where

$$F_{jj'}^{(n)}(\hat{q})=(n!)^{-1}\sum_{k\alpha;\,k'\beta} w_{k\alpha}{}^{0}(j)C_{\alpha\beta}{}^{(n)}(kk';\mathbf{q})\times w_{k'\beta}{}^{0}(j'). \quad \text{(A10)}$$

Equation (9) is the familiar eigenvalue problem with solutions given by

$$|[\omega_0{}^2(j)-\omega^2(j\mathbf{q})]\delta_{jj'}+[q^2F_{jj'}{}^{(2)}(\hat{q})+q^4F_{jj'}{}^{(4)}(\hat{q})+\cdots]|=0, \quad \text{(A11)}$$

where use has been made of the fact that

$$F_{jj'}{}^{0}(\hat{q})=\omega^2(j,\,q=0)\delta_{jj'}\equiv\omega_0{}^2(j)\delta_{jj'}. \quad \text{(A12)}$$

The acoustic eigenvectors at $q=0$ consist of the uniform translations

$$w_{k\alpha}{}^{0}(j_a)=m_k{}^{1/2}v_\alpha(j_a)\,, \quad \text{(A13)}$$

where $\mathbf{v}(j_a)$ is an arbitrary vector. There are thus three linearly independent eigenvectors $\mathbf{w}_k{}^0(j_a)$ with eigenfrequencies $\omega_0{}^2(j_a)=0$. The $\mathbf{w}_k{}^0(j_a)$ can be completely defined by requiring in addition to $\mathbf{w}^0(j_a)\cdot\mathbf{w}^0(j_a')=\delta_{j_a,j_a'}$ [Eq. (A7)], that $F_{j_a,j_a'}{}^{(2)}=0$ if $j_a\neq j_a'$. If there are other degeneracies in the optic branches at $q=0$ any arbitrariness in the eigenvectors $\mathbf{w}^0(j_0)$ can also be removed by requiring within the degenerate set that $F_{j_0,j_0'}{}^{(2)}=0$ for $j_0\neq j_0'$.

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Effect of the Spin-Phonon Interaction on the Thermal Conductivity

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The effect of dilute concentration of the Kramers ion, Yb^{+++}, and the non-Kramers ion, Ni^{++}, on the thermal conductivity of CaF_2 has been measured as a function of magnetic field at various temperatures in the range 0.3–1.3°K. The results have been compared with a theory due to Elliott and Parkinson based on the Jacobsen and Stevens dispersion relations. It has been found that it is possible to account for the effect of temperature on the change in conductivity with magnetic field in both cases, for fields such that $g\beta H/kT<6$. If the temperature dependence is factored out of the expression for the change in conductivity, the remaining terms predict that at low fields it should increase as $H^{7/2}$ for the Kramers ions, and as $H^{5/2}$ for the non-Kramers ions, unless a zero-field splitting is present which dominates, and then the change in conductivity should increase as H^3 increases. The Yb-doped crystal yielded an $H^{7/2}$, and the Ni-doped yielded an H^3 dependence in agreement with the theory.

INTRODUCTION

THE first data on the thermal conductivity of a system for which the spin-phonon interaction is important were obtained by Morton *et al.*[1] for holmium ethylsulphate. The characteristic behavior of these systems lies in the variation of the conductivity K with magnetic field at fixed temperature. Typically, K is expected to first decrease with field, then reach a minimum, and recover finally to a value equal to the zero-field value if the magnetic ion obeys Kramers's rule, or an amount greater than this for the non-Kramers ions.

Qualitatively, this behavior is readily understood in terms of a strong interaction between the spins and a band of phonons whose frequencies are close to the Larmor frequency of the spin system (see Fig. 1); at low temperatures, the phonon carrier distribution is a function which has a maximum. The interaction suppresses the contribution of those carriers close to the Larmor frequency (see Fig. 2). As the field is increased, more important carriers are affected until the peak in the distribution is reached, after this the interaction occurs at less important frequencies until at very high fields the interaction is with phonons whose contribution is negligible.

Because the spin-phonon interaction affects the conductivity by suppressing a relatively narrow band of phonon frequencies, the variation of thermal conductivity with magnetic field forms a convenient phonon spectrometer,[2,3] which has been used[4] to study the resonant scattering by the Li ion in KCl. For this reason, it is important to understand in some detail how the spin-phonon interaction modifies the conductivity.

For those ions which do not obey Kramers's rule, an interaction is possible at zero magnetic field, which is removed at very high fields and, as McClintock *et al.*[5]

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* Research supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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[3] D. Walton, Phys. Rev. **151**, A267 (1966).

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[5] P. V. E. McClintock, I. P. Morton, and H. M. Rosenberg, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and the Physical Society, London, England, 1965), p. 455.

first demonstrated, the high-field conductivity can be considerably better than that at zero field. At low temperatures, this fact has rather important consequences because the interaction usually occurs with a band of low-frequency phonons. Some ions of this class are extremely strongly coupled; it has been found that as little as ~0.1 part per million of Fe^{++} in MgO can lead to a reduction in conductivity at 1°K of about 10%.

It has also been found that the high-field conductivity can be greater than the zero-field value even if the magnetic ions obey Kramers's rule. Briefly, this is due to a diminished velocity of sound over the greater part of the phonon spectrum, which is caused by the spin-phonon interaction (see Fig. 1). At high fields, the slope of the lower branch is reduced considerably.

The Kramers ions are simpler in principle because no interactions are possible through an electric field, which lead to a zero-field effect. In practice, however, at large concentrations dipole and/or exchange interaction can be expected to lead to internal magnetic fields with the same result. Nevertheless, in a crystal with a sufficiently small concentration of magnetic ions, it should be possible to neglect any zero-field effect of the spin system on K. The effect due to the change in velocity of sound is usually small.

