

duction in the frequency observed at largest  $n_0$  and  $E_0$  would be due to an increase in the ratio of  $C/Q_0$ . This brings the system close to the conditions of case 2, which lowers the frequency, as shown in Fig. 2. The increase in  $C/Q_0$  comes from overdriving the phonon distribution, as discussed above. The quantity  $Y$  in Eq. (3.59) depends on  $E_0$  and  $n_0$ .

The oscillations observed in GaAs may fit this analysis.<sup>2</sup> Larger values of  $n_0$ , smaller values of  $m^*$  and larger  $v_d$  will increase  $\Omega_0$ . For  $n_0 \approx 10^{14} - 10^{15}$ ,  $v_d \approx 10^7$ , and  $m_e^* \approx 0.02m_e$ , the value of  $\Omega_0 \approx 10^9$ . The fundamental mode of crystals, of the order of  $10^{-1}$  cm, would then be in the long- to intermediate-wavelength region, and the spontaneous oscillations observed would correspond roughly to the behavior exhibited in Fig. 4.

The large drift velocities required for oscillation could be necessary to bring the fundamental mode of the crystal to the high- $Q$  side of the cutoff, i.e.,  $v_d Q' \approx \Omega_0$ . Similarly, the high drift velocities may be necessary before strong electron-phonon coupling occurs. The theory developed in paper I should be limited to the cases where  $v_d - v_s/v_s < 1$ , and the extrapolation to oscillations in GaAs, where  $v_d/v_s \approx 100$ , should be viewed with caution.

#### ACKNOWLEDGMENTS

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### Thermoelectric Size Effect in Pure Gold\*

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The difference between the thermoelectric power of thin gold foils and a 0.010-in.-diam gold wire was measured between 77°K and room temperature. The electrical resistance difference between the foils and the wire was determined simultaneously. From the experimental results, the energy dependence of the electron mean free path and of the area of the Fermi surface in gold was obtained. Both the electron mean free path and the area of the Fermi surface decrease with increasing electron energy, which is opposite to the behavior expected from the free-electron model of a metal. The electron mean free path obtained from the resistance measurements is in agreement with the value derived from the anomalous skin effect.

#### I. INTRODUCTION

THE positive sign of the electronic component of the absolute thermoelectric power of the noble metals has been discussed recently in a series of theoretical papers.<sup>1-4</sup> The electronic component  $S_e^0$  of the thermoelectric power depends on the way in which the area of the Fermi surface and the electron mean free path vary with the electron energy. In the free-electron model of a metal the energy dependence of both the area of the Fermi surface and the electron mean free path yield a negative term in the electronic thermoelectric power. When it was found that the Fermi surface in the noble metals is distorted and touches the zone boundaries, it was suggested<sup>1</sup> that the area of the Fermi surface might decrease sufficiently rapidly with increasing energy of the electrons to yield a positive electronic thermoelectric power. However, it appears today that the positive value of  $S_e^0$  in the noble metals

is caused by deviations from the free electron value of both the term containing the area of the Fermi surface and the term containing the electron mean free path.<sup>2</sup>

Since in the electronic thermoelectric power of a pure metal, the term containing the area of the Fermi surface and the term containing the electron mean free path always appear combined, it is usually not possible to measure each term separately. However, the term of  $S_e^0$  containing the electron mean free path can be determined separately by measuring the effect of the specimen size on the electronic thermoelectric power. In the present investigation the influence of the specimen size on the electronic thermoelectric power is studied with high-purity gold foils in the temperature range between 77 and 296°K. From the results, the term of  $S_e^0$  containing the electron mean free path and the term containing the area of the Fermi surface are obtained separately.

#### II. THEORY

The absolute thermoelectric power  $S^0$  of a pure metal consists of a contribution  $S_e^0$ , arising from the non-equilibrium distribution of the conduction electrons, and a contribution  $S_\phi^0$ , caused by the interaction be-

\* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, England, 1960), p. 399.

<sup>2</sup> J. M. Ziman, *Advan. Phys.* **10**, 1 (1961).

<sup>3</sup> P. L. Taylor, *Proc. Roy. Soc. (London)* **A275**, 209 (1963).

