The $J=1$ state in absorption contains essentially all the oscillator strength and is lifetime broadened by spontaneous phonon emission to the $J=2$ state. In fluorescence, the $J=2$ state can decay in two ways: (1) directly (in a forbidden optical process), producing a sharp optical line, and (2) indirectly, by emitting (or absorbing) an acoustic phonon in a virtual transition to the $J=1$ state, followed by photon emission from the $J=1$ state. The energy of the photon is the energy of the direct transition minus (or plus) the phonon energy. The energy denominator for this second order transition is resonant for the absorption of acoustic phonons having energies near the $J=1$ to $J=2$ state splitting. With this model the shape of the entire emission spectrum of Fig. 2 at low temperatures (below 10°K) can be calculated in perturbation theory from the shape of the low-energy tail of the emission at one temperature and the measured constant width of the absorption line below 10°. These calculations give the theoretical curves of Fig. 2. (The assumption of weak coupling and the neglect of other phonon processes prevent precise agreement with experiment.) That the emission near the position of the $J=1$ symmetrical absorption line must be badly distorted when kT is comparable to the homogeneous linewidth of this state follows from thermodynamic arguments of detailed balance. If this linewidth were due to inhomogeneous effects, such distortion would not occur, as thermal quasi-equilibrium would not be attained.

The precise nature of the center is at present unknown. It seems clear, however, that it is either a compensated donor or acceptor. Annealing treatments in zinc vapor suggest that the center is associated with a stoichiometric defect.

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[1] R. E. Halsted and M. Aven, Bull. Am. Phys. Soc. 6, 312 (1961).

THERMAL RESISTANCE OF HOLMIUM ETHYL SULFATE*

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Recently, Morton and Rosenberg[1] reported the first observation of a change in the thermal conductivity of a paramagnetic salt with the application of an external magnetic field. It is the purpose of this Letter to examine their preliminary results for holmium ethyl sulfate in the light of the present theory of phonon-spin interactions in rare-earth salts, and to indicate some novel aspects of this problem which the theory predicts. We shall show that the peak in the thermal resistance-versus-magnetic field plot displayed in reference 1 is most likely not due to the attenuation of acoustic modes, but rather may be due to the attenuation of a low-level optical mode capable of carrying thermal currents. A second resistance-versus-field peak is predicted, which should fall at the fields predicted for acoustic phonons. Preliminary experimental results support this conclusion.

The thermal conductivity, κ, of a dielectric material is given by[2]

$$\kappa=\tfrac{1}{3}\sum_{\vec{f}s}C_{\vec{f}s}v_{\vec{f}s}\Lambda_{\vec{f}s}, \qquad (1)$$

where $\vec{f}$ represents the phonon wave vector; s is the polarization index;

$$C_{\vec{f}s}=[(\hbar\omega)^2/kT]\exp(\hbar\omega/kT)[\exp(\hbar\omega/kT)-1]^{-2},$$

the specific heat per phonon mode; $v_{\vec{f}s}$ is the phonon velocity; and $\Lambda_{\vec{f}s}$ is the phonon mean free path.

For a single phonon interacting with a two-level spin system, it has been shown[3] that

$$1/\Lambda_{\vec{f}s}=1/v_{\vec{f}s}\tau_{\vec{f}s}=(\pi\omega_{\vec{f}s}/\hbar M v_{\vec{f}s}^{3})$$
$$\times[\sum_m|\langle b|\sum_n V_n^{\,m}|a\rangle|^2]g(\omega_{\vec{f}s}-\omega_s)\Delta N_s, \qquad (2)$$

where $|a\rangle$ and $|b\rangle$ are the two spin states; $V_n^{\,m}$ is a phenomenological spin-phonon coupling constant[4]; and $g(\omega-\omega_s)$ is the spin-phonon line shape function,[5] equal, for a Lorentzian line, to $(T_2/\pi)\times[1+T_2^{\,2}(\omega-\omega_s)^2]^{-1}$. The spin frequency is $\omega_s=\delta_{ab}/\hbar$, δ_{ab} being the energy splitting between the two spin states, and $\Delta N_s=N_a-N_b$, the difference in population of the spin states. It is now straightforward to insert (2) into (1) and compute κ. For acoustic phonons in the Debye approximation, we find

