A PHYSICAL STUDY OF THE THERMAL CONDUCTIVITY OF SOLIDS.

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SINCE the physical interpretation of the variation of the specific heat of solids with temperature has been found to be of considerable theoretical importance, it is to be expected that a study of the physical nature of the thermal conductivity of solids may also bring interesting results. The present paper may be considered as a start at such a study.

In order not to be disturbed by thermal conduction due to electrons, we shall consider only non-metallic substances. For the sake of further simplicity we shall consider in the first place the conduction of heat through a crystal, in which the atoms are closely packed. Consider two infinite, parallel planes in such a medium, at a distance x apart, and maintained at a constant difference of temperature, $T_1 - T_0$. Let δx be the average distance in the x direction through which the energy of an atomic collision is transmitted. The temperature drop along this distance δx will evidently be

$$\delta T = \frac{\delta x}{x}(T_1 - T_0).$$

This quantity represents the average difference in temperature between the atom which gives out energy at each collision, and the atom or atoms which absorb it. According to ordinary kinetic theory, if the collisions of the atoms are elastic, the average amount of energy transmitted at each collision may be shown to be

$$\delta\epsilon = \frac{4m_1m_2}{(m_1 + m_2)^2} R\delta T,$$

where m_1 and m_2 are the masses of the atoms in collision, and R is the gas constant for a single molecule. This may be written

$$\delta\epsilon = bR\delta T,$$

where b is in most cases approximately equal to 1.

In the kind of a medium we are considering, the number of atomic collisions in unit time on unit area of the surface of a plane separating

adjacent layers of atoms will be equal to the number of atoms per unit area multiplied by the frequency of oscillation of each atom. That is,

$$\eta = n^2\nu,$$

where ν is probably equal to the natural frequency of the atoms as determined by optical methods, and n^2 is the number of atoms per unit area of the plane. n^2 will be equal to the $2/3$ power of the number of atoms in unit volume in the case of cubic crystals, but not necessarily for other kinds. The rate of transfer of energy per unit area across a plane perpendicular to the x axis will therefore be

$$\frac{dE}{dT} = \eta \cdot \delta\epsilon = n^2\nu \cdot bR \cdot \frac{\delta x}{x}(T_1 - T_0);$$

and since there can be no piling up of energy at any point of the substance this is also the rate of transfer of energy from one boundary plane to the other. But by definition,

$$\frac{dE}{dT} = k\frac{T_1 - T_0}{x},$$

where k is the coefficient of thermal conductivity, so that

$$k = bn^2R\nu\delta x,$$

or

$$\delta x = k/bn^2R\nu.$$

According to the experiments of Eucken,[1] the thermal conductivity of crystals is approximately inversely proportional to the temperature. If we call the factor of proportionality, c,

$$k = c/T,$$

and the distance through which the energy of an atomic collision is transmitted is

$$\delta x = c/T \cdot \frac{1}{bn^2R\nu}. \tag{1}$$

That is, as the temperature falls, and the atoms become more and more closely packed, the distance through which the effect of an atomic collision is transmitted increases, as appears plausible.

Thus we have the distance δx for a crystal expressed in terms of known quantities. For rock-salt at 0° C. these quantities are:

$$c/T = 1.36 \times 10^6 \text{ erg cm.}^{-1} \text{ sec.}^{-1} \text{ deg.}^{-1},$$
$$b = 0.955,$$
$$n = 3.58 \times 10^7 \text{ cm.}^{-1},$$
$$\nu = 5.8 \times 10^{12} \text{ sec.}^{-1},$$
$$R = 1.35 \times 10^{-16} \text{ erg deg.}^{-1};$$

[1] A. Eucken, Ann. d. Physik, 34, 185 (1911).

and thus

$$\delta x = 1.42 \times 10^{-6} \text{ cm.}$$

But the distance between two neighboring atoms in rock-salt is $d = 2.80 \times 10^{-8}$ cm., or $\delta x = 51d$. The value of δx for other crystals is of the same order of magnitude. We find, therefore, that the energy of a collision between two atoms in a crystal is transmitted through a distance which is approximately inversely proportional to the temperature, and many times the distance between two neighboring atoms.

