

## Thermoelectric size effect in noble metals\*†

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(Received 27 March 1975)

The difference between the thermoelectric power of thin foils ranging in size from  $2.54 \times 10^{-2}$  to  $1.52 \times 10^{-3}$  mm and a 0.254-mm wire of gold, copper, and silver was measured as a function of temperature from 4.2 to 333°K. The electrical resistance of the wire and the foils was measured at 4.2, 77.3, and 296°K. From the high-temperature results values were obtained for  $[\partial \ln l(\epsilon)/\partial \ln \epsilon]_{\epsilon_F}$  and  $[\partial \ln A(\epsilon)/\partial \ln \epsilon]_{\epsilon_F}$  of  $-0.58 \pm 0.08$  and  $-1.00 \pm 0.08$  for gold,  $-0.34 \pm 0.11$  and  $-1.20 \pm 0.11$  for copper, and  $+0.86 \pm 0.09$  and  $-1.91 \pm 0.09$  for silver, respectively. Analysis of the low-temperature results suggest that the thermoelectric size effect can be used to determine subparts per million concentrations of magnetic impurities in the noble metals.

### I. INTRODUCTION

The positive sign of the electronic thermoelectric power of the noble metals has been a nagging embarrassment to the theory of ordinary electron transport properties of solids for a number of years. The electronic thermoelectric power of a pure metal can be written<sup>1</sup>

$$S_e^0 = - \frac{\pi^2 k_B^2 T}{3e \epsilon_F} (U + V). \quad (1)$$

The parameters  $U$  and  $V$  are given by

$$U = \frac{\partial \ln l(\epsilon)}{\partial \ln \epsilon} \Big|_{\epsilon_F} \quad \text{and} \quad V = \left( \frac{\partial \ln A(\epsilon)}{\partial \ln \epsilon} \right)_{\epsilon_F}, \quad (2)$$

where  $k_B$  is Boltzmann's constant,  $T$  the absolute temperature,  $e$  the absolute value of the elementary charge,  $\epsilon_F$  the Fermi energy,  $l$  the mean free path of the conduction electrons, and  $A$  the area of a constant-energy surface. In a free-electron picture the energy dependence of  $U$  and  $V$  yields a negative electronic thermoelectric power if the carriers are electrons as determined by the Hall effect.

There have been several theoretical<sup>2-6</sup> attempts to explain the possible origin of the positive electronic thermoelectric power in the noble metals. All of these, except possibly that of Robinson,<sup>6</sup> have proven unsatisfactory in one way or another. Discussion of these attempts can be found elsewhere.<sup>7,8</sup>

These theoretical attempts to discover which term is causing the sign anomaly in the noble metals have been accompanied by experimental efforts to measure  $U$  and  $V$  separately, the most successful of which is perhaps that of Huebener.<sup>9</sup> He has shown that  $U$  can be experimentally determined by measuring the influence of sample size on the electronic thermoelectric power. Subsequently,  $V$  may be determined with the aid of Eq. (1) and the known value of  $S_e^0/T$  at high temperatures.

The thermoelectric size effect has been investi-

gated by numerous authors<sup>9-23</sup> in a series of metals. The first experiments of this kind were performed with thin-film samples prepared by evaporation.<sup>10-16</sup> Later experiments were carried out with thin foil samples obtained by cold rolling and subsequent annealing.<sup>9,17,20</sup> Recently, further experiments have been carried out with evaporated films of the noble metals.<sup>18,19,21-23</sup>

In this experiment the difference in thermoelectric emf between a well-annealed rolled foil and a well-annealed wire was measured as a function of temperature from 4.2 to 333°K, and the difference in the thermoelectric power between the foil and the wire was determined.

The high-temperature data are used to determine the values of  $U$  and  $V$  for each of the noble metals. These values are then compared to those predicted by Robinson.<sup>6</sup>

The low-temperature data are explained by the effect of minute concentrations of unoxidized magnetic impurities, chiefly iron. Analysis indicates that the thermoelectric size effect may provide a unique method of determining magnetic-impurity concentrations of less than 1 part per million (ppm) in the noble metals.

