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Phonon Scattering by Paramagnetic Ions and Scattering by Other Defects*

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When considering the effect of a magnetic field on the thermal conductivity of a crystal which contains paramagnetic ions, phonon scattering processes other than the spin-phonon interactions must be taken into account. The purpose of this note is: to point out how the effect of other phonon-scattering processes can be taken into account and show that semiquantitative agreement with experiment is possible; to suggest an experimental technique which permits the magnetothermal resistance to be used as a direct measure of the frequency dependence of the total zero-field phonon-scattering cross section without knowing the details of the line shape for the spin-phonon interaction.

WHEN considering the effect of a magnetic field on the thermal conductivity of a crystal which contains paramagnetic ions, phonon-scattering processes other than the spin-phonon interactions must be taken into account.[1] The effect of other phonon scattering processes can be taken into account and semiquantitative agreement with presently available experimental results is possible. However lack of information about the line shape for the spin-phonon interaction first, prevents more than the crude comparison between theory and experiment made here, and second, prevents the implementation of Berman's suggestion[2] that the magnetothermal resistance can be used to obtain information on phonon mean free paths.

Assume that the effect of the magnetic field is to tune the spin system to a particular phonon frequency ω_0 and to prevent phonons in a narrow band around this frequency from contributing to the heat transport.[2,3] The fractional change in the conductivity may be written in the limit where this band is narrow, neglecting multiple scattering effects, and the effect of normal processes as

$$\Delta K/K_0 = -AT^3 f(x)\Delta x/K_0$$

in which

$$A = k^4/2\pi^2\bar{v}\hbar^3,$$

$$x = \hbar\omega_0/kT = g\beta H/kT,$$

where $\bar{v}$ is an average sound velocity and the other quantities have their usual meaning. The function $f(x)$ characterizes the distribution of phonons responsible for the heat flow in the absence of a field. This transport function is

$$f(x) = [e^x/(e^x-1)^2]x^4/\Sigma[1/\tau(x)],$$

where $\tau(x)$ is a relaxation time determined by the phonon-scattering processes active at zero field.

In general the bandwidth Δx will depend on applied field, and the possibility of transport by spin waves also exists. Although these effects must be considered in a detailed treatment it is evident that to a crude approximation sweeping the magnetic field at a fixed temperature yields $f(x)$. Thus, the dependence of $\Delta K/K_0$ on magnetic field would be determined largely by the shape of the transport function.

It is interesting to consider the case of point-defect scattering. First assume that the scattering follows a Rayleigh law, then

$$f(x) = \frac{e^x}{(e^x-1)^2}\frac{x^4}{\bar{v}L^{-1}+BT^4x^4},$$

where B is a constant determined by the strength of the interaction between the phonons and the defects, $\bar{v}L^{-1}$ is the boundary scattering term, and L is the Casimir length. Again, the boundary scattering term is, in general, a function of the other scattering processes taking place,[4] but this effect is somewhat subtler than those being considered here.

It is well known that in the limit where BT^4 is very small compared with $\bar{v}L^{-1}$ the maximum in $f(x)$ occurs at about $x=4$. Also, in this limit the phonon frequency at the maximum in $f(x)$ occurs at about $x=4$. Also, in this limit the phonon frequency at the maximum and hence the applied field for which $\Delta K/K_0$ has a minimum will be directly proportional to the temperature. As B increases, however, it can be seen that the value of x_M which maximizes $f(x)$ becomes smaller and smaller. In the limit where x_M is small the maximum will occur where $BT^4x^4=\bar{v}L^{-1}$, and it is xT that is constant. Hence the phonon frequency and the magnetic field for which a minimum occurs in this case will be independent of temperature.

A crude comparison with existing data is possible: McClintock *et al.*[5] have measured the field dependence of the thermal conductivity of MgO containing various transition metal ions. It is interesting to observe that the field at which the maximum in the thermal con-

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[1] R. Orbach, Phys. Letters **3**, 269 (1963).

[2] R. Berman, J. C. F. Brock, and D. J. Huntley, Phys. Letters **3**, 310 (1963).

[3] D. L. Huber, Phys. Letters **20**, 230 (1966).

[4] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961); see p. 129.