If it should happen that the crystals of which a substance is composed are of smaller dimensions than the average distance through which the effect of a thermal disturbance is transmitted, a decrease in temperature will no longer mean a decrease in the δx of equation (1), since this distance will evidently be limited by the size of the component crystals. On the other hand, it is probable that the frequency of the collisions between the atoms of neighboring crystals will diminish as the amplitude of the vibrations becomes less, since the atoms will not be closely packed at the juncture of the crystals. This would result in a decrease in the conductivity with temperature, such as is actually observed in the case of all amorphous substances.

That something of this kind actually occurs in amorphous substances becomes evident when we consider a definite example. In the case of fused quartz at $-190°$ C., for instance,

$$k = 6.61 \times 10^{4} \text{ erg cm.}^{-1} \text{ sec.}^{-1} \text{ deg.}^{-1},$$

$$b = .95$$

$$\nu^{6} = 1.82 \times 10^{13} \text{ sec.}^{-1} \text{ (mean value)},$$

$$n = 4.1 \times 10^{7} \text{ cm.}^{-1},$$

and if we calculate δx according to equation (1) we obtain

$$\delta x = 1.7 \times 10^{-8} \text{ cm.} = 0.7d.$$

Thus if a collision occurred at each oscillation of an atom, we should have to conclude that the effect of the collision was transmitted through less than the distance between two atoms, which would be meaningless. It is evident, therefore, that some of the atoms in an amorphous substance must oscillate without affecting appreciably the atoms next to them, as suggested above.

The physical interpretation of this result, that the effect of each atomic collision in a crystal is felt at a considerable distance, is an interesting problem. According to the agglomeration theory of the variation of the specific heat of solids with temperature,[1] at low temperatures the

[1] C. Benedicks, Ann. d. Physik, 42, 133 (1913); A. H. Compton, PHYS. REV., 6, 377 (1915).

atoms of solids lose degrees of freedom in a manner very similar to that in which a degree of freedom is lost when two atoms combine chemically. It is evident that if large groups of atoms should thus be formed which would vibrate as units, the thermal conductivity would be greatly increased. Benedicks[1] has accordingly considered the sharp increase in the heat conductivity of crystals at low temperatures to be an indication of the formation of such groups, and hence as a support of the agglomeration hypothesis. If these atomic aggregations vibrate independently, the distance through which the effect of a collision will be transmitted will be equal to their average diameter. As we have seen above, for rock-salt at 0° C. this distance is some 50 times the distance between two neighboring atoms; but the probability that a degree of freedom shall be agglomerated is in this case only 1/3. Thus it is seen that the size of the groups formed by a possible agglomeration of the atoms is not of the proper order of magnitude to account for the thermal conductivity of crystals.

A more probable interpretation would seem to be that each atom transmits the greater part of the energy of every thermal disturbance which reaches it, retaining or scattering the remaining part, the atoms thus acting as if imperfectly elastic. If we assume that the energy of each collision is transferred from atom to atom, being diminished by a definite factor as it traverses each atom, it can be shown by reasoning similar to that above that the thermal conductivity of a crystal in which adjacent atoms are arranged in lines parallel to the axis of conduction is

$$k = bn^2dR\nu \cdot \frac{2-\alpha}{\alpha^2}; \tag{2}$$

where d is the distance between successive atoms in the direction of conduction, and α is the fraction of the energy absorbed by each atom as the thermal disturbance traverses it. This absorbed energy is given out again at the next collision of the atom. For other kinds of crystals the function of α is somewhat different, but is in any case approximately proportional to $1/\alpha^2$ as long as α is small. For rock-salt at 0° C.

$$\alpha = 0.202.$$

According to this explanation the energy of an atomic collision is not transmitted through a definite distance, but dies out gradually as it passes through a substance. The *mean* range, however, must be the same as the δx which we have used above.

If we assume that the fraction of the energy of each thermal disturbance which an atom retains is proportional to its amplitude of vibration, and

hence, according to ordinary kinetic theory, to the square root of the temperature, *i. e.*,

$$\alpha = c\sqrt{T},$$

we have,

$$k = bn^2dR\nu \cdot \frac{2 - cT^{\frac{1}{2}}}{c^2T}, \tag{3}$$

where c is determined by the conductivity at a given temperature. The following tables show how this expression compares with Eucken's experimental data. The first calculated values are found according to the expression

$$k = c/T,$$

and the second according to equation (3). The value of α at 273° K. is calculated according to equation (2), using the value of d determined by X-ray measurements,[1] and ν for quartz in the mean value, 1.82×10^{13}, determined from specific heat data.[2] k is expressed in calories cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$.

TABLE I.

