PHYSICAL REVIEW VOLUME 120, NUMBER 4 NOVEMBER 15, 1960

Effect of Point Imperfections on Lattice Thermal Conductivity

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(Received June 1, 1960)

The consequences of a simple, phenomenological, theory of lattice thermal conductivity with respect to the effect of point imperfections are summarized. The experimental results of Berman *et al.* on the effect of varying the concentration of Li^6 on the conductivity of lithium fluoride are analyzed in detail.

INTRODUCTION

THE principal object of this note is to show that a simple, phenomenological theory of lattice thermal conductivity[1] is capable of giving a reasonably good account of the experimental results concerning the effect of varying the concentration of the isotope Li^6 on the conductivity of lithium fluoride. It first seems desirable, however, to summarize the assumptions of this theory and to present its conclusions with respect to the effect of point imperfections on lattice thermal conductivity at both low and high temperatures. Some of the results given here have also been obtained by Ambegaokar[2] and by Blair.[3]

The theory incorporates the following rather sweeping assumptions: (1) A Debye spectrum is assumed for the phonons. Thus, effects due to anisotropy and dispersion are neglected. (2) It is assumed that all phonon scattering processes can be represented by frequency-dependent relaxation times. For scattering by point defects, we put

$$\tau_D^{-1}=A\omega^4, \tag{1}$$

where A is independent of temperature.[4] For phonon-phonon scattering processes we put

$$\tau_P^{-1}=S(T)\omega^2. \tag{2}$$

We shall suppose that $S(T)$ is proportional to temperature at high temperatures. At low temperatures, we assume that Herring's fifth-power law is obeyed[5]: Thus, $S(T)\propto T^3$. We may, however, expect a further temperature variation of $S(T)$ associated with Umklapp processes. Thus, for low temperatures, we shall put[6]

$$S(T)=B(T)T^3. \tag{3}$$

Finally, at low temperatures, we must take account of boundary scattering. This will be represented by a constant relaxation time

$$\tau_B^{-1}=v_s/L, \tag{4}$$

where v_s is the velocity of sound and L is a characteristic length.[7]

(3) We shall assume the additivity of the reciprocal relaxation times. In the body of this paper, we do not distinguish between normal three-phonon scattering and Umklapp processes, and thus neglect a correction resulting from the fact that normal processes conserve the total momentum of the phonon system.[1] The effect of this correction is considered briefly in an appendix for the case in which normal processes dominate the scattering.

The resulting theory is, of course, greatly oversimplified. It does have some advantages over previous approaches in that the additivity of thermal *resistivities* due to specific scattering mechanisms is not assumed. It is not necessary to impose arbitrary cutoff procedures on divergent integrals. It will be shown in particular that a specific thermal resistivity due to defect scattering can be defined only when this scattering is small in comparison to that produced by other processes.

From the combined relaxation time,

$$\tau_C^{-1}=\tau_D^{-1}+\tau_P^{-1}+\tau_B^{-1}, \tag{5}$$

the thermal conductivity, κ, is computed in the following way [reference 1, Eqs. (19) and (20)]:

$$\kappa=\frac{K}{2\pi^2 v_s}\int^{K\theta/\hbar}\tau_C(\omega)\left(\frac{\hbar\omega}{KT}\right)^2\frac{\exp(\hbar\omega/KT)}{[\exp(\hbar\omega/KT)-1]^2}\omega^2 d\omega.$$

We introduce the dimensionless variable $x=\hbar\omega/KT$. Then

$$\kappa=\frac{K}{2\pi^2 v_s}\left(\frac{KT}{\hbar}\right)^3\int_0^{\theta/T}\tau_C(x)\frac{x^4e^x}{(e^x-1)^2}dx. \tag{6}$$

In these equations, K is the Boltzmann's constant and

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[1] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[2] V. Ambegaokar, Phys. Rev. **114**, 488 (1959).

[3] J. Blair, Bull. Am. Phys. Soc. **5**, 164 (1960). See also P. G. Klemens, Phys. Rev, **119**, 507 (1960).

[4] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[5] C. Herring, Phys. Rev. **95**, 954 (1954). At low temperatures, considering normal three-phonon scattering processes, the relaxation times must obey $\tau^{-1}\sim\omega^q T^{5-q}$.

[6] The ordinary theory of Umklapp processes would give $BT^3e^{-\theta/aT}$, where θ is the Debye temperature and a is a constant characteristic of the vibrational spectrum. P. G. Klemens, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 198.

