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Influence of F Centers on the Lattice Thermal Conductivity in LiF*

ROBERT O. POHL
Laboratory of Atomic and Solid-State Physics, Cornell University, Ithaca, New York

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The influence of photochemically produced F centers in LiF on the thermal conductivity is investigated, the density of the F centers being determined optically. The F centers decrease the thermal conductivity appreciably at low temperatures. Additive coloration of KCl has a similar effect. The experimental results are quite different from the results obtained in the case of the isotope effect in Ge. Callaway's theory for the lattice thermal conductivity in the presence of point defects cannot explain the present observations satisfactorily, although it is superior to Klemens'. Two explanations are proposed: (1) The F centers are not randomly distributed (but the presence of clusters of F centers can be excluded in the experiments). (2) The long-range strain field around the F center does not scatter like a point defect. In support of Callaway's theory, it is shown that his model can explain an experimental observation (first reported by Toxen) about the influence of point defects on the thermal conductivity.

I. INTRODUCTION

IN perfect crystal lattices the thermal conductivity is determined by intrinsic processes or in other language, phonon-phonon collisions. Peierls[1] showed that these processes become less frequent as the temperature decreases. This explained the observations first reported by Eucken[2] that the thermal conductivity of crystals increases with decreasing temperature. In practice, crystals always are of finite size, and this perturbation of the lattice periodicity constitutes a second scattering source: Phonons are scattered at the crystal surfaces. At low temperatures this scattering mechanism becomes dominant with a constant mean free path given by the crystal dimensions. The boundary effect is characterized by a T^3 dependence of the thermal conductivity. It was discovered by de Haas and Biermasz[3] and has been discussed in several papers.[4–6]

In addition, crystals always contain imperfections. The thermal conductivity depends very sensitively on their presence. The phonon scattering by different lattice imperfections differs not only in magnitude, but also in its dependence on the phonon frequency and the temperature. As a result, measurements of the thermal conductivity should be a sensitive means of studying crystal imperfections once this method is sufficiently calibrated. It is therefore of interest to investigate the lattice thermal conductivity of crystals containing various amounts of different known imperfections. In 1951, Klemens worked out a detailed theory of thermal conductivity and the influence of lattice defects. He explained the existing experimental data and made quantitative predictions for the various lattice defects. We refer to his papers[7–10] also for a careful collection of references.

This paper considers "point" defects; "point" means here a lattice defect with a diameter which is small compared to the phonon wavelength. The second part of this section discusses what is known about the effect of point defects on the thermal conductivity and explains why the system LiF containing F centers was chosen for this investigation. In Secs. II, III, and IV this experiment is described. Section V gives a brief review of the theory in which the differences between the two theoretical approaches, the one by Klemens, the other by Callaway,[11] are compared. In Sec. VI a comparison between the experiment and the theory is made. It will also be pointed out that Callaway's model explains an observation of the dependence of the thermal conductivity on the density of point defects, first reported by Toxen[12]; this observation could not be understood with Klemens' model. In the concluding discussion (Sec. VII) several reasons for the disagreement between the experiment reported here and the theory are discussed.

Point defects disturb the periodicity of the lattice in at least one of three different ways: (1) A point defect has a different mass; (2) it changes the force constants; and (3) as a particular case of (2), the impurity atom has a different volume which produces a strain field, thus changing the force constants through the anharmonic parts of the lattice forces. If point defects are randomly distributed, they scatter phonons with a Rayleigh scattering law. The relaxation time for this process is given by

$$\tau_{\rm pt} \propto \omega^{-4}. \tag{1}$$

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The experiments on point defects can be divided into two distinctly different groups. The first group is characterized by the isotope effect, as first discussed by Pomeranchuk.[13] In this case the lattice periodicity is disturbed by the difference ΔM in mass between the different isotopes. Slack[14] first presented experimental evidence for the isotope effect, and it was investigated experimentally by Geballe and Hull.[15] They compared two germanium single crystals which differed (as far as possible) only in their isotope content. One was the natural isotopic mixture, the other contained 95.8% of Ge^{74}. The crystal containing the normal isotopic mixture had a thermal conductivity which was lower than that of the isotopically pure specimen over the entire temperature region. The temperature at which the maximum conductivity was observed was almost the same in both crystals. Callaway[11] recently explained these results quantitatively. Evidence was given by two other experiments that the introduction of point defects had a similar result on the thermal conductivity, even though the point defects were not isotopes. One of these experiments was performed by Williams[16] on mixed crystals of KCl and KBr; he varied the concentration of the KBr from zero to 50%. The other experiment was done on mixed crystals of germanium and silicon by Toxen,[12] who varied the concentration of Si from zero to 7 atomic percent. In both cases the mixing resulted in a large decrease of the thermal conductivity over the entire temperature range. Again the presence of point defects did not alter the temperature at which the maximum thermal conductivity occurred. So far no attempt has been made to explain these two experiments quantitatively, but they agree qualitatively with the results Callaway obtained for the isotope effect.

In the second group of experiments the introduction of a rather small concentration of point defects results in an unexpected large decrease of the thermal conductivity at the lower temperatures. Consequently, the temperature at which the maximum conductivity is observed increases with increasing concentration of point defects. These experiments were made on the following systems: (1) KCl doped with $\mathrm{CaCl_2}$; (2) neutron irradiated $\mathrm{Al_2O_3}$, also LiF irradiated with neutrons and 1.5-Mev γ-rays; (3) Ge and Si doped with group III acceptors. The first of these experiments was done by Slack.[17] The concentration of $\mathrm{CaCl_2}$ ranged from $0\text{–}3.4\times10^{18}\ \mathrm{cm}^{-3}$. The calcium ion is believed to replace two potassium ions, substituting for one and leaving the other site vacant. Slack found a small decrease of the thermal conductivity on the high-temperature side of his curves, but there was also a large decrease on the low-temperature side. This large decrease was explained assuming that 20% of the $\mathrm{CaCl_2}$ was precipitated in the form of clusters approximately 75A in size. (Rayleigh scattering requires particle sizes small compared to the wavelength. With a particle size of 75A this was no longer the case in Slack's experiment. He assumed that they would scatter phonons with a relaxation time τ_{cl} independent on the phonon wavelength and temperature.)

