

in these calculations, it is encouraging that the agreement between theory and experiment is as good as it appears. It seems unlikely at present that further refinements of the calculations of  $\epsilon_0$  will improve the agreement between calculated and measured intensities. Precise calculations of the contributions of thermal diffuse scattering, Compton scattering, etc., to the Borrmann effect in copper may be more significant.

### SUMMARY

Absolute values of integrated intensities in anomalous transmission have been measured for almost perfect Cu crystals varying in thickness from 0.014 to 0.22 cm. Mo  $K\alpha$ , Cu  $K\alpha$ , and Cr  $K\alpha$  radiations were used with a double-crystal spectrometer for measuring the intensities of the 111, 200, 220, and 222 reflections. Relative and absolute values of integrated intensities in anomalous transmission and in the Bragg case for several reflections were measured with Ag  $K\alpha$  and Mo  $K\alpha$  radiations for a crystal containing  $2 \times 10^8$  dislocation lines/cm<sup>2</sup>.

Integrated intensities were calculated by means of the formulas of the dynamical theory of x-ray diffraction. For these calculations the dynamical values of the photoelectric absorption coefficients as a function of the scattering angle were computed by using formulas of the semiclassical theory of absorption of radiation.

Two Debye temperatures, 315 and 300°K, were used for the evaluation of the Debye-Waller factor. For  $\Theta = 300^\circ\text{K}$ , the calculated intensities are in better agreement with the experimental ones, and there is some experimental justification for this value of the Debye temperature. These results should not be taken as proof that the Debye temperature of Cu is 300°K rather than 315°K. Apart from the above minor discrepancies, the agreement of the experimental intensities with those calculated by applying the dynamical theory of diffraction is satisfactory.

For  $\Theta_M = 315^\circ\text{K}$ , the generally accepted value, calculated intensities were systematically higher than experimental ones. This work shows clearly that there are a number of factors, such as (1) the thickness and the strain (or the defects) of the crystal, (2) the exact value of the "apparent" Debye temperature, and (3) other x-ray scattering effects which should be taken into consideration for any significant comparison between calculated and measured values of intensities diffracted in anomalous transmission.

### ACKNOWLEDGMENTS

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## Thermopower of Pure Aluminum\*

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The thermopower of 99.999% pure, polycrystalline aluminum has been measured from 4.2 to 300°K using Pb as the standard, and from 300 to above 700°K using Au and Cu as alternative standards. The thermopower is negative at all temperatures with a phonon-drag peak occurring at about 75°K. From 200 to 300°K the thermopower  $S$  is well-described by the relation  $S = -2.34 \times 10^{-3}T - 284/T$   $\mu\text{V}/^\circ\text{K}$ . The thermopowers determined against Au and Cu are not quite the same above 450°K, showing a difference of about 0.1  $\mu\text{V}/^\circ\text{K}$  at 700°K. However, each set of data is consistent with the form  $S = -AT - B/T$  ( $A$  and  $B$  are positive constants); and a reasonable average for the two standards is given by  $S = -3.00 \times 10^{-3}T - 229/T$   $\mu\text{V}/^\circ\text{K}$ , for  $T > 300^\circ\text{K}$ . These two terms are interpreted as representing diffusion thermopower and phonon-drag thermopower contributions, respectively. If this interpretation is correct, it represents the first clear example of a nonzero phonon-drag thermopower in a metal at temperatures above 300°K.