[7] Strictly, it is necessary to take account of the fact that boundary scattering occurs at the boundaries of the specimen and not in the bulk. C. Herring, Phys. Rev. **96**, 1163 (1954).

θ is the Debye temperature. We now have

$$\tau_C^{-1}(x)=Dx^4+Ex^2+v_s/L, \tag{7}$$

where

$$D=A(KT/\hbar)^4;\quad E=S(T)(KT/\hbar)^2.$$

It will be observed that the thermal conductivity, like the vibrational specific heat, is determined by an integral over the entire vibrational spectrum. If $\tau_C(x)$ were a constant, the thermal conductivity would be proportional to the specific heat. However, the strong inverse frequency dependence of τ_C indicates that relatively long-wavelength phonons are of principal importance for the heat current. Consequently, use of a Debye spectrum in the theory of thermal conductivity may be justified even for temperatures for which the specific heat is not given correctly. Of course, details of the vibrational spectrum are of much greater importance in the determination of the relaxation times themselves.

II. DEFECTS AT LOW TEMPERATURES

At very low temperatures, boundary scattering is dominant, although significant departures from the predicted T^3 dependence of the thermal conductivity will be observed if point defect or dislocation scattering is appreciable.[8] Our interest here will primarily concern temperatures high enough and samples large enough for the boundary scattering to be considered as a correction. This will be the case for temperatures greater than that for which the maximum of the thermal conductivity occurs. We insert (7) and (3) into (6) and define the quantities

$$y^2=E/D=\frac{\hbar^2}{K^2}\frac{B(T)T}{A};\quad z^2=v_s/LE=\frac{\hbar^2}{K^2}\frac{v_s}{LBT^5}.$$

The thermal conductivity may then be found from the integral

$$\kappa=\frac{K}{2\pi^2 v_s E}\left(\frac{KT}{\hbar}\right)^3\int_0^\infty \frac{x^2}{y^{-2}x^4+x^2+z^2}\,\frac{x^2e^x}{(e^x-1)^2}dx.$$

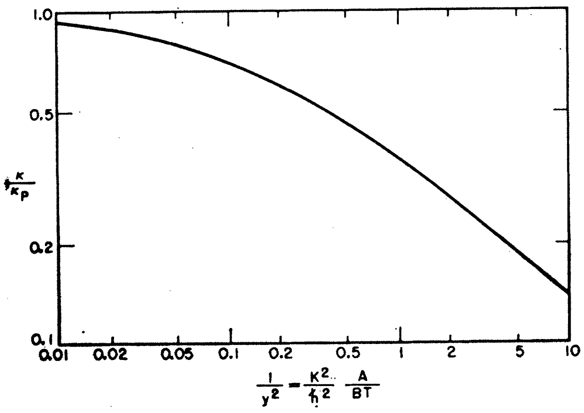

FIG. 1. The ratio of the thermal conductivities of material containing defects (κ) to that of pure material (κ_p) is plotted as a function of the variable $y^{-2}=K^2/\hbar^2A/BT$.

In general this integral requires numerical computation. Since it is a function of the two variables y, and z, we have found it desirable to express the result in the following approximate way, treating the size effect (terms involving z) as small:

$$\kappa=\frac{K^2}{2\pi^2 v_s\hbar BT^2}\left\{f(y)-\frac{\pi y}{2}\left[1-\left(1+\frac{2z}{y}\right)^{-\frac{1}{2}}\right]+z^2g(y)\right\}, \tag{8}$$

in which

$$f(y)=y^2\int_0^\infty\frac{x^2}{x^2+y^2}\,\frac{e^x}{(e^x-1)^2}dx;$$

$$g(y)=y^4\int\frac{dx}{x^2(x^2+y^2)^2}\left(1-\frac{x^2e^x}{(e^x-1)^2}\right).$$

Terms of order z^3 and higher have been neglected. The function $g(y)$ appears to be adequately represented by the following analytic approximation

$$g(y)=(\pi y/48)[1+y/\sqrt{3}+y^2/30]/[1+y/(12)^{\frac{1}{2}}]^2,\quad 0<y<12, \tag{9}$$

$$g(y)=\tfrac{1}{2},\quad y>12.$$

In many circumstances, it is permissible to make the further approximation

$$\kappa=\frac{K^2}{2\pi^2 v_s BT^2}\left[f(y)-\frac{\pi z}{2}\right]. \tag{10}$$

