Thermal Conductivity of Metals

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As indicated in a previous paper, elementary classical considerations suggested a relation between thermal conductivity k, atomic heat C, density ρ, and absolute temperature T of the form $k/C\rho=K/T+K'$. This is now shown to be in agreement with recent theories on the metallic state. The first term on the right relates to conduction by the crystal lattice, the second term, K', refers to conduction by electrons. It is found experimentally that K' is the conductivity in the molten condition. The present paper shows these relations for lead, tin, and zinc. The data reported for lead are new. A modification of the experimental method previously used for zinc was required for the work on lead (a much poorer conductor) and is here explained.

Introduction

In a previous paper[1] an attempt was made to explain the thermal conductivity of metals and its change with temperature on the basis of a transfer of heat partly by elastic waves in the crystal lattice and their rapid absorption and partly by atomic collisions as in a gas. The former introduced a temperature coefficient, the latter did not, the temperature coefficient being associated with the velocity of the elastic waves. Elementary classical considerations led to an equation of the type

$$k/\rho C=K/T+K' \tag{1}$$

where k is the thermal conductivity; C, the atomic heat; ρ, the density; T, the absolute temperature, and K and K' constants. The theory suggested that the intercept should be the value of $k/\rho C$ for the liquid state. The present paper offers data on lead, tin and zinc confirming this suggestion and interprets the equation in the light of recent theory.

Theory

A. H. Wilson[2] from the standpoint of modern theory shows that thermal conductivity should require two terms, one due to the lattice, which as given by classical physics is $k_g=\frac{1}{3}\rho Clu$, and one due to electrons, which on the basis of modern theory is

$$k_e=\frac{\pi^2}{3}\cdot\frac{n\tau k^2T}{m}.$$

l is the mean free path in the lattice; u, the velocity of sound in the lattice; n, the number of free electrons per unit volume; k, the molecular gas constant; T, the temperature; m, the mass of the electron; and τ, the "relaxation time," the average time between collisions.

We may write $k=k_g+k_e$ (although these are not independent, since the electrons afford a mechanism for scattering the lattice waves). Hence

$$k=\tfrac{1}{3}\rho Clu+\frac{\pi^2}{3}\cdot\frac{n\tau k^2T}{m}. \tag{2}$$

According to Wilson, k_e becomes constant at high temperatures, while k_g reaches a maximum and then decreases as T^{-1}. The experimental data on lead, tin and zinc here reported do not yield straight lines when k is plotted against $1/T$; but straight lines are obtained if $k/\rho C$ is plotted against $1/T$. The theoretical equation in the form

$$\frac{k}{\rho C}=\tfrac{1}{3}lu+\frac{\pi^2}{3}\cdot\frac{n\tau k^2T}{m\rho C} \tag{3}$$

must then be equivalent to

$$\frac{k}{\rho C}=K\frac{1}{T}+K'. \tag{1}$$

According to this $\tau\propto T^{-1}$ and $lu\propto T^{-1}$. The *International Critical Tables* give data on the velocity of sound for platinum and copper at 20° C, 100° C and 200° C. For these data $u\propto T^{-1}$. According to Wilson, l depends on the grain size and is therefore only slightly affected by the temperature. Thus with ρ and C approximately compensating

[1] C. C. Bidwell, Phys. Rev. **32**, 311–314 (1928).
[2] A. H. Wilson, *Semi-Conductors and Metals* (Macmillan, New York, 1939).

