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High-Temperature Thermal Conductivity of Insulating Crystals: Relationship to the Melting Point

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The Lindemann melting rule is used to eliminate the elastic constant from the thermal conductivity formula proposed by Lawson. The thermal conductivity is thus obtained as a function of density, atomic weight, and melting temperature. The introduction of a dependence on bond character allows a major fraction of the available high-temperature thermal conductivity data to be reproduced within a factor of two. A dependence of thermal conductivity on mass ratio of the type found theoretically by Blackman for diatomic crystals is observed.

I. INTRODUCTION

IN insulators, in which the thermal current is carried by phonons, the thermal conductivity, λ, is given by the formula[1] $\lambda=\frac{1}{3}Cvl$, where C is the specific heat per unit volume, v is an average velocity of sound, and l is an average phonon mean free path. At high temperatures in sufficiently pure and perfect crystals l is determined by phonon-phonon scattering. At temperatures high enough so that the lattice oscillators are classically excited, C has the Dulong and Petit value and l is proportional to the reciprocal of the temperature. The thermal conductivity under these last circumstances is referred to as the high-temperature thermal conductivity.

Various expressions which relate l or λ in the high-temperature range to other mechanical properties (e.g., thermal expansion coefficient, Debye temperature) of the crystal have been proposed.[2–6] Unfortunately all of these expressions involve properties which are known only for rather intensively investigated crystals.

For practically all materials which are intentionally prepared the density, atomic weights, and melting temperature are known. However, certain rules of a semiempirical nature connect the melting temperature with other physical properties of a crystal.[7,8] In this note such rules will be used to eliminate the less readily available parameters from the thermal conductivity formulas and to replace them with T_m, the melting temperature. The resulting expression will be compared with experimental data given in the literature.

A correlation of lattice thermal conductivity with melting temperature has been suggested previously: Eucken[9] concluded on empirical grounds that many substances have the same thermal conductivity at the melting point. Such a rule appears to work fairly well for substances with low melting points, but is not valid for crystals melting above about 500°K.

II. DERIVATION OF THE FORMULA FOR λT

It has been shown by Lawson[5] and by White and Woods[10] that the various thermal conductivity formulas are essentially equivalent in the high-temperature region. The form proposed by Lawson[5] is most convenient for the present purpose. It is

$$\lambda=a/3\gamma^2T\chi^{3/2}\rho^{1/2}, \tag{1}$$

where a is the interatomic distance, γ is the Grüneisen constant, χ is the compressibility, and ρ is the density. The dependence of all of these quantities on the temperature is very weak, and λT is constant to a good approximation at high temperatures.

The Lindemann melting rule[7] can be used to eliminate χ from (1). The Lindemann rule is based on the assumption that melting takes place when the amplitude of thermal vibration of the atoms reaches some fixed fraction, ϵ, which is the same for all materials, of the interatomic distance. It can be put into the form

$$\chi=\epsilon^2V/RT_m, \tag{2}$$

where V is the volume per gram atom. Substituting (2) into (1) and setting $a=(V/N_0)^{1/3}$ and $V=A/\rho$, where A is the mean atomic weight and N_0 is Avogadro's number, gives

$$\lambda T=[R^{3/2}/3\gamma^2\epsilon^3N_0^{1/3}]T_m^{3/2}\rho^{2/3}/A^{7/6} \tag{3}$$

$$=B\Omega, \tag{4}$$

where B represents the bracketed factor in (3) and $\Omega\equiv T_m^{3/2}\rho^{2/3}/A^{7/6}$. Now most of the variations of physical properties among different materials has been combined into the second factor of Eq. (3), and it might be hoped that Eq. (4) with B regarded as constant would be a useful formula for the approximate

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[1] P. Debye, *Vorträge über die Kinetische Theorie* (B. G. Teubner, Leipzig, 1914).

[2] A. Akhieser, J. Phys. U.S.S.R. **1**, 277 (1939).

[3] G. Leibfried and E. Schlömann, Nachr. Akad. Wiss. Göttingen, Math-physik Kl **IIa**, 7 (1954).

[4] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **98**, 1751 (1955).

[5] A. W. Lawson, J. Phys. Chem. Solids **3**, 154 (1957).

[6] T. A. Kontorova, J. Tech. Phys. U.S.S.R. **26**, 2021 (1956) [translation: Soviet Phys. (Tech. Phys.) **1**, 1959 (1957)].