The function $f(y)$ is a monotonically increasing function of y. It has been computed numerically. For small y,

$$f(y)=y\left[\frac{\pi}{2}-0.477y\right]. \tag{11a}$$

An alternative, asymptotic, expansion can be made for large y:

$$f(y)=\frac{\pi^2}{3}\left[1-\frac{4\pi^2}{5y^2}+\frac{16\pi^4}{7y^4}+\cdots\right]. \tag{11b}$$

To study the effects of point defects in detail, consider samples sufficiently large or temperatures sufficiently high so that the size effect is negligible. Provided Umklapp processes dominate the phonon-phonon scattering, the thermal conductivity of pure material ($D=0$) is

$$\kappa_p=K^2/6c\hbar BT^2. \tag{12}$$

The ratio of the thermal conductivity of material containing defects to that of pure material is

$$\kappa/\kappa_p=W_p/W=(3/\pi^2)f(y). \tag{13}$$

This function is exhibited in Fig. 1. W is the thermal

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

resistance ($W=\kappa^{-1}$). When the defect scattering is large, the expansion (11a) for small y may be employed. Then

$$W/W_p=2\pi/3y+0.636+\cdots. \tag{14}$$

Equation (14) implies that for large defect scattering, the thermal resistance is proportional to $A^{\frac{1}{2}}$. For a two-component mixture, A is proportional to $c(1-c)$ where c is the relative concentration of one of the components. The thermal resistivity will be approximately proportional to the square root of the concentration when c is reasonably small. This result appears to be in qualitative agreement with the observations of Toxen.[9] Under these circumstances, the conductivity varies with temperature as $[B(T)T^3]^{-\frac{1}{2}}$.

When the defect scattering is small (large y), we use the expansion (11b). Including only the first term containing y, we have

$$\frac{W}{W_p}=1+\frac{4\pi^2}{5y^2}=1+\frac{4\pi^2}{5}\frac{K^2}{\hbar^2}\frac{A}{BT}. \tag{15}$$

W_p may now be found from (12). The additional thermal resistivity due to defects is

$$W_D=W-W_p=(24\pi^2/5)v_sAT/\hbar. \tag{16}$$

The defects then contribute an additional term to the thermal resistance which is proportional to temperature and independent of the phonon-phonon scattering (except for the numerical constant). This is in qualitative agreement with the results of Klemens[4] and of Ziman[10]; however, the coefficient of AT is different. It must be stressed that the large coefficient of the y^{-4} term in (11b) shows that the approximation (16) will be useful only when the defect scattering is very small. Further, Umklapp processes must dominate the phonon-phonon scattering.

Klemens gives an expression for A which may be written as[4]

$$A=\frac{\Omega_0}{4\pi v_s^3}\Gamma;\quad \Gamma=\sum_i f_i\left(1-\frac{M_i}{M}\right)^2. \tag{17}$$

In these expressions, Ω_0 is the volume of the unit cell, v_s is the velocity of sound, M_i is the mass of a unit cell, f_i is the fraction of unit cells with mass M_i, and M is the average mass of all cells. For a material containing one kind of impurity, present with relative concentration c,

$$A=\frac{\Omega_0}{4\pi v_s^3}c(1-c)\left(\frac{\Delta M}{M}\right)^2.$$

The defect thermal resistivity may now be given as

$$W_D=\frac{6\pi\Omega_0}{5\hbar v_s^2}\Gamma T=\frac{23.7\Omega_0}{hv_s^2}\Gamma T\quad (\hbar=h/2\pi). \tag{18}$$

The numerical coefficient in (18) is approximately twice that given by Klemens (who has 11.0 instead of 23.7).[11]

The dependence of the thermal resistivity in the case of large defect scattering on $A^{\frac{1}{2}}$ is intimately connected with the assumption that τ_p^{-1} is proportional to ω^2. If we put, instead of (2),

$$\tau_p^{-1}=S'(T)\omega^q, \tag{19}$$

where $q<3$ (in order that the integral will converge), we find after a short calculation that

$$W\propto S'(T)^{1/(4-q)}A^{(3-q)/(4-q)}. \tag{20}$$

Measurement of the dependence of thermal resistivity on A may yield information concerning the frequency dependence of the effective relaxation time for phonon-phonon scattering.

