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Thermal Conductivity of Elements with Complex Lattices: B, P, S

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The thermal conductivities of β-rhombohedral boron, orthorhombic (black) phosphorus, and orthorhombic sulfur have been measured down to 3°K. These results, as well as some from the literature on cubic (white) phosphorus and on boron carbide, have been interpreted by comparing them with the thermal-conductivity-versus-temperature curves expected for simple models of molecular solids and of monatomic solids. Sulfur and white phosphorus behave like simple molecular solids, and black phosphorus behaves like a monatomic solid, while the behavior of boron and boron carbide, whose lattices are composed of B_{12} icosahedra, lies between these two limits.

INTRODUCTION

BORON, phosphorus, and sulfur are nonmetallic elements with complex crystal lattices and are polymorphic. They differ, therefore, from the elements and compounds of simple crystal structure whose thermal conductivity K is more frequently studied. Previous measurements on the K of the elemental molecular solids hydrogen[1] and iodine[2] have, however, been reported in the literature. The present measurements on B, P, and S from 3 to 300°K combined with earlier ones on P and S show that the heat is transported by phonons and that the type of crystal lattice greatly affects the magnitude of K. The molecular or partially molecular lattices of β-rhombohedral B, cubic (white) P, and orthorhombic S have low thermal conductivities at 300°K. The orthorhombic (black) P has a simpler lattice, and its K is more nearly similar to that of monatomic nonmetallic solids such as Si and Ge. The purpose of this paper is to show how these results can be understood in terms of the differences in energy transport by the lattice modes and the internal molecular modes of the molecular crystals.

SAMPLES

The boron samples used were the β-rhombohedral form. Solid boron possesses at least three different crystallographic modifications.[3] The β-rhombohedral form appears to be the stable one near the melting point[4,5] of 2310°K, and is the form normally produced when boron crystals are grown from the melt.[6] One of these samples of β-rhombohedral boron, $R4$, was grown from partially purified boron by F. H. Horn of this laboratory, using the Czochralski technique and boron nitride crucibles. It was 3.8 cm long and had a somewhat irregular cross-section with an average diameter of 0.7 cm. A thin section was studied in transmission using infrared light and an infrared image converter. This study indicated the presence of some precipitate particles from 5 to 50 μ in diameter, and the total volume fraction of precipitate was estimated to be of the order of 10^{-3}. These may be boron nitride or silicon inclusions, or small voids in the sample. The sample was polycrystalline with numerous columnar crystals about 1 cm long with an average diameter of 0.3 cm. The second β-rhombohedral boron sample $R46$ was a polycrystalline sample from Eagle-Picher,[7] grown from the melt by a floating zone process.[8] It was 2.6 cm long, 0.6 cm average diameter. The crystallites of which it was composed were columnar with an average diameter of 0.1 cm and a length of 2 cm. The samples were analyzed for metallic impurities by emission spectrography and the major impurities found are listed in Table I. Silicon is seen to be the major contaminant in both, although $R46$ is considerably purer than $R4$. It is not known whether these impurities are present in solid solution in the boron or as a precipitate phase. The thermal conductivity results for both boron samples are nearly identical, so it appears that K is not too sensitive to the impurity concentration.

TABLE I. Major impurities in the samples of β-rhombohedral boron in units of 10^{18} atoms/cm^3.

Impurity	$R4$	$R46$
Al	20	0.3
Cu	4	0.04
Mn	20	···
Si	100	0.8
Ti	6	<0.3
W	7	···

The sample of black phosphorus was a polycrystalline rod of dimensions 1.2 cm ×0.35 cm ×0.35 cm. It was cut from a larger ingot prepared by R. H. Wentorf[9] of

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[2] A. Pochettino and G. Fulcheris, Atti Accad. Sci. Torino **58**, 493 (1923).

[3] J. L. Hoard and A. E. Newkirk, J. Am. Chem. Soc. **82**, 70 (1960).

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[7] Eagle-Picher Research Laboratory, Miami, Oklahoma, crystal reference number M6005CP.

[8] R. J. Starks and W. E. Medcalf, *Boron, Synthesis, Structure, and Properties*, edited by J. A. Kohn, W. F. Nye, and G. K. Gaulé (Plenum Press Inc., New York, 1960), p. 59.

[9] R. H. Wentorf, *The Art and Science of Growing Crystals*, edited by J. J. Gilman (John Wiley & Sons, Inc., New York, 1963), p. 176.

this laboratory in a high-pressure, high-temperature apparatus. The black P was the orthorhombic modification[10] first reported by Bridgman.[11] The present material was made from liquid P by cooling the melt from a temperature of 1200°C under a pressure of 2.3×10^4 atm. The resultant crystallite size as judged from microscopic observation was roughly 200 μ, with some preferred orientation of the anisotropic crystallites. The heat flow in the sample was approximately in the *a-b* plane of these crystallites. No analysis of the purity of the P was made, but the starting material was 99.8% pure from the Fischer Scientific Company.[12] The electrical properties of this specimen were measured by R. O. Carlson of this laboratory. He found that the sample was *p* type with an electrical resistivity of 3.1 Ω cm, and a Hall mobility of 110 cm^2/V sec at 300°K. Its carrier concentration from measurements at lower temperatures was 10^{15} cm^{-3}. These properties are similar to those found by Warschauer.[13]

The samples of sulfur were single crystals of the stable orthorhombic modification slowly grown from a CS_2 solution at room temperature during a period of about a week. No impurity analysis of the crystals was made, but the purity of the sulfur starting material was >99%. The as-grown samples had well-developed crystal faces, and were transparent with a yellow color. A few small internal growth flaws were visible even in the best samples studied. Rod-shaped samples about 0.7 cm long ×0.2 cm in diameter were cut from the crystals. Sample *R*124 was cut with its long dimension in the *a-b* plane so that the heat flow was perpendicular to the *c* axis. In sample *R*126 the heat flow was parallel to the *c* axis.