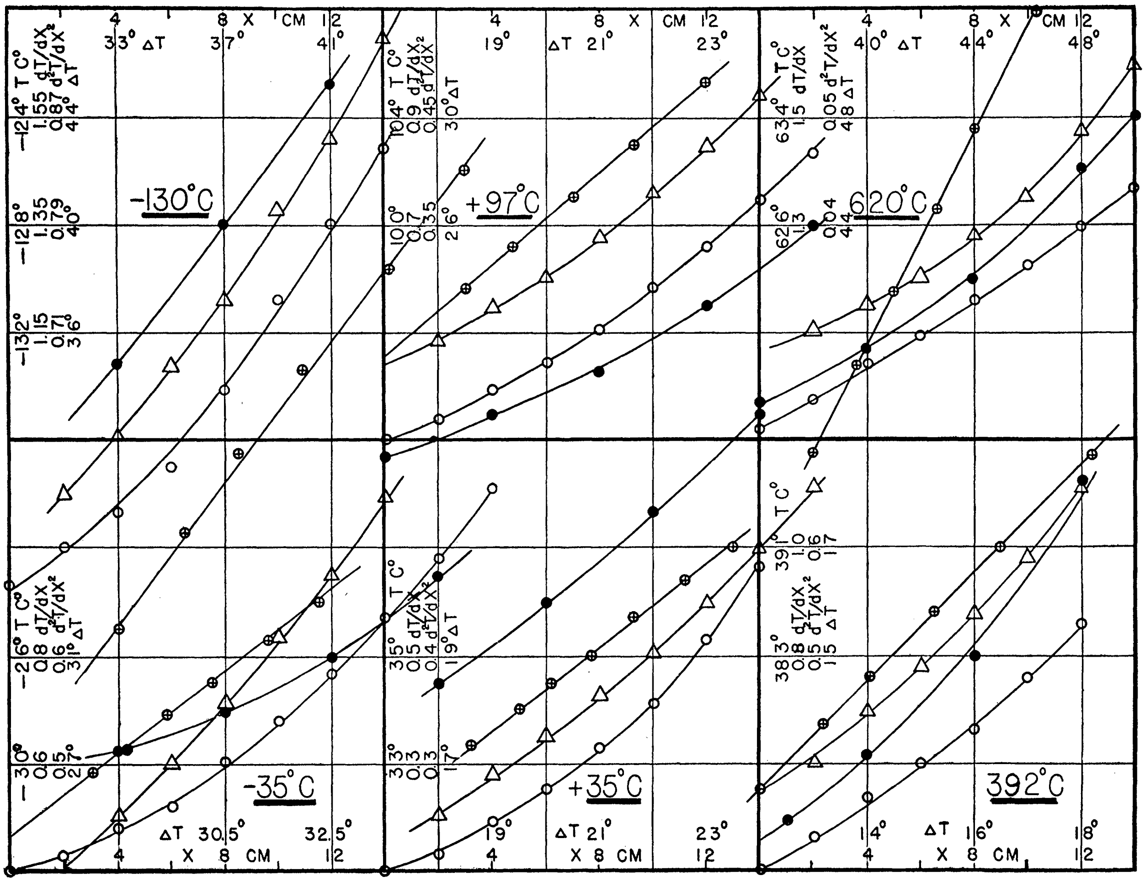

FIG. 1. Experimental data for lead at various temperatures.

in their temperature effects, Eqs. (3) and (1) are in agreement.

The intercept term must include the atomic as well as electronic conductivity for the liquid metal. If the atomic conductivity is that of an insulating liquid, it will be only one or two percent of the electron conductivity. Such conductivity increases with temperature and may thus account for the slight positive slope experimentally observed.

The experimental evidence

The data on zinc previously reported[3] were obtained by a new experimental method and agree closely with values found by Konno,[4] the only other data published for molten zinc. The data here presented on tin are Konno's, no work on tin having been done by the author. For lead, however, Konno's values for the molten state are far too low to give value of $k/C\rho$ in agreement with the intercept of the equation for the solid metal. Hence new observations were made on lead with the newly developed experimental method. These observations are shown graphically in Fig. 1. Figure 2 shows the author's values for the thermal conductivity of lead together with values obtained by Konno[4] and Van Dusen and Shelton.[5] Konno's values for the molten state are about 30 percent lower than the newer values here reported. Figures 3 and 4 show the course of the thermal conductivity curves for zinc and tin. For all these plots specific heats and densities were obtained from the published tables and are averages of what

[3] C. C. Bidwell, Phys. Rev. **56**, 594 (1939).
[4] S. Konno, Phil. Mag. **40**, 542 (1920).
[5] M. S. Van Dusen and S. M. Shelton, J. Research Nat. Bur. Stand. **12**, 429 (1934).

appear to be the best values. With the author's values for molten lead, the plots for tin, lead and zinc are seen to be in agreement with the suggested law, *the intercepts giving the value of k/Cp for the molten state.*

Modification of the Experimental Method in its Application to Lead

The experimental procedure as reported in a previous paper on zinc (reference 3) consisted, in brief, in establishing a flow of heat vertically down a specimen packed in Silocel, measuring the temperature at various levels (from which can be computed the gradient dT/dx and the change in gradient d^2T/dx^2) and measuring the lateral radial drop ΔT across the Silocel at the various levels.