[7] F. A. Lindemann, Physik Z. **11**, 609 (1910).

[8] D. van der Reyden, J. Appl. Phys. **22**, 363 (1951); M. E. Straumanis, J. Appl. Phys. **21**, 936 (1950); F. Zwikker, *Physical Properties of Solid Materials* (Interscience Publishers, Inc., New York, 1954).

[9] A. Eucken, Ann. Physik **34**, 35, 185 (1911).

[10] G. K. White and S. B. Woods, Phil. Mag. **3**, 785 (1958).

prediction of lattice thermal conductivities. In the subsequent text the evaluation of this idea will be undertaken, and references to Eq. (4) should be understood to mean Eq. (4) with B regarded as a constant.

III. EVALUATION OF THE FORMULA

For the purpose of evaluating Eq. (4), values of λT and of $T_m^{3/2}\rho^{2/3}/A^{7/6}$ are tabulated in Table I. An attempt has been made to include in Table I all of the available thermal conductivity data for which a temperature range has been observed in which λ varies, at least approximately, as T^{-1} and in which it appears that material of reasonably high structural perfection has been used. In some of these cases the measurements have been made at temperatures considerably less than the Debye temperature, and the assumption of classical excitation of the "optical" modes of vibration does not seem plausible, in spite of the T^{-1} dependence. However, the de-excitation of the optical modes will probably not make a difference of a factor greater than two in the thermal conductivity, and it will be seen that such a factor does not have an important effect on the considerations to be presented.

The data of Table I has been used to construct Fig. 1. It is seen that Eq. (4) with B regarded as constant is capable of defining the thermal conductivity to within about one order of magnitude. Since the independent variable in (4) varies over four orders of magnitude, some significance can be attached to Eq. (4).

In calculating Ω for crystals containing a molecular unit, e.g., (CO_3), (C_6H_6), the parameter A was taken to be the molecular mass. This amounts to ignoring the internal degrees of freedom of the molecule. The

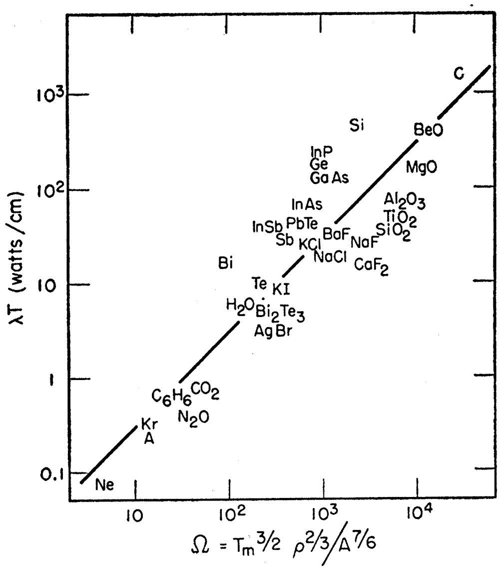

FIG. 1. The high-temperature thermal conductivity data of Table I plotted in the form suggested by Eq. (4). In the abscissa, T_m is expressed in Kelvin degrees, ρ in g/cm³, and A in grams per mole. A is the average atomic weight. The line indicates proportionality between λT and Ω.

TABLE I. A collection of high-temperature thermal conductivity data, taken from temperature ranges in which λ is approximately proportional to T^{-1}.

Material	λT (watts/cm)	Ω (cgs units)	Bonding[a]	Mass ratio
C (diamond)	1700[b]	31000	cv	
Si	440[c]	2500	cv	
Ge	180[c]	1000	cv	
Sb	28[d]	370	cv	
Bi	16[d, e]	110	cv	
Te	10[f]	230	cv	
Se	5[g]	190	cv	
Kr	0.27[h]	14.7	vW	
A	0.25[h]	14.4	vW	
Ne	0.075[h]	5.2	vW	
BeO	400[i]	14000	cv	1.78
MgO	160[j]	11900	i	1.52
Al_2O_3	75[j]	8100	i	1.69
InP	210[k]	930	cv	3.7
GaAs	150[l]	1200	cv	1.07
InAs	65[l, m]	650	cv	1.53
InSb	40[m, n]	280	cv	1.06
PbTe	40[o]	430	cv[p]	1.62
SiO_2	35[q]	4050	cv	1.75
TiO_2	35[j]	6000	i	3.0
BaF_2	33[q]	1500	i	7.2
KCl	40[r]	730	i	1.10
NaF	28[q]	2500	i	1.21
Mg_2S_n	23[s]	730	cv	4.9
NaCl	19[q]	1140	i	1.54
CaF_2	15[j]	3160	i	2.11
$Ca(CO_3)$	12[t]	1240[u]	i	1.50[u]
KT	8.4[q]	390	i	3.2
(H_2O)	6[v]	150[w]	vW	
Bi_2Te_3	5[x]	260	cv	1.63
AgBr	2.8[y]	320	i	1.35
(CO_2)	0.8[z]	50[w]	vW	
(C_6H_6)	0.7[z; aa]	28[w]	vW	
(N_2O)	0.4[aa]	36[w]	vW	