### INTRODUCTION

IT is generally assumed that the thermopower  $S$  of very pure, simple metals can be described as the sum of two terms: a diffusion contribution  $S_d$  associated with the spatial redistribution of conduction electrons in the necessary temperature gradient, and a phonon-drag contribution  $S_g$  arising from the interaction between

the electrons and the nonequilibrium part of the phonon distribution produced by this temperature gradient.  $S_d$  and  $S_g$ , in turn, contain contributions from two types of electron-phonon interaction: normal electron-phonon scattering, in which the total crystal momentum of the incoming electrons and phonons is transferred undiminished to the outgoing electrons and phonons; and umklapp scattering, in which some crystal momentum is given to the crystal lattice (a reciprocal lattice vector

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$K$  appears in the momentum-conservation equation). Although general formalisms for calculating the thermopower of metals exist, detailed predictions of the sign, magnitude, and temperature dependence of  $S_e$  and  $S_g$ , without resort to adjustable parameters, have so far been obtained only for a hypothetical metal whose electrons behave as a free-electron gas, whose phonons are described by a Debye spectrum, and whose phonon-electron interaction involves no umklapp scattering. The high-temperature thermopower of such a metal has the form

$$S = S_e + S_g = AT + B/T, \quad (1)$$

where  $A$  and  $B$  are negative constants, and  $T$  is the absolute temperature. For such metals as copper, silver, and gold, a simple calculation based on this model shows that  $S_g$  should be comparable in magnitude to  $S_e$  at  $T = 300^\circ\text{K}$ . For aluminum we will show that this same calculation yields  $S_g/S_e = 30$  at  $300^\circ\text{K}$ . Experimentally, the thermopower of Cu, Ag, and Au are found to be nearly linear at temperatures above about  $300^\circ\text{K}$ ,<sup>1</sup> consistent only with  $S_g$  equal to zero. In fact, no metal has yet been shown, unambiguously, to have a nonzero high-temperature phonon-drag thermopower. In this paper we present measurements of the thermopower of aluminum which, so far as we can tell, are consistent with Eq. (1), yielding a phonon-drag thermopower which at  $300^\circ\text{K}$  has nearly the same magnitude as the diffusion thermopower. This result, if correct, has double significance: first, because Eq. (1) allows a separation of the measured high-temperature thermopower of aluminum into the component parts  $S_e$  and  $S_g$ ; and second, because it would represent the first clear example of a metal with a nonzero phonon-drag thermopower at temperatures about  $300^\circ\text{K}$ .

### THEORY

For an electron gas whose scattering can be described in terms of a relaxation time  $\tau$ , the diffusion thermopower can be written as<sup>2,3</sup>

$$S_e = -\frac{\pi^2 k^2 T}{3e} \left[ \frac{\partial \ln \sigma}{\partial \epsilon} \right]_{\epsilon = \epsilon_f}, \quad (2)$$

where  $\sigma$  is the electrical conductivity,  $\epsilon_f$  is the Fermi energy,  $e$  is the magnitude of the electronic charge,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. The quantity enclosed in brackets is to be evaluated at  $\epsilon = \epsilon_f$ . In the free-electron approximation, when  $\tau$  is assumed to be "isotropic" (i.e., to depend only on the energy of an electron and not on its crystal mo-

mentum), Eq. (2) reduces to

$$S_e = -\frac{\pi^2 k^2 T}{3e\epsilon_f} \left[ \frac{3}{2} + \epsilon_f \frac{\partial \ln \tau}{\partial \epsilon} \right]_{\epsilon = \epsilon_f}. \quad (3)$$

The  $\frac{3}{2}$  is characteristic of a free-electron gas having a spherical Fermi surface. At high temperatures,  $\tau$  is dominated by electron-phonon scattering. If normal electron-phonon scattering predominates, Eq. (3) becomes

$$S_e = -\frac{\pi^2 k^2 T}{e\epsilon_f} = -7.35 \times 10^{-2} \frac{T \mu\text{V}}{\epsilon_f \text{ } ^\circ\text{K}}, \quad (4)$$

where  $\epsilon_f$  is measured in electron volts. No simple form equivalent to Eq. (4) has been derived for  $S_e$  when umklapp scattering predominates.