<sup>4</sup> F. J. Blatt, *Phys. Letters* **8**, 235 (1964).

tween the conduction electrons and the phonons, which are not in equilibrium:

$$S^0 = S_e^0 + S_g^0. \quad (1)$$

$S_e^0$  and  $S_g^0$  are usually called electronic thermoelectric power and phonon-drag thermoelectric power, respectively. The electronic thermoelectric power of a pure metal is given by

$$S_e^0 = -\frac{\pi^2 k_B^2 T}{3eE_F} \left\{ \frac{\partial \ln l(E)}{\partial \ln E} + \frac{\partial \ln \mathfrak{S}(E)}{\partial \ln E} \right\}_{E_F}. \quad (2)$$

Here  $k_B$  is Boltzmann's constant,  $T$  the absolute temperature, and  $e$  the absolute value of the elementary charge.  $l$  and  $E$  are the mean free path and the energy of the conduction electrons, respectively.  $\mathfrak{S}$  is the area of the Fermi surface.  $E_F$  is the Fermi energy. In order to yield a positive value of  $S_e^0$ , at least one term in the bracket of Eq. (2) must be negative. In the free-electron approximation we have

$$\alpha \equiv \left\{ \frac{\partial \ln \mathfrak{S}(E)}{\partial \ln E} \right\}_{E_F} = 1. \quad (3)$$

When it was found that the Fermi surface in the noble metals is distorted and touches the zone boundaries, it was suggested<sup>1</sup> that the area of the Fermi surface might decrease sufficiently rapidly with increasing energy of the electrons to make  $\alpha$  negative. However, from an analysis of the transport properties of the noble metals Ziman<sup>2</sup> concluded that  $\alpha$  is reduced below the free-electron value, but still remains positive. Ziman estimated  $\alpha$  to be in the range between 0 and 0.5. He pointed out that the positive sign of  $S_e^0$  of the noble metals must be due to the first term in the bracket of Eq. (2).

To explain the positive sign of  $S_e^0$  in the noble metals, we require an electron mean free path which decreases rapidly with increasing electron energy. In the free-electron approximation the term  $\partial \ln l(E)/\partial \ln E$  for scattering by lattice vibrations is positive and equal to 2. Ziman<sup>2</sup> noted that in the noble metals the electron mean free path should be anisotropic over the Fermi surface, with  $l_{\text{neck}} < l_{\text{belly}}$ , and that a more complete theory of the function  $l(E)$  is necessary to explain the thermoelectric power. Here  $l_{\text{neck}}$  and  $l_{\text{belly}}$  refer to the mean free paths of the electron-phonon scattering. A calculation by Taylor,<sup>3</sup> which took into account the anisotropy of the electron mean free path, again yielded a negative sign of the electronic component of the thermoelectric power of copper.

Blatt<sup>4</sup> suggested that electron-electron interaction could lead to an effective belly mean free path which decreases sufficiently rapidly with increasing electron energy to yield a positive electronic thermoelectric power.

The quantity  $\left\{ \frac{\partial \ln l(E)}{\partial \ln E} \right\}_{E_F}$  can be determined experimentally by measuring the influence of the specimen size on the electronic thermoelectric power.

The electrical resistivity  $\rho$  of thin wires or foils is larger than the resistivity  $\rho_0$  of the bulk material due to the scattering of the electrons at the surface of the specimen. The resistance increase due to surface scattering is for a cylindrical wire<sup>5</sup>

$$\Delta\rho \equiv \rho - \rho_0 = (3/4\kappa)\rho_0 \quad (4)$$

and for a foil<sup>6</sup>

$$\Delta\rho \equiv \rho - \rho_0 = (3/8\kappa)\rho_0. \quad (5)$$

Here  $\kappa = a/l$ , where  $a$  is the diameter of the wire or the thickness of the foil. In Eqs. (4) and (5) it is assumed that  $\kappa \gg 1$  and that the electrons are scattered diffusely at the specimen surface. The change of the electronic thermoelectric power due to additional scattering events in the bulk material, which cause a resistivity increase  $\Delta\rho$ , is given by<sup>6</sup>

$$\Delta S \equiv S_e - S_e^0 = \frac{S_e^0}{(\rho_0/\Delta\rho) + 1} \left\{ \frac{(\partial \ln \Delta\rho/\partial E)}{(\partial \ln \rho_0/\partial E)} - 1 \right\}_{E_F}. \quad (6)$$

Here  $S_e$  is the electronic thermoelectric power of the material, whose electrical resistivity is increased by  $\Delta\rho$  due to the additional electron-scattering events. In the derivation of Eq. (6) the following assumptions are required:

(1) The additional scattering of electrons, which causes the resistivity increase  $\Delta\rho$ , and all other electron scattering events in the crystal are independent of each other (Matthiessen's rule).