$$\kappa = \frac{6\rho v k^4 T^3}{\pi^2 \hbar^2 g\beta (N/V)[\sum_m |\langle b|\sum_n V_n^m |a\rangle|^2] T_2} \times \frac{1}{H}\left\{\zeta(3) + \frac{T_2^2}{\hbar^2}\left[(g\beta H)^2\zeta(3) - 8kTg\beta H\zeta(4) + 20(kT)^2\zeta(5)\right]\right\}, \quad (3)$$

where there are N/V spins per unit volume, we have set $\delta_{ab} = g\beta H$, and $\zeta(x)$ is the Riemann zeta function. To estimate κ, we need values for the V_n^m and for T_2. For the former, we use the crystalline field extrapolation procedure of Powell and Orbach[6] and the very approximate dynamic coefficient expressions of Orbach,[4] to find

$$V_2^2 \sim V_4^2 \sim 120 \text{ cm}^{-1}; \quad V_4^4 \sim 30 \text{ cm}^{-1};$$
$$V_6^2 \sim 80 \text{ cm}^{-1}; \quad V_6^4 \sim 200 \text{ cm}^{-1}.$$

The sum of the squares of the matrix elements in (3) is evaluated using the ground doublet wave functions of Baker and Bleaney.[7] We find

$$\sum_m |\langle b|\sum_n V_n^m|a\rangle|^2 \sim (140 \text{ cm}^{-1})^2.$$

We estimate T_2 by computing the second moment[8] of the spin line using the g values for holmium ethyl sulfate given by Baker and Bleaney and by Grohmann et al.[9] ($g_\parallel = 15.4$, $g_\perp = 0$), and the lattice sums for the ethyl sulfates as given by Daniels.[10] We find $T_2 \sim 10^{-10}$ sec. Our result for the thermal resistance ($1/\kappa$) incorporating these estimates is shown in Fig. 1. Note that the thermal resistance is asymmetrical about the peak, and that the maximum occurs at $\delta_{ab} \cong 4.5\,kT$, as can also be seen by direct differentiation of (3). This relationship between the field for maximum thermal resistance and the temperature is a general one for a Debye acoustic phonon spectrum and indicates the maximum must move to higher fields as the temperature is raised. However, a glance at the curves exhibited by Morton and Rosenberg[1] shows that this is not the case for holmium ethyl sulfate. There is no significant shift of the thermal resistance maximum even though the temperature changes by a factor of ~3 on their plot.

A hint at a solution to this dilemma comes from the specific heat measurements of Meyer and Smith[11] on diamagnetic lanthanum ethyl sulfate. They show that C_v/T^3 below 1.5°K rises anomalously as the temperature falls, changing by a factor of ~2 in less than one degree. We used a smooth extrapolation of their higher temperature (2-3°K) data to subtract off the "normal" acoustic lattice specific heat from the total lattice specific heat. The resultant "excess" of C_v/T^3 is plotted against T on Fig. 2. We suggest that this part of the low-temperature lattice specific heat of the ethyl sulfates arises from part of an optical mode which lies at a very low energy Δ somewhere in the zone. We assume this energy Δ to be the energy associated with the peak in the thermal resistivity of Morton and Rosenberg, i.e., $\Delta/k \cong 3.4$°K. This value at first sight appears rather small. However, the ratio $k\theta_D/\Delta \sim 15$ may not be unreasonable for the ethyl sulfates because they do contain large organic molecules which may interact weakly with the waters of hydration and the paramagnetic ion. If we assume this explanation to be correct, then the excess specific heat due to the low-lying part of the optical mode must be of the form,

$$C_v = \alpha N k \left(\frac{\Delta}{kT}\right)^2 \frac{e^{\Delta/kT}}{(e^{\Delta/kT} - 1)^2}, \quad (4)$$

where α is the fraction of the zone occupied by the low-lying part of the optical mode. We fit (4) to Meyer and Smith's result at 2.132°K, and find α on the order of a percent. Using this value we