A number of authors have solved the coupled transport equations describing electrons interacting with a nonequilibrium phonon distribution.<sup>4-6</sup> In the free-electron approximation, when the phonons are assumed to have a Debye spectrum, and in the absence of umklapp scattering, the high-temperature form of  $S_g$  can be written as<sup>7,8</sup>

$$S_g = -\frac{C_g}{3Ne} \frac{\tau_{pe}}{\tau_{pp} + \tau_{pe}}. \quad (5)$$

Here  $C_g$  is the lattice specific heat of the metal,  $N$  is the number of electrons per unit volume,  $\tau_{pe}$  is an average phonon-electron relaxation time, and  $\tau_{pp}$  is the average relaxation time for all other phonon-scattering events. At high temperatures  $\tau_{pp}$  is dominated by phonon-phonon scattering. Since at high temperatures  $\tau_{pe}$  is long compared to  $\tau_{pp}$ ,  $C_g$  and  $\tau_{pe}$  are nearly independent of temperature, and  $\tau_{pp}$  varies as  $1/T$ , Eq. (5) predicts that  $S_g$  should decay with increasing temperature as  $1/T$ . If we combine this result with Eq. (4), we obtain Eq. (1).

To estimate the relative magnitudes of  $S_e$  and  $S_g$ , we use an alternative form of Eq. (5)<sup>6</sup>

$$S_g/S_e = \frac{1}{3} N_a (\epsilon_f/kT) K_g/K_e. \quad (6)$$

Here  $N_a$  is the number of free electrons per atom, and  $K_g$  and  $K_e$  are the lattice and electronic thermal conductivities, respectively. For aluminum at  $300^\circ\text{K}$ , we use  $N_a = 3$ ,  $\epsilon_f = 15$  eV (both based on the free-electron approximation) and  $K_e = 2.1$  W/cm K.<sup>9</sup> Since  $K_g$  has not been directly determined for aluminum, we estimate its value by combining the measured  $K_g$  for copper,<sup>10</sup> extrapolated to  $300^\circ\text{K}$ , with the Leibfried-Schloemann

<sup>4</sup> M. Bailyn, *Phys. Rev.* **120**, 381 (1960).

<sup>5</sup> J. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), p. 409.

<sup>6</sup> I. I. Hanna and E. H. Sondheimer, *Proc. Roy. Soc. (London)* **A239**, 247 (1957).

<sup>7</sup> D. K. C. MacDonald, *Physica* **20**, 996 (1954).

<sup>8</sup> E. H. Sondheimer, *Can. J. Phys.* **34**, 1246 (1956).

<sup>9</sup> International Critical Tables **5**, 220 (1929).

<sup>10</sup> G. K. White and S. B. Woods, *Phil. Mag.* **45**, 1343 (1954).

<sup>1</sup> D. K. C. MacDonald and W. B. Pearson, *Proc. Phys. Soc. (London)* **78**, 306 (1961).

<sup>2</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1965), 2nd ed., p. 204.

<sup>3</sup> F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 200.

formula.<sup>11</sup> Values for the other necessary parameters are taken from Gschneidner.<sup>12</sup> In this manner we obtain

$$S_g/S_e = 30, \quad (7)$$

for aluminum at 300°K. Since the experimentally measured  $S_g/S_e$  ratio for copper is probably less than 1/20 of the ratio estimated using the above equation, we must view this ratio for aluminum with caution. It does show, however, that one would not expect to be able to neglect  $S_g$  with respect to  $S_e$  at 300°K.

Although no simple form equivalent to Eq. (5) has been derived for  $S_g$  when umklapp scattering predominates, two general comments can be made. First, at high temperatures, where large numbers of phonons are involved in umklapp scattering, it seems reasonable to expect the temperature dependence of the umklapp contribution to  $S_g$  to be dominated by the temperature dependence of  $\tau_{pp}$ , yielding a decay approximately proportional to the inverse absolute temperature. Second, although for a free-electron gas umklapp processes always contribute a positive phonon-drag thermopower, for aluminum, as we shall see below, they may well produce a net negative contribution.