(2) The heat which is transported by the conduction electrons is independent of other heat-transporting mechanisms (phonons).

(3) The electrical conductivity and the electronic component of the heat conductivity are determined by the same relaxation time (Wiedemann-Franz law).

Inserting Eqs. (4) and (5) into Eq. (6) and with the relation  $\Delta\rho \ll \rho_0$  we obtain for the difference between the electronic thermoelectric power of a foil of thickness  $a_1$  and a wire of diameter  $a_2$

$$\Delta S_e \equiv S_e^{\text{foil}} - S_e^{\text{wire}} = \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) \frac{\pi^2 k_B^2 T l}{4eE_F} \left\{ \frac{\partial \ln l(E)}{\partial \ln E} \right\}_{E_F}. \quad (7)$$

An equation similar to Eq. (7) has been derived by Justi, Kohler, and Lautz<sup>7</sup> from a solution of the Boltzmann equation for the case of thin films and wires. As seen from Eq. (7) thermoelectric measurements carried out with a thermocouple made of two fine specimens with different thickness yield information on the quantity  $\left\{ \frac{\partial \ln l(E)}{\partial \ln E} \right\}_{E_F}$ .

<sup>5</sup> E. H. Sondheimer, *Advan. Phys.* **1**, 1 (1952).

<sup>6</sup> R. P. Huebener, *Phys. Rev.* **135**, A1281 (1964).

<sup>7</sup> E. Justi, M. Kohler, and G. Lautz, *Z. Naturforsch.* **6A**, 544 (1951).

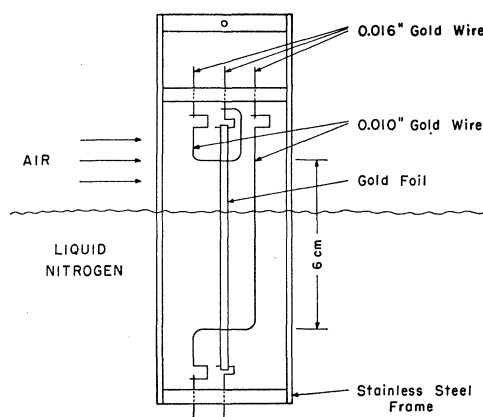


FIG. 1. Scheme of the specimen.

### III. EXPERIMENTAL

The specimen material was polycrystalline 99.999% pure gold wire of 0.010 in. diameter.<sup>8</sup> Foils with a thickness of  $1.5 \times 10^{-3}$  to  $2.5 \times 10^{-2}$  mm were manufactured from this wire by cold rolling. The wire was cold rolled between stainless-steel foils. The scheme of the specimen is shown in Fig. 1. The specimen consisted of a thermocouple made from a foil and two 0.010-in.-diam wires mounted on a stainless-steel sample holder. The specimen wires and the foil were spot welded to short pieces of 0.016-in.-diam gold wire which were attached to the sample holder. Before mounting, the specimen wires and foils were rinsed in nitric acid, distilled water, and acetone. After mounting, the foil and the wires of the specimen were annealed in air at about 850°C for 5 to 24 h and for 30 to 40 h, respectively, by passing direct current through them and were cooled gradually to room temperature. After annealing, the wires were spot welded to the foil to obtain the thermocouple consisting of both. The annealed specimen was handled carefully to introduce as little cold work as possible. The length of the foil between the hot and the cold junction was about 6 cm. The width of the foil was 3 to 6 mm.

During the thermoelectric measurements the sample holder was immersed into liquid nitrogen until the lower thermocouple junction was 1 to 4 cm below the liquid nitrogen level. Within this range the thermoelectric voltage varied by less than 10% with the position of the liquid-nitrogen level. The upper junction of the thermocouple was kept at room temperature by blowing air of the laboratory against it. An experiment, in which a thin thermocouple (gold 2.1% cobalt versus copper) was attached to a specimen, confirmed the fact that the upper region of the specimens was held at room temperature. The thermoelectric measurements were carried out using a Rubicon model 2768 microvolt potentiometer and a Rubicon model 3550 photoelectric

<sup>8</sup> Obtained from the Sigmund Cohn Corporation, Mount Vernon, New York.

galvanometer. The specimen was connected to the potentiometer with 99.999% pure gold wire.

