also to the coupling to the elastic waves whose velocities depend on the direction.

If $\Omega$ is close to the $\omega^i$'s, no clear separation of thermal wave propagation and diffusion of heat is possible. The situation can be analyzed by plotting our result [see Eq. (89b)] for the heat response function. We have done this explicitly for a specialized case.

The quasiparticle interaction, described by **I**, has been taken into account throughout the paper. Although this does not seem to be of direct experimental interest for low temperatures in a crystal, it might be of importance for higher values of $T_0$. Equation (19) shows how one has to determine **I** experimentally.

Obviously the theory developed is very closely related to the problems of deriving hydrodynamic equations for superfluid $\mathrm{He}^{\mathrm{II}}$.[15] There it is known that $\omega(p)$ varies strongly with temperature if rotons are excited. Our technique could be of interest in this field.

## ACKNOWLEDGMENTS

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# Effect of Boundaries and Isotopes on the Thermal Conductivity of LiF†

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In order to test thermal-transport theories with data involving readily calculable phonon scattering rates, the thermal conductivity of LiF has been measured between 1 and 100°K, first for a series of isotopically pure crystals with sandblasted surfaces ranging in mean width from 1 to 7 mm, and then for a series of crystals ranging in isotopic content of $^7$Li from 99.99 to 51%. These data are used to investigate Casimir's theory, the boundary scattering mechanism, and the importance of normal processes in LiF. Sandblasted crystals at the lowest temperatures are found to exhibit a boundary-limited conductivity proportional to crystal width and the cube of the temperature, in agreement with Casimir's theory. However, the proportionality constant is strongly influenced not only by the sandblasting procedure but also by dislocations in the crystal interior. Further measurements, coupled with annealing studies and etch-pit counts, show that dislocations introduced near the crystal surface during sandblasting play a major role in the frequency-independent surface scattering of phonons assumed in Casimir's theory. The importance of normal processes is assessed by comparing both the boundary and isotope data with conductivities calculated from Callaway's model with normal processes neglected. Berman and Brock have already fitted similar isotope data with Callaway's theory, and normal processes played a crucial part in the fit. The present fits demonstrate the necessity of considering normal processes in LiF by showing that, though boundary data can be matched, even a determined effort to match the isotope data does not succeed when normal processes are neglected. Furthermore, normal processes are shown to provide the only mechanism for improving the fit.

## I. INTRODUCTION

The importance of crystal boundaries and isotopic composition in determining the low-temperature thermal conductivity of dielectric crystals has been known since observation of the former effect by de Haas and Biermasz[1,2] and recognition of the latter effect by Berman *et al.*[3] and Slack.[4] Despite considerable further investigation of these effects, no adequate effort has been made either to measure them carefully in the same crystal or to exploit the advantages of using them together as a test of thermal-conductivity theory. It is to these problems that the work reported here is addressed.[5]

The observation by de Haas and Biermasz of a reduction in the conductivity on approaching their lowest temperatures was explained to them[2] by Peierls as a boundary effect. The phonon mean free path does not increase without limit as the temperature is decreased, but is limited by collisions with the crystal walls. This effect was further studied by Makinson[6] and especially by Casimir,[7] who calculated the con-

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ductivity when phonons scatter only at diffusely reflecting crystal walls. The isotope effect, on the other hand, was observed only after Pomeranchuck[8] predicted it. He used perturbation theory to calculate the scattering of phonons by variations in isotopic mass in a crystal. The result was later corrected as to numerical constant by Klemens,[9] extended by Carruthers,[10] and rederived using Green's functions by Klein.[11] As a consequence both of these theoretical studies and of the relative simplicity of the scattering mechanisms themselves, the relaxation rates for phonon scattering by boundaries and isotopes are the two best-known phonon relaxation rates in crystals.

Not well known, however, is how to start from given phonon relaxation rates and compute the thermal conductivity. Peierls[12] did work out a complete quantum-mechanical theory of thermal conductivity, but the necessary comparison with experiment could not be made without recourse to approximations developed by Klemens,[13] Ziman,[14] and Callaway.[15] Callaway[16] has since shown that his theory includes Ziman's in the limit of strong normal processes, and Callaway's basic approach has been justified in turn by Nettleton[17] and Krumhansl.[18] More recently, Guyer and Krumhansl[19] have obtained still another representation for thermal conductivity.

In spite of the proliferation of theories and a like increase in data, both of which are reviewed by Klemens[13] and Carruthers,[10] few theories could be validated with confidence. It is for just such a validation that the boundary and isotope effects are most important. Since the relaxation rates for phonon scattering by boundaries and isotopes are well known, the only unknown in fitting a theory to the experimental data is the theory itself.

The boundary and isotope effects are also important in their own right because the former dominates the conductivity of pure crystals at the lowest temperatures and the latter helps determine the height of the conductivity maximum. These effects can be unraveled by first studying the boundary effect alone in an isotopically pure crystal. Such an experiment also offers the advantage of studying the minimum number of phonon-scattering processes: intrinsic scattering and boundary scattering.

Before using boundary-effect data to test a theory at all temperatures, it is first necessary to verify Casimir's prediction that the low-temperature boundary-limited conductivity is proportional to the crystal width and the cube of the temperature. The first successful experiments to this end were reported by Berman, Simon, and Ziman[20] and Berman, Foster, and Ziman.[21] Working with sapphires in the latter paper, they showed that only chemically pure crystals with roughened (ground) surfaces had a conductivity agreeing with Casimir's predictions. They also computed modifications of Casimir's theory for crystals of finite length with varying amounts of specular surface scattering, and they related the reflection coefficient to the surface roughness. The small range of crystal diameters investigated by Berman *et al.* was extended by Dreyfus and Zadworny,[22] but the necessary proportionality to temperature cubed was not observed. Pohl[23] initiated boundary-effect studies of LiF as well as the process of sandblasting a crystal surface to ensure the diffuse phonon scattering assumed by Casimir. Numerous investigators have since found essential agreement with Casimir's theory, but no systematic effort has been made either to verify this theory or to use the boundary-effect data to test a theory at higher temperatures.

The first isotope-effect data were provided by Geballe and Hull.[24] Their comparison of the conductivity of two zone-refined germanium crystals showed the enriched $^{74}$Ge crystal to have a higher conductivity than the crystal of natural isotopic composition. Callaway[15] used their results to test his theory, though the test was weakened by insufficient data and a meager knowledge of intrinsic scattering rates. Berman *et al.*[25] first measured a series of isotopic additions by using LiF crystals with varying amounts of $^6$Li and $^7$Li. Even though the data extended over only a narrow temperature range, it was still possible to show that Klemens's theory and an early formulation by Ziman could not fit the experimental results. Callaway and von Baeyer[26] then attempted to fit the LiF data with Callaway's theory. The fit to the data was satisfactory, but the presumably reliable numerical constant in the isotope relaxation rate had to be increased by a factor of 5. The isotope effect has also been measured for mixtures of He$^3$-He$^4$, though strains and other effects complicate interpretation of the results. Recent discussions are

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given by Berman, Bounds, and Rogers[27] and by Bertman *et al.*[28,29]

In order to extend the temperature and composition range of the previous isotope-effect work in LiF and to appraise the effects of impurities, more thorough investigations were undertaken at both Oxford and Cornell. The Oxford data have already been reported by Berman and Brock[30] and compared with Callaway's theory. They find good agreement between theory and experiment, and normal processes play an important part in their fit. The Cornell data are included in the present paper and are compared with Callaway's theory with normal processes neglected. Such a comparison is undertaken in order to investigate carefully and independently whether or not the success of Berman and Brock can be achieved by a simpler approach similar to the one originally used by Callaway[15] to fit the germanium isotope-effect data and more recently tested by Pohl[31] against KBr:$KNO_2$ conductivity data. In essence, the importance of normal processes in LiF is under investigation.

## II. EXPERIMENT

The apparatus and techniques for measuring low-temperature thermal conductivity were standard in most respects.[32,33] An important difference was the use of a He exchange gas in the temperature range 1.2–2°K to decrease equilibrium times by shunting the cryostat heat sink to the He bath. The cryostat design is given by Worlock.[34]

The temperature gradient along the crystal was measured with matched 100-Ω, 0.1-W Allen-Bradley resistors from 1–20°K and 1500-Ω, 0.1-W Allen-Bradley resistors from 4–100°K. In the important range 2–20°K this choice of resistors maximized the sensitivity of the 25 Hz, narrow-band amplifier and bridge built by Seward[35] to measure the resistances. Measurement power dissipation in the resistors was held to $10^{-9}$ W below 5°K and to $10^{-8}$ W above 5°K to avoid self-heating.