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

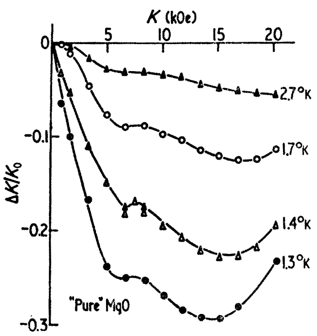

FIG. 1. Nominally pure MgO containing 30 parts per million of Fe.

ductivity occurs is proportional to T^n for Co^{2+} and Cr^{3+} where n is about 0.6. In the light of the preceding remarks this can be interpreted as due to Rayleigh scattering by point defects. If this interpretation is correct an increase in the concentration of the defects should increase B and hence decrease the value of n. Challis[6] has measured the field dependence of the thermal conductivity for MgO containing 0.3% Cr which is four times the concentration quoted in Ref. 5. Here the value of n is about 0.5. Finally, if strong Rayleigh scattering is present in these crystals the thermal conductivity at zero field should not vary as T^3. Challis[7] has measured the conductivity as a function of temperature at zero field and finds it to be proportional to T^1 for MgO+0.3% Cr.

Resonance effects are also characteristic of the interaction between phonons and defects. These have been observed through their effect on the thermal conductivity by a number of investigators.[8] The presence of resonance scattering will decrease the value of the transport function at a fixed frequency. When the spin system is tuned to that frequency $\Delta K/K_0$ should rise, because the phonons at resonance are already being strongly scattered and the effect of the additional scattering is less when the spin system becomes tuned to their frequency. The peak in $\Delta K/K_0$, or conversely a dip in the ratio of the thermal resistances should of course be independent of temperature and always occur at the same field. As shown in Fig. 1, such a peak has been observed by McClintock *et al.* in nominally pure MgO containing 30 parts per million of Fe in a field of 8 kG. Challis has also observed a change in slope of the thermal conductivity versus temperature at 3°K for MgO+0.3% Cr, which he has ascribed to a possible resonance. Since the point defect scattering is evidently very strong ($K\propto T^1$), the resonant frequency, if this discontinuity is in fact due to a resonance, should be such that $\hbar\omega=kT$. If this is so, then a characteristic dip in the magnetothermal resistance should occur at a field such that $g\beta M=\hbar\omega=3k$. Assuming a value of $g=1.98$ appropriate to Cr^{3+}, we observe that the dip should occur at 22.5 kG. It is interesting to note that such a temperature-independent dip does appear in his results[6] at a field of 25 kG.

To summarize, it appears that a useful (though not always rigorous) way to view the phonon scattering in a crystal which contains paramagnetic ions is to split the interaction into two parts: one is the resonant interaction of the phonon with the spin system; the other is the interaction of the phonon with all other defects (including the paramagnetic ion itself) at zero field. This, of course, is nothing more than the familiar assumption that the reciprocal relaxation times are additive.[9] If this is done it can be seen that the shape of $\Delta K/K_0$ as a function of applied field is determined to a large extent by the second interaction. In particular the value of $g\beta H/kT$ at which the minimum in $\Delta K/K_0$ occurs is determined by this interaction. If strong Rayleigh scattering is present, this minimum may even occur at a fixed field over a limited temperature range.

Finally, it should be emphasized that this is a potentially powerful technique for studying phonon scattering by defects. A relatively light doping of suitable ions would permit the transport function to be determined. The appropriate scattering cross section for the defect as a function of frequency can then be deduced from the transport function. However, it is necessary to know the details of the spin-phonon interaction to determine the transport function accurately. This information, on the other hand, would be necessary for the following experiment which depends on a differential measurement: $\Delta K/K_0$ as a function of magnetic field would be determined first for a crystal containing the paramagnetic ions alone. Then the defect whose effect is desired would be introduced and the experiment repeated. From the difference in the behavior of $\Delta K/K_0$ for the two specimens, the interaction of the defect with the phonons can be deduced. A resonance scattering by the defect which has been introduced, for instance, would be unmistakable. In this way it may well be possible to identify local modes associated with defects.

The variation of the thermal conductivity with temperature has been used extensively for just this purpose. However, the more direct relationship between the phonon-scattering processes and the transport function provides a marked advantage to the spin-phonon technique.

[6] L. J. Challis and D. J. Williams (private communications).

[7] L. J. Challis and D. J. Williams, in *Low Temperature Physics: LT9*, edited by J. G. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 1135.

[8] See, for instance, C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

[9] P. Carruthers, Rev. Mod. Phys. **33**, 123 (1961).