Unfortunately, the Kramers ions are usually weakly coupled to the lattice; typical spin-lattice relaxation times are of the order of a second at 1°K. To be useful at concentrations for interionic interactions to be negligible ($\ll 0.1\%$), the coupling has to be somewhat larger, i.e., leading to a relaxation time of the order of 10^{-3} sec or less at 1°K.

At the time of writing, most of the quantitative comparisons between theory and experiment have been for the non-Kramers ions.[6,7] Some success using a simplified model has been achieved by Brock and Huntley[8] for a concentrated Kramers's system. Some of their results, however, are difficult to understand, which suggests that the situation is considerably more complex than they assume. The most successful work is that of McClintock *et al.*[7] again on holmium ethylsulphate. Unfortunately, this is far from a simple system, and the large number of adjustable parameters necessary for the comparison make it difficult to make generalizations on the basis of their results.

Theoretically, the problem has received a good deal of attention. The approaches fall into two classes. The first group treats the problem from the scattering point of view, computing the scattering cross section for a single spin, summing the contributions of all spins, and calculating the thermal conductivity in the conventional way. Using this viewpoint, Orbach[9] discussed the experimental results of Morton and Rosenberg,[1] and this approach was employed in treating the more detailed measurements of McClintock *et al.*[7] Huber[10] emphasized the difficulties introduced by the unknown spin-phonon line-shape function.

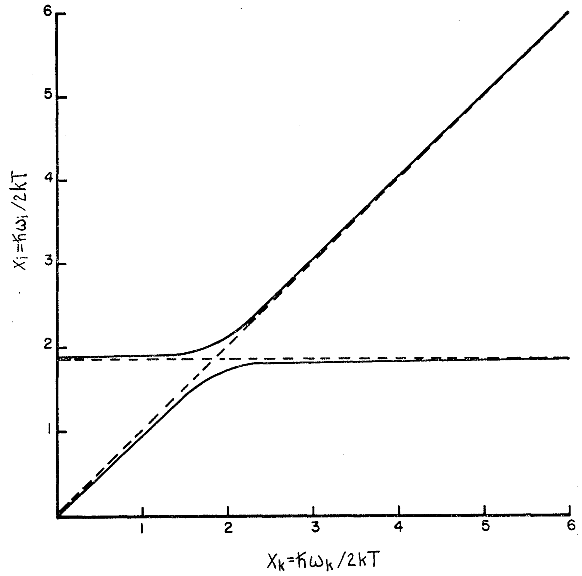

FIG. 1. Calculated dispersion relations for a crystal containing paramagnetic ions, assuming $\epsilon^2=0.033$, and $g\beta H/2kT=1.8$.

An alternative is to treat the spin system and lattice together, following Jacobsen and Stevens.[11] The effect of

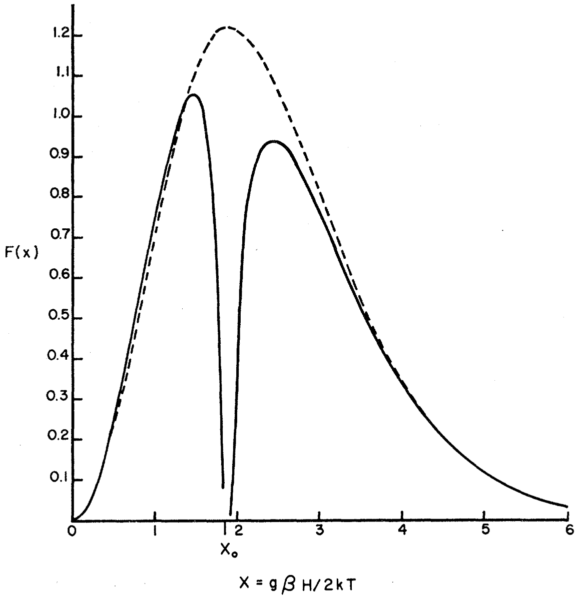

FIG. 2. Calculated values of the integrand in Eq. (6) using the dispersion relation shown in Fig. 1. The dashed line is the same function with no spin-phonon interaction.

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the spin-phonon coupling is then included in the normal modes. The important result is that an effective gap appears in the phonon spectrum near the Larmor frequency; carriers that originally contributed to the conduction are missing. The renormalization of the normal-mode frequencies has shifted their contribution to other frequencies (see Figs. 1 and 2). A conventional computation[12] of the thermal conductivlty reveals that it is less than it would have been in the absence of the interaction. This approach is preferable in concentrated systems where multiple scattering would have to be included in a scattering calculation. Of course, if the wavelength of the important phonons is greater than the mean separation between the spins, a scattering calculation becomes questionable. In the present case, the highest frequency of interest is about 2×10^{11} Hz, corresponding to a phonon wavelength of approximately 200 Å. This is about equal to the separation between paramagnetic ions, but the coupled-mode approach is probably safer. Finally, it should be emphasized that this latter point of view avoids the difficulties introduced by ignorance of the precise line-shape function inherent in a scattering calculation.

A theoretical calculation of the thermal conductivity using the modification of the phonon spectrum has been accomplished by Muller and Tucker.[13] However, a later treatment by Elliott and Parkinson[14] is more complete and will be followed here.

The objective of this work, which has only been partially achieved, is to compare theory and experiment for a simple system. The theory refers to ions of effective spin $\frac{1}{2}$. This does not mean, of course, that the real spin is $\frac{1}{2}$, it simply requires that a doublet, well separated from other levels, be the ground state of the spin system. A simplification is introduced, if the direct interaction between the spins is negligible. This, of course, is best fulfilled in a dilute system. While the theory to be used here was formulated for the concentrated case, it should apply just as well to the dilute case, if the concentration of magnetic ions is included in the expectation value of S_z.[14] The desired system should have a strong enough lattice interaction that a measurable effect is present at small concentrations. This was found to be the most difficult requirement to meet for the Kramers ions, since they are generally weakly coupled, i.e., their spin-lattice relaxation times at 1°K are typically 1 sec or longer.