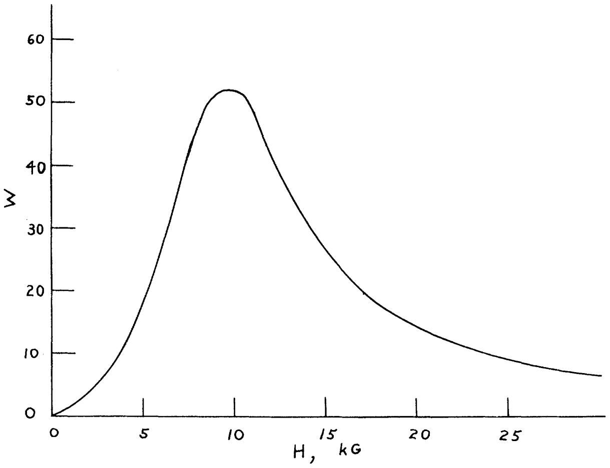

FIG. 1. The magnetic field dependence of the thermal resistance W due to acoustic phonon-spin interactions for holmium ethyl sulfate at $T = 2.2$°K. W is measured in watts^{-1} cm deg, H in kG, and a $g_\parallel$ value of 7.7 has been assumed.

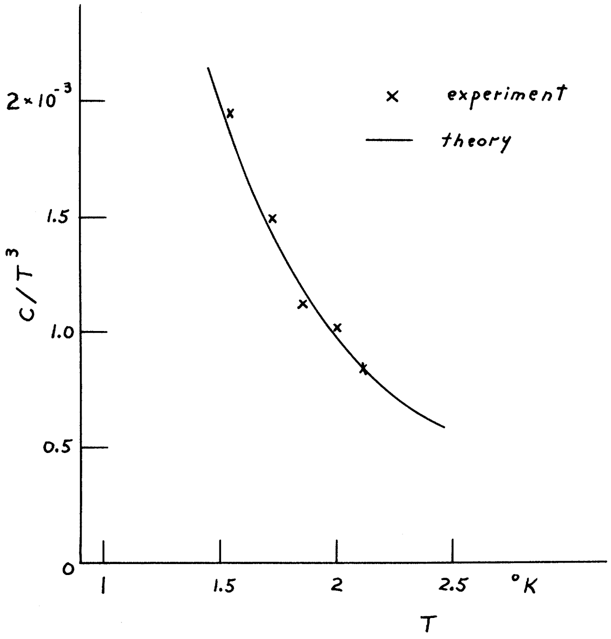

FIG. 2. The "anomalous" specific heat C_v/T^3 for lanthanum ethyl sulfate, plotted against T. The solid line is the computed C_v/T^3 for an optical mode with energy $3.4k$, and the crosses are Meyer and Smith's experimental points. The theoretical curve has been fitted at 2.132°K to the measured C_v/T^3.

then plot our calculated C_v/T^3 on Fig. 2, together with the experimental points. The excellent agreement with experiment is somewhat fortuitous as C_v was measured for lanthanum ethyl sulfate, and $\Delta/k \cong 3.4$°K refers to holmium ethyl sulfate. Nevertheless, the lattice specific heat would not be expected to change radically from one ethyl sulfate to another, so that the fit in Fig. 2 is at least a qualitative argument that our ideas are right.

Thus, we argue that the thermal resistance-versus-field peak displayed by Morton and Rosenberg is due to the scattering via phonon-spin interactions of a low-lying optical mode capable of carrying heat current (i.e., there must be some slope left) having an energy Δ of ~$3.4\,k$. The thermal conductivity would then no longer be given by (3), but instead would be just $\frac{1}{3}C_v v\Lambda$, where C_v is given in (4), and, for phonon-spin interactions,

$$\frac{1}{\Lambda}=\frac{1}{v\tau}=\frac{\pi(\Delta N_s/V)g(\Delta/\hbar-\omega_s)}{\rho v R^2\Delta}\sum_m|\langle b|\sum_n V_n{}^m|a\rangle|^2, \tag{5}$$

where R is of the order of the unit cell length. We can estimate κ for the optical mode in the absence of a field [where (5) vanishes] by using our computed values for C_v. We find at $T=1.7$°K, if we assume a velocity $v=10^5$ cm/sec, that $\kappa\sim4.3\,\Lambda$ watts/cm deg, where Λ is measured in cm. The observed value of κ, 4×10^{-3} watt/cm deg, is thus explained if there exists an intrinsic $\Lambda\sim10^{-3}$ cm, a figure which seems quite reasonable for water-of-hydration crystals. If now we tune the spin system so that $\hbar\omega_s=\Delta$, then for the constants appropriate to holmium ethyl sulfate Eq. (5) leads to a κ of the order of $4.1\times10^{-17}v^2$ watt/cm deg at $T=1.7$°K, where v is measured in cm/sec. For a reasonable choice of v, this leads to conductivities much smaller than those corresponding to the peak thermal resistances in Morton and Rosenberg's figures. Hence, the conduction properties of the optical modes must be completely quenched by the phonon-spin interaction at resonance, and what conductivity remains must be associated with the acoustic phonons which are carrying heat in parallel to the optical modes. Indeed, if we analyze the temperature variation of the peak thermal resistance, we find the following conductivities:

