THERMAL CONDUCTIVITY AND PHONON RESONANCE SCATTERING*

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A resonance interaction between phonons and the electron spin of paramagnetic ions has been observed by ultrasonic attenuation techniques.[1,2] Recently, Morton and Rosenberg[3] reported an experiment in which the thermal conductivity of a highly paramagnetic substance depended on an applied magnetic field. This they also explained as a resonance interaction between phonons and spins. In this Letter a resonance interaction between phonons and nonparamagnetic defects will be reported and the relaxation time $\tau_d(\omega)$ associated with these defects will be determined.

KCl crystals containing small concentrations of KNO_2 were investigated. The NO_2^- ions, which show no paramagnetism,[4] are believed to occupy substitutional sites in the chlorine sublattice. The optical and chemical properties of this system are well understood, and for our present purpose it is sufficient to mention that the characteristic absorption peaks of the nitrite ion were used to determine the NO_2 concentration in a given crystal. The crystals were grown in sintered Al_2O_3 crucibles from Cl_2-treated reagent-grade[5] KCl in an argon atmosphere, with the proper amount of KNO_2 added to the melt. KNO_2 concentrations as high as 4×10^{19} cm^{-3} could be produced easily without affecting the single-crystal character and without causing precipitation.

In lieu of a simple phonon spectrometer, the thermal conductivity of the specimen was investigated. The equipment used is standard and has been described elsewhere.[6,7] Figure 1 shows the experimental results. With increasing NO_2 concentration the thermal conductivity decreases considerably. In contrast to the "pure" KCl (no intentional doping) the thermal conductivity of the doped crystals exhibits a distinct structure that changes with the NO_2 concentration. From this structure (see, for instance, curve *C* and curve *D*) it follows that certain phonon frequencies (corresponding to roughly 8°K) interact very strongly with the defect.

For a quantitative analysis, the method suggested by Callaway[8] will be used. The thermal conductivity *K* is given by the following equation:

$$K=\int_0^{\omega_D} v^2\tau(\omega)(dC/d\omega)d\omega. \tag{1}$$

ω_D is the Debye frequency, v is the velocity of sound, and C is the specific heat per unit volume at constant volume. $\tau(\omega)$ is a combined relaxation time[8]

$$\tau^{-1}=\sum\tau_n^{-1}, \tag{2}$$

where τ_n describes the different scattering processes. For the undoped crystal, a combined relaxation time, τ_i, was determined to give an approximate fit (curve 1, Fig. 2). Then the effect of a resonance scattering term was studied by adding a relaxation time τ_d derived for a simple mechanical oscillator

$$\tau_d^{-1}=\frac{AH\omega^2}{(\omega_0^2-\omega^2)^2+(\Lambda/\pi)^2\omega_0^2\omega^2}. \tag{3}$$

H is the half-width, $H=\omega_0\Lambda/2\pi^2$, of the energy resonance curve, A is a proportionality factor containing the concentration of oscillators, ω_0 is the resonance circular frequency, and Λ is the logarithmic decrement $[\Lambda=(2Q)^{-1}]$. The results of the calculation are shown in Fig. 2 for different constants AH and the resonance circular frequency $\omega_0=6\times10^{12}$ sec^{-1}. Λ was chosen to be zero, but choosing $\Lambda>0$ did not change the calculated curves noticeably. Experimental and calculated curves show almost identical behavior. It should be emphasized that no attempt was made to achieve quantitative agreement. From the comparison of Figs. 1 and 2 we conclude that the present experiment most likely represents a case in which a resonance interaction between phonons and defects is observed with a relaxation time similar to Eq. (3). The question as to the nature of the resonators (the first possibility being the NO_2^- ions) will be further investigated experimentally and will be discussed later.

In the following the experimentally determined relaxation time τ_d will be discussed. From a comparison between calculated and experimental data it follows that the resonance scattering in curve *D* [30-parts per million (ppm) KNO_2] can be described by

$$\tau_d^{-1}=\frac{2\times10^{34}\ \mathrm{sec}^{-3}\omega^2}{(\omega_0^2-\omega^2)^2+(\Lambda/\pi)^2\omega_0^2\omega^2},$$