The primary temperature standard above 4.2°K was a variable-volume He gas thermometer calibrated by Moss. Below 4.2°K a Honeywell Type-II germanium resistor calibrated against the vapor pressure of liquid He was used. The advantages of such a resistor are discussed by Walker.[36] Both the germanium and carbon resistors were very reproducible during 75 cyclings from room to He temperatures, the germanium thermometer remaining within 0.5% of its original calibration and the carbon thermometers within 1% except for the first few cycles.

The measured data are expected to be in error by less than 5% below 5°K and by less than about 10% above. Most of this error arises from systematic deviations in the temperature calibration and from the computer's inability to fit exactly the thermometer resistances to a temperature calibration curve. Nevertheless, conductivities computed from the 100- and 1500-Ω resistor data always agreed within 3% in the temperature overlap region, and conductivities measured for one crystal with 1500-Ω and then 4600-Ω resistors agreed within 1% in their overlap region from 20–77°K. These results also show relative errors among measurements to be much smaller than absolute errors.

The crystals measured came from three sources. LiF of natural isotopic composition was purchased from the Harshaw Chemical Company no earlier than June 1963, to take advantage of the considerable increase in purity of their LiF in recent years. LiF of special isotopic composition was kindly loaned for both measurement and regrowth by the Reactor Chemistry Division of ORNL under the Research Materials Program. The purification and growth of LiF at Oak Ridge is described by Weaver *et al.*[37] The third source of LiF was through regrowth of ORNL and Harshaw starting material at the Cornell Crystal Growing Facility. The resulting Cornell crystals are among the purest yet grown when judged by the height of the thermal conductivity maximum, chemical analysis, and optical absorption. The details of crystal growth at Cornell and Oak Ridge will be reported elsewhere.

Spectrographic analysis by the Cornell Materials Science Analytical Laboratory of the isotopically pure boule used in this experiment showed copper, silicon, magnesium, and aluminum as the only detectable impurities. They were present in concentrations of less than 1 ppm. Optical-absorption measurements of the first crystals grown showed a strong, broad optical-absorption band at 3735 $cm^{-1}$ with narrow bands varying in strength from crystal to crystal at 3670, 3629, and 3577 $cm^{-1}$. Measurements were made on a Beckman IR-7 spectrophotometer. These bands were ascribed to $OH^-$ absorption[38] and were correlated both with a band which peaked below the 187-mμ cutoff of the Cary Model 14 spectrophotometer and with a band at

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about 10 eV in the vacuum ultraviolet. All these bands were eliminated in later crystals, but a band at 200 m$\mu$ remained, probably caused by an oxygen-containing impurity as suggested by Akpinar[39] and Klein.[40] The thermal conductivity was greatly reduced at low temperatures whenever $OH^-$ absorption was observed, but no correlation between thermal conductivity and the 200-m$\mu$ band was found as the band varied in absorption constant from $<5\times10^{-3}$ cm$^{-1}$ in one crystal to 0.5 cm$^{-1}$ in another.

## III. THEORY

The neglect of normal processes in Callaway's[15] theory results in the following expression for the lattice thermal conductivity $K$:

$$K=\frac{k}{2\pi}\left(\frac{kT}{\hbar}\right)^3\langle v^{-1}\rangle\int_0^{\Theta/T}\tau_R(x,T)\frac{x^4e^x}{(e^x-1)^2}dx. \quad (1)$$

$\langle v^{-1}\rangle$ is an appropriately averaged sound velocity, $\tau_R(x,T)$ is the total relaxation time for those mechanisms relaxing the phonon distribution to the stationary Planck distribution, and $x=\hbar\omega/kT$, where $\omega$ is the phonon frequency. Equation (1) is equivalent to Debye's[41] original expression for the thermal conductivity and was first obtained by Makinson[6] in the form used here. In order to contrast Callaway's model with the present approach, Eq. (1) will be referred to as the Debye model.

The Debye model achieves its simplicity at the expense of numerous assumptions reviewed by Pohl.[31] Perhaps the most important assumption involves the neglect of normal processes. According to Callaway,[15] such an assumption amounts to the neglect in Eq. (1) of a term proportional to $\sum_q \tau_R\tau_N^{-1}[N_q(\lambda)-N_q]\omega_q v_q$. $\tau_N^{-1}$ is the normal process relaxation rate, $N_q(\lambda)$ the phonon distribution stationary for normal processes, $N_q$ the actual phonon distribution, and $\omega_q$ the frequency of a phonon with wave vector $q$ and velocity $v_q$. This term can be important when $\tau_R\gg\tau_N$ (strong normal processes), is small when $\tau_R\ll\tau_N$, and vanishes when $\tau_R$ is independent of $q$ because of the quasi-momentum conserving properties of normal processes.[15] The term may also be small because it is the difference of two terms.

The Debye acoustic approximation, $\omega_q=vq$, is also assumed in the model and influences the values of $\langle v^{-1}\rangle$ and $\tau_R$ in Eq. (1). $\langle v^{-1}\rangle$ and $\tau_R$ are further dependent on averages over phonon angular direction and polarization. The polarization average may not be too critical at low temperatures. Holland,[42] for instance, found that a fit in which polarizations were averaged matched silicon conductivity data from 2–100°K as well as his approach in which the separate longitudinal and transverse phonon contributions to the conductivity were considered. However, above 200°K only Holland's polarization separation method agreed with the data.

TABLE I. Low-temperature sound velocities in LiF.

| Direction | Polarization | Velocity ($10^5$ cm/sec) |
|---|---|---|
| $\langle 100\rangle$ | Longitudinal | 6.87[a] |
| | Transverse | 4.95[a] |
| $\langle 110\rangle$ | Longitudinal | 7.49[a] |
| | Transverse | 4.95 |
| | Transverse | 3.94 |
| $\langle 111\rangle$ | Longitudinal | 7.67 |
| | Transverse | 4.30 |

Averages by Houston's method:

$\langle v^{-1}\rangle_H=(5.17\times10^5)^{-1}$ (cm/sec)$^{-1}$,
$\langle v^{-2}\rangle_H=(5.04\times10^5)^{-2}$ (cm/sec)$^{-2}$,
$\langle v^{-3}\rangle_H=(4.93\times10^5)^{-3}$ (cm/sec)$^{-3}$,
$v_{\text{Debye}}=k\Theta/\hbar(6\pi^2N)^{1/3}=4.88\times10^5$ cm/sec.

[a] Measured in Ref. 45.

Velocity averages were obtained by Houston's method[43,44] for lack of a more secure procedure. Directional velocities to be included in Houston's method were computed from low-temperature sound velocities in LiF measured by Briscoe and Squire,[45] the density, and equations reported by Betts *et al.*[44] The variation of the density with isotopic composition, about 2% for the present experiment, was neglected. Isotopic composition has little effect on the lattice parameter of LiF, at least at room temperature, as shown by Thewlis.[46]

Table I gives computed directional velocities in LiF and some velocities averaged by Houston's method (denoted by subscript H). The Debye velocity for LiF is included for comparison, and $v_{\text{Debye}}$ and $\langle v^{-3}\rangle_H^{-1/3}$ agree within 1% as they should. The Debye velocity, as well as the upper limit in Eq. (1), were computed using $\Theta_D=722$°K as reported by Scales.[47]

The total relaxation rate $\tau_R^{-1}$, which is inverted for use in Eq. (1), is assumed to be given by the sum of the relaxation rates for each individual scattering process. In the present experiment, relaxation rates are required for phonon scattering by boundaries, isotopes, and umklapp processes.

### A. Boundary Scattering and Casimir's Theory

Casimir's[7,10] expression for the boundary-limited conductivity is given most directly by

$$K=(2\pi^2/15)(kT/\hbar)^3\langle v^{-2}\rangle 1.12d, \quad (2a)$$

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where $d$ is the mean width of a rectangular crystal. If $d$ is expressed in centimeters and $\langle v^{-2}\rangle$ is set equal to $\langle v^{-2}\rangle_H$, Eq. (2a) becomes

$$K = 0.180dT^3 \text{ W cm}^{-1} \text{ deg}^{-1}. \qquad (2b)$$

The $\langle v^{-2}\rangle$ appearing in Eq. (2a) was derived on the assumption of isotropic velocities, and Table I shows velocities in LiF to be quite anisotropic. However, a direct solution for the boundary-limited conductivity of LiF including the angular dependence of velocities showed $\langle v^{-2}\rangle$ to be given by $\langle v^{-2}\rangle_H$ within 1%. It should further be noted that the acoustic approximation for velocities, which also enters into Casimir's theory, is well met for the boundary effect in LiF because Scales[47] showed $\Theta_D$ to be independent of temperature out to 14°K.