#### EXPERIMENTAL APPARATUS AND PROCEDURE

The pure metals used in this experiment were: 99.999% pure aluminum obtained as 0.016-in. diam wire from the Western Gold and Platinum Company, the Sigmund Cohn Company, and the Atomergic Chemetals Company; 99.999% pure lead obtained as 0.010-in. diam wire from Cominco, Inc.; 99.999% pure gold obtained as 0.016-in. diam wire from the Western Gold and Platinum Company; and 99.999+% pure copper obtained as 0.016-in. diam wire from Cominco, Inc. The resistance ratios,  $R_{300^\circ\text{K}}/R_{4.2^\circ\text{K}}$ , were about 2 000 for all three rolls of aluminum.

The thermopower of aluminum was determined from measurements of the temperature dependence of the voltage output from a thermocouple consisting of the aluminum and a suitable standard for which the thermopower could be independently estimated. One end of the couple was submerged in a constant temperature bath, and the other end was embedded in a metal block around which was wound a heating coil. The temperature of the block was raised in steps to the temperatures of interest and the voltage output of the couple was measured. The thermopower of the couple was determined by computer, using a program which smoothed the data and then differentiated it. The thermopower of the standard was then subtracted from the thermopower of the couple, yielding the thermopower of aluminum.

<sup>11</sup> P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1 (see p. 46).

<sup>12</sup> K. A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 276.

For measurements from 4 to 300°K, we used Pb as the standard, with its thermopower taken as that given by Christian *et al.*<sup>13</sup> This thermopower is probably accurate to better than  $\pm 0.1 \mu\text{V}/^\circ\text{K}$  at 300°K. For temperatures up to 100°K, liquid helium at 4.2°K was used as the constant-temperature bath; for measurements from 77 to 300°K, liquid nitrogen was used. The thermopowers measured with these different baths were generally the same in the region of overlap to within  $0.02 \mu\text{V}/^\circ\text{K}$ . The temperature of the hot junction was determined using a platinum resistance thermometer, and should be accurate to about  $\pm 0.2^\circ\text{K}$  over the entire temperature range. This temperature could be measured and held constant during a measurement to better than  $0.05^\circ\text{K}$ . Thermocouple voltage measurements were made every  $3^\circ\text{K}$  up to  $10^\circ\text{K}$ , every  $5^\circ\text{K}$  up to  $130^\circ\text{K}$ , and then every  $10^\circ\text{K}$  up to  $300^\circ\text{K}$ , with precautions being taken to insure that the system came to satisfactory thermal equilibrium. Repeated measurements at the same temperature yielded the same data. The system used for these measurements was similar to that described by Henry and Schroeder.<sup>14</sup>

For measurements above 293°K, gold and copper were used as alternative standards. They both have sufficiently small thermopowers at the temperatures of interest that small percentage errors in their estimated value will produce small errors in the thermopower of aluminum. Their thermopowers were measured against Pb from 77 to 300°K using the system described above. The thermopower of copper above 300°K was then obtained from the equation  $S = 0.08 + 5.45 \times 10^{-3}T \mu\text{V}/^\circ\text{K}$ , where the slope is taken from Nystrom,<sup>15</sup> and the constant term is chosen to make the equation coincide with our low-temperature data at 300°K. The thermopower for gold above 300°K was obtained by increasing the numbers given by Cusack and Kendall<sup>16</sup> by  $0.08 \mu\text{V}$ , so that they would agree with our low-temperature data at 300°K.

The constant-temperature bath consisted of stirred water, maintained at  $29.8^\circ\text{C}$  to within  $\pm 0.05^\circ\text{K}$ . The temperature of the hot junction was determined in earlier measurements with a Leeds and Northrup Chromel-Alumel thermocouple specified accurate to  $\pm 1^\circ\text{K}$  for  $T \leq 600^\circ\text{K}$ , and to  $\frac{2}{3}\%$  for higher temperatures. Later measurements were made with an annealed Leeds and Northrup Pt-Pt at. 10%Rh thermocouple specified accurate to within  $\pm 1^\circ\text{K}$  to above  $800^\circ\text{K}$ .