### II. THEORY

#### A. High-temperature thermoelectric size effect

At high temperatures the phonon-drag and second-order diffusion effects go to zero. This leaves the electronic thermoelectric power as the only remaining contribution to the absolute thermoelectric power.

By measuring the influence of specimen size on the electronic thermoelectric power Huebener<sup>7</sup> has shown that  $U$ , as given by Eq. (2), can be determined experimentally. He found that the difference between the electronic thermoelectric power of a foil of thickness  $a_1$  and a wire of diameter  $a_2$  is given by

$$\Delta S_e \equiv S_e^{\text{foil}} - S_e^{\text{wire}} = \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) \frac{\pi^2 k_B^2 T l}{4e \epsilon_F} \left( \frac{\partial \ln l(\epsilon)}{\partial \ln \epsilon} \right)_{\epsilon_F}. \quad (3)$$

As can be seen from Eq. (3), measurements of the size effect on the electronic thermoelectric power yield information on the quantity  $U$ . Using Eq. (1) and a knowledge of  $S_e^0/T$  at high temperatures we can obtain an estimate of the quantity  $V$ .

#### B. Low-temperature effects

At low temperatures there are two effects to be considered: effects due to magnetic impurities, and the effect of specimen size on the phonon-drag thermoelectric power.

"Pure" samples of the noble metals, i. e., the best material available from commercial sources, exhibit an anomalous thermoelectric power at temperatures less than 10 °K due to the presence of magnetic transition-metal impurities, chiefly iron.<sup>24-29</sup> Kondo,<sup>30-32</sup> in his investigation of dilute magnetic alloys, has shown that the thermoelectric power due to magnetic impurities can be approximated by

$$S_{Fe} = S_0 \frac{T}{T + T_0}. \quad (4)$$

$S_0$  is a constant and  $T_0$  the position of the low-temperature (10 °K) peak in the absolute thermoelectric power of the noble metals. For very dilute alloys,  $S_0$  is nearly independent of concentration while  $T_0$  increases with increasing concentration. Guenault<sup>28</sup> has had some success in fitting Eq. (4) to the experimental results in the noble metals.

When more than one type of scattering is present, the resultant thermopower is the average of the intrinsic thermopowers of the components weighted according to the expression<sup>33</sup>

$$S = \frac{\sum_i \rho_i S_i}{\sum_i \rho_i} = \frac{\sum_i \rho_i S_i}{\rho}. \quad (5)$$

$\rho_i$  is the resistivity due to the  $i$ th component of the scattering present and  $S_i$  its thermoelectric power. In the present case let us consider the electronic thermoelectric power of the pure metal  $S_1$ , due to surface scattering  $S_2$ , due to magnetic impurities  $S_3$ , and their respective resistivities:

$$S = \frac{\rho_1 S_1}{\rho} + \frac{\rho_2 S_2}{\rho} + \frac{\rho_3 S_3}{\rho}. \quad (6)$$

Defining  $\rho_{SE} = \rho_1 + \rho_2$  we can rewrite Eq. (6) in the following form:

$$S = \frac{\rho_{SE} S_{SE}}{\rho} + \frac{\rho_3 S_3}{\rho}. \quad (7)$$

$S_{SE}$  is the size-effect electronic thermoelectric power you would measure in a foil or wire separately and is given by

$$S_{SE} = \frac{\rho_1 S_1}{\rho_1 + \rho_2} + \frac{\rho_2 S_2}{\rho_1 + \rho_2}. \quad (8)$$

The difference in the electronic thermoelectric power between a foil and a wire is

$$\Delta S \equiv S^f - S^w = \frac{\rho_{SE}^f}{\rho^f} S_{SE}^f - \frac{\rho_{SE}^w}{\rho^w} S_{SE}^w + \frac{\rho_3^f}{\rho^f} S_3^f - \frac{\rho_3^w}{\rho^w} S_3^w \quad (9)$$

$$= \Delta S_{SE} + \frac{\rho_3^f}{\rho^f} (S_3^f - S_{SE}^f) - \frac{\rho_3^w}{\rho^w} (S_3^w - S_{SE}^w). \quad (10)$$