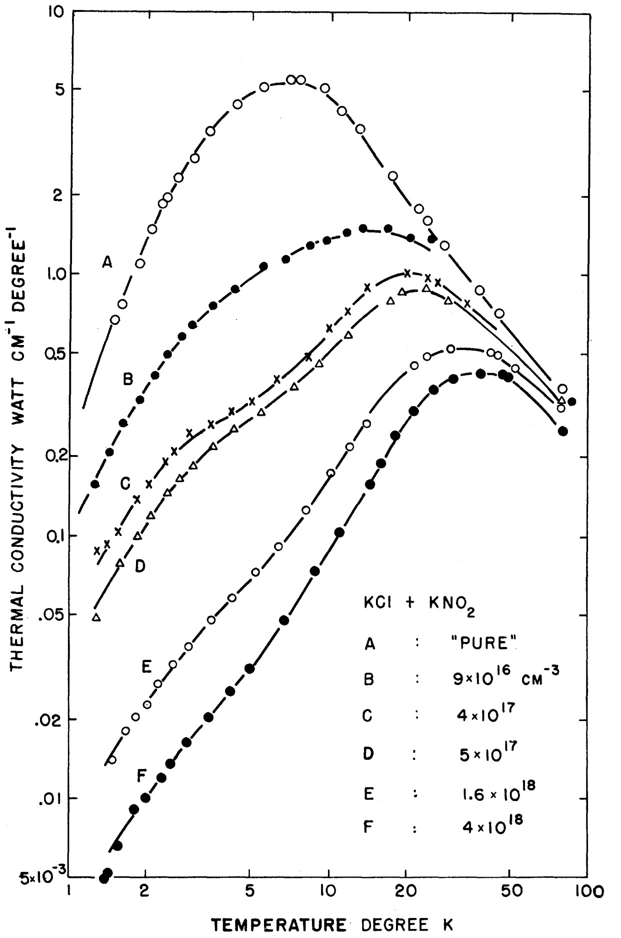

FIG. 1. Thermal conductivity of KCl single crystals containing various concentration c of KNO_2. Curve A: $c=0$, Curve B: $c=9\times10^{16}$ cm^{-3}, Curve C: $c=4\times10^{17}$ cm^{-3}, Curve D: $c=5\times10^{17}$ cm^{-3}, Curve E: $c=1.6\times10^{18}$ cm^{-3}, and Curve F: $c=4\times10^{18}$ cm^{-3}.

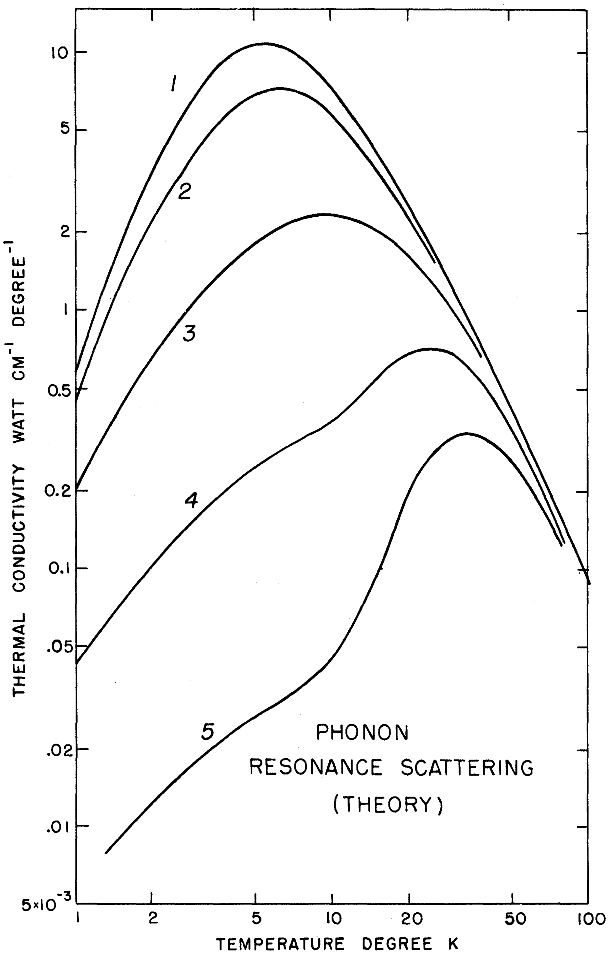

FIG. 2. Calculated thermal conductivity using Callaway's model as discussed in the text and a resonance expression as given in Eq. (3) with $\omega_0=6\times10^{12}$ sec^{-1} and $\Lambda=0$, for various constants (AH) (equivalent to various concentrations). Curve 1: $(AH)=0$, Curve 2: $(AH)=2\times10^{32}$ sec^{-3}, Curve 3: $(AH)=2\times10^{33}$ sec^{-3}, Curve 4: $(AH)=2\times10^{34}$ sec^{-3}, and Curve 5: $(AH)=2\times10^{35}$ sec^{-3}.