The radiation damage was studied by Berman[18] on $\mathrm{Al_2O_3}$ and by Cohen[19] on LiF. Both investigators attributed the decrease of the low-temperature thermal conductivity to the formation of clusters during the irradiation. The presence of clusters in these experiments was plausible, but not proved. As yet the influence of clusters on the thermal conductivity has not been independently studied.

The situation in the doped Ge and Si crystals investigated by Carruthers[20] and others is more complicated. The experimental results are similar to those just described, but the doping also produced mobile carriers. The decrease in thermal conductivity was believed to be caused by collisions of phonons with charge carriers in impurity bands.

In the present paper it will be shown that the same large decrease of the thermal conductivity on the low-temperature side of the maximum can be observed in a case where neither clusters nor charge carriers exist.

For studies of point defects alkali halides with *F* centers have many advantages. Some of them are summarized below: The nature of the *F* center, an electron trapped in a halogen vacancy, is well established. The *F* center is a defect of the general type mentioned in the introduction, disturbing the lattice by a different mass, changed force constants, and in particular by a strain field. Irradiation with x-rays is a simple way of producing *F* centers. A crystal containing *F* centers shows a characteristic absorption band which can be used to determine their density n_F (number of *F* centers per unit volume). The formation of clusters can be checked, again by means of optical absorption, and the crystal does not exhibit electrical conductivity in the absence of light. Successive irradiations make it possible to investigate the thermal conductivity as a function of temperature and the density n_F of the *F* centers on the same specimen, thus reducing to a minimum the error introduced by the geometry, the crystal surface, and the background imperfections of the specimen. Finally, annealing at moderate temperatures bleaches the *F* centers, and thus the reproducibility can be checked. LiF has the advantage over most of the other alkali halides of having a high Debye temperature ($\theta=722^\circ\mathrm{K}$). Therefore, its intrinsic ther-

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[13] J. Pomeranchuk, J. Tech. Phys. (U.S.S.R.) **6**, 237 (1942).

[14] G. A. Slack, Phys. Rev. **105**, 829 (1957).

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mal conductivity is high. Because of the small atomic numbers a very uniform coloration can be produced by using soft x-rays.

II. CRYSTALS

The crystals used were Harshaw LiF purchased in October, 1956. The crystals were 40 mm long. After the cleaving, the crystals were annealed 3 hr at 1100°K (40° below the melting point) and cooled at a rate of one degree/min to 500°K and then more slowly to room temperature before their thermal conductivity was measured. The chief purpose of this treatment was to provide the same thermal history for all crystals. The crystals could be cleaved to a size of $0.75\times 0.75\times 40$ mm without apparent plastic deformation.

III. EXPERIMENTAL PROCEDURE

The apparatus used was built and described by Williams[16] and is similar to the one designed by Slack.[17] Gold-Cobalt[21] vs constantan differential thermocouples were used to measure the temperature gradient in the crystal when a known heat flux (provided by an electric heater) was established in the crystal. The sensitivity of these thermocouples is roughly 1 μv deg^{-1} at 1°K. Voltages were measured with a dc breaker amplifier which had a sensitivity of 10^{-8} volt. Because of the high thermal expansion of the alkali halides, the thermocouples could not be cemented to the crystals. Instead, two indium-faced clamps, made entirely of aluminum, were attached to the crystal 15 mm apart. Phosphor bronze springs provided sufficient pressure at all temperatures. The thermocouples were soldered to the clamps. For the photochemical production of F centers the crystal was exposed to 60 kv x-rays filtered through 2 mm Al, without removing the aluminum clamps. For one experiment at the highest density, $n_F=2\times 10^{18}$ cm^{-3}, an additional exposure to 1.5-Mev γ-rays was used. The optical absorption was determined on thin slices of LiF which had been subjected to the same treatment as the pieces used to study the thermal conductivity. For the absorption measurements a Cary recording spectrophotometer was used, and the data were analyzed by Smakula's formula[22] assuming that the oscillator strength f was equal to unity. From their experiments on the magnetic susceptibility, Bate and Heer[23] deduced an oscillator strength $f_L=0.82$ for a Lorentz band shape; such a departure from unity for f is not significant in the interpretation of our experiments.

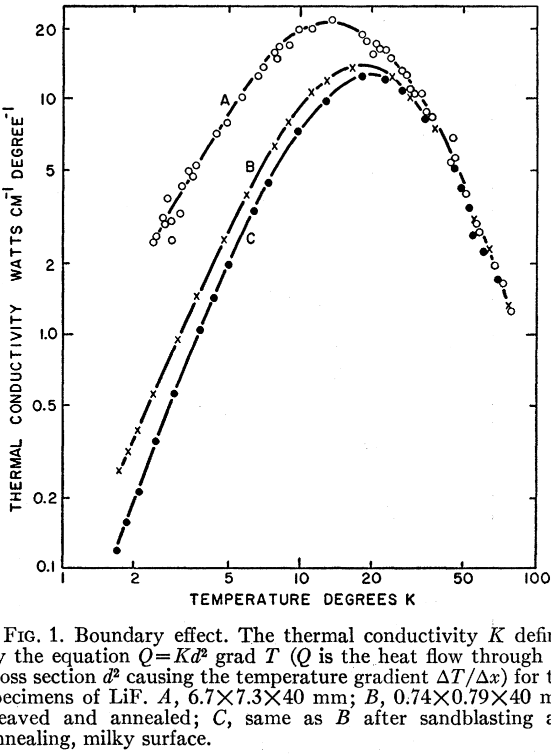

FIG. 1. Boundary effect. The thermal conductivity K defined by the equation $Q=Kd^2$ grad T (Q is the heat flow through the cross section d^2 causing the temperature gradient $\Delta T/\Delta x$) for two specimens of LiF. A, $6.7\times 7.3\times 40$ mm; B, $0.74\times 0.79\times 40$ mm, cleaved and annealed; C, same as B after sandblasting and annealing, milky surface.

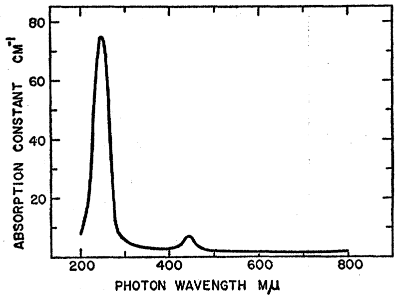

FIG. 2. Optical absorption spectrum of LiF after irradiation with 60 kv x-rays through 2 mm aluminium filter. $n_F=7\times 10^{17}$ cm^{-3}. Irradiated and measured at 300°K.

