

## A SIMPLE RELATION BETWEEN THERMAL CONDUCTIVITY, SPECIFIC HEAT AND ABSOLUTE TEMPERATURE

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### ABSTRACT

A relation of the form  $k/aC = K_1/T + K_2$ , between thermal conductivity  $k$ , atomic heat ( $aC$ ), and absolute temperature  $T$ , is shown to hold for zinc, sodium, lithium, copper, lead, aluminum and mercury. The possibility is indicated of an equation of this sort based on the assumption of a double mechanism of heat conduction—an atomic lattice along which energy is transmitted as elastic waves (Debye) and a structure of atoms (crystalline or amorphous), through which energy is transferred by impacts. The lattice and atomic contributions to the thermal conductivity may be obtained from the slopes and intercepts of the lines. The values at 0°C are as follows (lattice part being given first): lithium 0.150, 0.006; sodium 0.092, 0.169; zinc 0.084, 0.192; copper 0.920, 0.171; lead 0.018, 0.068; aluminum 0.127, 0.358; mercury 0.031, 0.033. The line for mercury suggests that the atomic part is at least approximately the conductivity in the liquid state. The single and poly-crystal zinc lines have the same intercept but different slopes indicating that the increased thermal conductivity of the single crystal specimen is in the elastic wave contribution.

A STUDY of recently obtained data on thermal conductivity and specific heat of lithium and sodium<sup>1</sup> and zinc and lead<sup>2</sup> over the temperature range  $-250^\circ\text{C}$  to  $+200^\circ\text{C}$  reveals a simple relation between these quantities, not hitherto specifically reported, namely the law

$$k/aC = K_1/T + K_2 \quad (1)$$

where  $k$  is the thermal conductivity; ( $aC$ ), the atomic heat;  $T$ , the absolute temperature and  $K_1$  and  $K_2$  constants. The values of  $k/aC$  when plotted against  $1/T$  fit straight lines with remarkable precision. These plots are shown in Figure 1.\* For lithium the law holds as far down as  $-200^\circ\text{C}$  below which the rapid increase in  $k$  causes a deviation. For zinc a deviation becomes noticeable only below  $-225^\circ\text{C}$ , while for sodium and lead there is no deviation as far as  $-240^\circ\text{C}$  below which temperature we have no data. The plot shows also lines for copper, aluminum and mercury using data from the Landolt-Börnstein tables.

<sup>1</sup> Bidwell, Phys. Rev. **28**, 475 (1926).

<sup>2</sup> Lewis and Bidwell, Phys. Rev. **31**, 1111 (1928).

\* The transformation at  $+50^\circ$  for lithium limits the upper temperatures since we have no data for the metal in the higher temperature modification. A transformation occurs in sodium between  $-40^\circ\text{C}$  and  $0^\circ\text{C}$ ; we have data above this region and the points are indicated. The following data for thermal conductivity of very pure zinc and lead, recently obtained by Bidwell and Lewis were used for this graph: For poly-crystal zinc:  $-250^\circ\text{C}$ , 0.341;  $-200^\circ\text{C}$ , 0.325;  $100^\circ\text{C}$ , 0.2975;  $0^\circ\text{C}$ , 0.273;  $+100^\circ\text{C}$ , 0.255;  $+200^\circ\text{C}$ , 0.2425;  $300^\circ\text{C}$ , 0.238. For single crystal zinc:  $-250^\circ\text{C}$ , 0.382;  $-225^\circ\text{C}$ , 0.373;  $-200^\circ\text{C}$ , 0.3615;  $-100^\circ\text{C}$ , 0.330;  $0^\circ\text{C}$ , 0.304;  $+100^\circ\text{C}$ , 0.286;  $+200^\circ\text{C}$ , 0.274. For lead:  $-250^\circ\text{C}$ , 0.128;  $-200^\circ\text{C}$ , 0.113;  $-100^\circ\text{C}$ , 0.097;  $0^\circ\text{C}$ , 0.084;  $+100^\circ\text{C}$ , 0.075. The lower range values for lead are higher than values reported by Meissner and Schott but agree with values found by Macchia.