The boundary-limited conductivity can be obtained from Eq. (1) by setting $\tau_R$ equal to the frequency-independent boundary relaxation time $\tau_B$. Since boundary scattering dominates only at the lowest temperatures, $\Theta/T \rightarrow \infty$; and when $\langle v^{-1}\rangle$ is taken from Table I and $\tau_B$ is expressed in seconds, Eq. (1) becomes

$$K = 7.88\times 10^4 \tau_B T^3 \text{ W cm}^{-1} \text{ deg}^{-1}. \qquad (3)$$

In principle $\tau_B$ can now be calculated from Eqs. (2) and (3). In practice, however, $\tau_B$ was chosen to make Eq. (3) fit the low-temperature data. This procedure was adopted because, though Eq. (2b) proved to be of the correct form, the proportionality constant did not quite describe the data.

### B. Isotope Scattering

The isotope-scattering relaxation rate is given by Klemens[9] and Carruthers[10] as

$$\tau_I^{-1} = \frac{\Omega_0\langle v^{-3}\rangle}{4\pi}\omega^4 \sum_i f_i\left(1-\frac{m_i}{\bar{m}}\right)^2 = Ax^4T^4. \qquad (4)$$

$\Omega_0$ is the volume of a unit cell, $f_i$ the fraction of unit cells having mass $m_i$, and $\bar{m}$ the average mass. $\Omega_0$ was obtained from the low-temperature lattice constant[48] of $a = 2.00$ Å. The $\langle v^{-3}\rangle$ was taken as equal to $\langle v^{-3}\rangle_H$, despite the fact that in calculating $\tau_I^{-1}$ it was assumed that all polarization branches have the same velocity and that that velocity is independent of angle and obeys the acoustic approximation. Resulting values of $A$ in Eq. (4) as a function of the percentage of $^7$Li in LiF are given in Table II for the crystals of this experiment.

### C. Umklapp-Process Scattering

The relaxation rate for umklapp scattering is by far the most difficult to treat theoretically, even after making the serious single-mode approximation. However, most attempts at fitting experimental curves have more or less successfully used a form for the umklapp relaxation rate $\tau_U^{-1}$ which combines results of Herring[49] and Peierls[12]:

$$\tau_U^{-1} \propto \omega^2 T^n e^{-\theta/bT} = x^2 f(T).$$

This form was also chosen for the present work.

$f(T)$ was computed by using Eq. (1) and the Cornell Computing Center's CDC 1604 computer to fit the conductivity data of the largest isotopically pure LiF crystal shown in Figs. 1 and 4. Only $\tau_B^{-1}$ and $\tau_U^{-1}$ should then enter into $\tau_R^{-1}$ since $\tau_N^{-1} = 0$ by assumption. Any effects of residual impurities, which become less important in less isotopically pure crystals, are included in $\tau_U^{-1}$. Once $\tau_B^{-1}$ was determined using Eq. (3), the integral was reduced to a form tabulated by Callaway[16] with limits 0 to $\infty$. $f(T)$ versus $T$ could then be determined and $f(T)$ fit by an analytic function. The resulting expression for $\tau_U^{-1}$ was

$$\tau_U^{-1} = 106x^2T^3[e^{-27/T} + 500e^{-186/T}]\text{sec}^{-1}. \qquad (5)$$

In view of the method of derivation, no great theoretical or physical significance can be attached to the parameters in this expression.

## IV. EXPERIMENTAL CHECK OF THEORY

### A. Casimir's Theory

The most striking confirmation of the boundary effect and Casimir's theory is shown in Fig. 1. The influence of crystal width on the low-temperature conductivity is easily seen, and the predicted $T^3$ dependence is evidenced by the straight lines of slope 3 on the graph of $\log K$ versus $\log T$. In order to ensure that only phonon scattering by boundaries varied among the crystals of Fig. 1, all crystals were cleaved from the same isotopically and chemically pure boule, and all were annealed before sandblasting the surfaces. Isotopically pure crystals were used because the $T^3$ region of dominant boundary scattering extends to 6°K, whereas increased isotope scattering in natural LiF limits the $T^3$ region to below 4°K.

The $T^3$ dependence was checked routinely by plotting $K/T^3$ versus $T$. Figure 2 shows the best such plot, obtained after recalibrating the germanium thermometer, and the exponent of $T$ is seen to be 3.005 within 0.5% from 1.25–6°K. The other plots, one including data extended to 0.3°K by Seward,[50] gave the exponent as 3 within 2%. The uncertainty in the exponent came from inaccuracies in the germanium thermometer calibration because the same pattern of scatter occurred on

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[48] The low-temperature lattice constant was obtained from the room-temperature value (Ref. 46) and the thermal expansion data of H. Adenstedt [Ann. Physik **26**, 69 (1936)]. See also G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 402.

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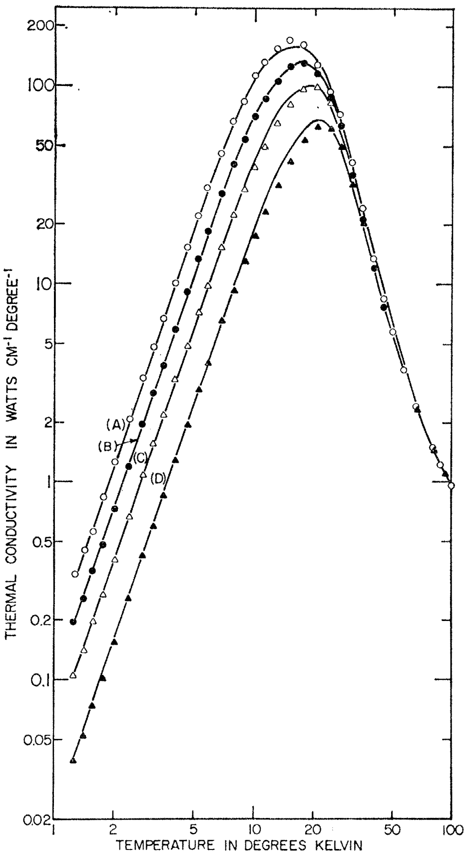

FIG. 1. Thermal conductivity of isotopically pure LiF showing the effect of boundaries for sandblasted crystals. Mean crystal widths: (A) 7.25 mm, (B) 4.00 mm, (C) 2.14 mm, (D) 1.06 mm. Solid curves are calculated from Eq. (1).

almost all plots. More recently, Harrison[51] has extended data on curve (B) in Fig. 1 to 0.06°K using his demagnetization cryostat. A least-squares fit to the data gave the exponent of $T$ as $3.005\pm0.007$. Boundary scattering must therefore be a frequency-independent phonon process. Any dependence of $\tau_B$ on $\omega=T(kx/\hbar)$, except for the unusual functional form $f(\omega/T)$, would change the temperature dependence of the conductivity from the $T^3$ appearing before the integral in Eq. (1).

The proportionality of conductivity to crystal width $d$ was determined by plotting $K/T^3$ versus $d$ as shown in Fig. 3. This figure includes data on all sandblasted LiF crystals measured to low temperatures in this experiment except for data on two abraded crystals and three containing dislocations. In particular, data on the four crystals of Fig. 1 appear as the filled circles in Fig. 3. The straight line gives the slope $K/dT^3$ averaged for all the points. All crystals which were annealed before sandblasting fell on this curve, so by such a procedure boundary scattering can be defined experimentally.

The form for the boundary-limited conductivity is found from Figs. 2 and 3 to be

$$K=(0.21\pm0.02)dT^{3.005\pm0.015}\ \mathrm{W\ cm^{-1}\ deg^{-1}},\qquad(6)$$

when $d$ is in centimeters. The 10% variation of the proportionality constant includes the maximum variation of the data. Equation (6) agrees with theory in the form of Eq. (2b) except that the experimental proportionality constant, and thus the phonon mean free path, is 15% larger than predicted. This 15% discrepancy is of some consequence to the investigation of boundary scattering, and it is important to trace the source of the discrepancy to some specific difference between experiment and the assumptions of Casimir's theory.

Casimir did his calculations for crystals of infinite length. Corrections for finite crystals must include end

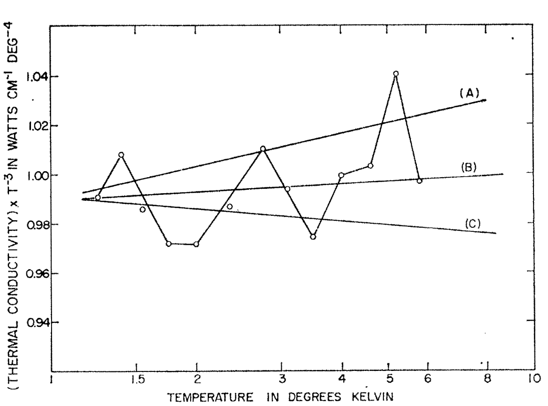

FIG. 2. Low-temperature thermal conductivity $K$ divided by $T^3$ and plotted against $T$. If $K\propto T^n$, then for (A), $n=3.020$; (B), $n=3.005$; (C), $n=2.990$. Curve (B) has been normalized to 1.00 W cm$^{-1}$ deg$^{-4}$ at 10°K.

