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Thermal Conductivities of Pure Metals at Low Temperatures. I. Aluminum*

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The thermal conductivities of three specimens of highly pure aluminum have been measured in the temperature range 2 to 20°K. All specimens showed maximum conductivities in the temperature range 14 to 17°K. The measured values are compared with the theory of Sondheimer. The number of effective conduction electrons per atom is found to be 0.061.

INTRODUCTION

At room temperatures and above, the thermal conductivity of most metals shows little change with temperature. As the temperature is lowered, the thermal conductivity of pure and well-annealed metal specimens first rises in magnitude, passes through a maximum and then declines more or less linearly toward zero at 0°K. The thermal conductivity of metals in the range of temperatures from 20°K up to room temperature has been the subject of numerous investigations by Grüneisen and his co-workers.[1] The range of temperatures below 20°K spans a region of considerable interest, for in this range extremely pure and strain-free metal specimens exhibit their maximum thermal conductivity. Furthermore, at these low temperatures the free electron theory of thermal conductivity reduces to a relatively simple form which facilitates comparison with experiment. Although there have been a number of investigations of the thermal conductivities of pure metals at temperatures below 20°K,[2–12] the majority have been concerned primarily with phenomena associated with the incidence and destruction of superconductivity and have employed a relatively restricted range of temperatures.

As the first of what is planned to be a systematic series of investigations of thermal conductivities of pure metals over the 2 to 20°K temperature range, we have studied the thermal conductivities of three highly pure aluminum specimens, two of them single crystals.

EXPERIMENTAL DETAILS

The three specimens reported in this paper were rods of exceptionally pure aluminum, approximately four inches in length and 0.15 inch in diameter. Details on the purity and crystalline state of these specimens are given in Table I. To facilitate mounting of the rods and the attachment of thermometers, a thin layer of copper was plated on each end of the rod for a distance of about $\frac{3}{4}$ of an inch.

The calorimeter used in this work was similar to that previously described by de Haas and Rademakers,[9] but differed in some details. The specimen rods were soldered with one end protruding through the bottom of a brass can which could be evacuated. A sufficiently high degree of thermal insulation was found for vacuums of better than 0.05 micron. To permit a measured flow of heat through the specimen, a heater coil of manganin wire was attached to the isolated end of the specimen inside the can.

For those measurements of the thermal conductivity at temperatures above that of the refrigerant bath, an auxiliary heater of manganin was wrapped around the end of the specimen protruding through the bottom of the calorimeter can. The whole bottom of the can was then partially insulated from the bath by means of a tight-fitting thin brass cap filled with vacuum grease.

The absolute temperature and temperature gradient along the specimen were determined by two gas thermometer bulbs, approximately 6 cm^3 in volume, attached to the specimen. These bulbs were separated by about 5 cm and were connected by means of small diameter thin-wall *K*-monel tubes to an external manometer system. This system consisted of two closed-end mercury manometers, which measured the absolute temperature of each of the thermometer bulbs, and a capillary differential oil manometer used for a precision determination of the temperature difference between the two thermometer bulbs. The temperature difference between the gas thermometers ranged from about 0.03°K in the measurements at 2°K up to about 0.15°K in the measurements at 20°K. A summary of the corrections due to departures of the thermometer system from ideal behavior at liquid helium temperatures is given by Hulm.[2]

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[1] A summary of the work of Grüneisen, together with a complete bibliography, is given in an obituary article appearing in the Ann. Physik **5**, V–XII (1949).

[2] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950) (Sn, In, Hg, Ta).

[3] K. Mendelssohn and J. L. Olsen, Proc. Phys. Soc. (London) **A63**, 2 (1950) (Ta, Nb).

[4] K. Mendelssohn and R. B. Pontius, Phil. Mag. **24**, 777 (1937) (Pb).

[5] A. Rademakers, Physica **15**, 849 (1949) (Pb, Sn).

[6] J. de Nobel, Physica **15**, 532 (1949) (W).

[7] J. F. Allen and E. Mendoza, Proc. Cambridge Phil. Soc. **44**, 280 (1948) (Cu).

[8] S. Shalyt, J. Phys. USSR **8**, 315 (1944) (Bi).

[9] W. J. de Haas and A. Rademakers, Physica **7**, 992 (1940) (Pb).

[10] H. Bremmer and W. J. de Haas, Physica **3**, 672 (1936) (Pb, Cu).

[11] de Haas, Gerritsen, and Capel, Physica **3**, 1143 (1936) (Bi).

[12] W. J. de Haas and H. Bremmer, Commun. Phys. Lab. Univ. Leiden 214d, 220b, 220c (1931) (Pb, Sn).