After the thermoelectric measurements the electrical resistance of the foil and of the lower wire of the specimen was measured at room temperature, in a liquid-nitrogen bath, and in a liquid-helium bath. To measure the resistance of the lower specimen wire an additional potential lead was spot welded to this wire. The resistance measurements were carried out with conventional potentiometric techniques.

After completion of the experiment, the foil was cut off, and the length and width of the foil were measured with a micrometer microscope. The thickness of the foil was then determined from its weight using  $19.3 \text{ g/cm}^3$  for the density of gold.

An experiment within a cryostat,<sup>9</sup> in which the cold junction of the thermocouple was kept at 77.3°K and the temperature of the hot junction was raised up to 300°K, showed that  $\Delta S_e$  did not vary appreciably with the temperature between 77 and 300°K. In this experiment a foil with a thickness of  $5.4 \times 10^{-3}$  mm was used.

The ratio of the electrical resistance of the annealed 0.010-in.-diam gold wire at 296°K to that at 4.2°K was 2500 to 2800.

The difference in the electrical resistivity of the gold foils and the 0.010-in.-diam gold wire was determined from the ratios of their resistance at 296°K to that at 77.3°K and at 4.2°K. With

$$\{\rho(296^\circ\text{K})/\rho(T^*)\}_{\text{foil}} \equiv A \quad (8)$$

and

$$\{\rho(296^\circ\text{K})/\rho(T^*)\}_{\text{wire}} \equiv B \quad (9)$$

the resistivity difference  $\Delta\rho$  between the foils and the wire is given by

$$\Delta\rho = \rho_{\text{foil}} - \rho_{\text{wire}} = \rho_{\text{wire}}(296^\circ\text{K}) \times [(1-A/B)/(A-1)], \quad (10)$$

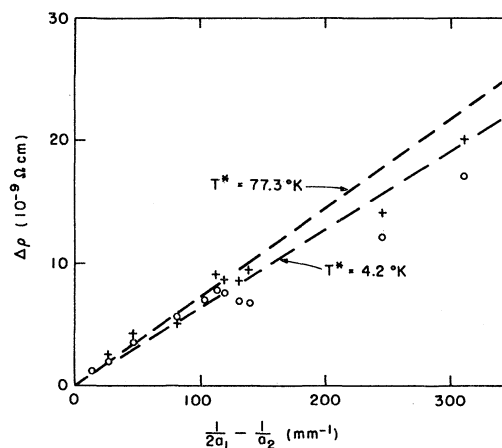


FIG. 2. Difference between the electrical resistivity of a gold foil of thickness  $a_1$  and a gold wire of diameter  $a_2 = 0.254$  mm, calculated from Eq. (10) for  $T^* = 77.3^\circ\text{K}$  (crosses) and  $T^* = 4.2^\circ\text{K}$  (circles).

<sup>9</sup> A description of the cryostat is given in Ref. 6.

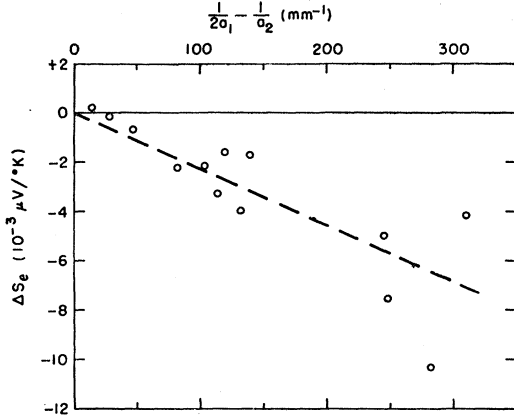


FIG. 3. Difference between the thermoelectric power of a gold foil of thickness  $a_1$  and a gold wire of diameter  $a_2=0.254$  mm in the temperature range between 77 and 296°K.