III. DEFECTS AT HIGH TEMPERATURES

At high temperatures ($T>\theta$), size effects may be ignored completely. The inverse relaxation time for phonon-phonon scattering should be proportional to temperature:

$$S(T)=CT. \tag{21}$$

We obtain from (6) instead of (8)

$$\kappa=\frac{K}{2\pi^2v_s}\left(\frac{KT}{\hbar}\right)^3\int_0^{\theta/T}\frac{x^2}{Dx^2+E'}\frac{e^x}{(e^x-1)^2}dx, \tag{22}$$

in which $E'=CT(KT/\hbar)^2$. Since the upper limit is less than unity, we may set $x^2e^x/(e^x-1)^2=1$. The integral is then elementary, and we have

$$\kappa=\frac{K}{2\pi^2v_s(DE')^{\frac{1}{2}}}\left(\frac{KT}{\hbar}\right)^3\tan^{-1}\left[\frac{\theta}{T}\left(\frac{D}{E'}\right)^{\frac{1}{2}}\right]$$

$$=\frac{K}{2\pi^2v_s(ACT)^{\frac{1}{2}}}\tan^{-1}\left[\frac{K\theta}{\hbar}\left(\frac{A}{CT}\right)^{\frac{1}{2}}\right]. \tag{23}$$

In the limit of small defect scattering ($A\rightarrow 0$), we have for pure material

$$\kappa_p=\frac{K^2\theta}{2\pi^2v_s\hbar CT}.$$

We then have, for the ratio of the conductivities of material containing defects to that of pure material,

$$\kappa/\kappa_p=W_p/W=(1/u)\tan^{-1}u \tag{24}$$

in which $u=(K\theta/\hbar)(A/CT)^{\frac{1}{2}}$. As before, two special cases may be distinguished: (1) Small defect scattering (small u). In this case, we expand and find

$$W=W_p(1+\tfrac{1}{3}u^2)=W_p+\frac{2\pi^2v_s\theta A}{3\hbar}. \tag{25}$$

This result agrees with that of Ambegaokar[2] if we use

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[9] A. M. Toxen, Phys. Rev. **110**, 585 (1958).

[10] R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).

[11] See also G. A. Slack, Phys. Rev. **105**, 829 (1957).

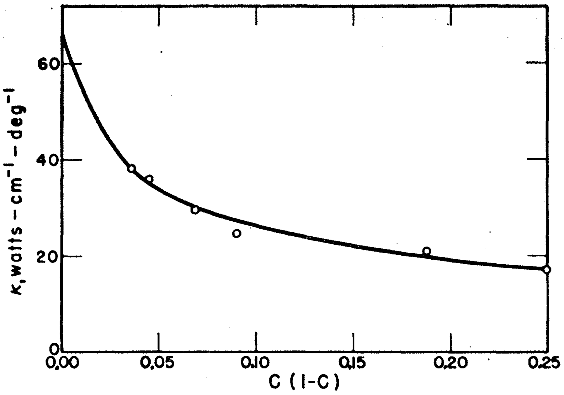

FIG. 2. Thermal conductivity of LiF at 20°K as a function of the relative concentration of Li^6. The circles represent experimental values inferred from the results of Berman *et al.*

the substitution (17) for A. The thermal resistance due to defects is independent of temperature and has the value

$$W_D = W - W_p = (\pi/6\hbar)(\Omega_0/v_s^2)\theta\Gamma. \tag{26}$$

Ambegaokar showed that this result is in reasonable agreement with the experiments of Geballe and Hull on germanium.[12]

The case in which defect scattering is large even at high temperatures is not very common, but is of interest in connection with the conductivity of solid solutions.[3] In this case, $\tan^{-1}u = \pi/2$, and

$$\kappa = K/4\pi v_s(ACT)^{\frac{1}{2}}. \tag{27}$$

The thermal conductivity now falls off with temperature as $T^{-\frac{1}{2}}$ and depends on the defect concentration as $A^{-\frac{1}{2}}$. This result is in agreement with the measurements of Blair.[3] The dependence on A and T given by (27) could also have been obtained directly from (20).

IV. APPLICATION TO LITHIUM FLUORIDE

This theory has previously been applied to germanium with considerable success.[1,2] It has also been used in a study of the influence of F centers on the thermal conductivity of LiF,[13] and of the conductivity of solid solutions of cadmium telluride in mercury telluride.[3] We discuss here the results of Berman *et al.*[14] who have measured the thermal conductivity of single crystals of LiF containing various relative concentrations of the isotopes Li^6 and Li^7.