IV. EXPERIMENTAL DATA

In Fig. 1 the thermal conductivity for two specimens of LiF is plotted vs temperature. The curves A and B were measured on two specimens which differed only in size. C is the same specimen as in B, but with roughened surfaces. These measurements are a verification of the boundary effect and show that except at high temperatures the conductivity depends strongly on the geometrical size and surface structure of the specimen measured.

Irradiation with x-rays at room temperature produces the characteristic absorption spectrum shown in Fig. 2. The graph shows the F absorption at 2450A and a comparatively small absorption at 4500A, which is ascribed to the M center. The introduction of F centers reduces the thermal conductivity quite markedly. Figure 3 gives an example. Curve A is the same as the top curve in Fig. 1. Three successive irradiations reduce the thermal conductivity on the low-temperature side (curves B, C, and D in Fig. 3). After D was measured,

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[21] G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, Commun. Kamerlingh Onnes Lab. Univ. Leiden No. 217, *c*, *d*, *e* (1932); W. H. Keesom and C. J. Matthijs, Physica **2**, 623 (1935).

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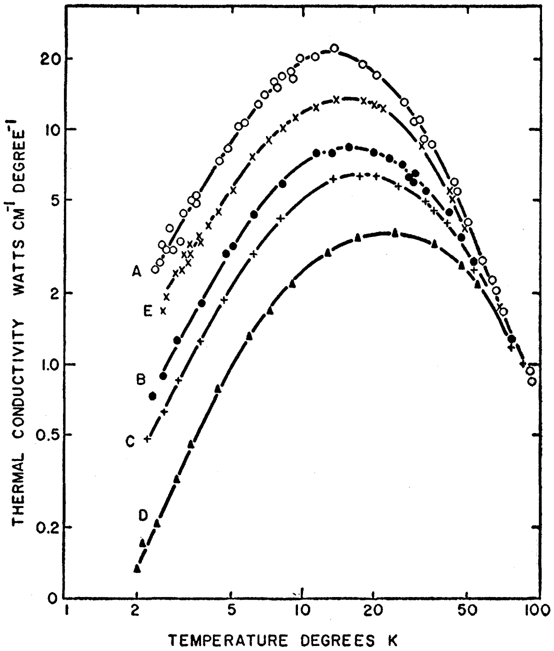

FIG. 3. Thermal conductivity of one crystal of LiF with successive irradiations at room temperature: *A*, same as in curve *A* of Fig. 1, 6.7×7.3×40 mm; *B*, x-rays, $n_F=4.2\times10^{17}$ cm^{-3}; *C*, x-rays, $n_F=7.1\times10^{17}$ cm^{-3}; *D*, x-rays plus 1.5-Mev γ-rays, $n_F=2\times10^{18}$ cm^{-3}; *E*, partly bleached.

the crystal was annealed for two hours at 570°K. This treatment bleached the *F* band, but a small band remains which peaks at around 2100A and is quite similar to the one described by Delbecq and Pringsheim.[24] The nature and oscillator strength of the centers responsible for this band is unknown. The thermal conductivity is given by curve *E*. Finally, after the crystal is bleached completely, curve *A* is obtained again. The process is completely reversible. Figure 4 shows the same effect of *F* centers on the thermal conductivity, but in this case of a thin crystal; again the presence of *F* centers is accompanied by a large decrease of the thermal conductivity at low temperatures. The particular shape of the curve is different because of the different conductivity in the unirradiated specimen (boundary effect).

These experiments show that a rather small concentration of defects results in a very large decrease of the thermal conductivity on the low-temperature side. They therefore belong to the second group of experiments described in Sec. I. But before drawing conclusions from the present experiments, it must be shown that explanations like those given for these earlier experiments cannot apply to the present investigation.

The *F* electron is very tightly bound. This excludes a phonon scattering by electrons. The formation of clusters with size comparable to the phonon wavelength—in this case colloidal Li metal—is a possibility that must be discussed in more detail. At temperatures much below the Debye temperature Θ the most numerous phonons in a Debye distribution have the wavelength $\lambda=a\Theta T^{-1}$, in which a^3 is the molecular volume. For LiF, $\Theta=722$°K, $a^3=(4\text{A})^3/4$, $a=2.5$ A, and therefore at 7°K, for example, $\lambda=250$ A. From the investigations by Miescher[25] and by Scott and Smith,[26] it follows that a neutral alkali metal in the lattice absorbs light with practically the same oscillator strength, independent of whether it is atomically dispersed or present in the form of clusters. A density $n_F=10^{16}$ cm^{-3} can be easily detected by means of optical absorption. Since the irradiated crystals do not show absorption apart from the *F* and *M* band, it is assumed that a maximum of 10^{16} cm^{-3} neutral Li atoms are present in form of clusters. For the present purpose their size would have to be 250A in diameter. This means the density n_c of the colloids is at most 2×10^{10} cm^{-3}. The geometrical cross section of the colloid is 5×10^{-12} cm^2. Upon setting the geometrical cross section σ of the colloid equal to the phonon scattering cross section according to Slack, the phonon mean free path l becomes

$$l=1/n_c\sigma\approx10 \text{ cm}.$$

This is 100 times as long as the mean free path as given by the boundary effect in the small crystal ($l_{\text{exp}}=0.88$ mm), and therefore phonon scattering by colloids should not be detectable.