At temperatures above 4.2°K the volume of that part of the manometer system at room temperature made necessary the calculation of a significant correction factor. In this case, the calculation of the temperature[13] and the temperature gradient was simplified if the thermometer system were "balanced"; that is, if the corresponding volumes on the two branches of the system were made equal. This was achieved by first carefully constructing and then etching the copper bulbs until their volumes were equal to within 0.1 percent. The *K*-monel tubes connecting these bulbs to the manometer system were made of equal lengths. Finally, the volumes of the two sides of the manometer system were made equal with the help of a small 0-ring-sealed cylinder and piston whose volume could be adjusted sensitively and reproducibly by a standard micrometer head attached to the piston. The position of the piston was adjusted until large changes of temperature of the bulbs, produced by warming them from the temperature of liquid nitrogen to that of the room, caused no net difference in pressure as observed on the oil manometer.

Total error in the thermal conductivity measurements in the temperature regions 2 to 4.2°K and 14.5 to 20.5°K is estimated to be approximately 4 percent. In the temperature region 4.2 to 14.5°K, uncertainty in evaluating the magnitude of the correction factors led to somewhat larger errors (up to 10 percent at 14°K).

The electrical conductivity measurements were made after the specimens had been removed from the calorimeter. A Wenner potentiometer and standard techniques were employed. Total error in these measurements is estimated to be less than 2 percent.

RESULTS AND DISCUSSION

The thermal conductivities of the three aluminum specimens are plotted against temperature in Fig. 1. An understanding of these curves may be gained from consideration of the theory of transport phenomena in free electrons. Assuming the simplest monovalent model in which the electrons are quasi-free, it is possible to set up an integral equation for the velocity distribution of the conduction electrons.[14] This equation includes scattering both by impurities and by thermal vibrations of the lattice. A complete solution of this equation has been recently given by Sondheimer[15] in the form of the infinite series:

$$K=K_0+K_1+\cdots. \tag{1}$$

At temperatures $T/\Theta<0.05$, where Θ is the Debye characteristic temperature, K_0 in (1) is given by:

$$(1/K_0)=(\rho_r/L_0T)+(1/K_\infty)(T/\Theta)^2 \times[95.3N_a^{\frac{2}{3}}-533(T/\Theta)^2], \tag{2}$$

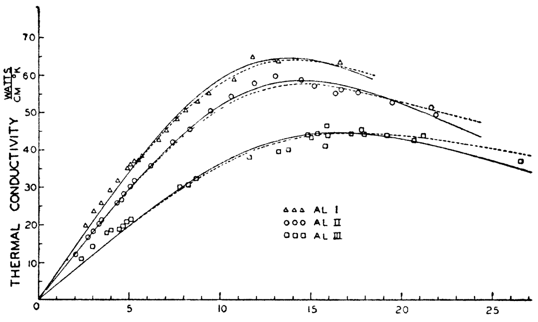

FIG. 1. Thermal conductivity of aluminum specimens as a function of temperature. The points represent experimental data. The solid curves are calculated from the theory of Makinson, Eq. (3), using *A* and *B* values of Table I, but neglecting the T^4 term. The dashed curves are calculated from the theory of Sondheimer, Eq. (1), using $N_a=0.061$ and $L_0=A\rho_r$.

where ρ_r = residual electrical resistivity, L_0 = Lorenz ratio, K_∞ = high temperature thermal conductivity, and N_a = number of effective free electrons per atom. This expression, previously derived by Makinson,[16] is of the form

$$(1/K_0)=(1/AT)+BT^2+CT^4. \tag{3}$$

Ignoring for the present the relatively small T^4 term, we may plot data for the three aluminum specimens on a graph of T/K *vs* T^3 getting nearly straight lines of slope *B* and intercept $1/A$. The values of *A* and *B* determined in this way are given in Table I. It is seen that *A* is proportional to the residual electrical conductivity whereas *B* is the same constant for all three specimens. From Eq. (2):

$$B=95.3(N_a)^{\frac{2}{3}}/K_\infty\Theta^2. \tag{4}$$

TABLE I. Characteristics of aluminum specimens.

	Al I	Al II	Al III
Source of metal	Aluminum Company of America	Aluminum Company of America	Johnson and Matthey
Purity of metal[a] Al:	99.996+ percent	99.996+ percent	99.995+ percent
Mg:	0.001	0.001	0.002
Si:	0.001	0.001	<0.001
Fe:	0.0006	0.0006	<0.0005
Cu:	0.0004	0.0004	<0.0005
Na:	0.0004	0.0004	faint trace
Crystalline form[b]	Single crystal	Single crystal	Annealed polycrystal
Residual resistivity, ρ_r in ohm-cm	3.04×10^{-9}	3.85×10^{-9}	5.51×10^{-9}
Resistance ratio, $\rho_{4.2}/\rho_{273}$	1.19×10^{-3}	1.48×10^{-3}	2.14×10^{-3}
Impurity constant, *A* in watts/cm(°K)^2	7.04	6.06	4.05
Lattice constant, *B* in cm/watt °K	2.70×10^{-5}	2.72×10^{-5}	2.72×10^{-5}

[a] The claims of purity stated here are based on spectrographic analyses performed by the suppliers of the metal.