THERMAL CONDUCTIVITY RESULTS

Boron

The thermal conductivity of all of the samples of boron, phosphorus, and sulfur was measured between 3 and 300°K by using a steady-state longitudinal-heat-flow technique previously described.[14] The results for boron samples *R*4 and *R*46 are shown in Fig. 1. The agreement with the results of Thompson and McDonald[15] for $4°\text{K}\leq T\leq 140°\text{K}$ is reasonable. Their measurements were made on a single crystal of β-rhombohedral boron grown by a floating-zone process, and are lower than the present ones by a factor of 4 in the 4 to 20°K range. This difference is probably caused by the presence of large dislocation densities or some physical or chemical imperfections in their crystal in spite of the fact that it was a "single crystal." In the region from 140 to 300°K the results of Thompson and McDonald are too high by a factor of roughly two. Their three data points in this region also give what is believed to be an incorrect temperature dependence for *K* near 300°K (see Fig. 1). The present results and those of Thompson and McDonald both give much higher *K* values than that found by Talley.[16] Talley's result is probably too low because he did not take account of the temperature drop between the boron sample and the water bath.

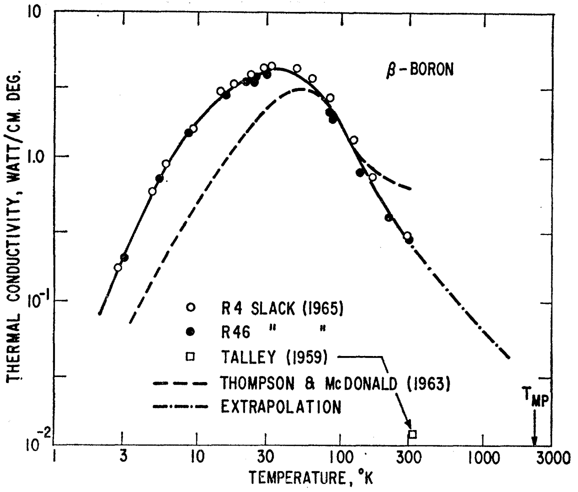

FIG. 1. Experimental data on the thermal conductivity of β-rhombohedral boron as a function of temperature. The melting point of boron is T_{mp}.

Phosphorus

The *K* results between 3 and 300°K for orthorhombic, black P are shown as the solid curve in Fig. 2 for the present sample measured in experimental run *R*21. The only previous mention in the literature on the *K* of black P seems to be Bridgman's observation[11] that near room temperature its *K* is much greater than that of glass. Since most silica glasses have a *K* of about 1.2×10^{-2} W/cm deg at 300°K, Bridgman's observation is in agreement with the present results. Figure 2 also shows some recent measurements by Kraemer and Schmeiser[17] for *K* of cubic and liquid white P from 290 to 350°K (mp=317°K). The *K* of black P is considerably higher than that of white P.

Sulfur

Figure 3 shows the *K*-versus-*T* curves for sulfur based on crystals *R*124 and *R*126 as well as data on polycrystalline material by Lees,[18] Eucken,[19] Kaye and

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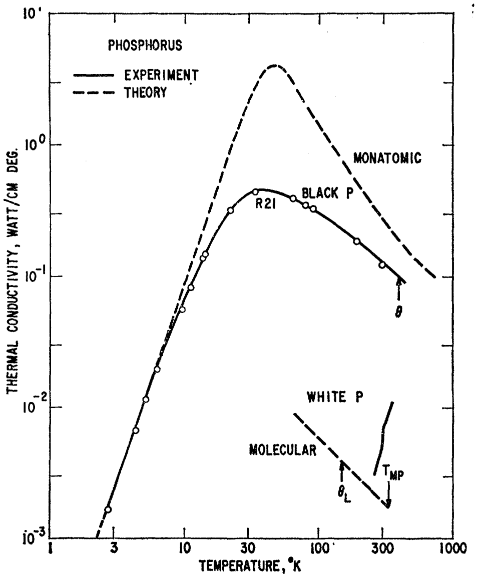

FIG. 2. The thermal conductivity of two allotropic forms of phosphorus (black and white) as a function of temperature. The dashed curves are theoretical estimates calculated from simple models for monatomic black P and for molecular white P. The melting point is $T_{\rm mp}$. The Debye temperatures θ and θ_L are explained in the text.

Higgins,[20] and Greene.[21] The single crystal data starts at 3°K and extends only up to 100°K. Above 100°K the thermal radiation losses in the present apparatus became too high too permit accurate measurements. Eucken's two results at 83 and 273°K on cast plates of sulfur cover the gap between 100°K and the results of the other authors whose measurements were all made above 273°K.