The Kramers system chosen was the Yb^{+++} ion in CaF_2. The majority of the magnetic ions are in cubic sites with most of the remainder in sites of tetragonal symmetry.[15] While the g value for the cubic sites is isotropic, that for the tetragonal ones is not. However, in the [111] directions, the g value for all the tetragonal sites becomes equal and is close enough to that for the cubic that the difference is less than the resolution of this technique. In this way, the effect of the anisotropy can be minimized.

The rare-earth Kramers ions in CaF_2 display fast relaxation times.[16] However, it appears likely that these are not the intrinsic times but are the result of cross relaxation.[16] In fact, recent measurements on Tm by Sabisky and Anderson reveal that the intrinsic times are of the order of seconds at 1°K.[17] Since Tm is isoelectronic with Yb, it seems likely that the intrinsic times for Yb will also be of this order.[18] The result of cross relaxation will be to complicate the interaction in at least two ways: (a) The spin damping due to the direct process is no longer directly related to the coupling constant and (b) additional levels may appear which couple to phonons of different energy, and the coupling can occur at more than one frequency.

Since Kramers's theorem forces the spin-lattice coupling to be so small, it is difficult to find a large enough effect (i.e., $\sim10\%$ change in thermal conductivity) at sufficiently small concentrations for the effects of interionic interactions to be neglected.

For the non-Kramers ion, Ni^{++} was chosen. Paramagnetic resonance due to Ni^{++} in CaF_2 has been observed by Zaripov *et al.*[19] at 77°K. They observed a $\Delta m=2$ transition with symmetry axes directed along the C_3 axes with $g_{\parallel}=5.2$ and $g_{\perp}=0$. The ground state of Ni^{++} in CaF_2 is an orbital singlet which splits into a doublet and a singlet. If the singlet is lowest, it is questionable whether or not the doublet responsible for the observed transition is populated at He^3 temperatures. However, a resonance similar to that observed by Zaripov *et al.* has been observed at ~1°K.[20] No resonances were observed corresponding to the $\Delta m=1$ transitions between the singlet and the doublet levels, although these should be considerably stronger than the $\Delta m=2$ transition observed.

The unique advantage of this system, of course, lies in the fact that it appears that only one transition need be considered. Since phonons couple with about equal strength to both the $\Delta m=2$ and $\Delta m=1$ transitions, the thermal conductivities of crystals containing non-Kramers ions normally reveal the effect of two transitions.[7]

Finally, for the purpose of simplifying the effect of phonon scattering and minimizing the effect of normal processes, the experiments were conducted at ^3He temperatures.

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THEORETICAL BACKGROUND

The Hamiltonian for the crystal can be written as the sum of three contributions, one from the phonons, another from the spins, and a third due to the spin-phonon interaction. It can be diagonalized with the result that the frequencies of the normal modes for the system can be obtained from the following expression, due to Elliott and Parkinson[14]:

$$(\omega^2-\omega_0^2)(\omega^2-\omega_k^2)-\omega^2\omega_0^2\epsilon^2\sigma=0\,, \tag{1}$$

where $\omega_0=g\beta H$ is the Larmor frequency, $\omega_k=V_0k$ is the unperturbed phonon frequency, and V_0 is the velocity of sound. ϵ^2 is the spin-phonon coupling constant, which is proportional to ω_0 for Kramers ions and inversely proportional to ω_0 for non-Kramers ions.

The expectation value of the z component of spin is σ, and in a dilute system it is multiplied by the fraction of occupied unit cells.[14]

The solutions to this expression are sketched in Fig. 1, and consist of two branches corresponding to the two possible solutions for each unperturbed phonon frequency.

The thermal conductivity can be obtained in the conventional way by summing the contributions of each of the normal modes.

The starting point is the expression for the thermal conductivity obtained from a Boltzmann equation[12]:

$$K=\sum\nolimits_k v(k)\Lambda(k)\hbar\omega(k)\frac{\partial N(k)}{\partial T}\,, \tag{2}$$

where $v(k)$ is the group velocity, $N(k)$ is the distribution function for the carriers, and $\Lambda(k)$ is the mean free path of carriers of wave vector k. If $\omega(k)$ is independent of temperature, $\hbar\omega(k)[\partial N(k)/\partial T]$ will just be the specific heat. Here, $\omega(k)$ depends on temperature and the more general expression must be employed. In a magnetic field, these three quantities will generally depend on k in a complicated way because of the modification of the dispersion relations by the spin-phonon coupling. It will be assumed that this coupling exists for the transverse as well as the longitudinal branches of the phonon spectrum, the only difference between them being the magnitude of the coupling constant so that the contributions are additive.

Transforming the sum to an integral, assuming isotropy, and averaging over all the angles between k and the heat-flow direction, Eq. (2) becomes, for each branch,

$$K_H=\frac{1}{6\pi^2}\int_0^{\omega m}\left[\hbar\omega\frac{\partial N(\omega)}{\partial T}\right]\Lambda(\omega)k^2(\omega)d\omega\,. \tag{3}$$

The distribution function may be computed from Elliott and Parkinson's expression for the energy,

$$U_i(k)/\hbar=\tfrac{1}{2}f_p{}^i\omega_i(k)\coth[\tfrac{1}{2}\beta\omega_i(k)]+f_s{}^i\left\{\frac{(\sigma-1-\epsilon^2\sigma)\omega_0{}^2+(\sigma+1)\omega_i(k)^2}{4\omega_i(k)}\times\coth[\tfrac{1}{2}\beta\omega_i(k)]-\tfrac{1}{2}(1+\sigma)\omega_0\right\}\,, \tag{4}$$

where $f_p{}^i$ and $f_s{}^i$ are quantities which measure the phonon and spin character of the mode.