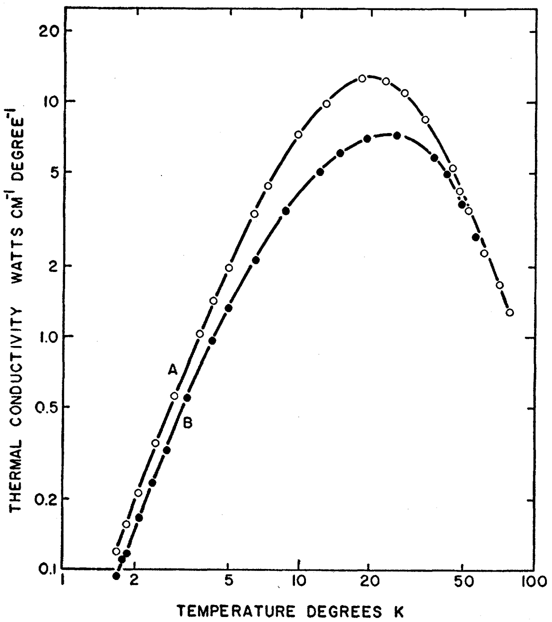

FIG. 4. Thermal conductivity of LiF. *A*, same as curve *C* in Fig. 1, 0.74×0.79×40 mm, sandblasted and annealed; *B*, after x-irradiation at 300°K, $n_F=2.2\times10^{17}$ cm^{-3}.

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[24] C. J. Delbecq and P. Pringsheim, J. Chem. Phys. **21**, 794 (1953).

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The foregoing calculations are based on one particular picture of phonon scattering by clusters. This picture has not yet been proved experimentally. An attempt was made to obtain experimental evidence that the formation of clusters is unimportant in our experiments by studying the effect of x-irradiation at 77°K on LiF, with the results shown in Fig. 5. Curve *A* is the unirradiated crystal; curve *B* was measured immediately after the x-irradiation at 77°K (without warming the crystal up). A short warmup to room temperature restores the original conductivity, curve *C*. The formation of colloids in alkali halides at 77°K during x-irradiation seems very unlikely. Besides it is known from investigations of colloids that it takes temperatures well above room temperature to redissolve them (see, for instance, Miescher[25] and Scott and Smith[26]). The fact that the original thermal conductivity is restored during a short warmup to room temperature indicates that the defects produced during the x-irradiation at 77°K anneal at or even below room temperature. It is therefore assumed that these defects cannot be colloids but are probably of atomic dimensions. A comparison of the data shown in Fig. 5 with those obtained with a crystal of same size which was irradiated at room temperature in order to produce *F* centers (Fig. 4) shows that the irradiation results in both cases in a very similar decrease of the conductivity. It is therefore concluded that the defects which produce the change in the conductivity after x-irradiation at room temperature also are of small size (or else the clusters would have to scatter in the same way as the small size defects produced at low temperatures).

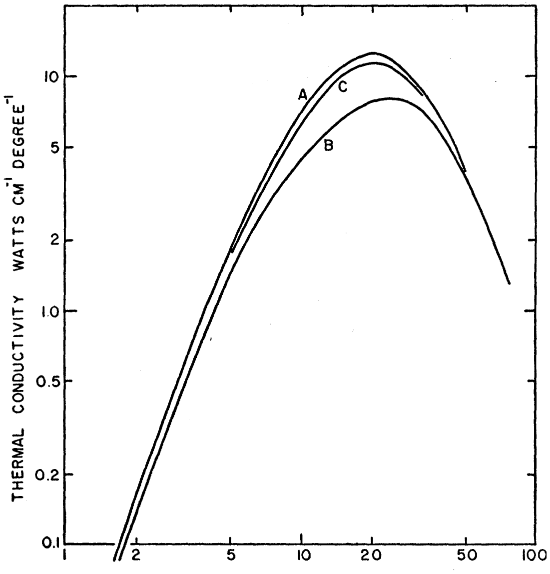

FIG. 5. Thermal conductivity of LiF, 0.94×0.92×40 mm, annealed and sandblasted. *A*, annealed, "pure"; *B*, after 60 kv x-rays at 77°K, measured without warming up after the irradiation; *C*, measured after a short warmup to 300°K. To improve the clarity, the experimental points have been omitted in this figure.

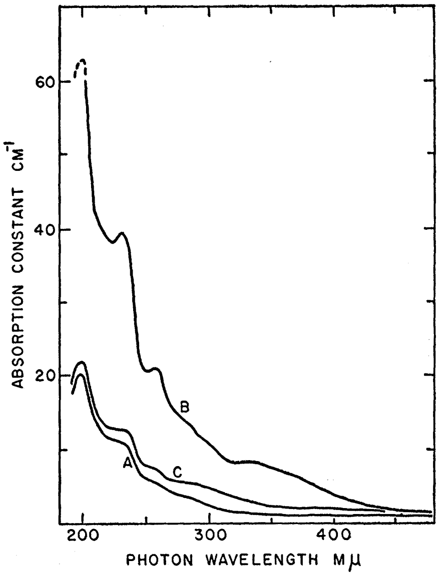

FIG. 6. Optical absorption of LiF after the same treatment as in Fig. 5. Measured and irradiated at 90°K.

It should be noted parenthetically that the particular reaction products of photochemical processes at low temperatures depend appreciably on the state of purity of the crystal. Figure 6 gives one example. Here the effect of the low-temperature irradiation on the optical absorption was measured. Curve *A* is the "pure" crystal. Although transparent at 300°K, it shows some absorption at 90°K. The absorption shown in *B* is produced by x-irradiation. In addition to a broad band at 3400A, three other bands whose nature is unknown are observed, but no *F* centers. A short warmup reduces *B* to almost the original value, curve *C*. These observations do not agree with the experiments of Pringsheim and Yuster.[27] They reported that irradiation with x-rays at 77°K produced the *F* band at 2420A and a broad band at 3400A. Warming to 138°K bleached this band, but not the *F* band. Warming to 300°K bleached half of the *F* centers. This discrepancy can probably be attributed to impurities in the specimen investigated here. Since this problem did not seem to be relevant to the questions investigated in this paper, no further attention was paid to it.

It is interesting to compare the results obtained on additively colored crystals with those observed on photochemically colored crystals. It has not been found possible to color LiF additively. Deviatkova and Stilbans[28] studied the thermal conductivity of additively colored KCl at 100°K, 200°K, and 300°K, using *F* center concentrations up to 5×10^{18} cm^{-3}. The changes in thermal conductivity which they found were small and showed appreciable scatter. Therefore, a study of the same substance was attempted, but extended to

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[27] P. Pringsheim and P. Yuster, Phys. Rev. **78**, 293 (1950).

[28] E. D. Deviatkova and L. S. Stilbans, J. Tech. Phys. (U.S.S.R.) **22**, 968 (1952).