The temperature of the hot junction could be measured and held constant during a measurement to better than  $0.05^\circ\text{K}$ . Voltages were measured about every  $10^\circ\text{K}$  with a precision of  $0.01 \mu\text{V}$ , using either a Honeywell No. 2779 potentiometer or a Honeywell

<sup>13</sup> J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).

<sup>14</sup> W. G. Henry and P. A. Schroeder, Can. J. Phys. **41**, 1076 (1963).

<sup>15</sup> J. O. Nystrom, Arkiv Mat. Astron. Fysik **34A**, 27 (1947).

<sup>16</sup> N. Cusack and P. Kendall, Proc. Phys. Soc. (London) **72**, 898 (1958).

No. 2768, 6-dial potentiometer, each with a photoelectric galvanometer. Measurements made with two completely independent sets of measuring equipment yielded results which were identical within our random measuring error.

A schematic drawing of the high-temperature measuring apparatus is shown in Fig. 1. The specimen and standard were spotwelded together at the hot junction, as were the two legs of the temperature-measuring thermocouple. The hot junctions were placed in a cavity within the cylindrical aluminum block. The ends of the two thermocouples were either pressed together, one on top of the other, between the block and an aluminum disk held down by a stainless-steel screw; pressed side by side between the block and the disk; or, in later measurements, spotwelded to  $\frac{1}{16}$ -in. thick gold disks between which they were pressed, side by side. No significant difference in output voltage resulted from these changes. The thermocouples were brought out of the aluminum block through thin, high-purity alumina tubes down to the bottom of the container, where they passed through electrically insulated lead-thru's out to the water bath. These lead-thru's were sealed with Apiezon wax to provide vacuum-tight connections. About 8 in. into the bath the leads were soldered to copper wires which were brought out of the bath to the measuring equipment. Although the system was usually evacuated by forepump during a measurement, the specimen versus standard output voltage was occasionally measured at constant temperatures between 250 and 350°C with air, nitrogen, or helium in the chamber, to test whether a change in temperature distribution along the wire would change the measured voltage. While the equilibrium output voltage usually changed by some microvolts from its vacuum value when a gas was admitted, the changes were reversible, systematically larger at higher temperatures, and so small as to cause changes in the thermopower of only a few hundredths of a microvolt per degree Kelvin. Measurements made while the temperature of the hot junction was decreasing, subsequent to measurements from room temperature up to above 700°K, usually yielded thermopowers which were a few hundredths of a microvolt per degree less negative than those obtained on the way up. Apparently some change in property of at least one component of the specimen-standard thermocouple occurred when we reached these high temperatures. Estimates of the amount of diffusion of gold or copper into aluminum which could occur in 5 min at 700°K suggest that the aluminum near the hot junction could have become strongly contaminated. After high-temperature measurements, visible changes of color were observed in those parts of both the aluminum and the copper or gold wires which were near the hot junction. We have therefore assumed that the thermopowers measured with increasing temperature are the most reliable. Finally, measurements of the thermopower at temperatures above 700°K were not

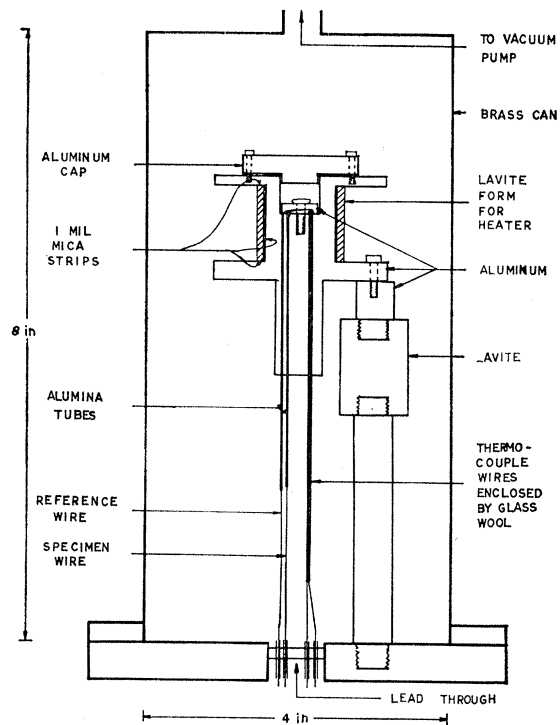


Fig. 1. Schematic drawing of experimental apparatus.

satisfactorily reproducible from specimen to specimen. Sometimes these data increased in magnitude less rapidly with temperature than the lower-temperature data, and sometimes they increased more rapidly. We will therefore present and discuss only data taken up to about 700°K.