For dilute systems $\sigma\ll1$, as discussed previously, and the contribution of the second term can be shown to be of order $\epsilon^2\sigma$ less than that of the first.

Subtracting the zero-point energy, it is found that to order $\epsilon^2\sigma$,

$$\frac{\partial N(\omega)}{\partial T}\cong f_p{}^i\frac{\partial}{\partial T}\coth x_i\,,$$

where

$$x_i=\tfrac{1}{2}\beta\omega_i\,.$$

The mean free path, again following Elliott and Parkinson, is given by

$$\Lambda^i(k)=v_i(k)/\gamma_i(k)\,,$$

where $\gamma_i(k)$ is the total damping of the mode. This will be the sum of the contributions of the boundaries and those processes which damp the phonon and spin part of the modes.

$$\gamma_i(k)=v_i(k)L^{-1}+f_p{}^i\gamma_p+f_s{}^i\gamma_s\,. \tag{5}$$

Therefore,

$$K_H=\frac{1}{6\pi^2}\int_0^{\omega n}\hbar\omega_i\left[\tfrac{1}{2}f_p{}^i\frac{\partial}{\partial T}(\coth x_i)\right]\times\frac{v_i(k)k^2(\omega_i)d\omega_i}{v_i(k)L^{-1}+f_p{}^i\gamma_p+f_s{}^i\gamma_s}\,. \tag{6}$$

As Elliott and Parkinson have observed, ω_i is a function of T, and this complicates the computation of the derivative in (6). However, the temperature dependence of ω_i occurs through the quantity $\epsilon^2\sigma$ in Eq. (1). For the dilute systems considered here, $\epsilon^2\sigma$ is small compared with unity and the dependence of ω_i on temperature may be safely neglected. With this approximation, and using (Ref. 21)

$$v_i=v_0f_p{}^i\omega_i/\omega_k\,, \tag{7}$$

$$K_H=\frac{k_B}{6\pi^2v_0}\int_0^{\omega m}\frac{f_p{}^ix_i{}^2\operatorname{csch}^2x_i\omega_k{}^2d\omega_i}{[v_0L^{-1}+(\omega_i/\omega_k)\gamma_p][1+\alpha f_s{}^i/f_p{}^i]}\,, \tag{8}$$

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[21] It should be noted that v_i for $\omega_i\to0$ and $k\to0$ is $v_0\omega_i/\omega_k$ but $\omega_i/\omega_k\to(1+\epsilon^2\sigma)^{-1/2}\simeq1-\frac{1}{2}\epsilon^2\sigma$. Thus, the effect of the dispersion introduced by the spin-phonon interaction is felt over the whole phonon spectrum. For the Kramer ions, ϵ^2 is proportional to the magnetic field, thus, at very high fields the conductivity at low temperatures should be larger than at zero field.

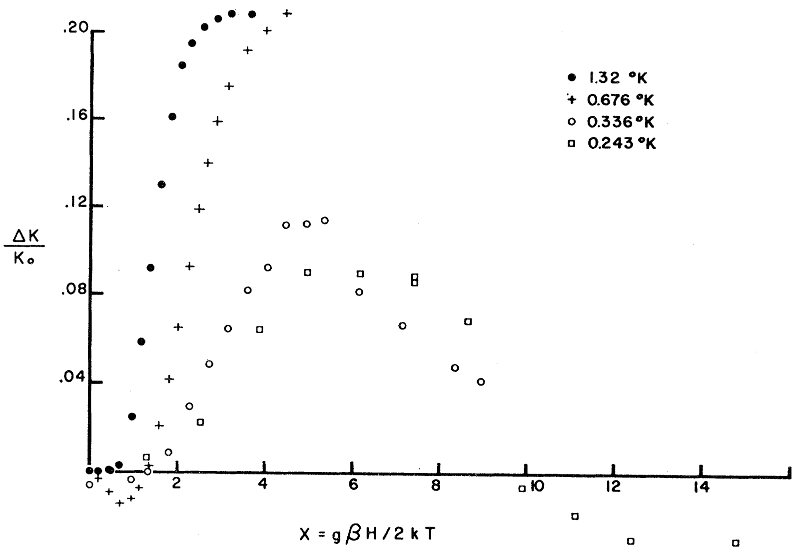

FIG. 3. The change in conductivity with magnetic field for $CaF_2+0.025\%$ Yb^{+++} plotted against $x_0=g\beta H/2kT$ with $g=3.45$.

where

$$\alpha=\frac{(\omega_i/\omega_k)\gamma_s}{v_0L^{-1}+(\omega_i/\omega_k)\gamma_p}.$$

The integration is to be performed separately for each of the two branches. However, the lower branch has values of ω only between 0 and ω_0, and the higher branch from $\omega_0(1+\epsilon^2\sigma)$ to ω_m. Thus, it is possible to simply allow ω to go from 0 to ω_m, and the contributions of both branches will be included in a single integral. In doing this, a contribution of order $(\epsilon^2\sigma)^2$ has been neglected, which comes from integrating between ω_0 and $\omega_0(1+\epsilon^2\sigma)$.