Because the sulfur crystals are orthorhombic they have three principal thermal conductivities K_a, K_b, and K_c along the a, b, and c crystallographic axes. Some idea of the anisotropy in K that is to be expected can be obtained from the measurements of the anisotropy in the elastic constants,[22] in the thermal expansion coefficients,[23,24] and in the intermolecular spacings.[25] The measurements show that these three properties are quite similar in the a and b directions, but that the c direction is different. Since the sound velocity along the c axis is 50% larger than along the a or b axes, and the thermal expansion coefficient along the c axis is $\frac{1}{4}$ of that along the a or b axes, one might expect $K_a = K_b < K_c$.

The conductivity ratios K_c/K_a and K_b/K_a were determined at 316°K by using a modification of deSenarmont's[26] melted wax method. For this measurement thin single crystal plates 1 cm in diameter and 0.1 cm thick were cut with the desired orientation. They were covered with a thin layer of phenyl salicylate (mp=316°K) and heated in air by a small central wire passed through a hole in the plate. The heat input was adjusted until about $\frac{1}{3}$ of the phenyl salicylate had melted. The melted portion has an elliptical boundary, and its eccentricity is related to K_c/K_a. These experiments indicated little if any anisotropy in K, and all three principal K values were equal to within ±20%. The measurements in Fig. 3 between 15 and 100°K indicate that K_c and K_{ab} do not differ by more than 20%, where K_{ab} refers to some arbitrary direction in the ab plane. [*Note added in proof.* A. V. Ioffe and A. F. Ioffe, Zhur. Tekh. Fiz. **22**, 2005 (1952) found an anisotropy, for crystalline sulfur, of 1.27 near 300°K (presumably K_c/K_{ab}). Their absolute values of K are about

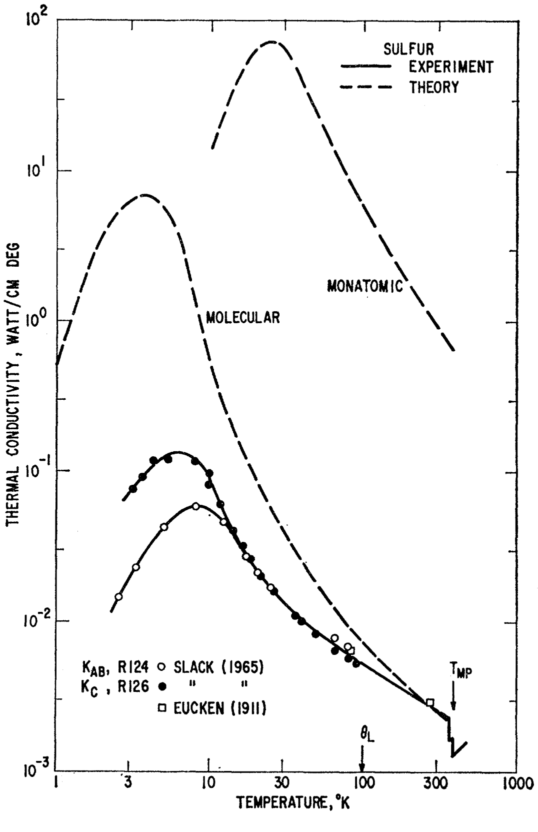

FIG. 3. The thermal conductivity of orthorhombic sulfur as a function of temperature. K_C means that K was measured with the heat flow parallel to the c axis, while for K_{AB} the heat flow was perpendicular to the c axis. The two steps in the experimental curve near the melting point $T_{\rm mp}$ are caused by the successive transitions to solid monoclinic and then to liquid sulfur with increasing temperature. The dashed curves show the predicted behavior of orthorhombic sulfur from simple molecular and monatomic models. The lattice Debye temperature of molecular sulfur is θ_L.

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[20] G. W. C. Kaye and W. F. Higgins, Proc. Roy. Soc. (London) A122, 633 (1929).

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twice as large as those in Fig. 3.] The large difference between $R124$ and $R126$ below 15°K is caused by differences in the crystal perfection and is not an intrinsic property of sulfur. Therefore, to a good approximation the K sulfur is isotropic and the previous results[18–21] on polycrystalline samples above 100°K can be combined with the present data below 100°K to yield a K-versus-T curve from 3 to 488°K as in Fig. 3. This temperature range covers the orthorhombic (below 369°K), monoclinic (369 to 392°K), and liquid (above 392°K) forms of sulfur. Notice the changes in K as the sulfur phases change, and that near the melting point the K of the solid is only slightly higher than that of the liquid. In the stable, low-temperature, orthorhombic phase between 3 and 369°K the K-versus-T curve exhibits a behavior typical of nonmetallic solids and reaches a maximum at 7°K. The most pronounced feature of the curve is the very small absolute value of K in the 10^{-2} W/cm deg range. The explanation of why the K value is so low is a major part of this paper.