T.	NaCl; $\alpha_{273} = 0.202$.			KCl; $\alpha_{273} = 0.175$.		
	k (Calc.$_1$).	k Obs.).	k (Calc.$_2$).	k (Calc.$_1$).	k (Obs.).	k (Calc.$_2$)
373°	0.0122	0.0116	0.0119	0.0121	0.0118	0.0118
273	0.0167	0.0167	0.0167	0.0166	0.0166	0.0166
195	0.0233	0.0249	0.0238	0.0232	0.0248	0.0237
83	0.0548	0.0636	0.0577	0.0545	0.0502	0.0567
22	———	———	———	0.206	0.125	0.215
	$SiO_2 \parallel$; $\alpha_{273} = 0.200$[3].			$SiO_2 \perp$; $\alpha_{273} = 0.309$[3].		
373	0.0236	0.0215?	0.0230	0.0127	0.0133	0.0123
273	0.0325	0.0325	0.0325	0.0173	0.0173	0.0173
195	0.0455	0.0467	0.0465	0.0242	0.0241	0.0250
83	0.1067	0.1170	0.1124	0.0569	0.0586	0.0620
22	———	———	———	0.214	0.58	0.234

The data are not sufficiently consistent to fit any formula accurately, but it is apparent that equation (3) fits the data in general somewhat more closely than does the strictly linear law except for quartz $\perp$, in which case equation (3) does not strictly apply.[3]

[1] Cf. W. H. Bragg and W. L. Bragg, "X-rays and Crystal Structure," pp. 88 and 160.

[2] The data used are those of Nernst (Ann. d. Physik, 36, 395) and F. Koref (Ann. d. Physik, 36, 64). ν is calculated according to the formula $\nu = \tau/\beta$, where β is a universal constant and τ is determined by the specific heat at a given temperature. Cf. A. H. Compton, loc. cit.

[3] According to the structure of quartz as found by Professor Bragg, the arrangement of the atoms parallel to the axis is probably not greatly different from a linear distribution; but perpendicular to the axis the arrangement is more irregular. Thus while the function of β for quartz $\parallel$ is probably nearly that given in equation (2), for quartz $\perp$ this function may be different. The value of n^2 which should be used in this case is also doubtful, which could account for the large value of α for quartz $\perp$.

We have so far been considering the average energy of a degree of freedom in a solid to be RT, instead of the somewhat different value which is found by a study of the specific heat. If we use instead the energy assigned by the quantum hypothesis,

$$h\nu\left\{\frac{1}{e^{\frac{h\nu}{RT}}-1}+\frac{1}{2}\right\},$$

two changes must be made. In the first place, the average amount of energy given out by an atom at each collision is no longer

$$\delta\epsilon = bR\delta T,$$

but is

$$\delta\epsilon = b\frac{\partial}{\partial T}\left\{h\nu\left(\frac{1}{e^{\frac{h\nu}{RT}}-1}+\frac{1}{2}\right)\right\}\delta T$$

$$= \frac{bh^2\nu^2}{RT^2}\frac{e^{\frac{h\nu}{RT}}\delta T}{\left(e^{\frac{h\nu}{RT}}-1\right)^2}.$$

In the second place, if α is proportional to the amplitude of vibration, or the square root of the energy, *i. e.*,

$$\alpha = c\left\{\frac{1}{e^{\frac{h\nu}{RT}}-1}+\frac{1}{2}\right\}^{\frac{1}{2}},$$

the expression for the thermal conductivity corresponding to equation (3) is

$$(4)\qquad k = bn^2dv\cdot\frac{h^2\nu^2}{RT^2}\frac{e^{\frac{h\nu}{RT}}}{\left(e^{\frac{h\nu}{RT}}-1\right)^2}\cdot\frac{2-c\left\{\frac{1}{e^{\frac{h\nu}{RT}}-1}+\frac{1}{2}\right\}^{\frac{1}{2}}}{c^2\left\{\frac{1}{e^{\frac{h\nu}{RT}}+1}+\frac{1}{2}\right\}}.$$

This expression makes the thermal conductivity approach zero at very low temperatures, giving values much smaller than are actually observed. This is shown clearly in the following table, for the cases of rock-salt and sylvine (calc.$_3$).

TABLE II.