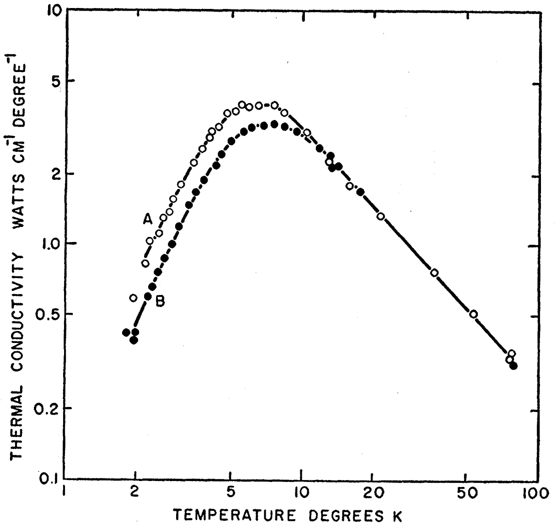

FIG. 7. Thermal conductivity of Harshaw KCl, 4×4.5×40 mm. *A*, cleaved and annealed; *B*, after additive coloration, $n_F=8\times10^{17}$ cm^{-3}. Since the surface was damaged during the coloration, it is not known how much of the low-temperature depression is caused by the change in specular reflection. Since the crystal is rather large, we expect this influence to be small.

lower temperature, where major changes were expected. The results of a preliminary investigation are shown in Fig. 7. The decrease below the maximum is well outside the experimental error, and the general behavior indicates that additive coloration reduces the thermal conductivity in the same way as does the photochemical coloration. The same density of *F* centers produces a smaller thermal resistivity (reciprocal thermal conductivity) in the additively colored KCl than in the photochemically colored LiF. An experimental investigation of both types of coloration in the same material is presently under way.

V. THEORY

In this section the theoretical expressions for the lattice thermal conductivity are briefly reviewed. In particular the difference between the models used by Klemens[7–10] and Callaway[11] are discussed. As first suggested by Debye in 1914 the lattice thermal conductivity *K* can be written as follows:

$$K=\tfrac{1}{3}C_v v l. \tag{2}$$

C_v is the specific heat per unit volume at constant volume, v is the velocity of sound, and l is an average phonon mean free path. A more detailed approach must take into account the fact that the phonon mean free path depends on the phonon circular frequency ω. Using the Debye expression for the specific heat one obtains[7,11]

$$K=\frac{1}{2\pi^2 v}\int_0^{\omega_D}\tau\frac{\hbar^2\omega^4}{kT^2}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega. \tag{3}$$

ω_D is the Debye limiting frequency. The relaxation time τ must take into account all the different scattering mechanisms. For those which lead to the same distribution of the phonon gas, namely a Planck distribution, the combined relaxation time τ is given by

$$\tau^{-1}=\sum\nolimits_i \tau_i^{-1}, \tag{4}$$

where τ_i is the relaxation time for the ith scattering mechanism.

Since the relaxation times τ_i in general depend on the phonon frequency ω and the temperature T, the combined relaxation time τ is a rather involved function. In the following discussion, consideration will be given separately to the Klemens and Callaway approaches.

(1) To reduce the mathematical difficulties Klemens confines himself to those cases where only one scattering mechanism is active. Klemens thus calculates the conductivity for the different scattering mechanisms separately. For instance, for point defects (randomly distributed imperfections with diameters small compared to the wavelength), the relaxation time τ_{pt} is

$$\tau_{\text{pt}}=A^{-1}\omega^{-4}. \tag{5}$$

(A is a constant containing the concentration of point defects.) In this case, Eq. (3) becomes

$$K=\frac{1}{2\pi^2 v}\int_0^{\omega_D}\frac{\hbar^2}{kT^2A}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega. \tag{6}$$

This integral diverges as ω approaches zero.

According to Klemens, the long wavelength phonons which would cause the divergence of Eq. (6) are scattered predominantly by "normal processes." These are three-phonon processes which conserve wave vector and therefore by themselves do not cause thermal resistance. The scattering process annihilates the long wavelength phonons and creates phonons with the typical frequency

$$\omega_1=kT/\hbar. \tag{7}$$

Then Eq. (3) becomes

$$K_{\text{pt}}=\frac{1}{2\pi^2 v}\int_0^{\omega_1}\frac{\hbar^2}{kT^2A}\frac{\omega^4}{\omega_1^4}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega+\frac{1}{2\pi^2 v}\int_{\omega_1}^{\omega_D}\frac{\hbar^2}{kT^2A}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega, \tag{8}$$

and thus

$$K_{\text{pt}}=\frac{0.9\hbar}{2\pi^2 vA}T^{-1}. \tag{9}$$

In the case of mass difference only (the isotope effect), Klemens showed that the constant A was given by

$$A=\frac{a^3}{4\pi v^3}\sum_i f_i\left(1-\frac{M_i}{\bar{M}}\right)^2. \tag{10}$$

In this expression, $\bar{M}$ is the average total mass of the molecule, M_j is the mass of the molecule containing the jth impurity, a^3 is the molecular volume, v is the velocity of sound, and f_j is the ratio of the number of molecules with mass M_j to the total number of molecules and equals $n_j a^3$ with n_j the number density of the jth impurity.

In order to compare his theory with experiments, in which several scattering mechanisms are always present, Klemens writes in the first approximation[29]:

$$K^{-1}=\sum_i K_i^{-1}. \tag{11}$$

(2) Callaway uses the fact that the boundary effect can act as a cutoff mechanism for the low-frequency phonons and avoids the low-frequency divergence by simply using Eqs. (3) and (4). He considers four different scattering processes: (1) boundary scattering, described by a constant relaxation time $\tau_B=Lv^{-1}$, where v is the velocity of sound and L some length characteristic for the specimen investigated; (2) "normal" three-phonon processes; their relaxation time τ_N is taken to be proportional to $\omega^{-2}T^{-3}$; (3) impurity scattering, including isotope scattering, whose relaxation time τ_{pt} is independent of temperature and proportional to ω^{-4}; (4) umklapp processes with a relaxation time τ_U proportional to $e^{\Theta/aT}\omega^{-2}T^{-3}$, where Θ is the Debye temperature and a is a constant characteristic of the vibrational spectrum of the material

