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Low-Temperature Thermal Conductivity of Boron*

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The thermal conductivity of a single crystal of boron has been measured between 4 and 300°K. The crystal structure is beta-rhombohedral, and the Debye temperature 1200°K. An exponential temperature dependence, $e^{\Theta/aT}$, was observed in the neighborhood of 150°K; the value of a was 2.4. This temperature dependence is characteristic of umklapp processes. The maximum conductivity is approximately 3 W/cm deg near 50°K. At low temperatures the conductivity obeys a $T^{1.8}$ law and has a magnitude one tenth that expected for boundary scattering. The latter effect may be associated with the presence of dislocations. The data are analyzed by the phenomenological model of Callaway.

INTRODUCTION

HEAT conduction by dielectric crystals is reduced by a number of scattering mechanisms.[1,2] Even in the purest of crystals the presence of several different isotopes will lead to a thermal resistance. However, in a material with a high Debye temperature the effect of the isotopic variety is diminished as the phonons effective in energy transport are shifted to longer wavelengths and, thus, are relatively unaffected by point defects, i.e., the isotopes. Other scattering agents include boundaries, dislocations, strains due to deionized impurities, etc. Each will contribute a characteristic temperature dependence to the conductivity in a given temperature range.

Interactions also occur between phonons due to anharmonic terms in the interionic potential. The phonon-phonon scattering may be divided into two classes: normal processes wherein crystal momentum is conserved; and umklapp processes wherein the crystal momentum is not conserved. Normal processes do not produce a thermal resistance, rather redistribute energy among the modes.

Quite recently, single crystals of boron have become available,[3] which provides an opportunity for the investigation of the various scattering mechanisms in an elemental semiconductor with properties intermediate between silicon and diamond. Boron has a Debye temperature over 1200°K and an energy gap of 1.35 eV. Unfortunately, the presence of dislocations obscures the low-temperature properties of the sample investigated.

EXPERIMENTAL

Boron has several allotropic forms. The sample used here was a single crystal of the beta-rhombohedral phase grown by Texaco Experiment, Inc.[4] Boron in this form is a semiconductor. The sample was a cylinder 3.8 cm in length and averaged 0.26 cm in diameter; as it was grown by the float-zone method it lacked a uniform cross section. From studies of electrical transport[3] made on similar specimens we may infer the band gap to be 1.35 eV; carbon was the major impurity (0.1%); the carbon acts as a donor with a level about 0.32 eV below the conduction band. The room temperature resistivity exceeds 5×10^6 Ω cm. The density is 2.342 ± 0.005 g cm^{-3} and the Debye temperature 1219°K.[5]

Measurements were made in the standard way[6,7] using gold-cobalt versus manganin thermocouples for temperature and temperature difference. The temperature difference across the sample was held to a few percent of the average temperature.

The results are shown in Fig. 1, where is also plotted a

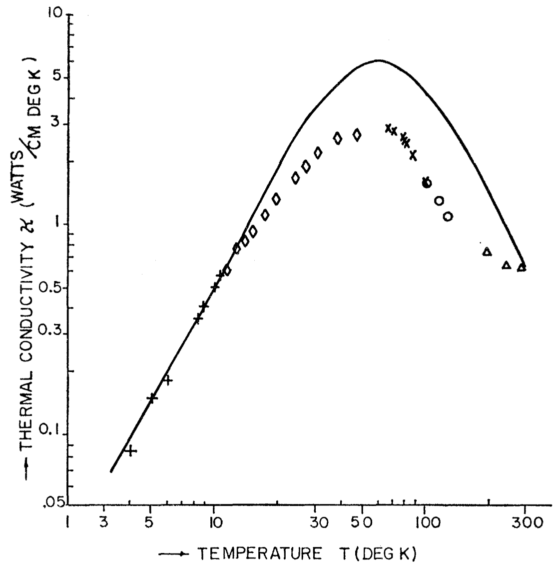

FIG. 1. Thermal conductivity as a function of temperature. The symbols refer to various runs. The solid line is based on isotope, boundary, and phonon-phonon scattering processes.

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[1] P. G. Klemens, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. VII, p. 1.

[2] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[3] C. P. Talley (private communication).

[4] The crystal was supplied to us through the good offices of C. P. Talley and T. S. Teasdale of Texaco, Inc.

[5] H. L. Johnston, H. N. Hersh, and E. C. Kerr, J. Am. Chem. Soc. **73**, 1112 (1951).

[6] J. C. Thompson and B. A. Younglove, J. Phys. Chem. Solids **20**, 146 (1961).

