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Scattering of Phonons by Lattice Defects*

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Phonon scattering by lattice defects in non-metals is being studied by measuring the thermal conductivity over a wide temperature range of crystals containing known concentrations of known types of defects. The relaxation times τ for different types of defects depend differently upon the phonon frequency, and types of defects can thus be distinguished by differences in the temperature dependence of the thermal conductivity. Experiments on phonon scattering by isotopes, *F*-centers, dislocations, chemical impurities, and colloids are discussed.

Thermal conductivity measurements at low temperatures provide a method of measuring the scattering of phonons by lattice defects. By studying the temperature dependence of the thermal conductivity over a wide temperature range (~1° to ~100°K), scattering can be measured as a function of phonon wavelength. By confining attention to non-metallic crystals, the complicating effects of phonon scattering by electrons are avoided. Such measurements are being carried out on a number of crystals into which known concentrations of known kinds of defects have been incorporated. In order to be suitable for such measurements, a crystal should be nearly pure chemically, free from strains and grain boundaries, and available in a large enough size that the phonon mean free path can be limited by the intentionally added imperfections rather than by the crystal boundaries (Casimir scattering).

The following experiments are in progress:

1) The scattering of phonons by isotopes provides a test of phonon scattering theory. Although isotopes as "defects" in solids are well-known,[1] the very fact that they are so well-known permits a crucial test of theory (which can then be applied to "unknown" defects). Studies are being made on LiF in collaboration with Dr. Clayton Weaver of the Oak Ridge National Laboratory.

2) Photochemically produced *F*-centers were studied earlier.[2] In these experiments, crystals of LiF were subjected to successive irradiations by both X-ray and γ-rays. The thermal conductivity as a function of temperature is shown in Fig. 1. Analysis of these curves by Callaway's approach[4] revealed that the phonon scattering by color centers was more complicated than the simple scattering (relaxation time $\tau \sim \omega^{-4}$, where ω is the phonon angular frequency) expected for a point defect.

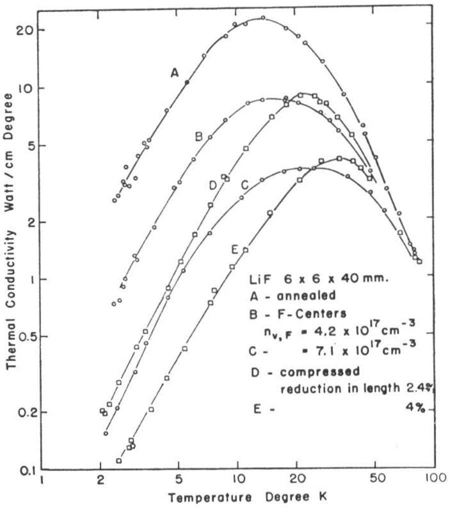

Fig. 1. Curve A is the thermal conductivity as a function of temperature for nominally pure LiF; curves B and C are for LiF with *F*-centers in the concentration indicated.[2] Curves D and E, for LiF with dislocations introduced by compression,[3] are included here to show how different kinds of defects can be distinguished by the different temperature dependences of the thermal conductivity.

Dr. C. T. Walker extending these measurements to NaF. He has discovered a quite different ω dependence near the maximum in *K vs T* for scattering by color centers and virtually no depression of *K* at the lowest temperatures (2°–5°K). The latter behavior is consistent with a $\tau \sim \omega^{-4}$ (point defect), but

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attempts to understand the former in terms of resonant scattering[5] have not yet been successful.

3) Earlier measurements[3] on dislocation scattering in LiF indicated a large effect of dislocations on phonon scattering. Mr. Marvin Moss is studying scattering in CaF_2, LiF, and Ge by dislocations whose edge components are predominantly aligned. No evidence for an effect of the angle between the predominant direction of edge components and the direction of heat flow has been observed in LiF, presumably because the screw components dominate[6] in dislocation loops in LiF. But in CaF_2, the phonon scattering is considerably less when the heat flow is perpendicular to the predominant edge dislocation array than when it is parallel. These experiments are being interpreted in terms of phonon scattering as a function of phonon-dislocation angle.

4) Dr. Anthony N. Taylor and the authors are studying the annealing of points defects and dislocations introduced by deformation by measuring the temperature dependence of the thermal conductivity at various stages of annealing of plastically deformed NaCl and KCl. The thermal conductivity of a crystal of KCl is shown in Fig. 2, first in the nominally undeformed state, then after 3% compression, and then after successive anneals at 400°C and at 650°C. Comparable experiments on NaCl are accompanied by a detailed study by Dr. Taylor of the distribution of etch pits after annealing at successively higher temperatures. He has found that about half of the individual dislocation has been removed by annealing at 400°C, the point at which half of the dislocation scattering of phonons has disappeared. He has found that dislocation wall formation begins at a still higher temperature and that the dislocations in walls do not scatter phonons strongly.