## DATA

The solid line in Fig. 2 represents the absolute thermopower of aluminum as determined using Pb as the standard. It is representative of data taken on five independent annealed specimens, from the three different manufacturers. Four additional unannealed speci-

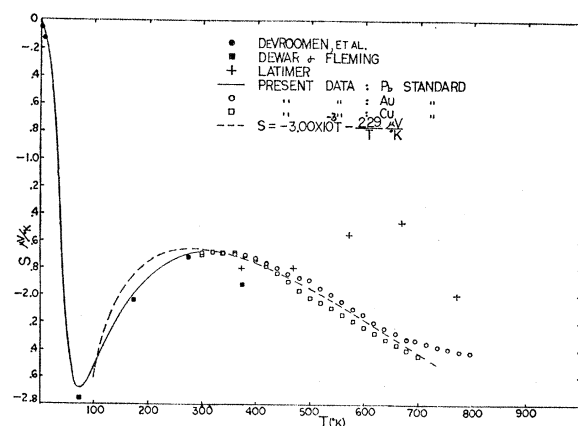


Fig. 2. The thermopower of pure aluminum.

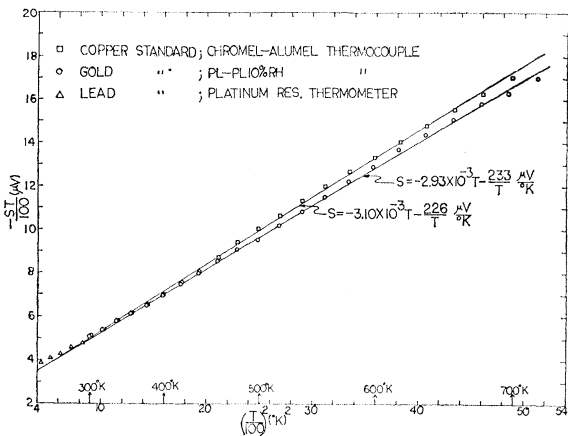


Fig. 3. Plot of  $ST$  versus  $T^2$  for the data of Fig. 2.

mens were also measured, and two independent Pb specimens were used. For temperatures above  $100^\circ\text{K}$ , all nine sets of data agreed with the curve shown to within  $\pm 0.02 \mu\text{V}/^\circ\text{K}$ . At lower temperatures, the reproducibility was poorer, with deviations of as much as  $0.1 \mu\text{V}/^\circ\text{K}$  occasionally occurring on the rapidly rising, low-temperature side of the phonon-drag peak, predominantly between specimens from different manufacturers. In this temperature region, the annealed specimens generally yielded thermopowers slightly smaller in magnitude than unannealed specimens from the same manufacturer; but this difference rarely exceeded  $0.1 \mu\text{V}/^\circ\text{K}$ .

Figure 2 also shows the computer-produced thermopower for two representative sets of measurements at temperatures above  $300^\circ\text{K}$ . The thermopower of aluminum using gold as standard was obtained using Pt-Pt at 10%Rh as the temperature measuring thermocouple; similar data obtained using Chromel-Alumel were in good agreement with those shown. For the measurement against copper, Chromel-Alumel was used to determine the temperature. From the observed insensitivity of the measured voltages to the perturbations noted in the previous section, and from the reproducibility between thermopowers obtained with different aluminum specimens coupled to independent standard specimens, we think it unlikely that random and systematic errors associated with our measuring technique and equipment could produce a standard deviation larger than  $0.05 \mu\text{V}/^\circ\text{K}$ . The difference between the two sets of data shown in Fig. 2 is probably due largely to errors in the estimated thermopowers of one or both of the standards.