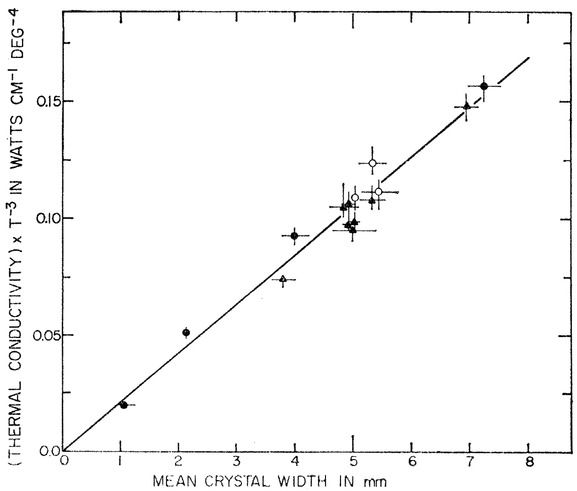

FIG. 3. Low-temperature thermal conductivity $K$ divided by $T^3$ and plotted against mean crystal width for 15 measurements and 13 different crystals. The vertical error bar on a point shows the maximum variation of $K/T^3$ over the $T^3$ region. The horizontal bar extends between the two widths of the rectangular crystal.

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[51] J. P. Harrison (Cornell University, private communication).

effects and possible effects of the heat-flow geometry. The heat flow is mentioned because, rather than heat entering and leaving symmetrically through the crystal ends in this experiment, heat entered through a clamp on the crystal side at the top and left through another clamp on the opposite side at the bottom. Effects of any resulting heat-flow asymmetry, such as nonplanar isotherms or a nonlinear temperature gradient, were minimized by placing gradient thermometers at least two crystal widths from the crystal heater or heat sink, and the resulting gradient was found to be linear within 5% below 4°K by a direct measurement using three thermometers along a crystal. Furthermore, the parameter of distance from thermometers to heat source or sink in units of crystal width varied from 1.8 to 7.7 among the crystals for this experiment with no effect on the measured conductivity. For one short, fat crystal, however, the parameter was 1.0. In this case the heat-flow geometry was important because the crystal failed to give even a $T^3$ dependence until its ends were sandblasted. Crystal ends were normally left unsandblasted to facilitate later optical measurements.

Other problems with the heat flow were reduced by minimizing $\Delta T$, the temperature difference between gradient thermometers. $\Delta T/T$ was never greater than 0.3% at any temperature and was usually about 0.1% for the measurement of a datum point. No variation in the low-temperature conductivity was noted when $\Delta T/T$ was increased to 1% as a check. $\Delta T$ is also a measure of the out-of-equilibrium phonon density, and a small $\Delta T/T$ simplifies theoretical interpretation of the data by ensuring that measurements are made using only a small departure from the equilibrium phonon distribution.

End-effect corrections for finite crystals have been calculated by Berman *et al.*,[20,21] but their assumptions of a symmetric heat flow and either all diffuse or all specular reflection at the crystal ends were not met in this experiment. If their correction were applied regardless of those assumptions, the constant in Eq. (2b) would be decreased between 3 and 10% for the crystals of this experiment and become about 20% lower than observed.

Casimir also assumed that phonons are not scattered in the crystal bulk. Any frequency-dependent scattering can be discounted in the $T^3$ region, but Worlock[34] has shown that impurity colloids can reduce the low-temperature conductivity below the boundary-limited value and still leave a $T^3$ slope, and Taylor *et al.*[52] have shown that dislocations may have the same effect. However, elimination of the effects of either scattering from the data would serve only to increase the observed conductivity and thus the discrepancy in the proportionality constant.

Casimir lastly assumed diffuse reflection of the phonons at the crystal boundaries. Relaxation of this assumption to include some amount of specular reflection is the only remaining way to explain the larger experimental proportionality constant. Specular reflection increases the phonon mean free path and thus the proportionality constant, as calculations and experiments of Berman *et al.*[20,21] have shown. It is surprising, however, that such specular reflection is independent of frequency. Experiments to clarify this problem and the question of dislocation scattering in the crystal bulk are taken up in Sec. V. Even though the precise nature of boundary scattering is yet to be investigated, the already demonstrated frequency independence of boundary scattering justifies use of Eq. (3) to calculate $\tau_B^{-1}$ for use in Eq. (1).

## B. The Debye Model

The test of the Debye model proceeded as follows[31]: Eq. (1) was fit to the data of the largest isotopically pure crystal shown in Fig. 1 by employing the method outlined in Sec. III. The results are given by the top, solid curve in Fig. 1, and the $\tau_U^{-1}$ so determined was considered fixed for all the other crystals. The model was then tested by observing its ability to predict the measured conductivities when calculated relaxation rates for first the boundary and then the isotope effects were varied over the maximum experimental range. Parameters relevant to the boundary and isotope fits are given in Table II.

### *Boundary-Effect Data*

Conductivities calculated for the boundary-effect data are given by the three lower, solid curves in Fig. 1. The Debye model is certainly able to describe the data when $\tau_B^{-1}$ is varied by a factor of 8, though curves for the two smallest crystals do rise about 15% above the data near the conductivity peak. The success of this fit is not sufficient to prove correct either the Debye model or the choice of $\tau_U^{-1}$, but such success is necessary before proceeding to a more demanding test employing the frequency-dependent $\tau_I^{-1}$. First, however, there

TABLE II. Various parameters for crystals used in testing the Debye model.[a]

| Crystals shown in Fig. | Curve | % $^7$Li in LiF | $A$ for $\tau_I^{-1}=Ax^4T^4$ [sec$^{-1}$ (°K)$^{-4}$] | $\tau_B^{-1}$ from Eq. (3) ($10^5$ sec$^{-1}$) | Sample dimensions (mm) |
|---|---|---|---|---|---|
| 1 | (A) | 99.99 | 0.0005 | 4.04 | 7.55 ×6.97 ×60 |
| | (B) | 99.99 | 0.0005 | 6.82 | 4.24 ×3.77 ×50 |
| | (C) | 99.99 | 0.0005 | 12.4 | 2.17 ×2.10 ×40 |
| | (D) | 99.99 | 0.0005 | 32.1 | 1.23 ×0.91 ×23 |
| 4 | (A)[b] | 99.99 | 0.0005 | 4.04 | 7.55 ×6.97 ×60 |
| | (B) | 97.2 | 0.126 | 5.09 | 5.58 ×5.10 ×60 |
| | (C) | 92.6 | 0.318 | 5.67 | 5.77 ×5.14 ×39 |
| | (D) | 50.8 | 1.20 | 5.83 | 5.06 ×5.00 ×40 |

[a] $\tau_U^{-1}$ as given by Eq. (5) is the same for all crystals.
[b] Curve (A) is for the same crystal in Figs. 1 and 4.

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[52] A. Taylor, H. R. Albers, and R. O. Pohl, J. Appl. Phys. **36**, 2270 (1965).

are two further points to be made about the boundary effect.

Carruthers[10] has challenged on theoretical grounds the addition of relaxation rates assumed in the fit. He showed that $\tau_B^{-1}$ could be added to the bulk relaxation rate only if $\tau_B^{-1}$ then depended on that bulk rate. This situation arises, in essence, because boundary scattering results in a boundary-value problem rather than the problem of a homogeneously dispersed scatterer. Using a simple model, Carruthers found that $\tau_B^{-1}$ must be decreased by a factor of 2 as the bulk scattering shifts from $\tau_U^{-1} \ll \tau_B^{-1}$ to $\tau_U^{-1} \gg \tau_B^{-1}$. If such an effect were included in the present fit to the boundary effect, the theoretical curves would rise even farther above the data. However, this result should be taken more as criticism of the Debye model or the choice of $\tau_U^{-1}$ than of Carruthers's results.