A fit has been made to these results, based on Eq. (8). We find that it is always possible to choose values of the constants in (8) so that the dependence of the conductivity on isotope concentration can be reproduced within experimental error. An example of such a fit is given in Fig. 2. No fit to the concentration dependence can be obtained with a point defect resistivity proportional to $c(1-c)$.

It is somewhat more difficult to fit the data over the entire range of temperatures, principally because of the behavior of the function $B(T)$. In germanium, it was possible to use the very crude approximation $B(T)=$constant over the entire range of temperatures studied.[1] Such is not the case here. The data of Berman *et al.* falls into two temperature ranges. The bulk of the measurements are at temperatures between 15° and 35°K. This data can be fit using a constant B, provided a size effect is included. In addition Berman *et al.* report some measurements between 55° and 80°K. These require a larger B, and one that increases with temperature. We have made the following choice of constants and functions:

$$A/c(1-c) = 8.25\times10^{-44}\ \mathrm{sec}^3,$$

$$B(T) = 1.8.\times10^{-22} \times[\exp(-115/T)+0.0903]\ \mathrm{sec\ deg}^{-3}.$$

LiF was considered to be a Debye solid with average sound velocity 4.95×10^5 cm/sec, obtained from the

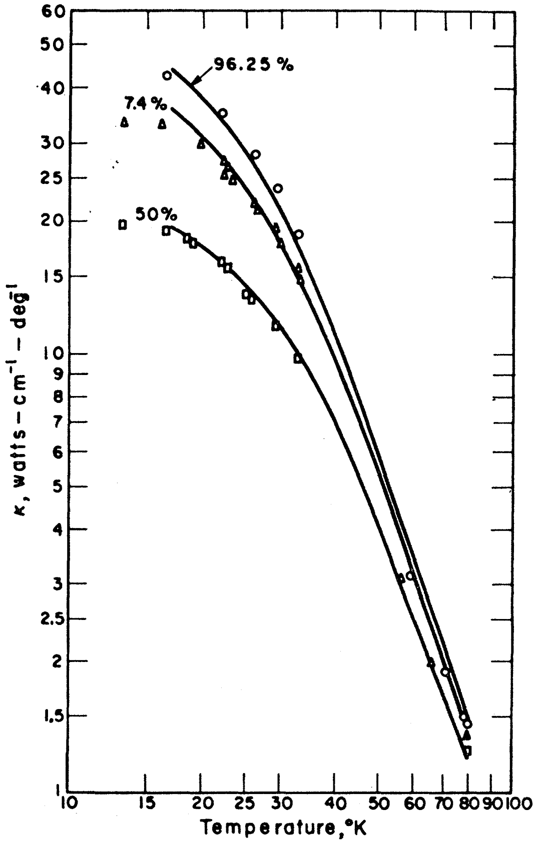

FIG. 3. Thermal conductivity of LiF as a function of temperature. The numbers labelling the curves are the Li^6 concentration. The boxes, circles, and triangles are the experimental points of Berman *et al.*

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[12] T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

[13] R. O. Pohl, Phys. Rev. **118**, 1499 (1960).

[14] 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). We are indebted to Dr. R. Berman for furnishing us the experimental results in detail.