ANALYSIS OF THE RESULTS

Sulfur

In order to analyze the results shown in Fig. 3 for sulfur one needs to know some of its other physical properties such as crystal structure, density, elastic constants, specific heat, and electrical conductivity. Some of these properties are given in Table II. Sulfur is a semiconductor[27,28] with a very small electrical conductivity. Hence, phonons will be the dominant carriers of the thermal energy at temperatures below 300°K. The stable, low-temperature modification of sulfur exists from 3 to 369°K and consists[25] of S_8 rings held together by Van der Waals forces. These S_8 rings of eight sulfur atoms are very stable and are the major constituents of monoclinic sulfur, of liquid sulfur just above its melting point, and of the vapor[29] over solid sulfur. These molecular S_8 units affect most of the other physical properties of sulfur. The sulfur-to-sulfur atom distance within the rings is 2.04 Å, while the nearest distance between atoms in adjacent rings is 3.69 Å. This large inter-ring distance yields a room-temperature density of 2.09 g/cm³. The measured[30] specific heat capacity per unit volume C_{TOT} of sulfur has been converted to values of effective Debye temperatures θ by assuming that at any temperature T the value of C_{TOT}, corrected to constant volume, is given by

$$C_{\text{TOT},V}=3k\delta^{-3}f_D(\theta_E/T)\,, \qquad (1)$$

where k = Boltzmann's constant, δ^3 = average volume occupied by a single sulfur atom, and f_D = the Debye function. A plot of this effective Debye temperature θ_E versus T is given in Fig. 4. From Fig. 4 it is quite clear that θ is not independent of temperature. Since θ is a parameter that enters into the calculation of K, it is necessary to understand the reason for the variation of θ with T.

TABLE II. Some physical properties of Sulfur, Phosphorus, and Boron.

Crystal	Density gm/cm³	N[a]	δ[b] (Å)	$\bar{v}$[c] 10^5cm/sec	θ_L[d] (°K)	θ[e] (°K)	T_{mp}[f] (°K)
Orthorhombic S	2.09	8	2.97	2.5	100	···	387
White P	1.82	4	3.00	1.6	100	···	317
Black P	2.69	1	2.67	4.0	···	400	1300
β-Boron	2.33	12	1.98	8.0	570	1300	2310

[a] N = number of atoms in a molecular group.
[b] δ^3 = average volume occupied by a single atom of the solid.
[c] $\bar{v}$ = average sound velocity.
[d] θ_L = average Debye temperature for the translational and librational lattice modes of the intermolecular vibrations.
[e] θ = normal Debye temperature of the monatomic solid.
[f] T_{mp} = melting point.

The θ-versus-T variation is intimately connected with the molecular nature of sulfur. In a molecular solid it is possible to divide the normal modes of vibration, i.e., the phonon frequencies, into two well-separated groups. We shall designate the "I" phonons as those associated with the internal vibrations of the S_8

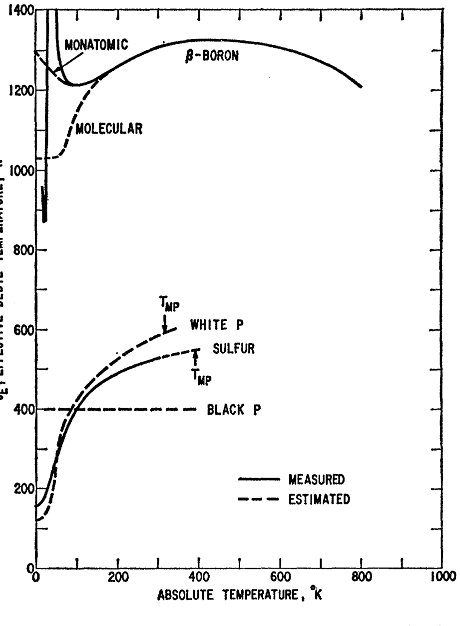

FIG. 4. The effective Debye temperature versus absolute temperature for several solids. This θ_E is that value which is calculated from specific heat data when the data are treated as if all of the solids were monatomic. The melting points are T_{mp}.

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molecules. The "L" phonons will be the lattice phonons associated with the relative motions of the various S_8 molecules considered as separate, rigid units. This is the type of separation of phonon modes used in interpreting the infrared and Raman spectra of molecular solids. The frequencies of the L phonons will generally be much lower than those of the I phonons because the intermolecular forces are much weaker than the intramolecular forces. Both types of phonons contribute to the total specific heat capacity per unit volume at constant volume, $C_{\mathrm{TOT},V}$. Thus $C_{\mathrm{TOT},V}$ is a sum over all the internal and external modes:

$$C_{\mathrm{TOT},V}=\sum_I c_I+\sum_L c_L=C_I+C_L. \tag{2}$$

The θ_E shown in Fig. 4 is a combination of contributions from C_I and C_L. The I phonons, which have rather higher frequencies than the L phonons, are present in substantial numbers at room temperature and have a characteristic temperature of 500 to 600°K. The effective θ increases continuously from 160°K near 0°K toward a θ_I value above room temperature. This temperature variation has been worked out by previous authors[31,32] and found to agree with the experimental C_{TOT} results.