Some values of the thermopower of aluminum obtained by previous investigators are also shown in Fig. 2. DeVrooman *et al.*<sup>17</sup> measured the thermopower of aluminum from 2 to  $9^\circ\text{K}$  against superconducting

Niobium. Dewar and Fleming<sup>18</sup> measured it against Pb in the range between  $78$  and  $373^\circ\text{K}$ .

All of the high-temperature measurements<sup>19-21</sup> were made against standards, Pt, W, and Ag, whose thermopowers are large, and not sufficiently well known for our present purposes. As an example, we show the data of Latimer,<sup>22</sup> measured relative to Ag. To obtain these data, we used the thermopower of Ag given by Cusack and Kendall.<sup>16</sup>

### INTERPRETATION OF DATA

Figure 3 shows the two sets of high-temperature data from Fig. 2 plotted in the form  $ST$  versus  $T^2$ . The data are indeed consistent with straight lines for temperatures above  $300^\circ\text{K}$ , determining values of  $A$  and  $B$  which satisfy the condition  $AT$  approximately equal to  $B/T$  at  $300^\circ\text{K}$ . Similar plots of  $S/T$  versus  $1/T^2$ , which weight the low-temperature points more heavily, yield essentially the same results. The equation determined from an average of these two sets of data is shown as a dashed line in Fig. 2. As can be seen, this line yields a reasonable approximation to the data all the way down to the phonon-drag peak. We suggest that this analysis represents the best presently available means for separating the high-temperature thermopower of aluminum into its two component parts.

Although our high-temperature data do have the temperature dependence predicted by Eq. (1), the magnitude of the measured  $S_e$  is only half that predicted by Eq. (4), and the magnitude of  $S_o$  is only a few percent of the value obtained by combining Eq. (7) with Eq. (4). In the following, we will describe conditions on the properties of aluminum which would allow our experimental data to be reconciled with Eqs. (3) and (5), taking care to distinguish between those properties of aluminum which appear reasonably well established, and those for which detailed calculations will be necessary.

We first consider  $S_e$  in terms of Eq. (3). Because the shape of the Fermi surface of aluminum is known to deviate but little from a free-electron sphere, except where this sphere intersects Brillouin zone boundaries,<sup>23</sup> we do not expect the number  $\frac{3}{2}$  appearing inside the bracket to be substantially changed. However, since the electronic specific heat<sup>24</sup> and the room-temperature Hall coefficient<sup>25</sup> of aluminum agree with the predicted free-electron values only to within 50%, we will allow this number to vary between 1 and 2. This means that Eq. (3) will yield the measured  $S_e$  if  $\partial(\ln\sigma)/\partial\epsilon$  lies between about  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . Since normal, isotropic

<sup>17</sup> J. Dewar and J. A. Fleming, *Phil. Mag.* **40**, 95 (1895).

<sup>18</sup> International Critical Tables **6**, 213 (1930).

<sup>19</sup> G. Borelius, *Handbuch Metall. Physik* **1**, 185 (1935).

<sup>20</sup> T. Ricker and G. Schaumann, *Physik Kondensierten Materie* **5**, 31 (1966).

<sup>21</sup> W. M. Latimer, *J. Am. Chem. Soc.* **44**, 2136 (1922).

<sup>22</sup> W. A. Harrison, *Phys. Rev.* **118**, 1182 (1960).

<sup>23</sup> F. A. Otter and D. Mapother, *Phys. Rev.* **125**, 1171 (1962).

<sup>24</sup> International Critical Tables **6**, 416 (1929).