For the comparison with the isotope experiment of Geballe and Hull,[16] Callaway writes:

$$\begin{aligned}\tau&=(\tau_B^{-1}+\tau_N^{-1}+\tau_{\text{pt}}^{-1}+\tau_U^{-1})^{-1}\\&=(vL^{-1}+B_1T^3\omega^2+A\omega^4+B_2T^3\omega^2)^{-1}.\end{aligned} \tag{12}$$

This expression for τ contains two simplifications: (1) The normal processes do not lead to a Planck distribution of the phonon gas. Therefore the use of Eq. (4) for the determination of a combined relaxation time introduces an error which Callaway discusses in his paper. (2) The exponential term $e^{\Theta/aT}$ in τ_U is neglected. This means $a=\infty$. The justification for this is found by comparison with the experiment: Introduction of Eq. (12) into Eq. (3) yields

$$K=\frac{1}{2\pi^2 v}\int_0^{\omega_D}\frac{\hbar^2\omega^4k^{-1}T^{-2}}{A\omega^4+(B_1+B_2)T^3\omega^2+vL^{-1}}\,\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega. \tag{13}$$

By choosing the parameters A and (B_1+B_2) properly, Callaway obtains a very good quantitative agreement between theory and the experiment in the temperature range from 2.5°K to 100°K.

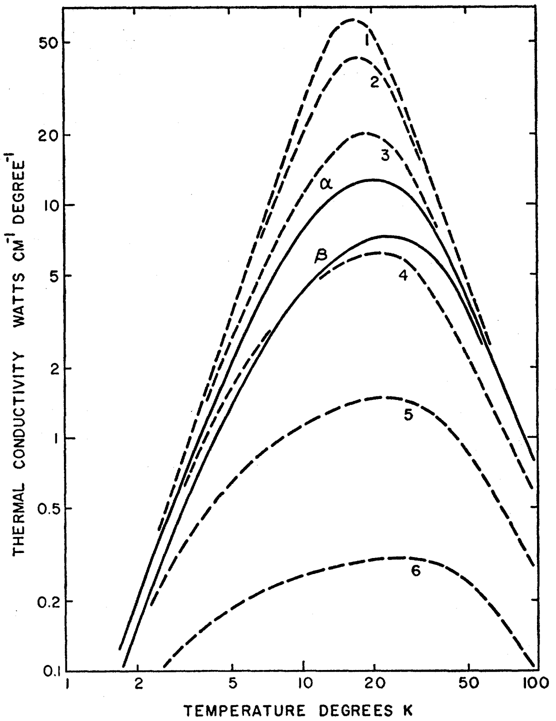

FIG. 8. Thermal conductivity of LiF. Comparison of theory with experiment. α and β are experimental curves, the same as curves *A* and *B* in Fig. 4. Curves 1 to 6 were computed, using Callaway's model, for various concentrations of point defects. The factor *A* is proportional to Γ discussed by Klemens, reference 10, and Toxen, reference 12, and for small *A* is proportional to the concentration of point defects. The value of the parameter *A* for the different curves is: Curve 1, $A=0$; curve 2, $A=5\times10^{-46}$ sec^3; curve 3, $A=5\times10^{-45}$ sec^3; curve 4, $A=5\times10^{-44}$ sec^3; curve 5, $A=5\times10^{-43}$ sec^3; curve 6, $A=5\times10^{-42}$ sec^3.

VI. COMPARISON OF THEORY WITH EXPERIMENT

The results of Callaway's theory agree well with the data obtained in the isotope experiment. Therefore, the same theory will be applied in this section to LiF, assuming the presence of point-defects scattering with a relaxation time $\tau_{\text{pt}}\propto\omega^{-4}$. The results will be used for the comparison with two experimental investigations: (1) They will be compared with the *F* center experiment reported in this paper. (2) They will be used to explain experimental results reported by Toxen,[12] and this comparison will furnish further support for Callaway's model.

Curve α in Fig. 8 is the thermal conductivity of "pure" LiF (curve *A* from Fig. 4). We assume that the thermal conductivity above 60°K is almost entirely intrinsic for our particular material. This conclusion is supported by many experiments on LiF from different sources and with different treatments. Berman and others,[30] for instance, investigated the thermal conductivity of LiF with various isotopic compositions be-

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[29] The error introduced by using Eq. (11) instead of Eq. (3) plus Eq. (4) has been estimated by Slack[17] for the case of the combination of point defect and umklapp scattering and the case of combination of boundary and point-defect scattering. For the point defects he used the cutoff mechanism by normal processes from Eq. (7).

[30] R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).

tween 13°K and 80°K. The natural isotopic mixture contains 92.6% Li^7 and 7.4% Li^6. They varied the concentration of Li^6 from 4.7% to 95.3%. Their specimens also seem to be of higher chemical purity. Nevertheless the thermal conductivity above 60°K is practically the same for all crystals and agrees with the data reported here. The theoretical curve for the pure LiF will be matched to the low-temperature data (boundary effect) and the high-temperature data (intrinsic effects) of the experimental curve α of the unirradiated LiF.

The constants needed for Eq. (13) are determined in the following way. The specific heat C_v of LiF has been determined experimentally by Clusius and co-workers[31,32] and by Scales[33] in the temperature range from 2°K to 270°K. From these data Θ can be determined. Below $T=25$°K the Debye Θ is constant and equals 722°K. Θ is defined by the following equation:

$$\frac{\Theta}{T}=\frac{\hbar\omega_{\mathrm{D}}}{kT}=\frac{\hbar v(6\pi^2N)^{\frac{1}{3}}}{kT}, \qquad (14)$$

where N is the total number of molecules per unit volume. From this, ω_{D} and v can be determined:

$$\omega_{\mathrm{D}}=9.4\times10^{13}\ \mathrm{sec}^{-1};\quad v=5\times10^5\ \mathrm{cm\ sec}^{-1}.$$

According to Casimir,[4] L for a crystal with a square cross section d^2 is given by $L=\pi^{\frac{1}{2}}d$. For the crystal measured in Fig. 4, $d=0.75$ mm and $L=1.33$ mm. A better agreement with the experiment in the region where the T^3 dependence is found is obtained by writing $d=0.88$ mm and $L=1.55$ mm. A possible explanation for this small disagreement might be that a small fraction of the phonons is reflected specularly at the crystal surfaces, but the Casimir expression is probably not sufficiently accurate to warrant this conclusion.