$\Delta S_{SE}$  is the size-effect electronic thermoelectric power one would measure if no other scattering events were present. The resistivity  $\rho_3$  and electronic thermoelectric power  $S_3$  due to magnetic impurities are a property of the impurity and not of sample configuration. Thus,  $S_3^w = S_3^f = S_3$  and  $\rho_3^w = \rho_3^f = \rho_3$ . Equation (10) then becomes

$$\Delta S = \Delta S_{SE} + \rho_3 \left( \frac{S_3 - S_{SE}^f}{\rho^f} - \frac{S_3 - S_{SE}^w}{\rho^w} \right). \quad (11)$$

We take the form of  $S_3$  from Eq. (4) and experimentally we know that  $S_0$  is of the order of 10  $\mu\text{V}/^\circ\text{K}$ .<sup>34</sup> We also know that<sup>9</sup>

$$\frac{S_{SE}^f}{T} \approx \frac{S_{SE}^w}{T} \approx \frac{S_e^0}{T} \approx 0.007 \mu\text{V}/^\circ\text{K}.$$

We will therefore neglect  $S_{SE}^f$  and  $S_{SE}^w$  in Eq. (11), giving us

$$\Delta S = \Delta S_{SE} + \rho_3 S_3 \left( \frac{1}{\rho^f} - \frac{1}{\rho^w} \right). \quad (12)$$

An estimate (see below) of  $\Delta S_{SE}$  at low temperature yields a value of the order of 0.01  $\mu\text{V}/^\circ\text{K}$ . Owing to the magnitude of the effect observed we will neglect the  $\Delta S_{SE}$  contribution in the following calculation. Thus,

$$\Delta S = \rho_3 S_3 \left( \frac{1}{\rho^f} - \frac{1}{\rho^w} \right) = \rho_3 S_0 \frac{T}{T + T_0} \left( \frac{1}{\rho^f} - \frac{1}{\rho^w} \right). \quad (13)$$

This form will be used to analyze the observed results in the low-temperature region.

In addition to the effect of magnetic impurities, the phonon scattering at the crystal surface causes a change in the phonon-drag component of the thermoelectric power. Studies of the size effect on the phonon-drag thermoelectric power should yield information on the average phonon mean-free path in the bulk material as a function of temperature. The boundary scattering of phonons is analogous to that of electrons. Therefore, the theory developed for electrons<sup>35</sup> can be used directly to describe the boundary scattering of phonons. Huebener<sup>17</sup> has found that the change in the phonon-drag thermoelectric power between a foil of thickness  $a_1$  and a cylindrical wire of diameter  $a_2$  can be expressed approximately as

$$-\frac{\Delta S_g^{\text{SE}}}{S_g^0} = \frac{3}{4} \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) A e^{T^*/T}, \quad (14)$$

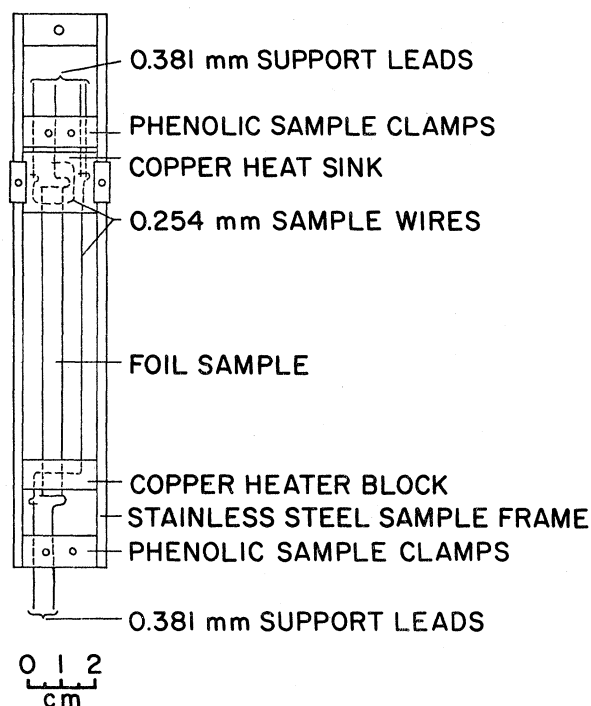


FIG. 1. Sample holder and sample.