<sup>17</sup> A. R. DeVrooman, C. Van Baarle, and A. J. Cuelenaere, *Physica* **26**, 19 (1960).

electron-phonon scattering yields a contribution to  $\partial(\ln\tau)/\partial\epsilon$  of  $\frac{2}{3}$ , such scattering cannot dominate  $\tau$ . Indeed, calculations of the electrical resistance of aluminum<sup>26</sup> imply that umklapp scattering is dominant at high temperatures. A similar calculation of  $\partial(\ln\tau)/\partial\epsilon$ , taking into account both anisotropic scattering and umklapp scattering, is necessary before we can say more.

We now turn to  $S_\theta$ . We can obtain the proper temperature dependence by assuming, as suggested above, that the temperature dependence of both the normal and umklapp contributions to  $S_\theta$  are dominated by  $\tau_{pp}$  (which decays with increasing temperature approximately as  $1/T$ ), provided that the phonon-dispersion relation for aluminum does not deviate too greatly from the form  $\omega=vq$ . ( $\omega$  is the phonon's energy,  $q$  is its crystal momentum, and  $v$  is a velocity comparable to the velocity of sound in aluminum.) Blatt<sup>27</sup> has shown that substantial deviations from this condition can produce a more rapidly decaying high-temperature thermopower. In fact, the phonon-dispersion curves for aluminum have nearly the form  $\omega=vq$ , except for the very highest energy phonons.<sup>28</sup> Since, in addition, the complete phonon spectrum of aluminum is similar to a Debye spectrum (although its high-frequency states are less numerous, and some middle-frequency states are more numerous than those in the Debye spectrum), we do not believe that deviations of either the phonon spectrum or the phonon-dispersion relation from Debye form can be the major cause for the small measured value of  $S_\theta$ . Rather, we suggest that this small magnitude is due mostly to a cancellation between the various contributions to  $S_\theta$  arising from normal and umklapp scattering from different parts of the Fermi surface of aluminum.

Although the Fermi surface of aluminum is so complicated that a correct description of the relative contributions of normal and umklapp scattering to  $S_\theta$  probably cannot be made without detailed calculations, some qualitative observations concerning the sign of these contributions can be made by assuming, as suggested by Ziman,<sup>29</sup> that this sign depends only upon whether the phonon crystal momentum vector involved in the electron scattering crosses a region in  $k$  space which is occupied or unoccupied by electrons. If the region crossed is occupied, the contribution to  $S_\theta$  is negative; if unoccupied, the contribution to  $S_\theta$  is positive. Figure 4 shows a schematic drawing in the repeated-zone scheme, of two-dimensional slices through

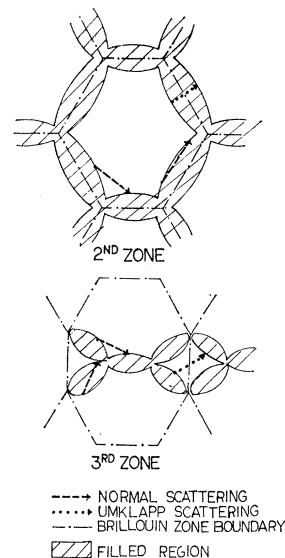


FIG. 4. Schematic representation of some electron-phonon scattering events in the 2nd- and 3rd-zone portions of the Fermi surface of aluminum.

the second- and third-zone portions of the Fermi surface of aluminum. We assume that the first zone is completely filled with electrons, and that the fourth zone is empty. A number of electron-phonon scattering events are also shown; normal scattering is designated by a dashed line, umklapp scattering by a dotted line. The Brillouin zone boundaries are indicated by broken lines. In the third zone, normal scattering will produce both positive and negative contributions to  $S_\theta$ , and umklapp scattering will produce mostly positive contributions. In the second zone, while normal scattering will again produce both positive and negative contributions to  $S_\theta$ , umklapp scattering will now produce mostly negative contributions. We can obtain qualitative agreement with our measured results by assuming that this second-zone umklapp scattering yields the dominant contribution, with the remaining scattering processes combining to produce either a smaller positive contribution, or nearly nothing at all. Clearly, this should be investigated through detailed calculation.

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