If the difference between ω_i and ω_k is neglected, it can be seen that the integrand in Eq. (6) is the expression for the phonon conductivity (i.e., the conductivity in the absence of the spin-phonon interaction) multiplied by $f_p{}^i/(1+\alpha f_s{}^i/f_p{}^i)$. If the phonon conductivity is subtracted, an expression for the change in conductivity due to the spin-phonon interaction may be obtained. Thus, on substituting Elliott and Parkinson's expressions for

$$f_s{}^i=(\omega_i^2-\omega_k^2)/(\omega_i^2-\omega_j^2),$$
$$f_p{}^i=[\omega_i^2-\omega_0^2(1+\epsilon^2\sigma)]/(\omega_i^2-\omega_j^2)$$

and neglecting quantities in $(\epsilon^2\sigma)^2$ compared with $(\epsilon^2\sigma)$, the change in conductivity is

$$\Delta K=\frac{k_B}{6\pi^2v_0}\int_0^{\omega_m}\frac{\omega^3x^3\,\mathrm{csch}^2x\,x_0^2(1+\alpha)\epsilon^2\sigma dx}{(v_0L^{-1}+\gamma_p)[(x^2-x_1^2)^2+\Gamma^2]},\qquad(9)$$

where

$$x_1=(\tfrac{1}{2}\hbar\omega_0/2kT)(1-\tfrac{1}{2}\alpha\epsilon^2\sigma)=x_0(1-\tfrac{1}{2}\alpha\epsilon^2\sigma)$$

and

$$\Gamma=x_0^2(1+\alpha)\epsilon^2\sigma.$$

The major contribution to Δk comes from values of x close to x_1, and this fact can be exploited to obtain an analytic form for Δk; if $\epsilon^2\sigma$ is small, then the change in α and $\omega^2(1+\alpha)\epsilon^2\sigma/(v_0L^{-1}+\gamma_p)$ over the important range of values for x will be small. Thus, the change may be approximated by

$$\Delta K=\frac{k_B(1+\alpha)\epsilon^2\sigma\omega_0^3x_0}{6\pi^2v_0(v_0L^{-1}+\gamma_p)}\int_0^{\infty}\frac{x^4\,\mathrm{csch}^2xdx}{(x^2-x_1^2)^2+\Gamma^2}.\qquad(10)$$

The integral may be evaluated by contour integration, and the final result is, letting $x_1=x_0$,

$$\Delta K=\frac{k_B(1+\alpha)^{1/2}\epsilon\sigma^{1/2}\omega_0^3}{12v_0(v_0L^{-1}+\gamma_p)}\left(\frac{x_0^2}{\sinh^2x_0}\right).\qquad(11)$$

This displays the important result that to a first approximation the phonon scattering function multiplied by the carrier distribution function is being scanned, as the magnetic field is varied, with a resolution of $\tfrac{1}{2}[(1+\alpha)\epsilon^2\sigma]^{1/2}$.

It should be observed that this procedure depends for its validity on the fact that the main contribution to the integral comes from the region about x_0. At large values of x_0 this contribution is diminished by csch^2x_0, i.e., $\mathrm{csch}^2x_0/(1+\alpha)\epsilon^2\sigma$. As long as this is large compared to the contribution to the integral from other values of x, far from x_0, the procedure outlined here is valid. As a very crude rule of thumb, this can be compared with the value of the integrand at $x=x_0/\sqrt{2}$, which is $\mathrm{csch}^2(x_0/\sqrt{2})$, i.e., $\mathrm{csch}^2x_0/(1+\alpha)\epsilon^2\sigma\gg\mathrm{csch}^2(x_0/\sqrt{2})$.

For a typical value of $(1+\alpha)\epsilon^2\sigma$ of say 10^{-2} (which would amount to a half-width for the Lorentzian of $10^{-1}x_0$), this would limit the approximate procedure outlined here to values of x_0 less than about 4 or 5. In any case, the contribution of phonons for which x is 4 (i.e., $\hbar\omega=8kT$) is sufficiently small to be uninteresting. Nevertheless, Δk may still be appreciable at values of x_0 larger than this because the contribution of the tails of the Lorentzian-like term become important.

The term $(1+\alpha)$ clearly demonstrates that there will be a nonzero effect in the absence of any spin damping, i.e., when $\alpha=0$. Since the spin-lattice contribution to the total damping is proportional to H^4 for the Kramers ions, it is expected that at low fields α will reflect the magnitude of the spin-spin contribution T_2. This T_2, however, refers to scattering by fluctuations in the spin system.[14] If the frequencies are low enough for the phonon damping to be solely due to the boundaries, a simple size-effect experiment determines the magnitude of $(1+\alpha)$, and hence T_2. Δk as a function of field is determined for a single crystal of relatively large cross section, then a thin slice is cut from the crystal and the experiment repeated. The values of Δk at low fields should be in the ratio of the crystal widths multiplied by $(1+\alpha)^{1/2}$.

EXPERIMENTAL DETAILS

The thermal conductivity was measured in the conventional potentiometric fashion in a ^{3}He cryostat capable of attaining 0.2°K.[22] The magnetic field was provided by a superconducting solenoid, and the field direction was parallel to the heat-flow direction.

The specimen used to investigate the effect of the Kramers ions was a single crystal of CaF_2 with 0.025 mole% Yb^{+++}, oriented such that the heat flow and magnetic field were parallel to the [111] direction. Initially, it was of square cross section, approximately 0.5 cm on the side. After a series of measurements were obtained on this sample, a thin slice was then cut from it and used for the bulk of the work. A single crystal of CaF_2 with 0.05% Ni^{++}, oriented with a [100] direction parallel to the heat flow and magnetic field, was used to obtain the data on the non-Kramers ions. Analysis of both specimens revealed no other paramagnetic impurities present in large enough concentrations to be of any importance.