where  $S_g^0$  is the phonon-drag thermoelectric power of the bulk material and  $T^*$  is about half the Debye temperature. Equation (14) should be valid between the temperature of the phonon-drag peak and the Debye temperature. Using an approximate<sup>17</sup> value of  $A = 1.1 \times 10^{-5}$  mm for the noble metals we estimate that  $|\Delta S_g^{SE}| \approx 0.01 \mu\text{V}/^\circ\text{K}$  and can be neglected as an explanation of the  $0.3\text{-}\mu\text{V}/^\circ\text{K}$  peak seen in this experiment at low temperatures.

### III. EXPERIMENT

The samples were prepared from 99.999%-pure wire. Gold wire was obtained from Sigmund Cohn Corp.,<sup>36</sup> copper wire from A. D. Mackay, Inc.,<sup>37</sup> and silver wire from Ventron Alfa Products.<sup>38</sup> Foils with a thickness of  $2.54 \times 10^{-2}$  to  $1.524 \times 10^{-3}$  mm were manufactured from this wire by cold rolling. This was done by Microfoils.<sup>39</sup> The samples consisted of a thermocouple made from a foil and two  $2.54 \times 10^{-2}$ -mm-diam wires. Before assembling, the components were acid etched, rinsed in distilled water, acetone, and finally methanol. Gold was etched in nitric acid, copper in a 25% (by volume) nitric acid solution, and silver in hydrochloric acid. The sample and sample holder are illustrated in Fig. 1. The wires were bent and the sample spot welded together. The length of the foil between the hot and the cold junctions was about 9 cm. The foils were from 2 to 8 mm wide.

Measurement of the thermoelectric size effect

requires a well-annealed specimen of high purity in order to detect the influence of the specimen surface only. It has been known for some time that a small percentage of iron is present in commercially available samples of the noble metals.<sup>24</sup> This produces giant negative thermoelectric powers in the case of gold and copper, and to a lesser extent in the case of silver.

The most comprehensive work investigating the annealing procedures designed to lessen the effect is that of Fickett<sup>40</sup> on copper, and Ehrlich<sup>41</sup> on silver. The procedure is to anneal the sample under a partial pressure of oxygen and measure the increase in the resistance ratio (RR), defined as the ratio of the resistance at room temperature to the resistance at  $4.2^\circ\text{K}$ . It is thought<sup>40</sup> that the oxygen diffuses into the metal and combines with the iron to give iron oxide. This presents a less energy-dependent scattering center than the unoxidized iron. The problem is to find that combination of temperature, time, and pressure which will yield the largest value of the resistance ratio. A temperature of  $800^\circ\text{C}$  was used because higher temperatures deformed the foils to a point where they could not be used. The largest resistance ratios were obtained in gold when samples were annealed in air for 30 h at atmospheric pressure, in copper when samples were annealed for 3 h at a pressure of  $1.5 \times 10^{-4}$  Torr, and in silver when samples were annealed for 5 h at a pressure of  $1.5 \times 10^{-4}$  Torr. In the thinner silver samples it was necessary to alter the annealing procedure somewhat. Owing to the high vapor pressure of silver the  $2.54 \times 10^{-3}$ -mm and thinner silver foils were destroyed when annealed as above. In those cases the wire portion of the sample was annealed at  $800^\circ\text{C}$  for 5 h at  $1.5 \times 10^{-4}$  Torr. The foil was then attached and the sample was raised to  $800^\circ\text{C}$  for a matter of minutes at a pressure of  $1.5 \times 10^{-4}$  Torr. In all cases the sample was cooled at a rate of less than  $150^\circ\text{C}$  per hour. Annealing was done on a high-density alumina block because that was found to introduce the least contamination of several attempted alternatives.