The extrapolation of θ_E to a value of 160°K at absolute zero is based on the following arguments. The heat capacity at the very lowest temperatures near 0°K in a molecular crystal is the sum[33,34] of a translatory vibration term and a libratory vibration term. These two terms each have their own Debye temperatures, θ' and θ''. Their sum is the total lattice specific heat capacity C_L. Thus

$$C_{L,V}=C_V'+C_V''=3kN^{-1}\delta^{-3}[f_D(\theta'/T)+f_D(\theta''/T)]. \tag{3}$$

Here we have made use of the fact that at $T\gg\theta$ the classical specific heat of a rigid mass is just k per degree of freedom, and there are $N^{-1}\delta^{-3}$ such masses per unit volume. Here N is the number of atoms in a sulfur molecule, i.e., 8. The translatory Debye temperature, θ', has been calculated[35] from the elastic constants[22] as $\theta'=103$°K. This θ' is somewhat larger than that used[31,32] before the elastic constants were known. Following Lord *et al.*[33] it will be assumed that $\theta'=\theta''$. Hence at temperatures near or below 1°K

$$C_{\mathrm{TOT},V}=C_L=6kN^{-1}\delta^{-3}f_D(\theta_L/T). \tag{4}$$

The right-hand side of Eq. (4) constitutes over 90% of the actual C_{TOT} from 0 to 20°K, and even 30% of C_{TOT} at 300°K. The lattice Debye temperature θ_L is given approximately by

$$\theta_L=\tfrac{1}{2}(\theta'+\theta''),$$

and is taken as $\theta_L=100$°K. Thus the effective θ_E at 0°K, calculated on the assumptions in Eq. (1) that sulfur is a monatomic lattice, is just

$$\theta_E=(N/2)^{1/3}\theta_L=160°\mathrm{K}. \tag{5}$$

This value is a reasonable extrapolation of the θ_E values determined from the specific-heat measurements, as shown in Fig. 4.

Now that θ versus T for sulfur is known, it is possible to make an estimate of the thermal conductivity of sulfur. This estimate can be based either on the assumption that sulfur is a monatomic solid or that it is a molecular solid. It is reasonably clear that the monatomic model won't work very well. However, its predictions are interesting.

For this calculation of K, we shall take the value of θ to be temperature independent at its high temperature limit of about 550°K. With this value of θ, an average sound velocity of 2.5×10^5 cm/sec derived from the elastic constants, and a boundary scattering mean free path equal to the sample diameter of 0.2 cm, the K versus T curve labeled "monatomic" in Fig. 3 was derived. This monatomic model is the same as that employed for Si and Ge.[36] The calculated curve clearly gives K values much higher than the observed ones. Even if a temperature-dependent θ for sulfur is put into the theory, the fit in Fig. 3 is not much better. The conclusion is that the K of sulfur cannot be computed from a monatomic model. However, much better agreement is found if explicit account of the molecular nature of sulfur is taken.

A simple model for computing K of a molecular solid will now be given. It is similar in sprit to that employed[37] for the K of a polyatomic gas. The thermal conductivity of a molecular solid can be considered as the sum of two terms:

$$K=\tfrac{1}{3}\sum_I v_I l_I c_I+\tfrac{1}{3}\sum_L v_L l_L c_L, \tag{6}$$

where v= average propagation velocity of phonons in a particular mode, l= their mean free path, and c= their contribution to the total heat capacity per unit volume. The sums are taken over both the I and L phonons, as was done in Eq. (2). In a molecular solid the molecular groups interact only weakly, and the high frequency internal vibrations do not propagate through the lattice. In this limit all the v_I are zero, and K is determined only by the L phonons. This zero or nearly zero group velocity of these internal or optical type phonons is a characteristic feature. In a monatomic solid, all of the

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[37] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids*, (John Wiley & Sons, Inc., New York, 1954), p. 498.

phonon modes are L modes, all (or almost all) of them have nonzero velocities, and hence all modes contribute to K. The main cause of the difference in K between molecular and monatomic solids, therefore, is the presence in molecular solids of many phonons that have zero group velocities. For evaluating Eq. (6) we shall use a crude theory of molecular crystals. It will be assumed that all $v_I=0$, all v_L for both translatory and libratory vibrations are equal to one another, and that l_L is the same for all of the L phonons. Thus

$$K=\tfrac{1}{3}v_L l_L C_L\,, \tag{7}$$

where C_L is given by Eq. (4). The next step is to estimate l_L, since v_L and C_L are known approximately. An exact calculation of l_L, which will depend on the anharmonic interactions and the detailed structure of the solid, is too involved for the present order-of-magnitude calculations. At the melting point T_{mp} of the molecular solid the value of l_L will be assumed to be as small as possible, that is comparable to the average distance between the molecular groups, i.e. $l_L\cong(N\delta^3)^{1/3}$. This type of assumption turns out to be reasonable for molecular solids, as we shall see. It gives too small a K for monatomic solids, since the average mean free path of phonons in Ge, Si, and diamond at their melting points as judged from K measurements[38] is about 20 interatomic distances. For temperatures $\theta<T<T_{\mathrm{mp}}$ the temperature variation of l_L will be approximately

$$l_L\cong N^{1/3}\delta(T_{\mathrm{mp}}/T)\,. \tag{8}$$

Hence for $T>\theta_L$ the value of K is given by substituting Eqs. (4) and (8) in Eq. (7) as