Temperatures were obtained from Speer carbon resistors whose nominal room-temperature resistance was 510 Ω. These were calibrated against the vapor pressure of ^{3}He, and the susceptibility of iron ammonium alum. Instead of using the Clement Quinnel equation, the following expression which gives significantly better results has been used as an interpolation formula[23]:

$$1/T=A+BR+CR^{1/2}.$$

The resistors were located about 5 cm above the magnet and supported by lengths of No. 14 copper wire attached to the thermometer clamps on the crystal. This minimized magnetoresistance effects. By judiciously adjusting the position of the two resistors in the residual field at the top of the magnet, magnetoresistance effects could be reduced to an undetectable level. There was, however, a small error introduced by the magnetoresistance of the crystal heater which was located in the main magnetic field.

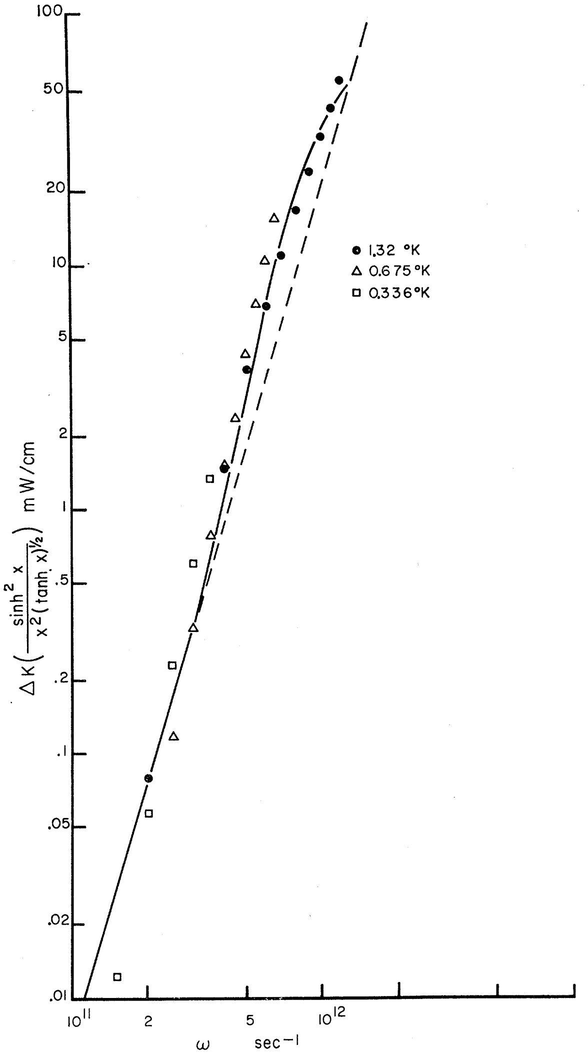

FIG. 4. The reduced change in conductivity as a function of phonon frequency for $CaF_2+0.025\%$ Yb^{+++}.

For this reason, and due to the unfortunately long time it took to sweep the magnetic field with the solenoid used, which prevented the effect of long term drifts from being eliminated, the over-all accuracy was limited to about 1% of the thermal conductivity. The relative accuracy of any two successive measurements is, however, much better than this.

RESULTS AND DISCUSSION

The results are shown in Figs. 3 and 4. In analyzing the experimental data it will be assumed that the coupling constant responsible for the direct-process spin-lattice relaxation time is the same as the one responsible for the effect on the conductivity, i.e., the simplification

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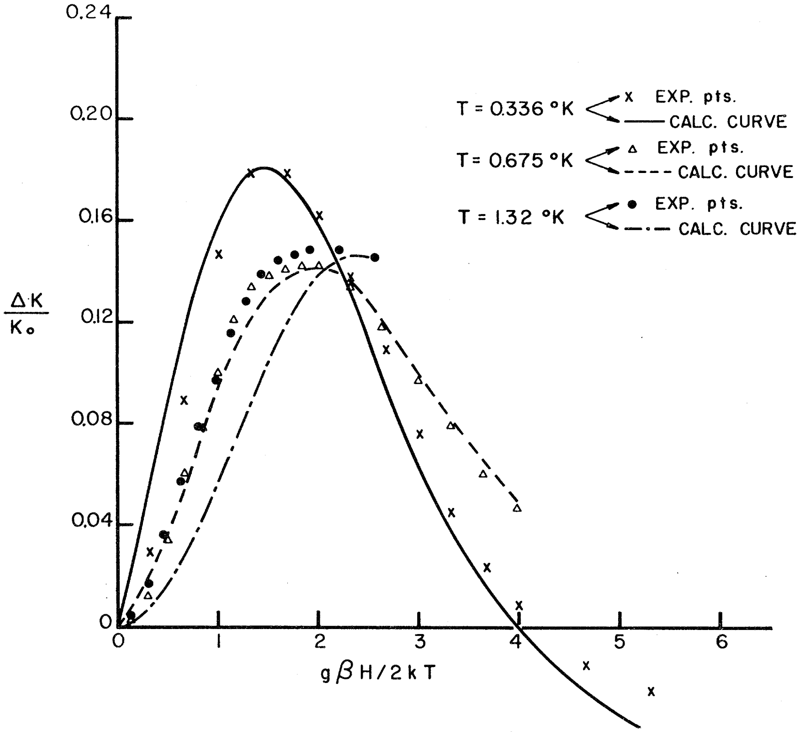

FIG. 5. The change in conductivity with magnetic field for CaF$_2$+0.05% Ni^{++}. The lines are calculated from Eq. (8).

will be made that the only effect of cross relaxation will be to increase the effective coupling constant.

In the scattering picture, this is easily justified; a phonon is absorbed or emitted at the center with the strongest coupling. As long as the time for cross relaxation is short compared with the spin-lattice time, all the spins linked by cross-relaxation should effectively be linked to the lattice through the strongly coupled center.