assuming that  $\Delta\rho$  is independent of the temperature. Here  $T^*$  is either 77.3 or 4.2°K. Under the condition that  $\kappa \gg 1$ , the difference in the electrical resistivity of a foil of thickness  $a_1$  and a wire of diameter  $a_2$ , according to Eqs. (4) and (5), is given by

$$\Delta\rho = \frac{3}{4}l\rho_0(1/2a_1 - 1/a_2). \quad (11)$$

The resistivity difference  $\Delta\rho$  between the gold foils and the 0.010-in.-diam gold wire, calculated with Eq. (10), is shown in Fig. 2 for  $T^*=77.3^\circ\text{K}$  and  $T^*=4.2^\circ\text{K}$  as a function of the geometric quantity  $(\frac{1}{2}a_1 - 1/a_2)$ . In the calculation of  $\Delta\rho$  the value

$$\rho_{\text{wire}}(296^\circ\text{K}) = 22.25 \cdot 10^{-7} \Omega \text{ cm} \quad (12)$$

was used. As seen from Fig. 2,  $\Delta\rho$  increases linearly with  $(1/2a_1 - 1/a_2)$ . The values of  $\Delta\rho$  obtained with the resistance data at 77.3°K are about 12% higher than the values obtained with the resistance data at 4.2°K. From the data of Fig. 2 for  $T^*=77.3^\circ\text{K}$ , the relation

$$l\rho_0 = (9.7 \pm 1.5) \times 10^{-12} \Omega \text{ cm}^2 \quad (13)$$

is calculated using Eq. (11). With the value of  $\rho_0(296^\circ\text{K}) \approx \rho_{\text{wire}}(296^\circ\text{K})$  given in Eq. (12) we then obtain

$$lT = (1.28 \pm 0.21) \times 10^{-3} \text{ cm}^\circ\text{K} \quad (14)$$

in the temperature range in which  $\rho_{\text{wire}}$  is linearly proportional to the temperature.

Figure 3 shows the thermoelectric power  $\Delta S_e$  of the thermocouple consisting of the gold foil and the gold wire as a function of the geometric quantity  $(1/2a_1 - 1/a_2)$ . For obtaining the data of Fig. 3 the thermoelectric voltage was divided by the temperature difference between the hot and the cold junction. Since, in gold, phonon-drag effects diminish at temperatures above about 100°K,<sup>6</sup> the phonon-drag contribution to the thermoelectric voltage was negligible. As seen from Fig. 3 a straight line going through the origin can be

fitted through the data. With Eq. (7) the value

$$\left\{ \partial \ln l(E) / \partial \ln E \right\}_{E_F} = -0.53 \pm 0.19 \quad (15)$$

was calculated from the data of Fig. 3. In the derivation of Eq. (15) the average value of  $l \times T$  given in Eq. (14) and the value  $E_F = 5.51$  eV were used. The value given in Eq. (15) is, of course, an average value over the Fermi surface. With Eqs. (2) and (15) and with the relation<sup>6</sup>

$$S_e^0 / T = 7.05 \times 10^{-3} \mu\text{V} / ^\circ\text{K}^2 \quad (16)$$

for gold, we obtain

$$\left\{ \partial \ln \mathcal{S}(E) / \partial \ln E \right\}_{E_F} = -1.05 \pm 0.19. \quad (17)$$

#### IV. DISCUSSION

The result given in Eq. (15) shows the decrease of the electron mean free path with increasing energy as suggested by theory.<sup>2,4</sup> Equation (17) indicates that also the Fermi surface decreases appreciably with increasing energy, in disagreement with Ziman's<sup>2</sup> estimate, mentioned above, that  $\alpha$  should have a positive value smaller than about 0.5.

Bailyn<sup>10</sup> calculated the thermoelectric power of a metal using the variational method. In the temperature range in which the Wiedemann-Franz law is valid he obtained for  $S_e^0$  the expression

$$S_e^0 = -\frac{\pi^2 k_B^2 T}{3eE_F} \cdot 2 \left\{ \frac{\partial n[v(E)\mathcal{S}(E)]}{\partial \ln E} \right\}_{E_F}. \quad (18)$$

Here  $v$  is the velocity of the electrons. Apparently in Bailyn's treatment the term in the electronic thermoelectric power which depends on the electron mean free path is replaced by quantities which are only functions of the geometry of the Fermi surface. Using Eqs. (18) and (16) together with Eq. (17) we find

$$\left\{ \partial \ln v(E) / \partial \ln E \right\}_{E_F} = 0.26 \pm 0.19. \quad (19)$$

The density of states  $n(E)$  is given by<sup>11</sup>

$$n(E) = \frac{1}{8\pi^3} \int \frac{d\mathcal{S}}{|\text{grad}_k E|}. \quad (20)$$