$$K=2kv_L T_{\mathrm{mp}}N^{-2/3}\delta^{-2}T^{-1}\,, \tag{9}$$

since f_D approaches unity. As T is lowered below $T=\theta_L$, Eq. (8) is no longer appropriate since the umklapp relaxation time τ_u increases exponentially with decreasing temperature. The experimental results for sulfur below 100°K show some indication of this exponential behavior in that, with decreasing T, K is definitely rising faster than T^{-1} between 30 and 10°K. For lack of a better approximation, it will be assumed[39] that

$$\tau_u^{-1}=(p\omega^2T/\theta_L)\exp(-\theta_L/3T)\,, \tag{10}$$

where p = some constant, and ω = the phonon frequency. The Debye temperature used in Eq. (10) is just the lattice Debye temperature θ_L. Note that Eq. (8) is equivalent to setting $\tau_u\cong\omega_L^{-1}$ at T_{mp}, where $\omega_L=k\theta_L/\hbar$. As T decreases, the phonon mean free path l_L increases until it becomes limited by isotope scattering and crystal boundary scattering. In the boundary scattering limit, K is calculated from Eqs. (4) and (7) with l_L set equal to the minimum dimension of the crystals in the sample studied. In this way the K-versus-T curve for sulfur was calculated in the molecular approximation. The various parameters used in calculating K are given in Table II. The results are shown in Fig. 3.

A comparison of the theory with the experimental results in Fig. 3 shows that the molecular model provides a much better approximation to the truth than does the monatomic model. The agreement is not perfect but it does give the right order of magnitude for K above 10°K and the correct type of temperature dependence. The theory is, of course, too crude to exhibit the change in K at 369°K at orthorhombic-monoclinic transition. The factor of $\sim10^2$ difference between theory and experiment at 3°K can be attributed to some unknown crystal defects, perhaps $\mathrm{CS_2}$ impurities[28] in these solution-grown crystals. Only above 10°K are the experimental results considered to be an intrinsic property of sulfur crystals.

Phosphorus

The results in Fig. 2 show that the two allotropic forms of phosphorus have considerably different thermal conductivities. At 300°K the K of black P is 25 times that of white P. In both types of P, the electrical conductivity is so low that the heat is transported almost entirely by phonons. The difference can be attributed to the difference in crystal structure and interatomic bonding. White P is a molecular solid composed of $\mathrm{P_4}$ molecules[40] held together by Van der Waals forces. The black P is a three-dimensional network of single P atoms held together by covalent bonds[10]; it has no distinguishable molecular groups. Thus the K of white P will be estimated using the same molecular model that was used for sulfur. The K of black P will be computed from the monatomic model.[36] The physical parameters used in this calculation are given in Table II, and the results are shown in Fig. 2. For black P the θ and v_L values of $\theta=400$°K, $v_L=4.0\times10^5$ cm/sec were estimated from the bulk compressibility[41] of 2.9×10^{-12} cm²/dyn and the density of 2.69 g/cm³. The crystallite size was chosen in order to make the theoretical and experimental K curves agree for $T<10$°K. This size is about 10% of the visual size of $\sim2\times10^{-2}$ cm, but is plausible since the visible grains may have possessed considerable internal damage. The value of θ_L for white P of $\theta_L=100$°K is based on the measured[42] compressibility of 2.13×10^{-11} cm²/dyn and the density of 1.82 g/cm³. The calculated v_L is 1.6×10^5 cm/sec. The estimated θ_E-versus-T curve for white P is shown in Fig. 4. The value of $\theta_E=130$°K at 0°K is obtained from Eq. (5) using $N=4$. At higher temperatures the internal vibrations[43] of the $\mathrm{P_4}$ molecule in the 350 to 600 cm⁻¹ wave-number range become excited. These correspond to a characteristic temperature of 600°K. There do not appear to be any

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published measurements of the specific heat capacity of white P in the 0 to 273°K range[44] to serve as a check on the estimated θ_E curve in Fig. 4. Therefore, it has been drawn to resemble the curve for sulfur.

The theoretically calculated K-versus-T curves for the two forms of P are shown in Fig. 2. The monatomic curve computed for a single crystal of black P is not a terribly bad approximation to the truth. Perhaps the experimental K curve would have been higher if a single crystal instead of a polycrystalline sample had been studied. The theoretical molecular curve for white P gives the correct order of magnitude for K, and is clearly different from the monatomic curve for black P. The predicted temperature variation is, however, not correct. If the theory had been more detailed, and had taken into account the phase transition[45] in white P at 196°K, and had included the apparent rotation[40,45] of the P_4 groups above 196°K, perhaps better agreement would have resulted. The important point is that the crude monatomic and molecular models do explain the large difference in K between the white and black allotropic forms of P and give semiquantitative estimates of the magnitude of K.