Thermoelectric emf measurements were carried out using a Guildline 9176-G nanovolt potentiometer. Thermoelectric connections to the cryostat were made with Guildline type SCW low thermal wire, in order to minimize thermal emf's in the measuring circuit. A standard four-probe technique was employed to make resistance measurements.

The temperature of the hot junction was measured by calibrated platinum and germanium resistors embedded in the heater block. The germanium resistor was used in the temperature range  $4.2\text{--}100^\circ\text{K}$ , and the platinum resistor was used in the temperature range  $77\text{--}333^\circ\text{K}$ . The resistors were symmetrically placed in the heater blocks and po-

sitioned within less than 1 mm of the hot junction. The heater consisted of two 125- $\Omega$  heaters of manganin wire wound concentrically around each heater block and resistor, and connected in series.

The temperature was controlled and measured simultaneously by an ac resistance bridge and temperature controller patterned after that of Ries and Moore.<sup>42</sup> A modified version of the Ries and Moore controller was built which gives 2.5 W to a 250- $\Omega$  heater and allows accurate control of the temperature in the range 0.03–300 °K.

The temperature drift of the heat sink was checked with both liquid helium and liquid nitrogen in the inner Dewar. The change in the temperature of the heat sink, with a maximum temperature gradient across the sample, was found to be less than 1 °K in each case.

The resistance ratio (RR) was measured for the sample and if it fell in a range predetermined by the previously mentioned annealing experiments, then the thermoelectric measurements proceeded. The thermoelectric emf measurements were made using the integral technique. One junction was maintained at 4.2 °K and the other raised in temperature. At each temperature the thermoelectric emf was measured. This was done over the range 4.2–100 °K with liquid helium in the inner Dewar, and over the range 77.3–333 °K with liquid nitrogen

in the inner Dewar.

The thermoelectric emf's were then differentiated, yielding a point-by-point slope which is the change in the thermoelectric power between the foil and the wire as a function of temperature.

After completion of each experiment, the foil was cut off, and the length and width of the foil were measured with a micrometer microscope. The average thickness of the foil was then determined from its weight using the density of the particular material.

#### IV. RESULTS AND ANALYSIS

The difference in the thermoelectric power between a well-annealed foil and a well-annealed wire was found by differentiating the thermoelectric emf with respect to temperature. Typical results are given in Fig. 2. The important features of these results are the position of the peak, the rate of decrease of  $\Delta S$  with increasing temperature after the peak, and the high-temperature behavior of  $\Delta S$ .

##### A. Analysis of high-temperature results

The high-temperature results were analyzed by the techniques developed by Huebener for gold<sup>9</sup> and platinum.<sup>17</sup>

The difference in the electrical resistivity of the foils and the 0.254-mm wires was determined from the ratio of their resistance at 296 to that at 77.3 °K and at 4.2 °K. With

$$[\rho(296 \text{ °K})/\rho(T')]_{\text{foil}} \equiv A \quad (15)$$

and

$$[\rho(296 \text{ °K})/\rho(T')]_{\text{wire}} \equiv B \quad (16)$$

the resistivity  $\Delta\rho$  between a foil and a wire is given by

$$\Delta\rho = \rho_{\text{foil}} - \rho_{\text{wire}} = \rho_{\text{wire}}(296 \text{ °K})[(1 - A/B)/(A - 1)] \quad (17)$$

assuming that  $\Delta\rho$  is independent of temperature. Here  $T'$  is either 77.3 or 4.2 °K. We know that<sup>9</sup>

$$\Delta\rho = \frac{3}{4} \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) \rho_0 l, \quad (18)$$

for the difference in the electrical resistivity of a foil of thickness  $a_1$  and a wire of diameter  $a_2$ .