H (kG)	κ (milliwatts/cm deg)	T (°K)	κ/T^3
3.3	6.3	1.55	1.7
3.3	19	2.03	2.3
3.3	36	2.59	2.1

which go roughly at T^3. This is exactly what we should expect for acoustic phonons whose mean free path is limited by gross crystal imperfections, the usual scattering mechanism at very low temperatures.

Finally, there is yet another check on the theory which we have not yet applied. There must still exist another maximum in the thermal resistance-versus-magnetic field corresponding to the resonance scattering of the acoustic phonons, which will lie at $\delta_{ab}\cong4.5\,kT$, and which thus shifts as the temperature changes. It is, however, now expected to be smaller than the peak due to the optical modes, since the optical modes interact to order $(1/fR)^2$ more strongly with the paramagnetic ion than the acoustic modes, as can be seen by comparing (2) and (5). Very recent experiments of Morton and Rosenberg at higher magnetic fields have now confirmed this prediction and their preliminary results are shown in Fig. 3. Indeed, a second peak is found; its height is roughly that given by Eq. (3) (see Fig. 1), and its maximum does appear to shift to higher fields as the temperature is raised.

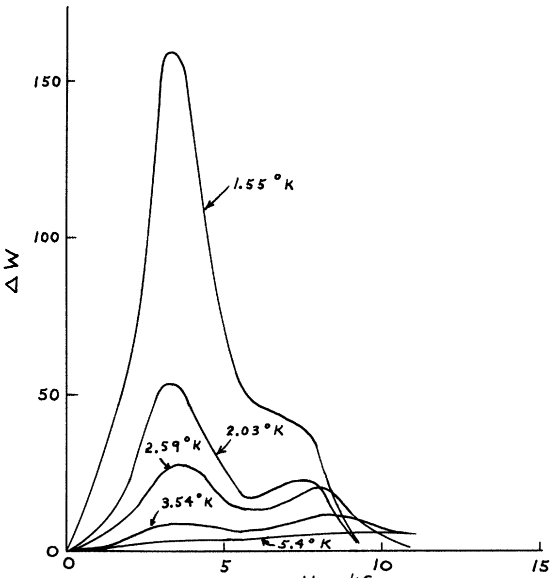

FIG. 3. A plot of the change in thermal resistance of holmium ethyl sulfate as a function of magnetic field, as recently found by Morton and Rosenberg (private communication). W is measured in watts^{-1} cm deg.

It must be emphasized that much of the experimental work quoted here is preliminary and that much remains to be done to check all the features of the theory. Nevertheless, we believe this analysis to show that paramagnetic ions via their interaction with the phonon system can shed much light on the phonon spectrum in a complicated crystal which might otherwise not be detectable. Indeed, this is closely analogous to a suggestion of Kittel[12] that phonon saturation of paramagnetic resonance lines be used as a detector of the level of high-frequency sound waves.

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[1] I. P. Morton and H. M. Rosenberg, Phys. Rev. Letters 8, 200 (1962).

[2] P. G. Klemens, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

[3] R. Orbach, thesis, University of California, 1960 (unpublished); copies are available from the University of California, Berkeley, California, upon request.

[4] R. Orbach, Proc. Roy. Soc. (London) A264, 458 (1961).

[5] R. Loudon, Phys. Rev. 119, 919 (1960).

[6] M. J. D. Powell and R. Orbach, Proc. Phys. Soc. (London) A78, 753 (1961).

[7] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) A245, 156 (1958).

[8] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[9] I. Grohmann, K. H. Hellwege, and H. G. Kahle, Z. Physik 47, 277 (1960).

[10] J. M. Daniels, Proc. Phys. Soc. (London) A66, 673 (1953).

[11] H. Meyer and P. L. Smith, J. Phys. Chem. Solids 9, 285 (1959).

[12] C. Kittel, Phys. Rev. Letters 1, 5 (1958).