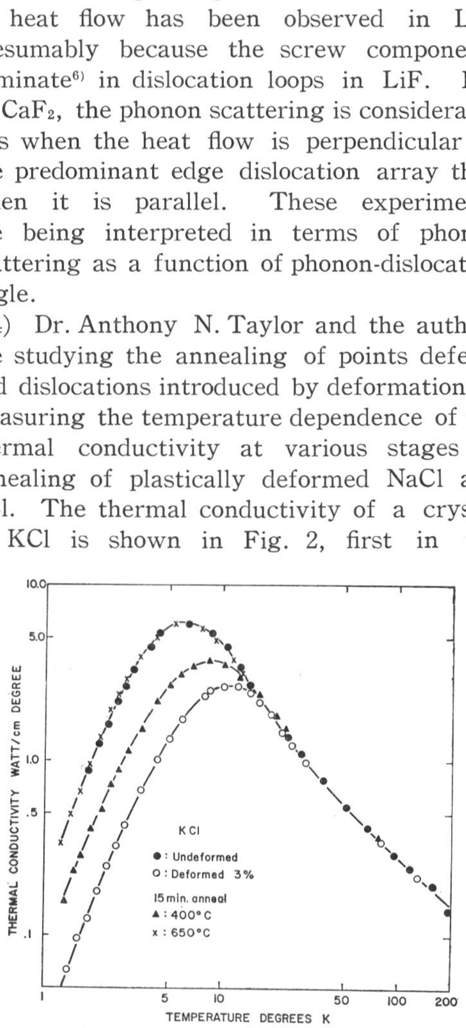

Fig. 2. Thermal conductivity of a KCl crystal as grown, after a 30% compression, and after successive 15-minute anneals at 400°C and at 650°C. Similar and more extensive experiments have been performed on NaCl.

5) KCl crystals containing small concentrations on KNO_2 exhibit a resonance scattering of phonons.[5] This pronounced scattering at a single phonon frequency produces a profound depression in the plot of thermal conductivity as a function of temperature near 10°K, as shown in Fig. 3. A Callaway[4] calculation shows reasonably good agreement with the data if an inverse relaxation time with a resonance denominator ($\omega_0=6\times10^{12}$ sec^{-1}) is added in the expression for the conductivity, as shown in Fig. 4. The remarkable effectiveness of NO_2 as a phonon scatterer is demonstrated by the fact that at 2°K less than 1% NO_2 incorporated into a KCl or KBr

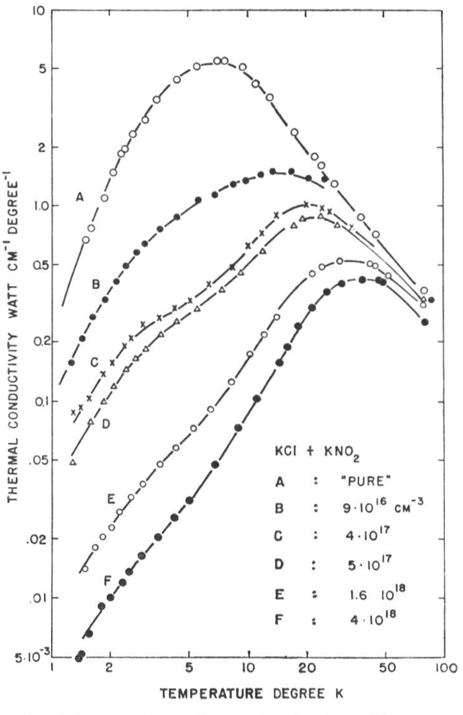

Fig. 3. Thermal conductivity[5] of KCl crystals containing various concentrations of KNO_2. The densities of NO_2^- ions for the various curves are given.

crystal reduces the thermal conductivity to about that of nylon. The possible explanation of several other phonon scattering experiments in terms of such resonance scattering is being studied.

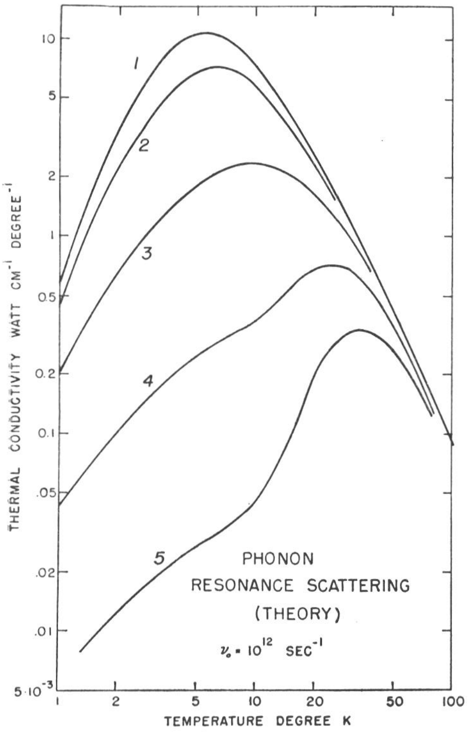

Fig. 4. Calculated thermal conductivities to compare with the curves of Fig. 3. An inverse relaxation time with a resonance denominator was included in the expression for conductivity. Curve 1 is a fit to the "pure" crystal. Curves 2–5 correspond to successively larger strengths of the resonant scattering term, each one a factor of 10 stronger than its predecessor, but all with $\omega_0 = 6\times10^{12}$ sec^{-1}.