[a] cv: covalent; i: ionic; vW: van der Waals or molecular bonding. The classification according to bonding type is based on structural considerations as described by F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), Chap. I; and A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1945).

[b] Berman, Simon, and Ziman, Proc. Roy. Soc. (London) **A220**, 171 (1953).

[c] Carruthers, Geballe, Rosenberg, and Ziman, Proc. Roy. Soc. (London) **A238**, 502 (1957); G. K. White and S. B. Woods, Phys. Rev. **103**, 569 (1956).

[d] G. K. White and S. B. Woods, *Low-Temperature Physics and Chemistry* (University of Wisconsin, Madison, 1958), p. 362.

[e] G. K. White and S. B. Woods, Can. J. Phys. **33**, 58 (1955).

[f] Fischer, White, and Woods, Phys. Rev. **106**, 480 (1957).

[g] White, Woods, and Elford, Phys. Rev. **112**, 111 (1958).

[h] G. K. White and S. B. Woods, Phil. Mag. **3**, 785 (1958).

[i] D. A. Ditmars and D. C. Ginnings, J. Research Natl. Bur. Standards **59**, 93 (1957).

[j] F. R. Charvat and W. D. Kingery, J. Am. Ceram. Soc. **40**, 306 (1957).

[k] H. Weiss, Vortrag auf der Physikertagung in Essen, October 3–7, 1958 (unpublished).

[l] E. D. Wilson (private communication).

[m] Bowers, Ure, Bauerle, and Cornish (to be published).

[n] A. Stuckes, Phys. Rev. **107**, 427 (1957).

[o] A. F. Joffe, *Semiconductor Thermoelements and Thermoelectric Cooling* (Infosearch, London, 1957), p. 66.

[p] Although substances crystallizing in the NaCl structure are generally to be regarded as ionic, the high electrical conductivity of PbTe indicates that this is not the case here.

[q] Data from *American Institute of Physics Handbook* (McGraw-Hill Book Company, New York, 1957).

[r] R. Berman and E. Foster, Proc. Roy. Soc. (London) **A237**, 344 (1956).

[s] G. Busch and M. Schneider, Physica **20**, 1084 (1954).

[t] A. Eucken, Ann. Physik **34**, 185 (1911).

[u] Calculated regarding (CO_3) as an atomic entity.

[v] M. Jakob and S. Erk, Z. ges. Kälte-Ind **35**, 125 (1928); **36**, 229 (1929). R. Powell, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1958), Vol. **7**, p. 276.

[w] Calculated using the weight of the molecule for A.

[x] C. B. Satterthwaite and R. W. Ure, Phys. Rev. **108**, 1164 (1957); H. J. Goldsmid, Proc. Phys. Soc. (London) **B69**, 203 (1956).

[y] T. E. Pochapsky, J. Chem. Phys. **21**, 1539 (1953).

[z] A. Eucken, *Lehrbuch der chemischen Physik* (Akademische Verlagsgesellschaft, Leipzig, 1949), p. 753.

[aa] A. Eucken and E. Schroeder, Ann. Physik **36**, 609 (1939).