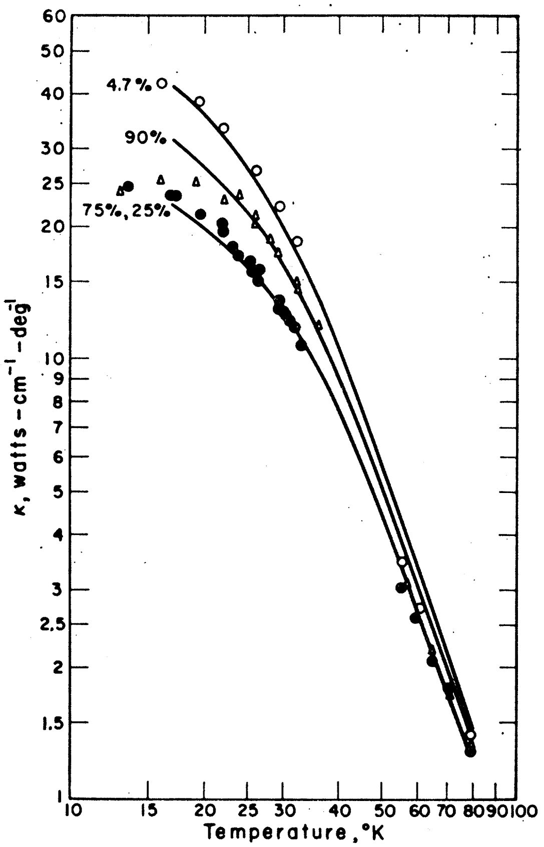

FIG. 4. Thermal conductivity of LiF as a function of temperature. The numbers labelling the curves are the Li^6 concentration. The boxes, circles, and triangles are the experimental points of Berman *et al.*

Debye temperature $\theta = 734°K$ found by Briscoe and Squire.[15] A size effect correction, corresponding to a phonon mean free path for boundary scattering of approximately 1 cm, was included. The curves, representing this fit to the data, are shown in Figs. 3 and 4.

The fitting is seen to be reasonably satisfactory, particularly in the lower temperature region. The approximations on which the calculation is based, in which the size effect is treated as a correction, do not permit us to extend the curves much below 20°. The fit is not unique: The value of B in the low-temperature region is determined to about $\pm 15\%$ by the data; the exponential part of B is rather uncertain in detail. A strong temperature dependence of B in the temperature region 20°–35°K does not appear compatible with the observations. The constant A is determined within about $\pm 30\%$. The curves are not particularly sensitive to the size effect correction. The mean free path mentioned above is reasonably consistent with the size of the specimens employed, but by suitable readjustments of A and B it is possible to make an acceptable fit to the data with a mean free path for boundary scattering greater than 10 cm.

It finally has to be observed that the value of A employed is approximately five times greater than that predicted from the theory of Klemens.[4] This result is similar to that of Pohl, who also found that a large value of A was required.[13] The constant term in the expression for $B(T)$ probably should be interpreted as representing the effect of normal three-phonon scattering processes. The correction to the expression for the thermal conductivity used here [Eq. (6)] arising from the conservation of the total wave vector of the phonon system may then be evaluated according to the prescription of reference 1. (This correction is also discussed in the Appendix.) The correction turns out to be only of the order of four or five percent of the conductivity as previously computed, even at 20°K for the purest material employed in the experiments discussed here. This result indicated that the fit to the data presented here is consistent.

Additional evidence will be required in order to determine whether the disagreement with to the theory of Klemens in respect to the value of A is significant. The present considerations do not rule out the possibility of obtaining a good fit to the data with a smaller value of A and a larger value of B in which the previously mentioned normal process correction would be much larger. Experiments showing the effect of isotope concentration on the thermal conductivity at temperatures below the maximum of the conductivity where phonon-phonon scattering can be neglected would determine A in an unambiguous manner.

ACKNOWLEDGMENTS

One of us (J.C.) wishes to acknowledge very helpful conversations with Dr. P. G. Klemens.

APPENDIX

There is one important case in which the expression (6) for the thermal conductivity is not valid. If normal three-phonon processes are the dominant scattering mechanism, Eq. (6) must be corrected by the addition of a term which takes explicit account of the conservation of the total wave vector of the phonon system by the normal processes. According to reference 1, Eqs. (16), (19), and (21), this term is

$$\kappa_1 = \frac{K}{2\pi^2 v_s}\left(\frac{KT}{\hbar}\right)^3 \frac{I_2^2}{I_3},$$

where

$$I_2 = \int \frac{\tau_c}{\tau_N}\frac{x^4e^x}{(e^x-1)^2}dx;$$
$$I_3 = \int \frac{1}{\tau_N}\left(1-\frac{\tau_c}{\tau_N}\right)\frac{x^4e^x}{(e^x-1)^2}dx. \qquad \text{(A-1)}$$

In these equations, τ_N is the relaxation time for scat-

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[15] C. V. Briscoe and C. F. Squire, Phys. Rev. **106**, 1175 (1957).

tering by the normal processes, which are included in τ_P, and τ_c, is the combined relaxation time of Eq. (5). As usual, x is the dimensionless variable $\hbar\omega/KT$.

The evaluation of the correction κ_1 is in general quite complicated. In reference 1, the case of large defect scattering at low temperature (small y in the terminology of the present paper) was considered; the result obtained was

$$\kappa_1 = 7B\hbar^3/96\pi^4K^2v_sA^2. \qquad \text{(A-2)}$$

The dependence of κ_1 on $1/A^2$ does not persist when A becomes small.