[7] M. G. Holland and L. G. Rubin, Rev. Sci. Instr. **33**, 923 (1962).

Table I. Isotope scattering effects in several materials.[a] The symbols are defined in the text.

Material	Θ (deg K)	V/N (cm^3) ($\times 10^{-24}$)	c (cm/sec) ($\times 10^5$)	Γ ($\times 10^{-4}$)	A (sec^3) ($\times 10^{-44}$)
diamond	1960	5.68	11.8	0.76	0.00216
boron	1219	7.7	8.1	12.9	0.150
sapphire	1010	42.6	8.0	0.025	0.0016
silicon	668	19.9	6.2	2.64	0.133
germanium	390	22.6	3.8	5.72	1.87
germanium[b] (enriched)	390	22.6	3.8	0.38	0.124

[a] Taken in part from Ref. 9.
[b] See Ref. 10.

theoretical curve based on isotope, dislocation, and boundary scattering, as well as the usual anharmonic effects.

DISCUSSION

The presence of two abundant isotopes with a 10% mass difference would be expected to preclude the observation of umklapp scattering effects. However, Klemens[1] has shown that the relaxation time τ_I for isotopic scattering can be written

$$\tau_I^{-1}=(V/N)(4\pi c^3)^{-1}\Gamma\omega^4=A\omega^4, \tag{1}$$

where we follow the notation of Callaway[8] with c the speed of sound, V/N the atomic volume, and

$$\Gamma=\sum_i f_i\left(1-\frac{M_i}{M}\right)^2. \tag{2}$$

In Eq. (2) f_i is the fraction of isotopes of mass M_i present in a crystal of average atomic mass M. The presence of c^{-3} in the coefficient of ω^4 implies that a wide variety of isotopic masses can be offset by a large sound speed. As c is proportional to the Debye temperature, we expect a large c in boron. Slack[9] has surveyed the variation of isotopic effects and Table I shows a comparison between several elements. One sees that boron is no more affected by isotope scattering than the enriched germanium sample used by Geballe and Hull.[10] It is nevertheless surprising that umklapp scattering should be observed here since the value of A is no smaller than in Si. However, one cannot make a prediction without detailed knowledge of the vibration spectrum.[10] Of the materials listed in the table only diamond and sapphire have heretofore been shown to exhibit an exponential thermal conductivity.

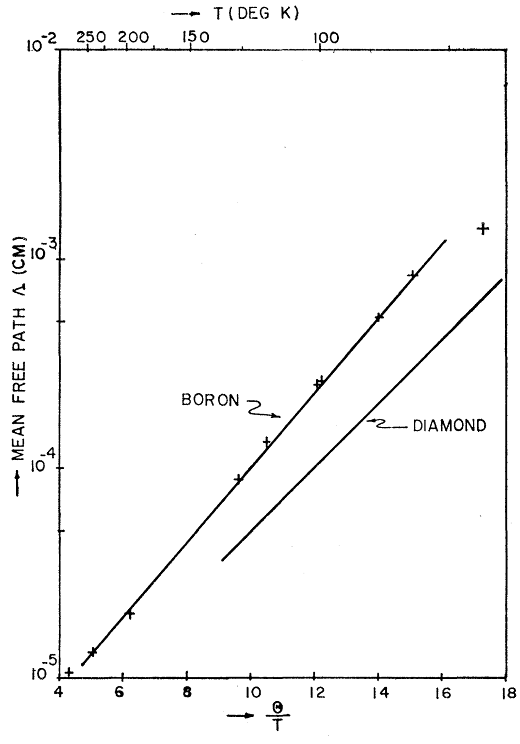

Fig. 2. The phonon mean free path as a function of temperature in the umklapp region. The mean free path is defined by $\kappa=\frac{1}{3}Cc\Lambda$, where κ is the thermal conductivity, C the heat capacity, and c the speed of sound. A similar curve for diamond is shown for comparison.

Figure 2 shows the mean free path Λ of boron as a function of Θ/T at temperatures above the maximum in the conductivity. An exponential dependence is indicated. The mean free path is calculated from the thermal conductivity by $\kappa=\frac{1}{3}Cc\Lambda$, where C is the specific heat expected from the Debye theory. Though simple arguments lead one to expect a value of 2 for a, the value of 2.4 reported here is not out of line with the value of 2.6, for example, reported for diamond.[2]

It should be noted that the 0.1% carbon present may be included as an "isotope" but alters the value of Γ by less than 1% since the carbon mass is so close to that of boron.