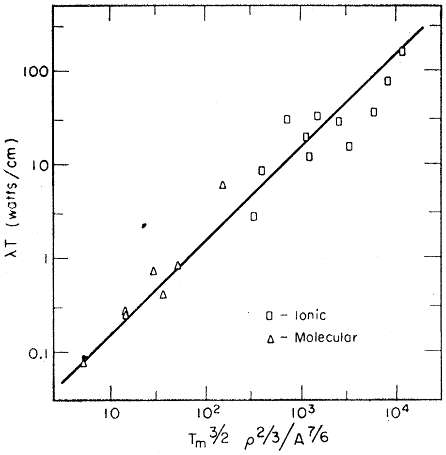

FIG. 2. The high-temperature thermal conductivity data plotted in a form similar to that of Fig. 1 for the ionic and van der Waals crystals.

justification for this is mainly empirical: the use of the molecular mass fits the molecular crystals into the present scheme in the most satisfactory way. However, it is also true that in a case for which a contribution to the thermal conductivity from internal degrees of freedom has definitely been observed, the temperature dependence of λ is not T^{-1}, but is more nearly $\lambda=$ constant.[11]

There are some general features of Fig. 1 which are worth noting: (1) Eq. (4) holds quite accurately for some sets of very similar substances, namely: neon, argon, krypton, and silicon, germanium, GaAs, InSb, InAs; (2) the covalently bonded solids tend to lie above the ionic and van der Waals solids for a given value of Ω; (3) the elements tend to have higher values of λT than compounds with the same value of Ω; (4) in the units of Table I, $B=0.03$, which is about the order of magnitude to be expected from Eq. (3).

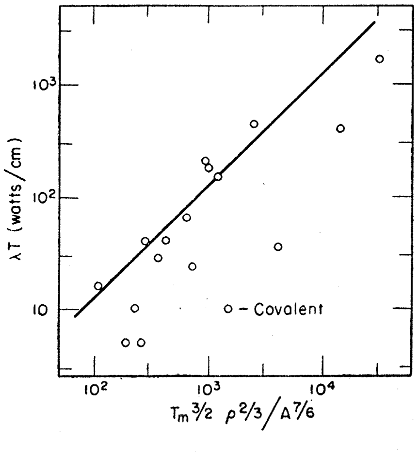

FIG. 3. The high-temperature thermal conductivity data plotted in a form similar to that of Fig. 1 for the covalent crystals.

The suggestion provided by observation (2) is examined in Figs. 2 and 3, in which the points derived from the covalent and the ionic and van der Waals solids are plotted separately. The division of the solids into types is as in Table I. The lines of Figs. 2 and 3 constitute a good representation of the data; two thirds of the points fall within a factor of two of the line to which they are assigned by the structural criterion. Many of the large deviations are cases in which a real question could be raised about the bonding classification, e.g., Se and Te, in which the bonding between chains is certainly not covalent. The value of B for the covalent line is 0.13, for the ionic–van der Waals line it is 0.015.

IV. THE MASS RATIO EFFECT

Observation (3) of the preceding section is a result first appreciated by Eucken and Kuhn,[12] who noted that in the alkali halides the thermal conductivity tends to be highest for those crystals in which the anion and cation masses are most nearly the same. The theoretical explanation of the effect was given by Blackman.[13] Blackman considered the case of a linear chain of atoms. If all of the atoms of the chain are identical there is no thermal resistance in the linear case, as shown by Peierls.[14] The reason is that the conservation laws for energy and for crystal momentum have only trivial simultaneous solutions for the linear chain. Blackman showed, however, that if the lattice is diatomic the additional dispersion introduced by the splitting of the vibrational spectrum into two branches allows nontrivial solutions to be found. Thus the diatomic linear chain has a nonvanishing thermal resistance, which depends on the mass ratio of the atoms, increasing as the ratio is increased from one.

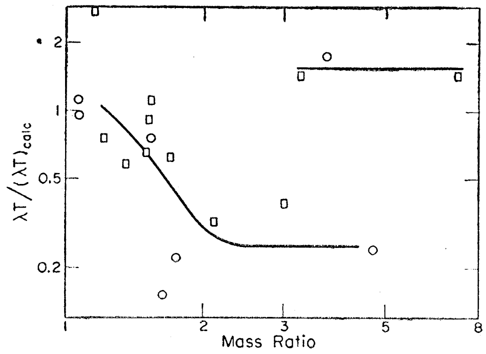

FIG. 4. The deviations of the points from the lines of Figs. 2 and 3, $\lambda T/(\lambda T)_{calc}$, plotted against the ratio (heavy atomic weight/light atomic weight) for the diatomic crystals.

In addition, however, Blackman showed that this thermal resistance persists only up to mass ratios of

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[11] A. Eucken and E. Schroeder, Ann. Physik **36**, 609 (1939).

[12] A. Eucken and E. Kuhn, Z. physik Chem. (Frankfurt) **134**, 193 (1928).