T.	NaCl; $\alpha_{273}=0.202$.			KCl $\alpha_{273}=0.175$.		
	k (Calc.$_3$).	k (Obs.).	k (Calc.$_4$).	k (Calc.$_3$).	k (Obs.).	k (Calc.$_4$).
373°	0.0124	0.0116	0.0118	0.0127	0.0118	0.0117
273	0.0167	0.0167	0.0167	0.0166	0.0166	0.0166
195	0.0214	0.0249	0.0240	0.0223	0.0248	0.0240
83	0.0263	0.0636	0.0590	0.0323	0.0502	0.0577
22	———	———	———	0.0015	0.125	0.217

In order to obtain a satisfactory expression for the thermal conductivity, if the energy of a degree of freedom is that assigned by the quantum hypothesis, it is necessary to assume that α is at least approximately proportional to the expression

$$\left\{\frac{h^2\nu^2}{RT}\cdot\frac{e^{\frac{h\nu}{RT}}}{\left(e^{\frac{h\nu}{RT}}-1\right)^2}\right\}^{\frac{1}{2}},$$

which is the square root of the product of the heat capacity of a degree of freedom according to Einstein's formula by the absolute temperature. It is hard to conceive of any possible direct connection between this quantity and the amount of "inelasticity" α of an atom. It seems difficult, therefore, to obtain on the basis of the quantum hypothesis a justifiable formula for the heat conductivity.

The case is different, however, if use is made of the agglomeration hypothesis. According to this hypothesis, the number of existing degrees of freedom is less than the greatest possible number by the factor $e^{-\frac{\beta\nu}{T}}$, where β is a universal constant; but the degrees of freedom which actually exist have the amount of energy assigned by equipartition, that is RT. This being the case, the energy given out at each collision is, as originally,

$$\delta\epsilon = bR\delta T;$$

but the number of collisions is diminished, since the number of existing degrees of freedom is reduced, in such a manner that

$$\eta = n^2\nu e^{-\frac{\beta\nu}{T}}.$$

The average energy of each *atom* is, however, $3RTe^{-\frac{\beta\nu}{T}}$, and if as before we consider the fraction of the passing energy which each atom absorbs to be proportional to its amplitude of vibration, we have

$$\alpha = cT^{\frac{1}{2}}e^{-\frac{\beta\nu}{2T}}.$$

The expression for the thermal conductivity then becomes:

$$k = bn^2dR\nu\cdot e^{-\frac{\beta\nu}{T}}\cdot\frac{\frac{1}{2}2-cT^{\frac{1}{2}}e^{-\frac{\beta\nu}{2T}}}{c^2Te^{-\frac{\beta\nu}{T}}},$$

$$= bn^2dR\nu\cdot\frac{2-cT^{\frac{1}{2}}e^{-\frac{\beta\nu}{2T}}}{c^2T}. \tag{4}$$

That this expression is practically equivalent to equation (2) will be seen on comparing the values of k(calc.$_4$) in Table II, with the corresponding

values of k(calc.$_2$) of Table I. Thus the agglomeration hypothesis leads directly to a satisfactory formula for the heat conductivity while the quantum hypothesis apparently does not.

The essential difference between these two hypotheses is that while according to the quantum hypothesis all of the possible degrees of freedom possess energy, but in an amount which differs from that assigned by equipartition, according to the agglomeration hypothesis only a part of the possible degrees of freedom possess energy, but those which have it carry the amount assigned by equipartition. The fact that the latter of these hypotheses leads naturally to a satisfactory formula for the thermal conductivity while the former seems to give such an expression only with the use of a highly improbable assumption may be taken as evidence against the quantum hypothesis, and as a verification of the law of equipartition of energy as applied to the degrees of freedom of solids.

SUMMARY.

In the first place it has been shown that the average distance through which the energy of an atomic collision in a crystal is transmitted is approximately inversely proportional to the temperature, and is many times the distance between the atoms.

This result may be explained on the assumption that each atom in a crystal absorbs or scatters a small fraction of the energy of every thermal disturbance which traverses it and transmits the rest.

In order to obtain a satisfactory formula for the thermal conductivity on the basis of the quantum hypothesis it seems necessary to make certain improbable assumptions; the agglomeration hypothesis, on the other hand, leads to such a formula with much more plausible assumptions.

This study of the thermal conductivity therefore brings evidence against the quantum hypothesis, and supports the law of the equipartition of energy as applied to the degrees of freedom in a solid.

I am indebted to my brother Professor Karl T. Compton for his suggestions and to Professor E. P. Adams for his helpful criticism in connection with this paper.

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December 9, 1915.