The theory of thermal conduction is in a unsettled condition because of our lack of any certain knowledge of the mechanism involved. It has been suggested frequently that two distinct mechanisms are concerned in heat conduction in a metal; namely, a non-metallic part, i.e., transfer by atomic

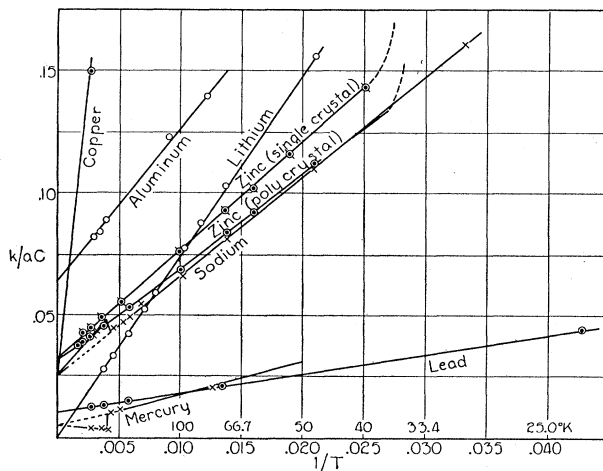


Fig. 1. Variation of  $k/aC$  with  $1/T$ .

collisions, and a metallic part, usually assumed as a transfer of heat by electrons. The equation above given likewise indicates a double mechanism and further shows that one part is a function of temperature, the other not.

Debye<sup>3</sup> has suggested the transfer of heat by elastic waves down a space lattice in which the energy of the wave is continually reabsorbed as heat, i.e., converted to atomic vibrations. His expression is

$$k_1 = \rho v' l' C_v / 4 \quad (2)$$

in which  $\rho$  is the density of the metal;  $C_v$ , the specific heat;  $v'$ , the velocity of sound in the metal; and  $l'$ , a dissipation factor, the distance the wave travels before its energy is reduced to  $1/e$  of its value. It is reasonable to suppose that dissipation of the wave energy is greater at higher temperatures. Therefore, if we tentatively place  $l' = A/T$ , where  $A$  is a constant and divide the expression by  $aC$  (where  $a$  is the atomic weight) we have  $k_1 = A\rho v' / 4aT$ , which corresponds to the first term of the experimental law, the term upon which the slopes of the lines depend. The increased slope of the single crystal zinc line is in agreement with this interpretation. The factor  $A$  should presumably not be affected by the crystal size but the elastic constants and therefore  $v'$  should be so affected. Measurement of  $v'$  in the single and polycrystal zinc rods should be of interest in this connection.

It is possible that the second term on the right, that is, the intercept, is the value of  $k/aC$  which has to do with the transport of heat by atomic

<sup>3</sup> Debye, *Vorträge über die kinetische Theorie der Materie und Electricität*. Teubner, 1914.

collisions. According to the experimental law this term is independent of the temperature. The behavior of the mercury line suggests that this has approximately the same value as for the liquid metal. An expression for the liquid state which is independent of the temperature is readily obtained. Thus the heat transferred through unit area in unit times by collisions of individual atoms is  $dH/dt = (1/3)vlNdE/dx$ , where  $E$  is the kinetic energy of the atoms;  $N$  the number of atoms per unit volume;  $l$ , the mean free path;  $v$ , the root-mean-square velocity. We may write this as

$$\frac{dH}{dt} = \frac{1}{3} vl\rho \left[ \frac{N}{\rho} \frac{dE}{dT} \right] \frac{dT}{dx}$$

in which  $(N/\rho)(dE/dT) = C_v$ , and  $\rho$ , the density. By definition  $dH/dt = k_2(dT/dx)$ , in which  $k_2$  is the thermal conductivity. Therefore

$$k_2 = \rho v l C_v / 3 \quad (3)$$

There is some experimental evidence from other quarters that  $l \propto 1/T^{1/2}$  or that  $l \propto 1/v$ . The expression thus is independent of the temperature.