Another aspect of the boundary value problem gives information about the normal process relaxation rate $\tau_N^{-1}$. Klemens[13] and then Sussman and Thellung[53] have shown that when $\tau_N^{-1} \gg \tau_B^{-1}$ and $\tau_B^{-1}$ is greater than other resistive scattering rates, a Poiseuille flow of the crystal phonons results. The low-temperature conductivity should then be proportional to $d^2T^7$ or $d^2T^8$. The same result was obtained by Gurzi,[54] and the problem has been examined more recently by Guyer and Krumhansl.[19] The Poiseuille flow region has apparently been observed by Mezhov-Deglin[55] in the conductivity of solid He$^4$, but since the observed conductivity of LiF goes as $dT^3$ up to 6°K and then decreases because of resistive scattering, no Poiseuille flow region exists in even isotopically pure LiF. Furthermore, it must be that $\tau_N^{-1} < \tau_B^{-1} \approx 10^6$ sec$^{-1}$ below 6°K. This result could not have been obtained from the usual use of Callaway's theory because that theory neglects the boundary-value nature of surface scattering and would predict no effect of normal processes when $\tau_R$ is independent of frequency, as is the case for the boundary-limited conductivity.

### *Isotope-Effect Data*

The depression of the conductivity with increasing isotopic disorder is shown in Fig. 4. The symmetry of this depression on a log-log plot should not obscure the fact that while isotope scattering causes the separation of the curves near 100°K, boundary scattering causes the separation near 1°K. The dominance of boundary scattering at low temperatures, which is required in order to calculate $\tau_B^{-1}$ for a crystal from its low-temperature data, is shown in Fig. 3 where open circles for the smaller crystals of Fig. 4 and a closed circle for the largest crystal, which was used for both the boundary and isotope effects, agree well with the average slope. All crystals in Fig. 4 were annealed before sandblasting the surfaces.

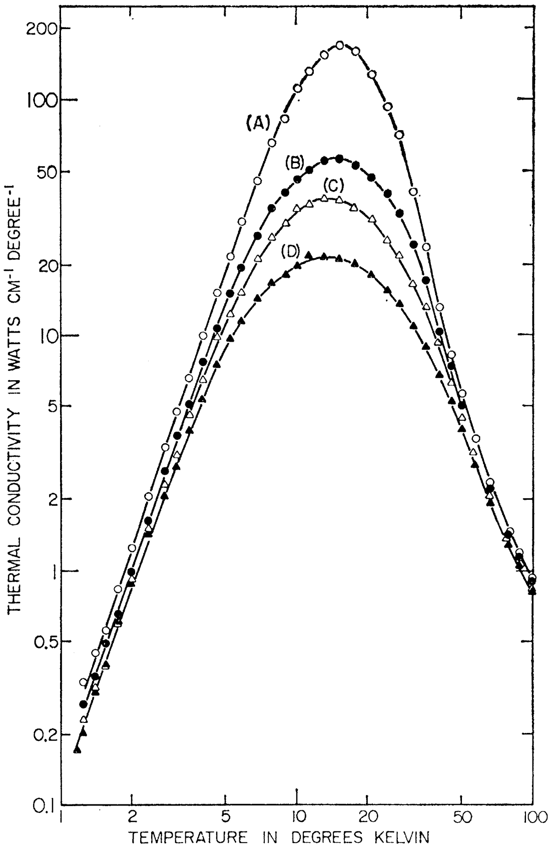

FIG. 4. Thermal conductivity of LiF showing the effect of isotopes. % $^7$Li in LiF: (A) 99.99, (B) 97.2, (C) 92.6 (natural LiF), (D) 50.8. Mean crystal widths: (A) 7.25 mm, (B) 5.33 mm, (C) 5.44 mm, (D) 5.03 mm. Crystals A, B, and C were regrown at Cornell from ORNL and Harshaw starting materials. Crystal D, and crystals of 87.6% and 69.1% $^7$LiF which are not included because of close duplication of existing data were grown at ORNL.

The results of the Debye-model fit are shown as the solid curves in Fig. 5. These curves have a skewed peak near 20°K rather than a symmetric peak at 15°K, and the calculated isotope effect is about a factor of 2 weaker than that shown by the data.

One must first suspect the data, especially as to the effect of crystal impurities which may mask or even duplicate the isotope effect. Such impurity effects are of concern, but convincing evidence that Fig. 4 represents only the isotope effect, except near the peak of the purest crystal, is shown in Fig. 6 where the data of Fig. 4 are compared with the recent isotope-effect data of Berman and Brock.[30] The disagreement at low temperatures and at the peak of the highest curves is discussed in Sec. V and undoubtedly results from scattering by the dislocations Berman and Block observed in their crystals. The close agreement at higher temperatures of data taken by separate experimenters on dif-

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[53] J. A. Sussman and A. Thellung, Proc. Phys. Soc. (London) **81**, 1122 (1963).

[54] R. N. Gurzi, Zh. Eksperim. i Teor. Fiz. **46**, 719 (1964) [English transl.: Soviet Phys.—JETP **19**, 490 (1964)].

[55] L. P. Mezhov-Deglin, Zh. Eksperim. i Teor. Fiz. **49**, 66 (1965) [English transl.: Soviet Phys.—JETP **22**, 47 (1966)].

ferent cryostats using crystals grown at four different locations is convincing proof that both sets of data are reliable. The theoretical model must therefore be examined.

In the next attempt at explaining the poor isotope-effect fit without invoking normal processes, the effects of various possible corrections to the relaxation times entering into the theory were assessed: (a) The constant term in $\tau_I^{-1}$ was increased on the assumption that $\langle v^{-3}\rangle$ had been underestimated by Houston's approximation. However, even with the $A$ for 51% $^7$LiF doubled, the theoretical peak was 25% above the data and still had the same skewed shape. (b) $\tau_U^{-1}$ was modified by replacing $e^{-27/T}$ by a constant. This exponential term adjusted the peak conductivity of the isotopically pure crystal and was the term most likely to be influenced by residual impurities. Though the isotopically pure crystal could no longer be fit, the addition of isotope scattering still resulted in skewed curves similar to those in Fig. 5. (c) $\tau_U^{-1}$ was again modified, this time by replacing $x^2T^3e^{-27/T}$ by a dislocation scattering rate proportional to $\omega$. However, dislocations scattering as $\omega$ were not observed in this experiment because as soon as dislocation scattering visibly depressed the computed conductivity peak, the low-temperature conductivity varied less strongly than $T^3$. (d) An extra term in $\tau_U^{-1}$ proportional to the $A$ of Eq. (4) was considered. The possibility of such a variation was calculated by Carruthers[56] after being used by Toxen[57] to fit his conductivity data on Ge-Si alloys. However, $A$ increases by a factor of 10 in going from the 97% to the 51% $^7$LiF crystal, whereas the theoretical curves of Fig. 5 deviate from the data by about the same factor of 2 for those crystals.

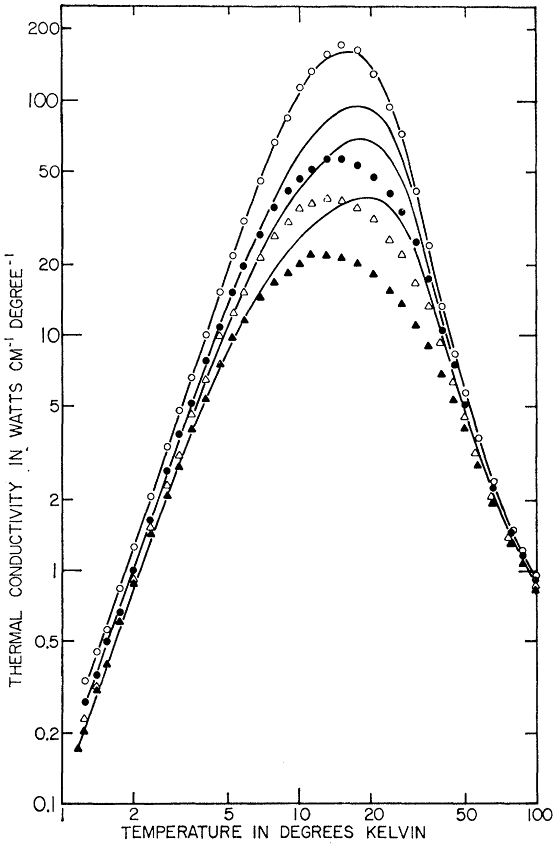

FIG. 5. Theoretical fit to the isotope-effect data. Symbols represent the same data as shown in Fig. 4. Solid curves are calculated from Eq. (1) in which the effects of normal processes are not included.