The resistivity difference  $\Delta\rho$  was calculated for the various foil sizes in gold, copper, and silver with Eq. (17). This is shown in Fig. 3 for  $T' = 77.3 \text{ °K}$  and  $T' = 4.2 \text{ °K}$  as a function of the geometric quantity  $(1/2a_1 - 1/a_2)$ . In the calculations of  $\Delta\rho$  the values

$$\rho_{\text{wire}}^{\text{Au}}(296 \text{ °K}) = 22.25 \times 10^{-7} \Omega \text{ cm}, \quad (19)$$

$$\rho_{\text{wire}}^{\text{Cu}}(296 \text{ °K}) = 17.24 \times 10^{-7} \Omega \text{ cm}, \quad (20)$$

and

$$\rho_{\text{wire}}^{\text{Ag}}(296 \text{ °K}) = 15.9 \times 10^{-7} \Omega \text{ cm} \quad (21)$$

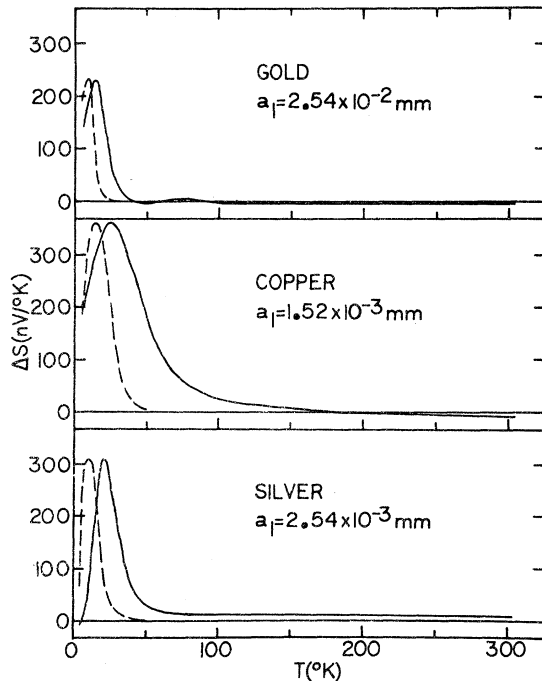


FIG. 2. Difference  $\Delta S$  between the thermoelectric power of a foil of thickness  $a_1$  and a wire of diameter  $a_2 = 0.254 \text{ mm}$  as a function of temperature for typical samples of the noble metals (solid line, experimental; dashed line, calculated).

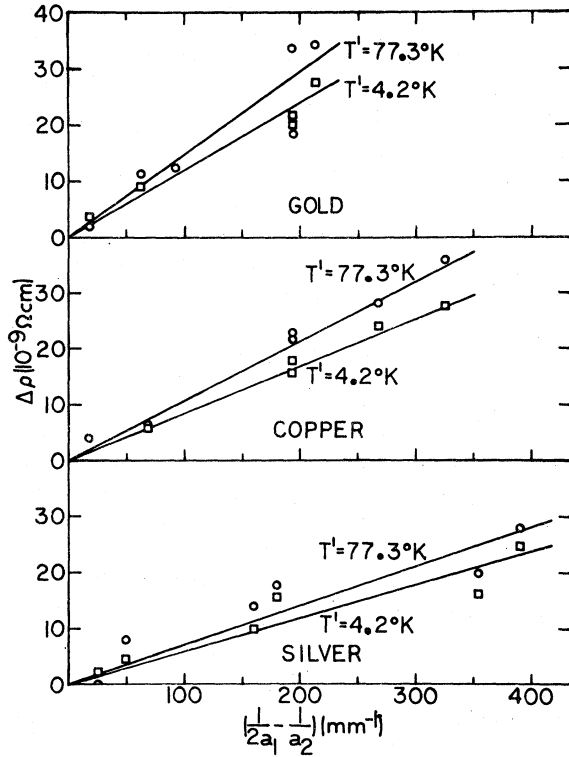


FIG. 3. Difference between the electrical resistivity of a foil of thickness  $a_1$  and a wire of diameter  $a_2 = 0.254$  mm, calculated from Eq. (24) for  $T' = 77.3^\circ\text{K}$  (circles) and  $T' = 4.2^\circ\text{K}$  (squares).