6) The scattering of phonons by colloidal defects in alkali halides has been investigated by Dr. John M. Worlock.[7] The scattering defects were silver and alkali metal colloids whose sizes and spatial distributions were studied by optical absorption.
Fig. 5 shows the effect of silver colloids in depressing the thermal conductivity. The principal conclusion of this work is that the thermal conductivity at very low temperatures is proportional to T^3 when limited by colloidal scattering. Thus in many previous experiments, colloidal scattering was probably mistaken for a failure of the Casimir (boundary) formula. Dr. Worlock's experiment now makes it possible to use thermal conductivity measurements to study the coagulation of point defects into colloids.

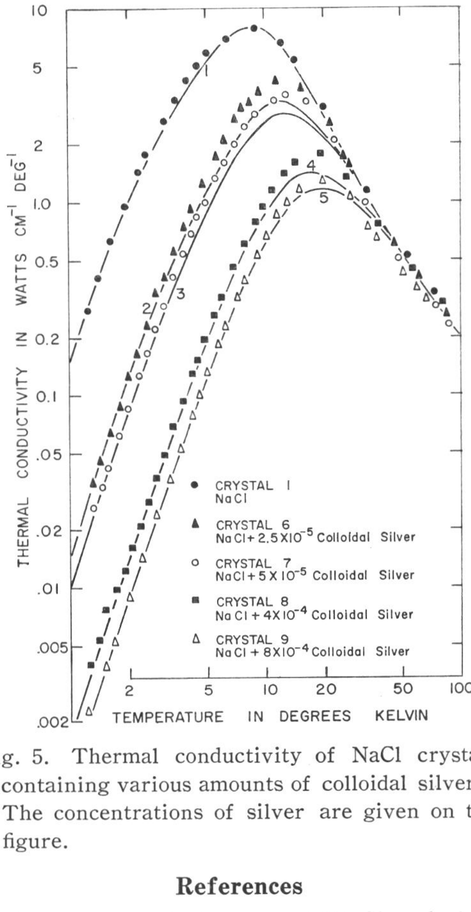

Fig. 5. Thermal conductivity of NaCl crystals containing various amounts of colloidal silver.[7] The concentrations of silver are given on the figure.

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DISCUSSION

Mendelssohn, K.: (1) When you referred to the T^3 dependency of the thermal conductivity of crystals containing colloids as "to be expected from theory", did you mean boundary scatter? The size of the particles is surely not large compared with the phonon wavelengths.

(2) Are the experiments which you mentioned first in agreement with the conclusions of Berman on the brass of similar work?

Sproull, R. L.: In reply to your first question, the "theory" I referred to is *not* so naive as to consider the colloids simply as if they were crystal boundaries. Dr. Worlock used the theory of Prof. R. Truell and others published in the J. Appl. Phys. several years ago to complete the scattering cross section for colloidal particles. This cross section is independent of the phonon frequency even for particles of size comparable to the phonon wavelength, and thus at sufficiently low temperatures, a thermal conductivity proportional to T^3 is predicted. The size of the Ag particles was *not* large compared to typical phonon wavelengths.

In reply to your second question, it is a pleasure to acknowledge the vision of Dr. Robert Berman of Oxford in studying the thermal conductivity of crystalline solids at very low temperatures and in pointing out in 1948 how sensitive this conductivity could be to imperfections. Even earlier, investigators at Leiden had opened this field. The experiments I have described today are the most recent of a series that began in 1952. We have been "standing on the shoulders" (to use Newton's expression) of the Leiden and Oxford work. Our particular "flavor" has been to study crystal systems consisting of known concentrations of known types of defects, in crystals where the imperfections intentionally introduced dominate the uncontrolled impurities and other imperfections.

Koehler, J. S.: In the experiments on the thermal conductivity after deformation, have you deformed the crystals at temperatures low enough so that point defects do not move between the time of deformation and the time of the thermal conductivity measurement?

Sproull, R. L.: Probably no, but Dr. Anthony Taylor is studying vacancy production and annealing in connection with these measurements, and he has reported the present status of this work at the Stuttgart Conference.

Truell, R.: In your slide on lithium fluoride (the second I believe) there is a rather notable difference in the sharpness of the peaks as compared with the sample having color centers. Is this difference understood?

Sproull, R. L.: The shape of the curves for color centers in LiF is not well understood, especially since the current experiments by Dr. C. T. Walker reveal a striking difference in shape between NaF and LiF. If the strain-field scattering predicted by Klemens is the predominant scattering mechanism for dislocations, the *shape* of the curves for deformed crystals is well understood. But there remains the problem of the *magnitude* of the scattering power of dislocations; but dynamic scattering theories such as those by Granato and by Ishioka and Suzuki give higher power of T than T^2 at low temperatures.