From Eq. (11), we note that all the temperature dependence of ΔK should be contained in the term $x_0^2 \tanh^{1/2}x_0/\sinh^2 x_0$. Thus, the results have been divided by this quantity and replotted in Fig. 4. The results for values of $x_0 > 3$ were not used, since the approximation involved in deriving (11) is invalid for large x_0.

If boundary scattering is the only damping mechanism, Eq. (11) predicts a $\omega_0^{7/2}$ dependence for ΔK $(\sinh^2 x_0/x_0^2)$. Figure 4 reveals that this is approximately true. If the effects of all damping other than boundary scattering are ignored, the only parameter in Eq. (11) is ϵ, since the velocity of sound is known. It is possible to obtain a value for the spin-lattice coupling constant from the data of Bierig *et al.*[16] It is interesting that this value agrees well with a coupling constant deduced from our data. This provides, at least, a phenomenological justification for including the cross relaxation effects in an increased coupling constant.

Our neglect of spin damping, at least at low frequencies, is borne out by a size-effect experiment; a slice was cut from the crystal changing its thickness from 6 to 0.77 mm which changed ΔK by a factor of 7. This implies that α is small at low frequencies. From Eq. (11), ΔK is proportional to the crystal thickness in the boundary scattering limit. We observe that since α is small, this implies that the damping due to spin-spin relaxation T_2 is small compared with that due to boundary scattering. This may not seem to be entirely reasonable at first sight, since accepted values for T_2 are usually an order of magnitude or more faster than τ for boundary scattering. It should be emphasized, therefore, that this T_2 refers to the scattering by fluctuations in the spin system.[14]

At this point, moderately satisfactory agreement has been obtained between theory and experiment. It is clear, however, that the neglect of spin damping is not justified at the higher frequencies. It is possible to include this without introducing any additional parameters by using Elliott and Parkinson's expression for the spin-lattice relaxation time, but this will result in an $\omega_0^{11/2}$ dependence at high frequencies. Better agreement results if a Rayleigh law for phonon scattering is also introduced; the solid line in Fig. 4 then is the result of including the direct process damping for the spins, and a Rayleigh term $b\,\omega_0^4$ for the phonons where $b = 3\times10^{-41}$. There is no justification for doing this if the relaxation occurs via exchange-coupled pairs. It would be expected that the ϵ for the damping corresponds to the coupling of the pairs, whereas the ϵ leading to the coupled modes should correspond to the single ions. However, in keeping with the simplified approach used here these have been considered to be equal.

Finally, two features of the experimental data are incompletely understood. The first is the unusually large value of x_0 at which $\Delta K/K_0$ reaches its peak, namely, 5–6 at the lowest temperature. The maximum in the function $x_0^n/\sinh^2 x_0$ occurs at $x_0=n/2$, thus the anticipated position of the maximum is at $2.75 \leq x_0 \leq 3.75$. The second feature is the initial improvement of K with field as the field is first turned on. These effects may be understood if the interaction between the spins, which is undoubtedly present in our crystals, is taken into account explicitly. The large value of x_0 at which the maximum in $\Delta K/K_0$ occurs can be caused by transitions to additional levels in the spectrum of exchange-coupled pairs.

If there are effective internal fields due to interactions between ions these will be random at zero field because of the random orientation of the dipoles. The internal field then would vary between zero and that due to the strongest possible interaction at different sites. The effect would be to suppress the contributions of all phonons whose frequency is less than the Larmor frequency corresponding to the maximum possible field. When a magnetic field is applied which is great enough to orient most of the dipoles along the field direction the interaction will only be with phonons at a single Larmor frequency, and fewer carriers will be suppressed. Thus, the conductivity should improve until $g\beta H/kT \sim 1$, which agrees with the observed behavior.

If internal fields are responsible, then at very high external magnetic fields the unperturbed phonon conductivity should be better than that at zero field. This is, in fact, observed at the lowest temperature investigated; the high-field conductivity is 3% better than the zero-field conductivity. (However, because of the large differences in magnetic field at which the measurements were made, the accuracy is only a little better than the 3% change observed.)

A change in K of this magnitude would require an internal field of the order of a few kOe. At a concentration of 0.025%, dipole interactions cannot possibly lead to internal fields that are this large unless some clustering is present.

However, it is also possible that the improvement in conductivity is caused by an increase in the number of carriers available for thermal transport at high fields, as discussed in the Introduction and Theoretical Background sections of this paper.

Ni^{++}

The results are shown in Figs. 5 and 6. Since this ion is not a Kramers ion, some spin-phonon interaction is expected at zero field. If this is due to static strains, the shift in the Larmor frequency is directly proportional to the strain. Thus, if this shift is ω_s, then $\omega_0 = g\beta H/h + \omega_s$. Elliott and Parkinson include the effect of a zero-field splitting by taking $\omega_0 = [(g\beta H/h)^2 + \omega_s^2]^{1/2}$, however, this cannot be used if the zero-field splitting is due to internal strain. In fact spin-lattice coupling constants are measured directly by observing the shift in resonant frequency with stress. In the analysis of our results, ω_s was obtained as follows: It can be seen from Fig. 5 that the minimum in the conductivity occurs at a lower value of $x = g\beta H/2kT$ at the lower temperatures. In the boundary scattering limit, the minimum should be independent of temperature, and if other sources of phonon scattering are present, the frequencies should move to higher values of x_1 as the temperature decreases. The zero-field spin-phonon coupling, however, will lead to an observed decrease in the value of $g\beta H/2kT$ for minimum conductivity. Ignoring all sources of phonon scattering except the boundaries, the minimum should