If we approximate the integral in Eq. (20) by  $\mathcal{S}(E) / \hbar v(E)$  ( $\hbar$  = Planck's constant) we obtain from Eqs. (20), (17), and (19)

$$\left\{ \partial \ln n(E) / \partial \ln E \right\}_{E_F} = -1.31 \pm 0.38. \quad (21)$$

The average value of  $\left\{ \partial \ln v(E) / \partial \ln E \right\}_{E_F}$  given in Eq. (19) is somewhat smaller than the value of 0.5 obtained with the free electron model. In the free-electron approximation the derivative  $\left\{ \partial \ln n(E) / \partial \ln E \right\}_{E_F}$  is positive with a value of 0.5. Equation (21) indicates that the energy dependence of the density of

<sup>10</sup> M. Bailyn, Phys. Rev. **120**, 381 (1960).

<sup>11</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

states deviates in gold appreciably from the value expected from the free-electron model.

Since in the present experiment the thermoelectric measurements were carried out above 77°K, no information on the effect of the specimen size on the phonon-drag component of the thermoelectric power could be obtained. However, the influence of the specimen size on the phonon-drag component of the thermoelectric power can be measured by extending the present investigation to temperatures below 77°K. Such experiments would yield information on the relaxation time for phonon scattering by the crystal surface and would be very interesting.

The result of the present investigation is in disagreement with earlier attempts to measure thermoelectric size effects in the noble metals. These experiments were carried out with thin films of copper<sup>12</sup> and silver.<sup>13</sup> The films were prepared by evaporation and had a thickness lower than 2000 to 4000 Å. The thermoelectric power of the films was measured between 16 and 50°C<sup>12</sup> and between 0 and 200°C,<sup>13</sup> respectively. In the copper films<sup>12</sup> the film thickness was found to have no effect on the thermoelectric power. In the silver films<sup>13</sup> a thermoelectric power larger than that of the bulk material was observed. In both investigations the films were deposited on a substrate and could not be annealed at sufficiently high temperatures. Therefore, the thermoelectric size effect was probably masked by the presence of large concentrations of lattice defects within the films.

Nossek<sup>14</sup> measured the thermoelectric power of evaporated films of potassium, rubidium, and cesium

<sup>12</sup> L. Reimer, *Z. Naturforsch.* **12A**, 525 (1957).

<sup>13</sup> F. Savornin, J. Savornin, and A. Donnadieu, *Compt. Rend.* **254**, 3348 (1962).

<sup>14</sup> Reported by H. Mayer in *Structure and Properties of Thin Films*, edited by C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea (John Wiley & Sons, Inc., New York, 1959), p. 242.

as a function of the film thickness. The thermoelectric measurements were carried out by him between 60 and 90°K. From his experimental results Nossek calculated the quantity  $\{\partial \ln l(E)/\partial \ln E\}_{E_F}$ . For potassium, rubidium, and cesium he obtained the values 2.0, 2.1, and 2.3, respectively, which are in good agreement with the value of 2.0 expected from the free-electron model. In potassium, rubidium, and cesium the Fermi surface seems to be somewhat distorted, the distortion being larger in the last two metals than in the first one.<sup>15</sup> However, it does not appear that in any of these metals the Fermi surface touches the zone boundary. The electronic component of the thermoelectric power of these metals is negative, which one would expect from a free-electron model. It is therefore not surprising that in potassium, rubidium, and cesium the quantity  $\{\partial \ln l(E)/\partial \ln E\}_{E_F}$  is close to the free-electron value.

According to Fig. 2, the resistivity difference  $\Delta\rho$  between the gold foils and the 0.010-in.-diam gold wire measured at 4.2°K is the same, within about 12%, as the value obtained between 77 and 296°K. It appears therefore that for the scattering of electrons by the crystal surface the deviations from Mathiessen's rule are relatively small.

The value of  $l\rho_0$ , given in Eq. (13), is in good agreement with the value  $l\rho_0=12\cdot 10^{-12}\Omega\text{cm}^2$  obtained experimentally for gold from the anomalous skin effect.<sup>16</sup>

#### ACKNOWLEDGMENTS

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<sup>15</sup> M. H. Cohen and V. Heine, *Advan. Phys.* **7**, 395 (1958).

<sup>16</sup> D. K. C. MacDonald, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XIV, p. 188.