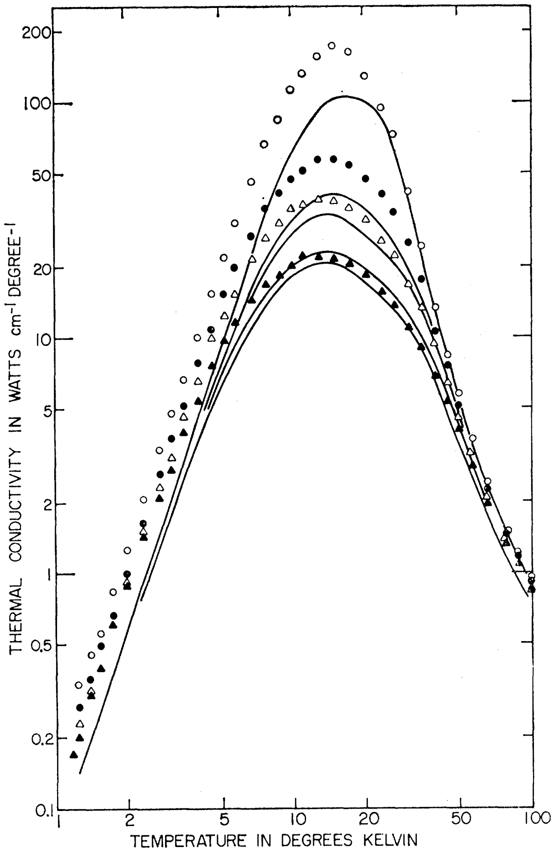

FIG. 6. Comparison of Fig. 4 with the isotope-effect data of Berman and Brock. Symbols represent the same data as shown in Fig. 4. The solid curves give data from Berman and Brock (see Ref. 30) for the following percentages of $^7$Li in LiF starting with the top curve: 99.98, 95.4, 9.6(=90.4), 75.0, and 49.9.

Since no straightforward correction to $\tau_R$ improved the isotope fit, the effects of the acoustic approximation and Debye density of states were considered. Calculations by Karo[58] and by Karo and Hardy[59] show that the frequency distribution in LiF is not well described by the Debye density of states, and measurements by Clusius *et al.*[60] of the temperature dependence of

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[56] P. Carruthers, Phys. Rev. **126**, 1448 (1962).

[57] A. M. Toxen, Phys. Rev. **122**, 450 (1961).

[58] A. M. Karo, J. Chem. Phys. **31**, 1489 (1959).

[59] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

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

$\Theta_D$, which indicates the departure from a Debye density of states, showed $\Theta_D(70°K)=610°K$ as opposed to the 0°K extrapolated value of 722°K reported by Scales.[47] Though dispersion could therefore seriously modify the assumed density of states, the fact that Scales has shown $\Theta_D$ to be linear up to 14°K implies that the Debye density of states is a reasonable approximation at least up to the conductivity maximum. It can also be shown that separation of the polarization contributions to the conductivity is of little help in matching the isotope data, at least up to 14°K.

The major approximation yet to be considered is the neglect of normal processes. Though normal processes can offer no resistance to the heat flow in a nondispersive crystal, they can funnel phonons into modes already depleted by isotope scattering and thereby increase the effective isotope-scattering rate. No other process appears capable of giving the enhanced isotope-scattering rate required to fit the data. In this indirect way the poor Debye-model fit shows the importance of normal processes in LiF and the necessity of using some theory, such as Callaway's, which includes normal processes in the computation of the thermal conductivity.

Berman and Brock[30] arrived at the same conclusion and then went on to show directly that Callaway's theory could fit their isotope-effect data. They also showed that Klemens's theory, Ziman's theory, and the first term of Callaway's theory would not fit the data. Their computed normal process contribution to the conductivity varied rapidly with $A$, as was expected, and peaked sharply at 20°K. It is interesting to note that just such a contribution is required to make the curves of Fig. 5 fit the data. Though substantial dislocation scattering is exhibited by Berman and Brock's crystals, it is likely, as discussed in the next section, that such scattering had no serious effect on their fit. Their paper should be consulted for the best relaxation rates presently available for LiF. $\tau_U^{-1}$ as given by Eq. (5) has been proved incorrect.

Further progress in understanding the isotope effect, and thermal conductivity generally, now depends on several factors. More reliable theoretical values for $\tau_N^{-1}$ and $\tau_U^{-1}$ are certainly required. The present forms are at best only indicated by theory and experiment, though ultrasonic attenuation experiments in LiF by de Klerk and Klemens[61] lend support to Berman and Brock's choice of $\tau_N^{-1}$. However, other experiments by Baumann[62] and Pohl[63] show that even a more careful single-mode approximation to $\tau_N^{-1}$ and $\tau_U^{-1}$ may not suffice because they apparently find a strong interaction between impurity scattering and intrinsic processes. Further theoretical and experimental work is also required on boundary and dislocation scattering. This point is amplified in the next section. Future theories should also consider dispersion and phonon polarization in the actual crystals, a project already initiated by Holland.[42] Despite these difficulties, Callaway's theory is sufficient to match the LiF isotope effect data. The success of the Debye model at matching the boundary-effect data most likely resulted from a small interaction between frequency-independent boundary scattering and normal processes.

## V. BOUNDARY SCATTERING

### A. The Mechanism

Boundary scattering in crystals with sandblasted or otherwise roughened surfaces has usually been considered as a diffuse reflection of phonons from rough crystal surfaces much as light is diffusely reflected from ground-glass surfaces. On that assumption, Berman *et al.*[21] have theoretically related phonon scattering and surface roughness. However, Worlock[34] has more recently suggested that boundary-scattering results when phonons are scattered from a large density of dislocations just beneath a roughened surface. Though the details of the scattering mechanism are as yet unknown, the evidence to be described greatly favors Worlock's model. In particular, etch and polish experiments not only show the presence of dislocations below a roughened surface but also demonstrate their important effect on the thermal conductivity. Furthermore, a similarity is observed between boundary scattering and scattering by dislocations introduced during growth.

The necessary initial evidence that a large density of dislocations exists beneath a sandblasted surface was provided by sandblasting a crystal, cleaving perpendicularly to the sandblasted surface, and etching. The observed dislocation density was greater than $10^8$ cm$^{-2}$ in the first 0.02 mm below the surface, fell to $10^7$ cm$^{-2}$ by 0.05 mm, and reached the average value of $5\times10^5$ cm$^{-2}$ by 0.5 mm. Only the average density was observed below a cleaved surface. The etching solution was that reported by Gilman and Johnston.[64]

The effect of the greatly damaged surface layer was ascertained by chemically polishing off 0.05 mm from a crystal sandblasted after an anneal. The low-temperature conductivity of this polished crystal varied as $T^{2.91}$, and $K/T^3$ was approximately 40% higher than before the polish. Though this experiment showed that a greatly damaged layer is required for obtaining the usual boundary scattering, the contributions of surface roughness and dislocations to the scattering in that layer were not separated. In effect, polishing removed both sources of scattering by not only smoothing the surfaces but also eliminating the most dislocated region. Nonetheless, the experiment did isolate the effect of scattering by dislocations more than 0.05 mm below a

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[61] J. de Klerk and P. G. Klemens, Phys. Rev. **147**, 585 (1966).

[62] F. C. Baumann and R. O. Pohl (to be published).

[63] R. O. Pohl (to be published).

[64] J. J. Gilman and W. G. Johnston, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 148.

sandblasted surface if the polished surface itself is assumed to offer no thermal resistance.

In order to assess the amount of dislocation scattering below the polished surface, the crystal was vacuum annealed for 1 h at 50°C below the melting point and cooled to room temperature over 10 h. This procedure, which was used for all crystal annealing, reduced the dislocation density at the surface[65] from about $10^7$ cm$^{-2}$ to a pattern of small-angle grain boundaries separated by about 0.2 mm with dislocation densities less than $10^4$ cm$^{-2}$ in between. The boundary-limited conductivity varied approximately as $T^{2.4}$ and was a factor of 2 higher than after the polish. Therefore, except for ambiguities caused by differences in surface scattering between polished and thermally etched surfaces, dislocation densities found more than 0.05 mm below sandblasted surfaces are sufficient to contribute greatly to the thermal resistivity. Dislocations in the first 0.05 mm must contribute even more so. This information could not have been obtained by annealing a sandblasted surface because annealing both removes dislocations and greatly smooths the surface by thermal etching.

Further evidence for a dislocation mechanism in boundary scattering is shown in Fig. 7 by the similarity of curves for sandblasted crystals with and without a high dislocation density in the crystal interior. Curves (A) and (C) are taken from Fig. 1 and represent annealed and sandblasted crystals approximately $4\times4$ mm and $2\times2$ mm, respectively, in cross section. Curve (B) is for a $5\times5$-mm crystal cleaved from the same boule but not annealed before sandblasting. The enhanced "boundary" scattering in the $5\times5$-mm crystal results from a dislocation density of $1\times10^7$ cm$^{-2}$ introduced by chance into the original boule during growth. These dislocations gave, in conjunction with a sandblasted surface, the same effect as boundary scattering in a $3\times3$-mm crystal even up to and over the conductivity peak where intrinsic scattering is important. Taylor *et al.*[52] observed the same apparent boundary effect with dislocations introduced into LiF by bending.