Boron

Now that the K of both monatomic and molecular crystals can be explained, at least partially, by simple models, an attempt can be made to explain the K of β-rhombohedral boron. Boron is a semiconductor. The β-rhombohedral form has a band gap[46] of about 1.6 eV and an electrical resistivity of greater than $10^3\ \Omega$ cm for the samples studied for all $T \leq 300$°K. The electronic contribution to the thermal conductivity can, therefore, be neglected, and all of the heat is transported by phonons. The crystal structure of boron is complex, and there are several allotropic forms. Hughes *et al.*[47] have worked out the crystal structure of the β-rhombohedral form, and found that it is a network of icosahedra of 12 atoms of B, and these icosahedra are linked together directly or through an occasional extra B atom. The α-rhombohedral form[48] and the tetragonal form[49] of B also consist mainly of icosahedral units of 12 B atoms linked together in slightly different ways. These icosahedra also occur in several boron compounds[50,51] such as B_4C and $K_2B_{12}H_{12}$. As can be seen in the pictures[48] of the structure of α-rhombohedral B, the 12 atoms in the icosahedral units are rather tightly bound together, and each icosahedron can be thought of as a large-mass-molecular-unit of B_{12}. Boron thus resembles phosphorus and sulfur in that its lattice is built up of molecular subunits. The P_4 and S_8 units have all of their bonding requirements satisfied with bonds inside the molecular units. Hence the intermolecular forces are of a Van der Waals nature. The single B_{12} units have unsatisfied bonds, so that in solid boron the various B_{12} units are joined to each other by covalent bonds. This strong bonding between molecular B_{12} units means that, in contrast to white phosphorus and sulfur, the lattice phonons and internal phonons may have comparable frequencies. Thus a distinct separation of the phonons into I and L modes as is done in Eq. (2) is probably no longer possible for β-rhombohedral boron or any of the other elemental forms of boron. Such a separation could probably be made in a solid such as $K_2B_{12}H_{12}$, where the B_{12} icosahedra are isolated[52] by the intervening K and H atoms which satisfy the bonding requirements of the B_{12} units. An indication of this effect of separation into I and L modes is given by the temperature variation of the low temperature heat capacity data[53] of $B_{10}H_{14}$, where the nearly complete icosahedra are separated by hydrogen atoms. Therefore, solid boron is neither a simple monatomic solid like Ge, Si, and black P, nor is it a molecular solid like white P or S. It lies somewhere in between.

The effective Debye temperature θ_E, as a function of T for β-rhombohedral B, has been computed from values of the specific heat at constant volume C_V derived from the constant-pressure (C_P) data in the literature.[54–56] The results are shown in Fig. 4 as the solid curve. Note the rather erratic behavior below 100°K. The θ_E at 0°K can be estimated, using Bridgman's compressibility data[57] and the density, for either the monatomic model or a molecular model with $N=12$. The average sound velocity calculated from the compressibility is 8×10^5 cm/sec. On the monatomic model, the result at 0°K is $\theta_E=1300$°K, and is given in the upper dashed curve in Fig. 4. The θ_E values have been defined by Eq. (1) and are the true θ values if the solid is monatomic. On the other hand, if boron is considered to be a molecular solid, then the θ_L at 0°K is $1300°\mathrm{K}/N^{1/3}$ or 570°K, and θ_E from Eq. (5) is 1030°K. This result is shown by the lower dashed curve. These two dashed curves show what C_V measurements would yield for θ_E if β boron were either a monatomic or a molecular solid. The actual data below 100°K are open to question.[54]

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New measurements of the heat capacity of a well-defined boron allotrope are needed to settle the problem. At present either model is as good as the other in fitting the θ-versus-T curve. Table I shows the two possible values of the Debye temperature for β-rhombohedral boron, i.e., $\theta = 1300$°K (monatomic) and $\theta_L = 570$°K (molecular).

The K-versus-T curves calculated for boron with a boundary-scattering mean free path equal to the crystallite size of 0.2 cm are shown in Fig. 5. Here both the monatomic and molecular models [see Eq. (9)] have been used. At 3°K both models are in reasonable agreement with the results in the boundary-scattering range. The two models both predict a higher maximum K than is observed at 40°K. Above 100°K the experimental results lie somewhere between the molecular and monatomic curves, as might have been anticipated from the discussion of the crystal structure. This complex crystal structure of boron gives it a K in the intrinsic phonon-phonon scattering range above 30°K which is quite low compared to its neighboring nonmetallic elements with high melting points and high Debye temperatures, i.e. diamond, silicon. It is also low compared to K values for light-mass, high-melting-point compounds such as BeO,[58] BN[59], and SiC[38], which have much simpler crystal structures.

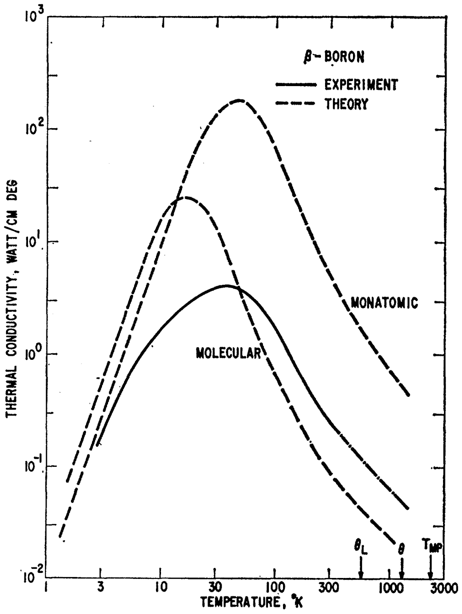

FIG. 5. The thermal conductivity of β-rhombohedral boron versus temperature. The dashed curves show the predicted behavior for boron treated as if it were either a simple molecular solid with a lattice Debye temperature $\theta_L = 570$°K or a simple monatomic solid with a Debye temperature $\theta = 1300$°K. The melting point is T_{mp}.