The procedure as reported in the work on zinc was improved by centering the graphite cylinder containing the test metal in an iron cylinder of about 12 cm inside diameter on which was wound a Nichrome heater ribbon. The space between the graphite cylinder (5 cm diameter) and the iron cylinder was filled with Silocel as was also a space between the iron cylinder and an outer asbestos cylinder of about 20 cm diameter. The Nichrome windings on the iron cylinder were in parallel with similar winding on the graphite. By adjustment of currents in these two windings, the radial temperature drop across the Silocel could be reduced to small values or zero. The addition of the intermediate iron cylinder with its heater coil is found to be a great improvement.

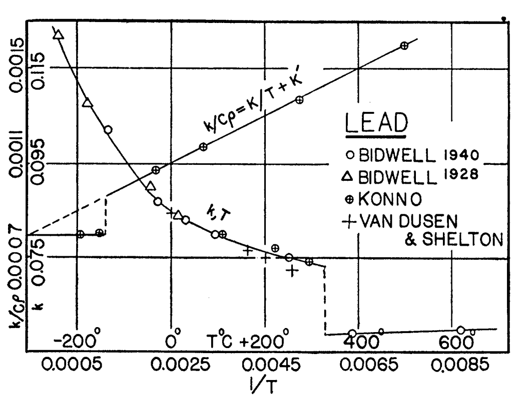

FIG. 2. Thermal conductivity of lead. k in cal. per sec. per cm per degree C.

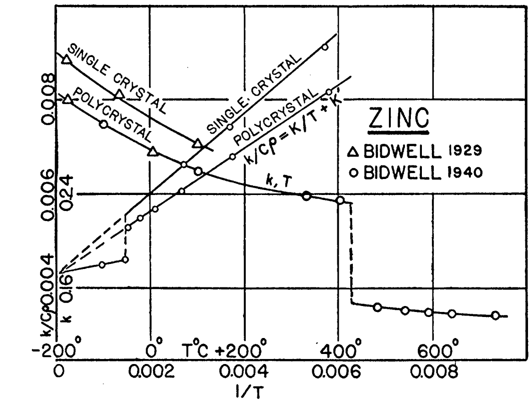

FIG. 3. Thermal conductivity of zinc. k in cal. per sec. per cm per degree C.

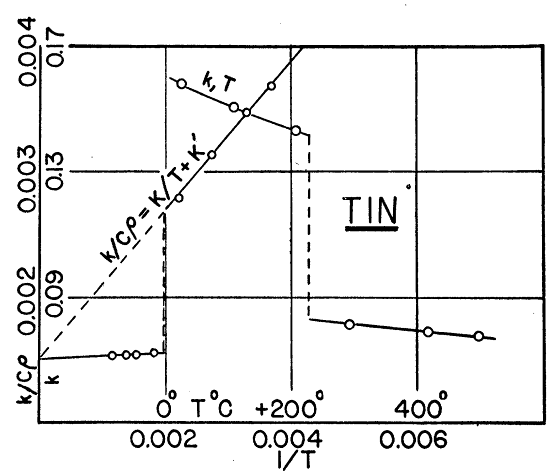

FIG. 4. Thermal conductivity of tin. k in cal. per sec. per cm per degree C.