were used. As seen in Fig. 3,  $\Delta\rho$  increases linearly with  $(1/2a_1 - 1/a_2)$ . From Fig. 3 and Eq. (18) we find

$$l\rho_0^{\text{Au}} = (19.64 \pm 1.97) \times 10^{-12} \Omega \text{ cm}^2, \quad (22)$$

$$l\rho_0^{\text{Cu}} = (14.25 \pm 0.35) \times 10^{-12} \Omega \text{ cm}^2, \quad (23)$$

$$l\rho_0^{\text{Ag}} = (9.386 \pm 0.95) \times 10^{-12} \Omega \text{ cm}^2. \quad (24)$$

With the values of  $\rho_0(296^\circ\text{K}) = \rho_{\text{wire}}(296^\circ\text{K})$  given in Eqs. (19)–(21) we then obtain

$$lT = (2.61 \pm 0.26) \times 10^{-3} \text{ cm } ^\circ\text{K} \quad (25)$$

for gold,

$$lT = (2.45 \pm 0.06) \times 10^{-3} \text{ cm } ^\circ\text{K} \quad (26)$$

for copper, and

$$lT = (1.75 \pm 0.18) \times 10^{-3} \text{ cm } ^\circ\text{K} \quad (27)$$

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

Figure 4 shows the average change in the electronic thermoelectric power of a thermocouple consisting of a foil and a wire as a function of the geometric quantity  $(1/2a_1 - 1/a_2)$ . The points for Fig. 4 were obtained by averaging the thermoelectric-power values for each foil in the region where the thermoelectric-power curves were constant.

In this region the phonon-drag contribution is negligible. For gold this is good for  $T > 100^\circ\text{K}$ , for copper  $T > 250^\circ\text{K}$ , and for silver  $T > 100^\circ\text{K}$ . To check the values of  $\Delta S_e$  plotted in Fig. 4 an average measurement of  $\Delta S_e$  between  $77.3$  and  $296^\circ\text{K}$  was performed in the same manner as Huebener for gold.<sup>9</sup> This was only possible for gold and silver, but the results in these two cases agreed with our point-by-point measurements to within 16%. As seen in Fig. 4 a straight line going through the origin can be fitted through the data for each of the noble metals. With Eq. (3) and the results of Fig. 4 the values of  $[\partial \ln l(\epsilon)/\partial \ln \epsilon]_{\epsilon_F} = U$  were calculated. These values are given in Table I. In these calculations the average values of  $lT$  given in Eqs. (25)–(27),  $\epsilon_F(\text{Au}) = 5.51$  eV,  $\epsilon_F(\text{Cu}) = 7.0$  eV, and  $\epsilon_F(\text{Ag}) = 5.5$  eV, were used. The values of  $U$  given in Table I are, of course, an average value over the Fermi surface. With the values of  $U$ , Eq. (1), and the values

$$S_e^0/T = 7.05 \times 10^{-3} \mu\text{V}/^\circ\text{K}^2 \quad (28)$$

for gold,<sup>43</sup>

$$S_e^0 = 5.4 \times 10^{-3} \mu\text{V}/^\circ\text{K}^2 \quad (29)$$

for copper,<sup>24</sup> and

$$S_e^0/T = 4.7 \times 10^{-3} \mu\text{V}/^\circ\text{K}^2 \quad (30)$$

for silver,<sup>44</sup> we obtain the values of  $V$  for the noble metals given in Table I. Along with the values for  $U$  and  $V$  calculated in this experiment, other published values for these quantities are included in Table I for comparison.