We consider here the case in which the relaxation time for defect scattering is long compared to τ_N. However, since the normal processes cannot be themselves lead to a nonzero thermal resistance, the conductivity will be primarily determined by the defect scattering. Equation (A-1) has been evaluated in this limit (large y), neglecting boundary scattering and umklapp processes. The result is (retaining only the two leading terms of an asymptotic expansion in powers of y^{-2})

$$\kappa_1 = \frac{\hbar}{120\pi^2 v_s A T} + \frac{13}{462}\frac{K^2}{v_s\hbar B T^2}. \qquad \text{(A-3)}$$

The first term in (A-3), when dominant, yields a thermal resistance $120\pi^2v_sAT/\hbar$, twenty five times as great as that obtained from Eq. (16) as a defect resistance. This result is in exact agreement with that obtained by Ziman from a variational principle.[10,14] The second term in (A-3) is of the same order as κ_p [Eq. (12)]. Combining the two, we have

$$\kappa = \kappa_p + \kappa_1 = \frac{\hbar}{120\pi^2 v_s A T} + \frac{15}{77}\frac{K^2}{v_s\hbar B T^2}. \qquad \text{(A-4)}$$

Equation (A-4) shows the extent to which the thermal resistance is overestimated by Ziman's formula, and indicates an explicit contribution from the normal processes to the conductivity. In these equations the constant B pertains to the normal processes only; Umklapp processes are neglected.

PHYSICAL REVIEW VOLUME 120, NUMBER 4 NOVEMBER 15, 1960

Coloration of Pure and Doped Calcium Fluoride Crystals at 20°C and −190°C[*]

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(Received July 14, 1960)

Coloration of pure CaF_2 crystals with 2.5-Mev electrons at room-temperature results in bands at 580, 400, 335, and 225 mμ. In YF_3-doped crystals the bands are in the same spectral positions as in pure crystals. They are, however, enhanced and their intensity ratios are significantly changed, the 400-mμ band being predominant. NaF-doped crystals show an even more drastic change: Coloration at room temperature produces bands at 605, 385, and 330 mμ and is deeper than in either pure or YF_3-doped crystals. Since the 400-mμ band is strongly enhanced by YF_3 addition which forms F^- interstitials, it is correlated to neutral fluorine atoms in interstitial positions. Similarly, the 605-mμ band in crystals doped with NaF, which creates F^- vacancies, is correlated to electrons trapped in F^- ion vacancies (F centers). The enhancement of the 385-mμ band by NaF is explained by the reduction of the activation energy required for formation of interstitials and vacancies. Of several possible correlations the 330-mμ band is probably connected with a hole trapped in a Ca^{2+} vacancy and that at 225 mμ with an electron trapped by a Ca^{2+} interstitial. The bands at 440 and 200 mμ which appear in NaF-doped crystals only must be connected with Na ions. Coloration at −190°C produces strong changes in the absorption spectrum. In pure and YF_3-doped crystals bands appear at 550, 320, and 270 mμ while in NaF-doped crystals bands are formed at 440, 390, 315, and 200 mμ in addition to the 550-mμ band. The primary process of coloration at low temperature cannot differ from that at room temperature but the secondary processes are strongly influenced by temperature.

COLOR centers in CaF_2 can be produced just as in alkali halides, i.e., additively by heating in Ca vapor or by irradiation with γ rays, x rays, electrons, or other ionizing radiation.[1]

Additive coloration in CaF_2 usually produces two strong bands at 375 and 525 mμ (denoted by Mollwo[2] α and β, respectively), while irradiation produces four bands at 580, 400, 335, and 225 mμ.[3] In the alkali halides both methods produce identical F bands although additional bands (V bands) are formed by irradiation only. By proper control of temperature and quenching rate, either the two- or four-band system can be produced by additive coloration.[4] Crystals that have been

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[*] Sponsored by the Office of Naval Research, the Army Signal Corps, and the Air Force; based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the Massachusetts Institute of Technology.

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[1] See e.g., K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press, New York, 1956).

[2] E. Mollwo, Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl. **1**, 79 (1934).

[3] A. Smakula, Phys. Rev. **77**, 408 (1950).

[4] F. Lüty, Z. Physik **134**, 596 (1953).