Combining expressions (2) and (3) gives

$$k/aC_v = A\rho v'/4aT + \rho vl/3a \quad (4)$$

This equation is of the form required by the law. The second term on the right, however, applies to mobile atoms, whereas in the solid metals we are dealing with atoms spaced rigidly in a lattice.

The observed intercept for zinc is 0.032. Assuming the above term, we get  $l$  as of the order of  $10^{-5}$  whereas the atomic spacing in the lattice is of the order  $10^{-8}$ . Evidently then the term as derived for a liquid metal cannot be taken over, as it stands, for the solid. It should be possible, however, to obtain for the solid a term of this character.

Table I shows the values of  $\rho v'/4a$ , compared with the observed slopes, and also the computed values of  $A$  for the different metals. It is of interest to note that we have approximately the same value for  $A$  for lithium, sodium, zinc and copper, or that the slopes for these four metals are proportional to  $\rho v'/4a$ .

TABLE I. Values of  $\rho v'/4a$  and of  $A$ .

Metal	$\rho v'/4a^*$	Observed slope	$A$
Lithium	1910	7.5	0.00390
Sodium	1030	3.9	0.00378
Zinc (poly crystal)	994	3.8	0.00383
Zinc (single crystal)	—	4.4	—
Copper	12250	44.7	0.00365
Lead	1360	.8	0.00059
Aluminum	12700	6.3	0.00050
Mercury	7100	1.3	0.00018

\* The values of the velocity of sound were taken from the Smithsonian tables for copper, zinc and aluminum. For lithium, sodium and mercury, this was assumed as of the same order as for lead, which is about 1060. For these metals the value of 1000 was taken.

It is also of interest to observe on the basis of the equation and its interpretation as here given to what extent the thermal conduction is due to elastic waves and to what extent it is due to atomic collisions. Table II shows the value of  $k_1 = K_1(aC/T)$  and  $k_2 = K_2aC$  for the various metals at  $0^\circ\text{C}$ .

TABLE II. *Elastic and non-elastic portions of thermal conductivity at  $0^\circ\text{C}$ .*

Metal	Elastic wave portion $k_1 = K_1 aC/T$	Atomic portion $k_2 = K_2 aC$
Lithium	0.150	0.006
Sodium	0.092 ( $-10^\circ\text{C}$ )	0.169
	0.124 ( $+10^\circ\text{C}$ )	
Zinc (poly crystal)	0.084	0.192
Zinc (single crystal)	0.098	0.192
Aluminum	0.127	0.358
Copper	0.920	0.171
Lead	0.018	0.068
Mercury	0.0308 (solid-extrapolated)	0.0335

The theory suggests that the intercepts give a measure of the non-elastic or atomic portion of the thermal conductivity and that this portion is independent of the temperature if the atomic heat has become constant. The mercury data indicate that this is approximately at least the thermal conductivity for the metal in the liquid state. (The slight negative slope of the liquid mercury line may be due to inaccurate data on  $k$  and  $C$ .) The line for single-crystal zinc shows a greater slope than the line for poly-crystal zinc but exactly the same intercept. The increased thermal conductivity, therefore, is entirely in the elastic wave portion as we would expect on the theory presented. Likewise the change in the sodium line just below  $0^\circ\text{C}$  indicates that the increased conductivity is entirely in the elastic wave portion since the slope is increased while the intercept remains the same.

We expect for the metals  $k_1$  to be much larger than  $k_2$  and this is borne out for lithium and copper but sodium, zinc and lead curiously enough show  $k_1$  smaller than  $k_2$ , while mercury shows about an equal division. The difference between a metal and a non-metal is usually ascribed to the presence of mobile electrons in the metal. It is not clear just what part the electrons play in thermal conduction. Possibly we may think of an electron lattice upon which the atoms act as drags. This would account for the rapid attenuation of the wave while also explaining the high thermal conductivity of metals. We would have to assume the absence of such a mobile electron lattice in non-metals. Data on other metals are being obtained to test the equation and theory further, particularly, for the liquid state.

LEHIGH UNIVERSITY,  
March 25, 1928.