The precise role played by dislocations in boundary scattering must now be analyzed by theory, and the question of whether surface roughness plays any role at all will probably await that analysis because of the experimental difficulties in separating completely the effects of surface roughness and dislocations. Calculations by Carruthers[10] and Bross[66] of phonon scattering from arrays of dislocations give no clue as to the origin of boundary scattering. Theories for phonon scattering from single dislocations worked out by Klemens[9,13] and Carruthers[10] predict a $T^2$ dependence of the low-temperature conductivity rather than the $T^3$ required for boundary scattering, though a $T^2$ dependence has indeed been observed by Sproull *et al.*[67] and Moss[68] for dislocations introduced into LiF by compression. However, even when a $T^2$ dependence is observed, neither Klemens's nor Carruthers's theory can predict the observed magnitude of the scattering, as has been most recently pointed out by Moss.[69]

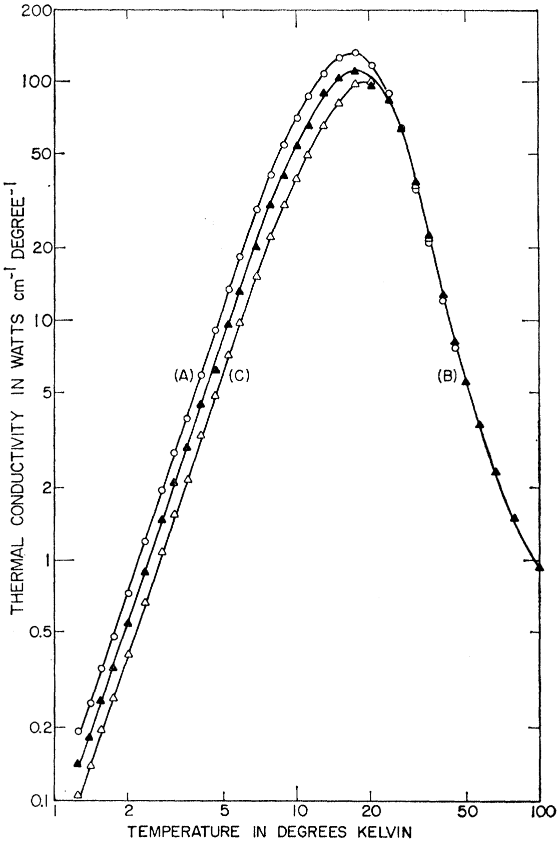

FIG. 7. Thermal conductivity of isotopically pure LiF showing an apparent boundary effect caused by dislocations. Mean crystal widths: (A) 4.00 mm, (B) 5.03 mm but containing $1\times10^7$ dislocations cm$^{-2}$, (C) 2.14 mm. Curves (A) and (C) are taken from Fig. 1. All crystals are sandblasted.

### B. Characteristics of the Mechanism

Several characteristics of boundary scattering, such as the influence of flame-polished or ground crystal surfaces on the temperature variation of the conductivity, have already been described by Berman *et al.*[21] The present experiments represent an extension of their efforts to include more controlled variations of the surface damage and associated dislocation densities.

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[65] Annealing is especially effective on dislocations less than 0.2 mm below the surface. See A. D. Podlesnaya, E. I. Raikhel's, I. V. Smushkov, and V. M. Trembach, Dokl. Akad. Nauk SSSR **161**, 821 (1965) [English transl.: Soviet Phys.—Doklady **10**, 358 (1965)].

[66] H. Bross, Z. Physik **189**, 33 (1966).

[67] R. L. Sproull, M. Moss, and H. Weinstock, J. Appl. Phys. **30**, 334 (1959).

[68] M. Moss, J. Appl. Phys. **36**, 3308 (1965).

[69] M. Moss, J. Appl. Phys. **37**, 4168 (1966).

The close control of the surface damage given by the usual sandblasting has already been evidenced in Eq. (6) by the 10% reproducibility of the boundary-limited conductivity. A further demonstration of this control was obtained by an experiment shown in Fig. 8 on a $K/T^3$ plot. A Harshaw crystal was first annealed and sandblasted with results given by the open triangle below the solid line, which has the same average slope determined in Fig. 3. The crystal was then annealed to remove surface dislocations (top triangle) and resandblasted; and, as is shown by following the arrows, the resandblasting very nearly restored the original boundary scattering. Such reproducibility was obtained by sandblasting all crystals with an S. S. White Industrial Airbrasive Unit using 27-$\mu$ $Al_2O_3$ particles powered with dry nitrogen at 80 psi. The crystal was held about 2 in. from the unit's nozzle, and sandblasting was continued until all sides scattered light diffusely to the naked eye.

The surface damage variations evident in Fig. 8 not only demonstrate reproducibility, but also force another, rather startling conclusion. The proportionality of the boundary-limited conductivity to $T^3$ is not at all unique for any one crystal size but varies greatly depending on the density and distribution of dislocations in the crystal. This conclusion, which had been indicated by Worlock,[34] is most graphically illustrated by the experiment shown by the filled circles at $d=5.5$ mm in Fig. 8. The lowest circle represents an abraded and sandblasted crystal of natural LiF regrown at Cornell and containing dislocations. The results of two anneals and a sandblasting are shown by subsequent circles as indicated by the arrows. Even though $K/T^3$ was varied by more than a factor of 3, the boundary-limited conductivity was still proportional to $T^3$, and boundary scattering was therefore still independent of phonon frequency. Furthermore, since the phonon mean free path after the second anneal was more than twice the crystal width, the boundary scattering was largely specular.

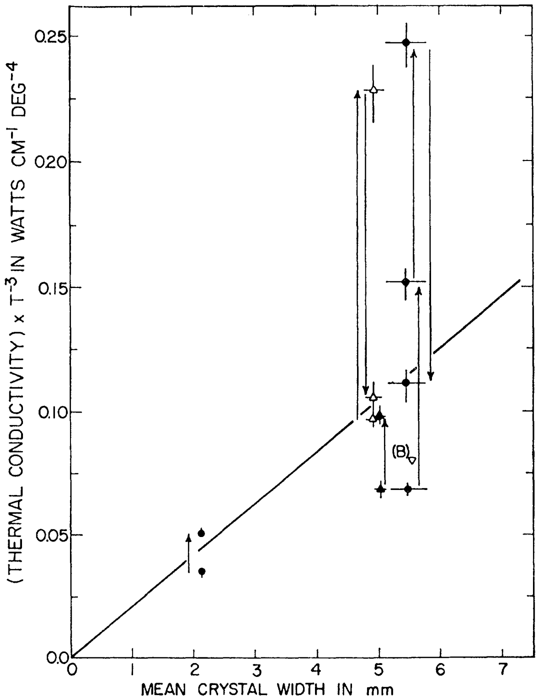

FIG. 8. Low-temperature conductivity divided by $T^3$ and plotted against crystal width to show annealing effects. The solid line is that determined in Fig. 3. Error bars also have the same meaning as in Fig. 3. Arrows show the order of the experiments discussed in the text.

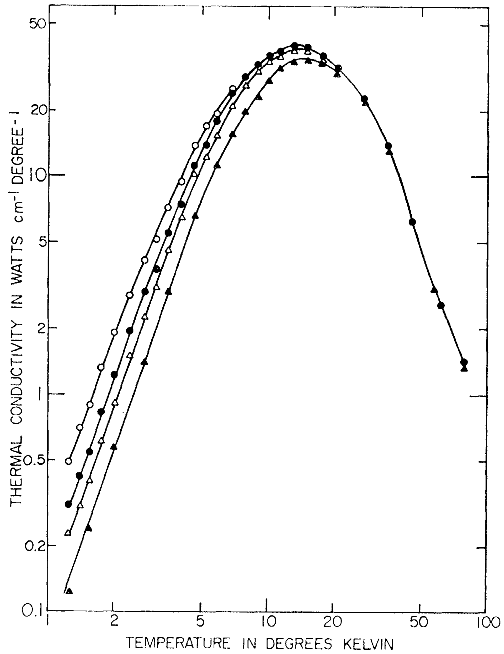

FIG. 9. Thermal conductivity of a natural LiF crystal showing annealing effects on sandblasting damage and internal dislocations. Closed triangles: cleaved from boule containing dislocations, abraded, and sandblasted. Closed circles: annealed. Open circles: annealed again. Open triangles: sandblasted.