Callaway's method of determining (B_1+B_2) in Eq. (13) will now be briefly reviewed. The correct sum of the reciprocal relaxation times according to Callaway is given by

$$\tau_U^{-1}+\tau_N^{-1}=(B_1e^{-\Theta/aT}+B_2)\omega^2T^3.$$

Callaway points out that in the case of germanium a might be of-the-order-of 8, because of the extreme dispersion in the vibrational spectrum. He then simplifies:

$$\tau_U^{-1}+\tau_N^{-1}=(B_1+B_2)\omega^2T^3,$$

in which (B_1+B_2) is a constant and which implies that $a=\infty$. He then gives an equation [his Eq. (36)] which permits calculation of (B_1+B_2). A rough estimate shows that in doing the same thing for LiF the temperature dependence of the thermal conductivity above 60°K does not come out correctly. Hence, we seek another expression for the combined intrinsic relaxation times. A better agreement with the experiment is obtained empirically by choosing

$$\tau_U^{-1}+\tau_N^{-1}=(B_1+B_2)\exp(-50°\mathrm{K}/T)\omega^2T^3.$$

A more theoretical determination of $(\tau_U^{-1}+\tau_N^{-1})$ would be desirable, but seems premature at the present state of the experiment, where too little is known about the thermal conductivity of an ideal LiF crystal.

At a given temperature (in this case 77°K), one can write

$$(B_1+B_2)^*=(B_1+B_2)\exp(-50°\mathrm{K}/T),$$

and thus use Callaway's equation to determine $(B_1+B_2)^*$ and thereafter (B_1+B_2):

$$(B_1+B_2)=1.35\times10^{-22}\ \mathrm{sec\ deg}^{-3}.$$

The computation of Eq. (13) for different concentrations of point defects, i.e., different constants A, is not difficult if a high-speed electronic computer is available. The results are shown in Fig. 8. One can draw the following conclusions:

(1) The experimental curve α of the unirradiated LiF can be represented reasonably well by a theoretical curve. By interpolation, one determines $A\approx10^{-44}$ sec³. Using Eq. (10) one calculates for the isotope effect alone $A=1.1\times10^{-45}$ sec³. This value is smaller than the experimentally determined A, which is reasonable since the LiF crystal used in the experiments also contained chemical impurities. Their nature is unknown, but one can expect divalent ions and vacancies. These impurities or imperfections might also be the reason why the shape of the curve α does not conform exactly to the set of calculated curves.

Curve β is the thermal conductivity for the crystal containing 2.2×10^{17} cm^{-3} F centers (curve B from Fig. 4). It is obvious that β cannot be accurately represented by a parameter A. This means that the defects introduced during the x-irradiation do not scatter phonons like point defects, i.e., with a relaxation time $\tau_{\mathrm{pt}}=A^{-1}\omega^{-4}$. Three possible reasons will be presented in Sec. VII.

It should be mentioned in passing that the experimental results cannot be explained with Klemens' formulas at all. He predicts $K_{\mathrm{pt}}^{-1}\propto T$ [Eq. (9)]. With $K^{-1}=\sum K_i^{-1}$, one obtains from the experiments (Figs. 3 and 4) approximately $K_{\mathrm{pt,exp}}^{-1}\propto T^{-1.5}$ at low temperatures ($T<8$°K) and $K_{\mathrm{pt,exp}}^{-1}=$constant at high temperatures. Thus the Calloway model is much closer to the experimental facts, especially at low temperatures.

(2) Another interesting application of the calculations is to the problem first pointed out by Toxen. According to Klemens, point defects change the thermal conductivity by causing a thermal resistivity

$$W_{\mathrm{pt}}=(2\pi^2vA/0.9\hbar)T. \qquad (9)$$

A is the proportionality factor in the expression for the point-defect relaxation time

$$\tau_{\mathrm{pt}}=A^{-1}\omega^{-4}\,. \qquad (15)$$

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[31] K. Clusius, J. Goldmann, and A. Perlick, Z. Naturforsch. 4A, 424 (1949).

[32] K. Clusius and W. Eichenauer, Z. Naturforsch. 11A, 715 (1956).

[33] W. W. Scales, Phys. Rev. 112, 49 (1958).

At constant temperature W_{pt} should be proportional to A:

$$W_{\mathrm{pt}} \propto A. \tag{16}$$

Toxen tried to verify Eq. (16) experimentally in the following way: Klemens gives an expression for the constant A used in Eq. (15). For mass difference only, for instance, A is given in Eq. (10). To make a comparison between differential materials, Toxen used Klemens' expression:

$$A = (a^3/4\pi v^3)\Gamma_{\mathrm{th}}.$$

Then,

$$W_{\mathrm{pt}} = (\pi a^3 \Gamma_{\mathrm{exp}}/1.8\hbar v^2)T. \tag{17}$$

According to Klemens these two Γ's should be equal. The subscripts indicate what Toxen did. Γ_{th} was calculated, using the expression given by Klemens. Γ_{exp} was determined from the experiment in the temperature range where the thermal conductivity varies more or less in inverse proportion to the temperature. A double logarithmic plot of Γ_{exp} vs Γ_{th} should give a straight line with unit slope. Figure 9 shows the results, taken from different investigators and materials. Γ_{exp} rises much slower than Γ_{th}. In particular, the deviation for large Γ is significant. Here the contribution from the intrinsic scattering processes should be small, and therefore the determination of W_{pt} from the experiment should be reliable. This seemed to reveal an interesting experimental fact: In the concentration range where point defects outweigh all other scattering mechanisms, the resistivity does not change in the same way as the point-defect relaxation time: Eq. (16) is in disagreement with the experiment.

Callaway's approach gives a very simple explanation of this observation: In Fig. 8 the conductivity is plotted for several point-defect concentrations. A varies over four orders of magnitude. Using Eq. (17), Γ_{th} can be calculated. At $T = 60°\mathrm{K} = 0.08\Theta$, W_{pt} is determined by simply subtracting the resistivity of the pure case, $A = 0$. Γ_{exp} and Γ_{th} are plotted in Fig. 9. The dependence is quite similar to what Toxen found by comparison with the experiment, and not linear as predicted by Klemens.