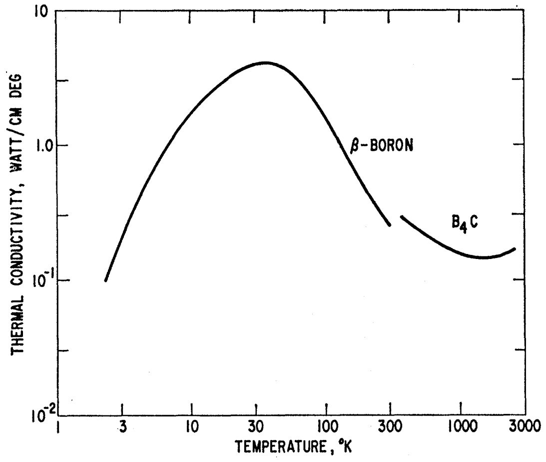

FIG. 6. The thermal conductivity of β-rhombohedral boron and of boron carbide as a function of temperature. The boron data are taken from Fig. 1.

Boron Compounds

Since the complex crystal structure of β-rhombohedral boron is believed to be the cause of its low K, then the other polymorphs of boron or those boron compounds that possess B_{12} units are also expected to have low thermal conductivities. None of the other boron polymorphs have yet been studied. There is some data on the K of B_4C which is really an interstitial compound[51] of α-rhombohedral boron, and which is built up of B_{12} and C_3 units. Figure 6 shows the K-versus-T curve based on results for several polycrystalline, ceramic samples of boron carbide which were close to the theoretical density.[60,61] Its K is also low and comparable to that of β-rhombohedral boron. The other parameters of B_4C such as melting point (2720°K), average atomic mass, density (2.52 g/cm^3), and its Debye temperature[62,63] ($\theta_E = 1300$°K) are also comparable to those of β-rhombohedral boron. The conclusion is that the low K of B_4C is also caused by its complex crystal structure. The occurrence of low K values coupled with high melting points and good high-temperature stability suggests that boron, boron carbide, and some other boron compounds may be useful for thermoelectric applications[64] at temperatures above 1000°C.

CONCLUSIONS

The thermal conductivities of orthorhombic sulfur, orthorhombic (black) P, and β-rhombohedral boron

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have been measured over the temperature range from 3 to 300°K. Phonons are the dominant carriers of the thermal energy. It is suggested that the thermal conduction in the molecular solids such as orthorhombic sulfur and cubic (white) phosphorus is caused by lattice phonons only; the phonons associated with the internal vibrations of the S_8 or P_4 units do not contribute to the conduction because their propagation velocities are zero. Since only a fraction of the phonons can carry heat and since their mean free path in the solid at the melting point is only about one molecular diameter, the molecular solids have thermal conductivities much lower than those of monatomic solids of similar average atomic mass. In monatomic solids such as orthorhombic (black) phosphorus there are no molecular groups. Thus all of the phonons contribute to the heat transport, their mean free paths at the melting point are of the order of twenty interatomic distances, and the thermal conductivities of such solids are high.

The β-rhombohedral form of boron has a crystal structure somewhere between the molecular and monatomic types. Its measured thermal conductivity has a value intermediate between the limits predicted by the molecular and monatomic models. Because of the similarity in the crystal structures of the several polymorphs of boron, it is believed that the other polymorphs as well as many of the interstitial compounds of boron will also have low thermal conductivities quite close to that of the β-rhombohedral form.

ACKNOWLEDGMENTS

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Nuclear Resonance of Solids Doped with Paramagnetic Impurities*

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This paper is an extension of the work of Rorschach on the interactions of dipolar nuclei with paramagnetic impurities in dielectric crystals. The influence of the average "static" moment on the nuclear resonance linewidth is considered. It is suggested that by measuring T_1 and the nuclear resonance linewidth as a function of temperature, magnetic field intensity, and sample orientation it is possible to determine the autocorrelation time of paramagnetic ions as a function of these parameters.

INTRODUCTION

Since Bloembergen[1] showed that nuclear spins could be relaxed in an insulating crystal by small amounts of paramagnetic impurities, several publications have appeared indicating information could be obtained concerning paramagnetic ions using nuclear magnetic resonance. Most of the attention has been given to the effect of impurities on the spin-lattice relaxation time T_1 of the nuclei. However, Verber, Mahon, and Tantilla[2] have demonstrated that paramagnetic ions also broaden the nuclear resonance at low temperatures. By utilizing the results obtained from both T_1 and linewidth measurements it is possible to eliminate most of the uncertainties of the theory, and thereby get more reliable information concerning the paramagnetic ions and their behavior in the crystal. In the theory section an expression is derived for the effect of paramagnetic ions on the nuclear-resonance linewidth based on Van Vleck's[3] method and Rorschach's[4] treatment of the motion of the paramagnetic moment. This calculation gives rise to an expression for the second moment containing the autocorrelation time of the paramagnetic ion, the ion concentration, and the average of the square and the square of the average of the z component of the magnetic moment for the paramagnetic ion. Also a discussion is given for T_1 based on Rorschach's paper.

THEORY

Linewidth

The nuclear-resonance linewidth of a system of nuclear spins can be calculated using Van Vleck's moment theory, and is in excellent agreement with experiment. If electron paramagnetic impurities are

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