A further modification of the method of handling the data in the case of such a relatively poor conductor as lead was found necessary. In the method used, the lateral, radial heat loss between two levels is equated to the difference between the heat entering at the upper level and leaving at the lower level. The equation is

$$k_xA_m(dT/dx)_1 - k_xA_m(dT/dx)_2 = \int_{r_1}^{r_2} k_s 2\pi rl dT/dr. \quad (5)$$

This becomes

$$k_xA_m d^2T/dx^2 = \frac{2\pi k_s \Delta T}{2.3 \log (r_2/r_1)}, \quad (6)$$

since $(dT/dx_1 - dT/dx_2)/l = d^2T/dx^2$. k_x is the thermal conductivity of the test metal; k_s, that of the Silocel; A_m, the cross section of the test metal; ΔT, the radial temperature drop across the Silocel at the level in question; r_2, the outer radius of the Silocel (inside the iron cylinder); r_1, its inner radius.[6]

In the case of molten metals it becomes necessary to add to the left side a term to cover the heat flow down the walls of the graphite-containing cylinder. The equation then becomes

$$k_x A_m (d^2T/dx^2)_m = \frac{2\pi k_s \Delta T}{2.3 \log (r_2/r_1)} - k_{\text{gr}} A_{\text{gr}} (d^2T/dx^2)_{\text{gr}}. \quad (7)$$

This may be written

$$(d^2T/dx^2)_m = \frac{2\pi k_s}{k_x A_m 2.3 \log (r_2/r_1)} \Delta T - \frac{k_{\text{gr}} A_{\text{gr}} (d^2T/dx^2)_{\text{gr}}}{k_x A_m}. \quad (8)$$

It is found for lead that values of d^2T/dx^2 plotted against corresponding values of ΔT give straight lines in all cases. The intercept term is small and the variation of $(d^2T/dx^2)_{\text{gr}}$ from top to bottom of the cylinder appears to be negligible. This is reasonable, at least when the contained metal is a comparatively poor conductor like lead, where the graphite has about five times the conductivity of the solid lead and about ten times that of molten lead. The comparatively high conductivity of the graphite means a correspondingly small temperature gradient in the graphite, changing at an approximately constant rate. In the case of zinc (see reference 3), the conductivity of the metal was about the same as that of the graphite and, for zinc, d^2T/dx^2 was found to be constant over a considerable range. This is in agreement with the above explanation of the constancy of $(d^2T/dx^2)_{\text{gr}}$.

In the case of zinc it was necessary merely to add the cross section of the graphite to that of the zinc and use Eq. (7), ΔT and the slope of the dT/dx line both being constant. For lead however, d^2T/dx^2 and ΔT are not constant but, when d^2T/dx^2 is plotted against ΔT, a straight line results as indicated by Eq. (8). From the slope of this line the thermal conductivity k_x is obtained. No correction for the graphite walls is required since the quantities having to do with the heat flow down the walls all appear in the intercept.

Precautions

In the use of this method it is of the utmost importance that stable unchanging temperature conditions be attained before starting the heat flow down the specimen. Four $\frac{1}{8}''$ quartz tubes were inserted at the outer radius of the Silocel (just inside the iron cylinder) and two such tubes in the molten specimen (or frozen in the solid specimen). Only three junctions were used, the Chromel wires welded at a common point and the copper leads connected to binding posts. One of the junctions was kept at the bottom of one of the quartz tubes in the metal, the second raised or lowered to the various levels in the other quartz tubes and temperature differentials between these junctions read on a galvanometer. The third junction was kept in ice and differentials between it and either of the others read on a potentiometer indicator gave actual temperatures.

It is usually necessary to wait two or more hours before unchanging conditions are attained. Readings up and down the specimen and across the Silocel at all levels are taken and then the downward heat flow started by applying heat in the d.c. heater at the top of the specimen. Final readings may be taken after another hour and corrections made for the initial readings. The fact that one gets smooth curves and straight lines as required by the equations is no guarantee of the correctness of the result. Only from absolutely stable conditions can satisfactory results be obtained.

[6] For temperatures $-130°$, $-35°$, $+35°$, $+97°$, $+250°$, $r_1 = 2.6$ cm; r_2, 4.5 cm; $A_m = 13.83$. For 392°, 620°, $r_1 = 2.5$ cm; r_2, 5.65 cm; $A_m = 13.83$. Values of k_s for various temperatures are shown in the previous paper. The lead specimen was prepared by slow freezing from the bottom. This was effected by lowering the molten lot slowly through a furnace at the rate of about two cm per hour.