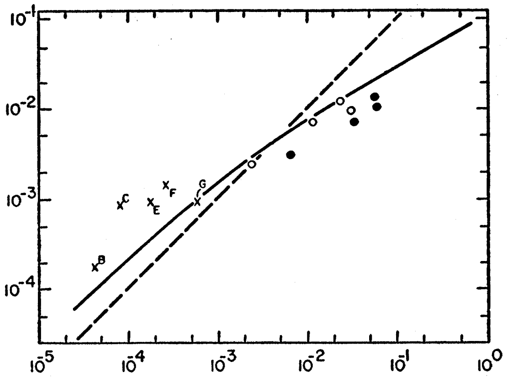

FIG. 9. A plot of Γ_{exp} versus Γ_{th}. The materials shown are: *B*, Ge^{74} enriched germanium, reference 15; *C*, diamond [R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956)]; *E*, KCl, reference 17; *F*, Si, reference 20; *G*, Ge, reference 20. The open circles are for Ge-Si mixtures, reference 12. The Si contents in the order of increasing Γ_{th} are 0.5%, 3%, 6%, and 7%. The solid circles are for KCl-KBr mixtures, reference 16. The KBr contents in the order of increasing Γ_{th} are 1.5%, 9.5%, 49%, and 28.3%. The dashed line represents Klemens' theory. The solid curve was determined using the computed curves in Fig. 8 as described in the text. It can be seen that Callaway's approach for point scatterers yields results quite similar to those obtained experimentally.

This means that the phenomena can be explained by simply using a combined relaxation time which automatically provides the boundary cutoff mechanism. This comparison of Γ_{th} and Γ_{exp} is an example of the difficulties one encounters by using Klemens' cutoff mechanism and simply adding resistivities, and shows how the crystal boundary cutoff mechanism as worked out by Callaway gives far better agreement with experiment.

VII. DISCUSSION

The present state of our knowledge about the influence of point defects on the lattice thermal conductivity is summarized in the following: The experiments can be divided into two groups. The first group is characterized by the isotope effect, i.e., the periodicity is disturbed by the difference in mass only. These experiments can be explained using Callaway's model. The other group of experiments deals with point defects of the general type. The experiment reported here belongs to this second group and cannot be quantitatively understood with Callaway's model and the assumption of point-defect scattering with a Rayleigh scattering mechanism. The nature of the defect, the *F* center, is reasonably well understood. There are no conduction electrons present which might scatter phonons. The influence of clusters can be ruled out. Therefore other explanations for the disagreement between theory and experiment must be considered. The following three will be discussed:

(1) The *F* centers might not be randomly distributed. As pointed out by Klemens,[8] a nonrandom distribution of point defects would cause a scattering with a different relaxation time τ. The model for the photochemical formation of *F* centers proposed by Seitz[34] would support this assumption. He suggests that *F* centers are mainly produced near the path of a climbing dislocation jog. From the preliminary results on additively colored KCl, the conclusion may be reached that both kinds of coloration affect the thermal conductivity in the same way. However it is possible that the *F* centers in the additively colored specimen are nonrandom just as in the irradiated specimens and thus cause the thermal conductivity to decrease the same way in the two cases. As shown by Cottrell,[35] defects might migrate to dislocations to release the

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[34] F. Seitz, Revs. Modern Phys. **26**, 80 (1954).

[35] A. H. Cottrell and B. A. Bilby, Proc. Phys. Soc. (London) **A62**, 49 (1948).

total strain in the crystal, which conceivably would affect the thermal conductivity in two ways: The release of the strain would increase the thermal conductivity, and the lining up of defects would decrease it by the introduction of coherent interference effects. The resulting change in thermal conductivity would have to be qualitatively the same as in the case of the x-irradiation.

(2) The scattering power of the long-range strain field around crystal imperfections may not be negligible. Carruthers[36] has pointed out that the effect of this strain field may be considerable. In particular, the strain field might be large enough in spatial extent so that only at very low temperatures—well below the conductivity maximum—a Rayleigh scattering mechanism can be expected. At higher temperatures, the defect would be large compared to the phonon wavelength, and the scattering power would be changed and perhaps strongly decreased.

(3) So far the applicability of Callaway's theory has been shown only in the case of point defects in Ge and Callaway makes only modest claims for his model. The phonon polarization, the fact that the normal processes do not lead to a Planck distribution, and the great importance of the normal processes for long wavelength phonons, as pointed out by Klemens, might have important influences on the thermal conductivity in other materials. In view of the great qualitative difference between the two groups of experiments described in the first section however, it seems unlikely that the experiments of the second group can be accurately described by assuming point-defect scattering proportional to ω^4, no matter what theory is used. This question could be answered experimentally by studying the isotope effect in LiF over a wider temperature range. The data available extend down to 13°K[30] and are qualitatively similar to those shown in Fig. 3, but the range which is important for this problem is the low-temperature region below the conductivity maximum.

VIII. CONCLUSION

(1) The effect of F centers on the thermal conductivity is distinctly different from that found with other point defects, such as isotope scatterers.

(2) The theory for the thermal conductivity in the presence of point defects developed by Callaway cannot explain the F-center experiments. Three possible explanations are suggested for the latter disparity: (a) the F centers are not randomly distributed. (b) The scattering power of the strain field connected with an F center might account for the depression of the thermal conductivity. This question requires a better theoretical understanding of these strain fields. (c) The F centers do scatter like point defects with a relaxation time $\tau_{\mathrm{pt}}=A^{-1}\omega^{-4}$ but the theoretical model by Callaway fails in materials like LiF. This question can be answered experimentally, for instance, by studying the isotope effect in LiF down to temperatures well below the conductivity maximum.

(3) The high sensitivity of the thermal conductivity to the presence of F centers indicates that the thermal conductivity can become a useful tool for the investigation of color centers.

(4) Toxen presented experimental evidence that the influence of point defects on the thermal conductivity did not agree with the model proposed by Klemens. The thermal conductivity was lowered much less than Klemens predicted. Evidence is presented that Callaway's model explains Toxen's observations.

IX. ACKNOWLEDGMENTS

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[36] P. Carruthers, Bull. Am. Phys. Soc. 5, 48 (1960).