We have analyzed our data by using the phenomenological model of Callaway.[8] We assume that the thermal resistance is due to the following effects: (a) boundaries, (b) dislocations, (c) phonon-phonon scattering, (d) isotope scattering. Each process is described by a relaxation time according to the following scheme:

(a) boundaries:

$$\tau_B^{-1}=C/L, \tag{3}$$

where L is the sample diameter;

(b) dislocations:

$$\tau_D^{-1}=n\gamma^2b^2\omega=H\omega, \tag{4}$$

where n is the density of dislocations, γ the Grueneisen constant, and b the "diameter" of the dislocation;

(c) phonon-phonon:

$$\tau_N^{-1}=B_2T^3\omega^2 \tag{5}$$

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[8] J. Callaway, Phys. Rev. **113**, 1046 (1959).
[9] G. A. Slack, Phys. Rev. **105**, 829 (1957).
[10] T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

for normal processes, with B_2 a constant; and

$$\tau_U^{-1}=B_1'T^3[\exp(-\Theta/aT)]\omega^2=B_1T^3\omega^2 \qquad (6)$$

for umklapp processes, with B_1 taken to be a constant; and (d) isotopes have already been discussed. One now combines the relaxation times and obtains the following expression for the thermal conductivity. The details of the calculation are given in the article by Callaway, who does not discuss dislocations, though their effect may be included by a straightforward process.

$$\kappa=\left(\frac{k}{2\pi^2c}\right)\left(\frac{kT}{\hbar}\right)^3 \times\int_0^{\Theta/T}(e^x-1)^{-2}\left(Dx^4+Ex^2+Fx+\frac{c}{L}\right)^{-1}x^4e^xdx. \qquad (7)$$

In Eq. (7) the parameters are k = Boltzmann's constant, $x=\hbar\omega/kT$, $D=A(kT/\hbar)^4$, $E=(B_1+B_2)T^3\times(kT/\hbar)^2$, and $F=H(kT/\hbar)$. The equation was numerically evaluated using Simpson's rule and a CDC 1604 computer.

A is evaluated from Klemens' expression, Eq. (1). A value is obtained for $B=B_1+B_2=5.4\times10^{-24}$ by setting $F=0$ and matching the integral to the measured thermal conductivity at 300°K. H is finally evaluated by matching the data at 5°K. The thermal conductivity may then be calculated at intermediate temperatures. The results are shown in Fig. 1. One cannot hope to obtain the exponential umklapp behavior, as that is removed when B_1 is taken to be temperature-independent. The value of A is undoubtedly low, as has often been noted.[2,11] One might then seek a "best" value for A by fitting the data curve. This we have not chosen to do. The discrepancy between theory and data above the maximum is due in part to this decision. The presence of umklapp effects, as noted above, does not improve the agreement.

Below the maximum the data obey a $T^{1.8}$ law. Neither magnitude nor temperature dependence agree with boundary scattering. However, the specific heat shows a hump,[5] in the neighborhood of 25°K, probably indicative of a phase change in view of the many alloptropic forms of boron. One is thus led to expect a considerable number of dislocations to be present. Dislocations should produce a T^2 temperature dependence.[2] If we determine the dislocation density at 5°C by fitting the data and Eqs. (4) and (7), we obtain a dislocation density of 10^9 cm^{-2}. This result depends upon assumed values of 2 and 3×10^{-8} cm for the Grueneisen γ and for the dislocation core size b, respectively. The result is reasonable if a phase change occurs.

We do not expect to explain our result in terms of strains induced by the deionization of the carbon donor atoms as has been done by Keyes[12] for Ge. This effect leads to a temperature dependence stronger than T^3, as does the presence of mobile defects.[13]

CONCLUSIONS

We have reported here the third observation of umklapp scattering processes among the elements, helium and diamond being the other two. The coefficient in the exponential term a has a value of 2.4 which compares well with the values of 2.3 and 2.6 for He and C, respectively. The presence of two abundant isotopes of boron, with masses differing by 10%, does not lead to the large isotope scattering observed in Ge, as the Debye temperature is high in boron.

The thermal conductivity below the maximum is limited by the presence of dislocations. Heat capacity measurements lead one to believe that a phase change occurs in this temperature range. Thus, the presence of 10^9 dislocations per cm^2 is not unreasonable.

The authors would like to acknowledge a stimulating conversation with P. G. Klemens.

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[11] B. K. Agrawal and G. S. Verma, Phys. Rev. **126**, 24 (1962).

[12] R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

[13] A. Granato, Phys. Rev. **111**, 740 (1958).