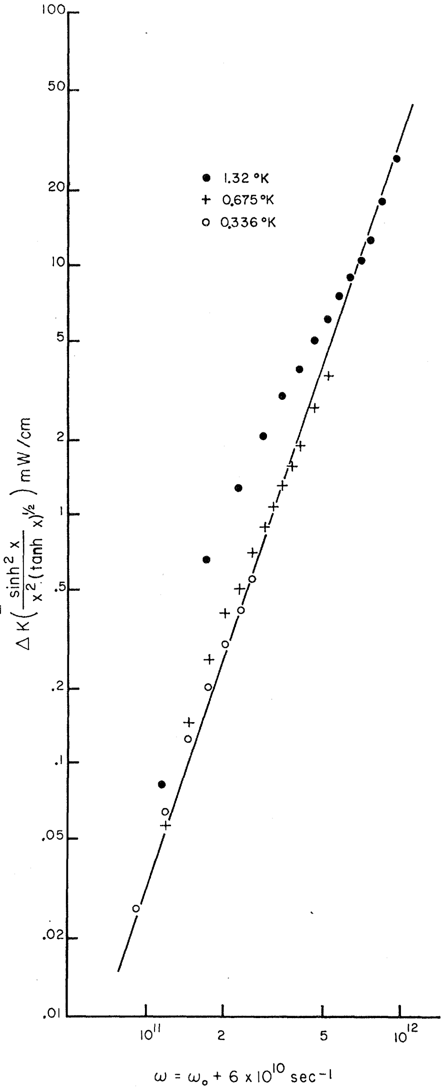

FIG. 6. The reduced change in conductivity as a function of phonon frequency for $CaF_2 + 0.05\%$ Ni^{++}.

occur at the same value of $(g\beta H+\hbar\omega_s)/2kT$ at all temperatures, and ω_s may be calculated from the data. The value of ω_s obtained in this way is 6×10^{10} sec^{-1}.

The data was then divided by the factor $x_0^2(\tanh x_0)^{1/2}/\sin\hbar^2 x_0$, where $x_0=(g\beta H+\hbar\omega_s)/2kT$, with the results shown in Fig. 6. There is adequate agreement except for the data obtained at 1.32°K and low fields. This departure is believed due to the effects of normal processes in extending the strongly damped region to other modes which otherwise would not be affected as strongly. A more detailed treatment of this question is in progress and will be the subject of a future publication.

Equation (11) predicts that, for a non-Kramers ion and small α, ΔK should vary as $\omega_0^{5/2}$, since ϵ is proportional to $\omega_0^{-1/2}$. It can be seen that the data agrees best with a ω_0^3 dependence. This can be understood if the width of the effective band of phonons removed is independent of frequency. In fact the levels of a non-Kramers ion should be split by internal strains, and since these are of different magnitudes, there should also be a distribution of splittings. The result should be that the strong interaction between the phonon and the spin system also occur over a range of frequencies, and if this range is broad enough and the interaction strong enough, the stop-band will be determined by the internal strains. If the width of the band is large compared to $(1+\alpha)^{1/2}\epsilon^2\sigma\omega_0$, the effective stop-band would be independent of applied field. Of course, if this is true the change in conductivity would also be insensitive to the phonon and spin damping.

By treating the spread in the zero-field splittings, their average value, and ϵ as adjustable parameters, it has been possible to fit a computer calculation of K_H from Eq. (8) to the data in Fig. 5 with moderate success. The solid lines are the calculated values of $(\mathrm{K}_H-K_0)/K_0$, where K_0 is the thermal conductivity in zero external field. Again the poor agreement at 1.32°K is believed to be due to the neglect of normal processes.

Of course, the average spread in zero-field splitting corresponds to ω_s above. The value obtained in this way is 5×10^{10} sec^{-1}, and the spread $\Delta\omega_s$ is 3×10^{10} sec^{-1}.

SUMMARY AND CONCLUSION

Equation (11) indicates that for temperature-independent phonon scattering, the temperature dependence of the change in thermal conductivity ΔK with magnetic field for fields such that $g\beta H/kT<6$ is contained in the term $x_0^2 \tanh^{1/2}x_0/\sinh^2 x_0$. If ΔK is divided by this quantity the result should be proportional to $H^{7/2}$ for the Kramers ions, $H^{5/2}$ for the non-Kramers ions, and H^3 if the levels are strongly broadened or split by a field-independent interaction.

It is found that the temperature dependence is, in fact, as predicted, and for the Kramers ions ΔK varies as $H^{7/2}$. The latter result is, however, weakened by the neglect of cross relaxation effects in these crystals. For the non-Kramers ion investigated, it appears that field-independent broadening mechanisms are important and the reduced ΔK varies as H^3.

A numerical integration of Eq. (8) yields the result that at very high fields and in the absence of any zero-field interaction, the conductivity is higher than the zero-field conductivity for both the Kramers and non-Kramers ions. This result is easy to understand. Equation (7) shows that the group velocity of modes of $\omega<\omega_0$ will be approximately $v_0[1-\omega_0^2\epsilon^2\sigma/(\omega^2-\omega_0^2)]^{1/2}$, which for $\omega\ll\omega_0$ is approximately $v_0(1-\frac{1}{2}\epsilon^2\sigma)$. Therefore, since the group velocity is less, the conductivity is greater. An equivalent statement is that for $\omega<\omega_0$ the energy of the coupled mode for a given k is less than that of the uncoupled phonon mode, and at a given temperature a greater number are excited.

It is possible that this is the reason for the improved high-field conductivity observed in the Yb-doped crystal. Unfortunately, as indicated above, coupled pairs can also lead to a diminished conductivity at zero field.

In conclusion, it is obvious from the foregoing that the idealized system to which the theory applies has not found its experimental counterpart as yet. Nevertheless, it is clear that the main features of the theory are correct, and that it provides a sound basis for understanding the effect of the spin-phonon interaction on the thermal conductivity.