with $\omega_0=6\times10^{12}$ sec^{-1}. This equation determines τ_d except in the vicinity of ω_0, where τ_d is strongly dependent on the damping, but the experiment is unfortunately quite insensitive to Λ. In an attempt to obtain an upper limit of the relaxation time in this frequency range, $\Lambda=1$ was chosen, which describes a very strong damping for mechanical oscillators. For $\omega=\omega_0$ one obtains $\tau_d=1.8\times10^{-10}$ sec or (as lower limit) an extinction constant $k=(\tau_d v)^{-1}=1.85\times10^4$ cm^{-1}. In investigating phonon spin interaction by ultrasonic attenuation, i.e., at much lower frequencies, Tucker[1] found in ruby a maximum acoustic attenuation constant $\alpha_d=0.04$ cm^{-1} for the phonon amplitude at the frequency $\nu=9\times10^9$ sec^{-1}, and Bolef and Gosser[2] found in MgO containing 100-ppm Fe^{2+} $\alpha_d=10^{-7}$ cm^{-1} at $\nu=2\times10^8$ sec^{-1}. Another comparison might help to visualize the strength of the scattering observed in this experiment: F centers in the same concentration (5×10^{17} cm^{-3}) produce in KCl at room temperature an optical extinction constant $k=129$ cm^{-1}. For a proper comparison, one has to take the different wavelengths into account, i.e., one has to compare the extinction coefficients $\kappa=(1/4\pi)k\lambda$, where λ is the wavelength. One finds for KNO_2 in KCl, $\kappa_{\text{phonon}}=4.4\times10^{-4}$, and for F centers in KCl, $\kappa_{\text{photon}}=5.7\times10^{-4}$. This shows that the attenuation is comparable in magnitude in these otherwise so different cases.

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ANISOTROPY OF EXCHANGE IN YTTERBIUM IRON GARNET

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A measurement has been made of the g tensors and of the exchange splittings of the Yb^{3+} ion in ytterbium iron garnet (YbIG) for both the ground-state doublet and for an excited state doublet. From these measurements one can conclude: (1) that the g tensor of Yb^{3+} is substantially the same in the iron garnet as in the gallium garnet[1]; (2) that the anisotropy in the exchange splittings is caused by anisotropy in the Yb^{3+}-Fe^{3+} exchange as well as in the Yb^{3+} g tensor. The purpose of this Letter is to describe the measurements leading to these conclusions, and to present a theory of exchange anisotropy which, considering its simplicity, fits the data remarkably well.

A spectroscopic study of the exchange splittings of Yb^{3+} in YbIG has already been reported in some detail.[2] The optical transition investigated is between the Γ_7 doublet of the ground $J=\frac{7}{2}$ state and the Γ_7 doublet of the excited $J=\frac{5}{2}$ state of the Yb^{3+} ion. These are the lowest-lying doublets of each J manifold. At the time of the original measurements only the g tensor of the $J=\frac{7}{2}$ doublet was known (from paramagnetic resonance in the isomorphic gallium garnet) and the substantial increase in anisotropy of the exchange splittings over the g tensor could have been due either to anisotropy in the exchange fields[3] or a difference in the Yb^{3+} g tensor in the iron garnet as compared to the gallium garnet. To remove this ambiguity and to give also further data on the upper state, a set of experiments was performed in which the effect of a large magnetic field upon the exchange splittings was observed. Fields up to 36 000 Oe were obtained using a PEM 12-in. electromagnet, and the spectra were taken photographically using the 30 000 line/inch grating of a Bausch and Lomb dual-grating spectrograph. From the change in splittings under an applied field, the g tensors for both upper and lower states were deduced. For the $J=\frac{7}{2}$ state the applied field acted to diminish the splittings; for the $J=\frac{5}{2}$ state the applied field increased the splittings.[4] The precision obtained in the g-tensor measurement was limited primarily by the optical linewidths encountered in the iron garnets.

The results of the measurements are given in Table I. Also given are the g values for Yb^{3+} in the gallium and aluminum garnets as determined by paramagnetic resonance and very recent optical Zeeman studies,[5] and both the experimental and theoretical exchange splittings.

In comparing the g tensors and exchange splittings in the iron garnet one finds that the two are markedly different, and in the $J=\frac{5}{2}$ state even topologically dissimilar. For $J=\frac{5}{2}$ the smallest exchange splitting is associated with the largest g value, the intermediate exchange splitting with the smallest g value, and the largest exchange splitting with the intermediate value. For the $J=\frac{7}{2}$ state the order of g values and of exchange splitting is the same, but the degree of anisotropy is much larger in the exchange splittings.

One can explain the above data only by assuming that the Yb^{3+}-Fe^{3+} exchange interaction contributes to the anisotropy, that is, has a magnitude which depends not only on relative spin orientation (as $S_1 \cdot S_2$) but also on the orientation of the spin vectors relative to the crystalline axes. That such an exchange is physically plausible can be seen as follows. The Yb^{3+} $4f$ wave