The behavior of this specular reflection is better seen in Fig. 9 by direct examination of conductivity data for the experiment just described. The lowest curve in the figure is for the abraded and sandblasted crystal, closed circles give the first anneal, open circles the second, and open triangles the results of the sandblasting. The most interesting observation is that the higher the boundary-limited conductivity, the lower the temperature below which the conductivity varies as $T^3$. Therefore, the lower the dislocation density near the surface, the more specular reflection given by boundary scattering, and the lower the temperature (and thus phonon frequency) below which the scattering is independent of phonon frequency. Eventually, as in the chemical polish experiment, the dislocation density can be lowered to such an extent that the conductivity never varies as $T^3$, at least above 1°K. Theory must now cope with a frequency-independent dislocation scattering which can be both diffuse and specular, though it may well be that lower dislocation densities give a less effective shielding of a specularly reflecting surface and that such shielding improves with increasing phonon wavelength. More quantitative measurements of dislocation densities produced both after sandblasting and after annealing would prove valuable for any theoretical efforts.

The puzzling frequency-independent specular reflection found necessary in Sec. IV to explain the 15 to 20% difference between theory and Eq. (6) has now been shown to be a basic property of the boundary-scattering mechanism. It can no longer be assumed that sandblasting will give a boundary-limited conductivity in agreement with Casimir's theory. Agreement with Casimir's theory could have been obtained in LiF only by introducing more dislocations than given by the standard sandblasting. In fact, two crystals abraded with fine sandpaper did follow Casimir's predictions, $K/dT^3$ being, respectively, 17 and 22% below the experimental average; but the crystal surfaces were severely scratched, the region of dislocation densities greater than $10^8$ cm$^{-2}$ extended to 0.1 mm below the surface, and the average interior dislocation density was double that observed after a normal sandblasting.

### C. Dislocation Effects

The effects of grown-in dislocations not only complement information already obtained on surface scattering but also lead to a better understanding of annealing effects and bulk dislocation scattering in both the present crystals and in those measured by Berman and Brock. For instance, it has already been shown in Fig. 7 that a sandblasted crystal with $1\times10^7$ cm$^{-2}$ grown-in dislocations gives a $T^3$ conductivity. Such behavior proves that these dislocations scatter phonons independently of frequency or at least very nearly so. It also follows that great densities of dislocations, such as those found below a sandblasted surface, are not necessary for frequency-independent scattering by these dislocations. The $T^{2.91}$ conductivity measured during the polish experiment probably resulted from some phonon scattering from the specularly reflecting surfaces rather than from a frequency dependence in the dislocation scattering.

The influence of scattering from smooth surfaces on scattering by dislocations in the bulk is better demonstrated in Fig. 10, where curve (A) shows the effect of $1\times10^7$ cm$^{-2}$ grown-in dislocations in an as-cleaved crystal. The conductivity varies as $T^{2.80}$ from 1.25–7°K. Since the same dislocation densities in a sandblasted crystal gave a $T^3$ conductivity, the $T^{2.80}$ variation can only have resulted from frequency-dependent specular reflection at the cleaved crystal surfaces. Some estimate of the surface scattering alone was gained by two successive anneals of the crystal resulting in curves (B) and (C). However, though the dislocations were largely annealed out so that only the surface should have been scattering, the curve's height and slope of about $T^{2.4}$ were partly dependent on measurement geometry because the average phonon mean free path of about 2 cm was greater than the 1.5 cm between a gradient thermometer and crystal heater or heat sink.

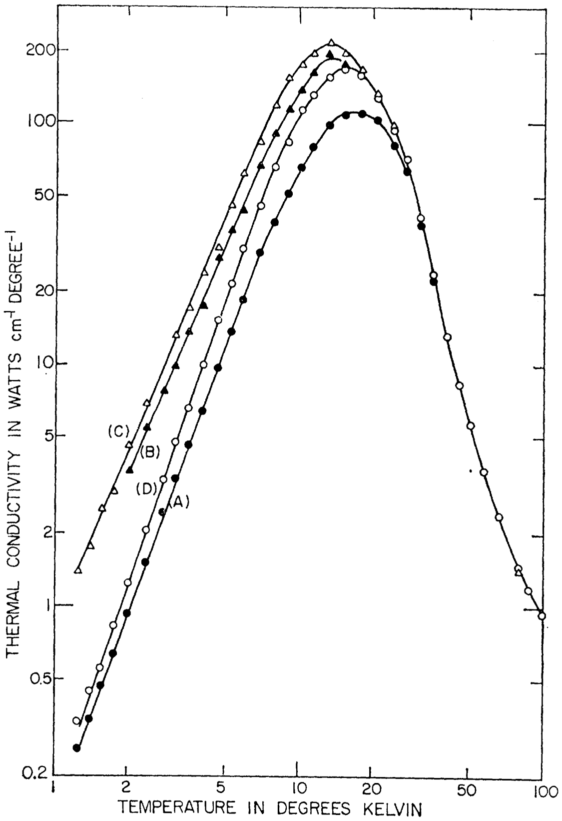

FIG. 10. Thermal conductivity of an isotopically pure LiF crystal showing effects of dislocations and annealing. (A) as-cleaved crystal containing $1\times10^7$ dislocations cm$^{-2}$; (B) annealed; (C) annealed again; (D) sandblasted. Curve (D) is the top curve in Figs. 1, 4, and 5.

Curve (D) in Fig. 10 resulted after sandblasting the annealed crystal. The increase in conductivity in going from the as-cleaved crystal containing dislocations to the annealed and sandblasted crystal proves that annealing out of dislocations rather than colloid production was responsible for the change in conductivity during annealing. Though Worlock[34] also found a $T^3$ slope after annealing his crystals to produce colloids, his conductivities were greatly reduced by colloid production even though his initial crystals were sandblasted.

The effectiveness of annealing for removing dislocation scattering in the crystal bulk is further demonstrated in Fig. 8. $K/T^3$ before and after annealing and sandblasting the crystal in Fig. 7 which contained

$1\times 10^7$ cm$^{-2}$ grown-in dislocations is given by the closed triangles. The same experiment on the abraded and sandblasted crystal for which $K/T^3$ was 22% below the average line is given by the closed circles at 2 mm. The closed circles at 5.5 mm have already been discussed.

The data in Fig. 8 also show that the point in the figure labeled (B), which gives the average $K/T^3$ for six LiF crystals measured by Berman and Brock, must represent an important amount of dislocation scattering. They report a dislocation density of about $2\times 10^6$ cm$^{-2}$. Therefore, as soon as boundary and dislocation scattering are better understood, Callaway's theory should be tested against the data of Fig. 4, especially since Berman and Brock partly determined $\tau_N^{-1}$ from low-temperature data which were strongly influenced by dislocation scattering. Nonetheless, the effect of dislocations on their isotope effect fit may well be slight because the Debye-model fit to the boundary effect in Fig. 1 and similarity of boundary and dislocation scattering in Fig. 7 show that there is little interaction between normal processes and both surface and interior dislocation scattering, at least for dislocations introduced into the interior during growth. Nor should any interaction be expected when such dislocations scatter independently of frequency.

## VI. SUMMARY

Analysis of thermal conductivity data for LiF crystals of varying size, surface treatment and isotopic composition has led to the following conclusions: (a) The Debye-model formulation of the thermal conductivity, in which normal processes are neglected, is not able to fit the isotope-effect data, and normal processes are shown to provide the only means for improving the fit. The data agree with similar data reported by Berman and Brock and fit by them using Callaway's theory. (b) No Poiseuille flow region is observed in isotopically pure LiF, so $\tau_N^{-1}<\tau_B^{-1}\approx 10^6$ sec$^{-1}$ below 6°K. (c) The Debye model is able to fit boundary-effect data for sandblasted crystals. Such success implies a small interaction between boundary scattering and normal processes in LiF. (d) Sandblasting an annealed (dislocation-free) crystal results in a boundary-limited conductivity proportional to crystal width and $T^3$. For the particular sandblasting procedure used, the proportionality constant was reproducible to 10% but was 20% higher than predicted by Casimir. (e) Sandblasting produces dislocation densities greater than $10^8$ cm$^{-2}$ just below the crystal surface, which, as Worlock suggests, cause frequency-independent boundary scattering by some unknown mechanism. Annealing experiments show this mechanism to include a frequency-independent specular reflection, perhaps from the crystal surfaces, which is required to explain the 20% disagreement with Casimir's theory. (f) The proportionality of boundary-limited conductivity to $T^3$ can be varied by up to 250% in LiF, so exact agreement with Casimir's theory is very likely fortuitous in any crystal. (g) Grown-in dislocations in LiF scatter phonons independently of frequency.

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