[b] We are very much indebted to Dr. F. Rosi of the Sylvania Company for supplying us with a number of very fine single crystals of pure aluminum.

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[13] The characteristics of helium gas thermometers with large dead space are given by A. H. Woodcock, Can. J. Research **A16**, 133 (1938).

[14] A. H. Wilson, Proc. Cambridge Phil. Soc. **33**, 371 (1937); *The Theory of Metals* (Cambridge University Press, London, 1936), p. 157 et seq.

[15] E. H. Sondheimer, Proc. Roy. Soc. (London) **A206**, 75 (1951).

[16] R. E. B. Makinson, Proc. Cambridge Phil. Soc. **34**, 474 (1938).

TABLE II. Values of the coefficients α, β, and γ in relationship (6) evaluated at $T/\Theta=0$.

Function	α	β	γ
a	78.4	-438	0.823
b	2.37×10^3	-4.16×10^3	11.4
c	1.64×10^5	6.83×10^3	355
d	4.25×10^3	6.20×10^3	0

TABLE III. Lorenz ratios of aluminum specimens at low temperatures.

Temperature (°K)	$(\rho K/T)\times10^8$ (watt-ohm/deg^2) Al I	Al II	Al III
4.2	2.21	2.34	2.41
14.5	1.55	1.80	1.88
20.4	...	1.40	1.57

Calculating K_∞ from the Wiedemann-Franz law and the Handbook value[17] of room temperature electrical resistivity and taking Θ to be 390°K,[18] Eq. (4) yields $N_a=0.040\pm0.001$ effective free electrons per atom. This value is in good agreement with the values of N_a found in tin, indium and mercury by Hulm.[2]

To this order of approximation, the thermal resistivity may thus be considered to be a simple addition of resistivities due to two scattering mechanisms:[19]

(1) The thermal resistivity due to impurity scattering $(1/AT)$.

(2) The thermal resistivity due to scattering by thermal vibrations of the lattice (BT^2).

The remaining terms of the series expression for the thermal conductivity (1) appear to converge and are of increasing difficulty of calculation. They include scattering by impurities and by the lattice in a manner such that they may not be separated and distinguished. The K_1 term in (1) is of the form:

$$K_1=7.60\times10^{-2}K_\infty[d^2/(a^2c-ab^2)](T/\Theta), \tag{5}$$

where a, b, c, and d are each functions of the form:

$$\alpha N_a^{\frac{2}{3}}(T/\Theta)^3+\beta(T/\Theta)^5+\gamma\rho_r/\rho_\Theta. \tag{6}$$

Here ρ_Θ is the electrical resistivity at $T=\Theta$, and the numerical coefficients α, β, and γ have the values given in Table II. These values are valid in the temperature range $0<T/\Theta<0.05$.

Extending the approximate solution, Eq. (1), to include K_1 and the T^4 term in K_0 and once again adjusting N_a, the number of free electrons, to fit our measurements, we obtain a value $N_a=0.061\pm0.002$. This is about 50 percent larger than the value obtained using Eq. (4). The T^4 term in Eq. (3) and K_1 contributed roughly equal amounts to this increase.

A disparity in order of magnitude is found in comparing these values of N_a with the number of free electrons calculated from measurements on aluminum of electron specific heats[20] and of soft x-ray emission[21] which yield values of N_a close to the valence number. This disparity might be resolved by modification of the transport theory to account for the role of filled and nearly filled zones occurring in multivalent metals.

Values of the Lorenz ratio, $K\rho/T$, as measured in our three specimens are given in Table III. At low temperatures, where impurity scattering predominates, the Lorenz ratio agrees moderately well with the value 2.45×10^{-8} watt-ohm/(°K)^2 predicted by the Sommerfeld theory.[22] At higher temperatures, where coherent scattering by the lattice plays a more important role, the values of the Lorenz ratio drop significantly below the theoretical value. This is in qualitative agreement with the predictions of Makinson.[16]

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[17] *Metals Handbook* (Am. Soc. Metals, Cleveland, 1948), p. 810.

[18] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 14.

[19] This is analogous to the well-known Mattheissen rule of electrical resistivity and was first established empirically for the case of thermal resistivity by Grüneisen, Z. Physik **44**, 615 (1927).

[20] J. A. Kok and W. H. Keesom, Physica **4**, 835 (1937).

[21] H. M. O'Bryan and H. W. B. Skinner, Phys. rev. **45**, 370 (1934).

[22] A Sommerfeld, Z. Physik **47**, 1 (1928).