[13] M. Blackman, Phil. Mag. **19**, 989 (1935).

[14] R. Peierls, Ann. Physik **3**, 1055 (1929).

about three. If the mass ratio becomes larger than three, the separation of the acoustical and optical branches of the vibrational spectrum becomes so great that interactions involving phonons in both branches become impossible. Since these are the interactions which produce the thermal resistance, the resistance then vanishes.

Although Blackman's calculations applied only to the linear chain, he believed that a similar effect should appear in the three-dimensional case, superimposed on the ordinary three-dimensional resistance.[14]

In order to see the relationship of Blackman's result to the present analysis of thermal conductivity data, it will be assumed in this section that the procedure of the preceding section has been successful in normalizing out of the thermal conductivity most of the variation from material to material which is due to variation of the average mass, the interatomic forces, and the crystal structure. The remaining variation can be studied by calculating the ratio of the measured λT to that predicted by the straight lines of Figs. 2 and 3, hereafter denoted by $(\lambda T)_{\mathrm{calc}}$.

An attempt is made in Fig. 4 to attribute this remaining variation to the mass ratio effect. In Fig. 4 values of $\lambda T/(\lambda T)_{\mathrm{calc}}$ are plotted against the ratio (heavy atomic weight/light atomic weight), column five of Table I, for the diatomic crystals. Although the points for high mass ratios are rather sparse, the trend can be recognized. For mass ratios from one to three, the ratio $\lambda T/(\lambda T)_{\mathrm{calc}}$ decreases with increasing mass ratio. However, at a mass ratio of about three there is a discontinuity at which the value of $\lambda T/(\lambda T)_{\mathrm{calc}}$ increases to the value which characterizes the compounds with mass ratio near unity. The disappearance of the Blackman-type scattering does not take place sharply at mass ratio three, but this is not surprising in view of the simplicity of Blackman's model.

V. DISCUSSION

The value of the present correlation, as compared to previous ones dealing with the same subject, is that it associates the thermal conductivity with more easily measurable, and hence more frequently available, parameters. The calculation of the abscissa in Fig. 1 requires only a knowledge of chemical formula, density, and melting temperature. The use of the plots of Figs. 2 and 3 requires, in addition some understanding of the crystal structure.

In some cases, notably that of silicon and germanium, Eq. (4) predicts the relationship of the thermal conductivities of the solids in question with greater accuracy than the Lindemann rule gives the relationship of their melting temperatures. The derivation of Eq. (4) given in Sec. II should therefore be regarded as suggestive rather than quantitative. In this connection it should be pointed out that a result similar to Eq. (4) can be obtained using the semiempirical relationships in different ways; for example, one might substitute the relationship of Zwikker,[8] $\alpha T_m=\text{constant}$, into the Dugdale and MacDonald[4] formula for l, $l=a/\alpha\gamma T$, where α is the thermal expansion coefficient.

The physical essence of the Eqs. (3) and (4) is that the melting temperature is used as a measure of the force constant of the crystals and it is assumed that the anharmonicity (in a dimensionless sense) is the same for all materials. Reasons why the covalent crystals do not fall into the pattern of the ionic and van der Waals crystals are not hard to find. Firstly, the Grüneisen number is generally smaller for covalent materials than for other types, being only one or less for the former. Secondly, the melting phenomenon is different for the covalent materials, in that they usually melt with a contraction in volume to form a metallic liquid, whereas there is little change in structure or bonding involved in the melting of the other crystals.

In all of the preceding discussion the anisotropy of the thermal conductivity of the noncubic substances has been ignored. This is principally because the simple semiempirical ideas used provided no way of taking the anisotropy into account. No improvement in the final correlation is to be expected from an inclusion of the effects of anisotropy, however, as, for most of the anisotropic substances of Table I the anisotropy of the thermal conductivity is not known, and in the remaining cases the anisotropy is usually less than a factor of two.[15]

A final point worthy of attention is the validity of the frequently used assumption that thermal conductivity is a decreasing function of atomic weight. Although A appears in the denominator of Eq. (3), and the statement appears to represent a trend in the covalently bonded solids, it is by no means universally true. The outstanding example here is found among the noble gases, where neon has the lowest atomic weight and the lowest thermal conductivity. The highest and lowest values of λT are represented by diamond and neon, respectively, the two elements of lowest atomic weight which are included.

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[15] W. A. Wooster, Z. Krist. **95**, 138 (1936).