#### B. Analysis of low-temperature results

In Eq. (13) we have expressed the change in the electronic thermoelectric power due to magnetic

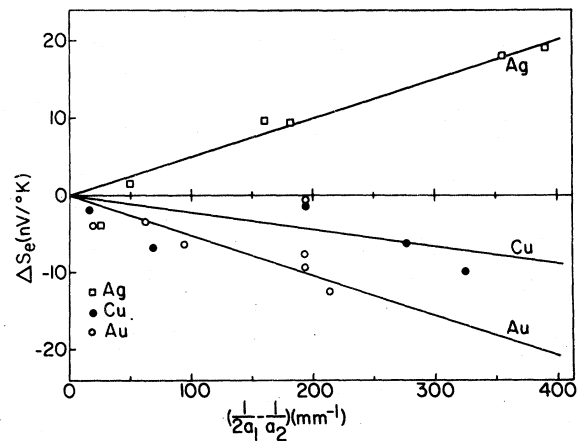


FIG. 4. Difference between the thermoelectric power of a foil of thickness  $a_1$  and a wire of diameter  $a_2 = 0.254$  mm, in the temperature range between  $100$  and  $296^\circ\text{K}$  for gold and silver, and between  $250$  and  $296^\circ\text{K}$  for copper.

TABLE I. High-temperature results. [The error indicated in the values of  $U$  and  $V$  obtained in this experiment represent only the standard deviation resulting from a least-squares fit of the data. The error indicated in the results of Lin and Leonard (Ref. 23) also include measurement errors. It is not known how Huebener (Ref. 10) and Worobey *et al.* (Ref. 24) obtained their larger stated error of  $\pm 0.19$  and  $\pm 0.20$ , respectively. Using Huebener's (Ref. 10) published data, a value of  $\pm 0.06$ , based on the standard deviation, for the error in  $U$  and  $V$  was calculated.]

	$\left(\frac{\partial \ln I(\epsilon)}{\partial \ln \epsilon}\right)_{\epsilon_F}$					
	This experiment	Huebener (Ref. 10)	Lin and Leonard (Ref. 23)	Worobey <i>et al.</i> (Ref. 24)	Angus and Dalglish (Ref. 22)	Gouault (Ref. 19)
Au	$-0.58 \pm 0.08$	$-0.53 \pm 0.19$	$-0.60 \pm 0.04$	$-0.61 \pm 0.20$	+0.9	...
Cu	$-0.34 \pm 0.11$	...	...	...	+2.3	+2.1
Ag	$+0.86 \pm 0.09$	...	...	...	+2.7	...

	$\left(\frac{\partial \ln A(\epsilon)}{\partial \ln \epsilon}\right)_{\epsilon_F}$					
Au	$-1.00 \pm 0.08$	$-1.05 \pm 0.19$	$-0.85 \pm 0.04$	$-0.98 \pm 0.20$	-2.5	...
Cu	$-1.20 \pm 0.11$	...	...	...	-3.8	-3.6
Ag	$-1.91 \pm 0.09$	...	...	...	-3.8	...

impurities as

$$\Delta S = \rho_3 S_0 \frac{T}{T + T_0} \left( \frac{1}{\rho^f} - \frac{1}{\rho^w} \right), \quad (31)$$

where  $\rho^{f,w} = \rho_0^{f,w} + \rho^{f,w}$ . The change in the resistivity  $\Delta \rho$  was obtained from the resistance ratio of each foil or wire and  $\rho(296^\circ\text{K})$  for each of the noble metals.  $\Delta S$  was then calculated from Eq. (13) and fitted to the experimental curves giving the dashed curves in Fig. 2.

The product  $\rho_3 S_0$  was used as a fitting parameter to adjust the height of the peak to that of the experimental peak. The values of  $T_0$ , for thermo-electric-power measurements in gold and copper, were taken from Daybell and Steyerl<sup>45</sup> as 9 and 30 °K, respectively. For silver  $T_0$  was also used as a fitting parameter to adjust the peak position. As  $T_0$  increases, the calculated peak position becomes fixed due to the rapid falloff of  $1/\rho^f - 1/\rho^w$  [see Eq. (13)]. Thus,  $T_0$  could not be determined uniquely in this way. The calculated peak position for silver did not change significantly for  $T_0$  values higher than 25 °K, so we chose to use the value of  $T_0$  in silver as 25 °K.

After obtaining values of  $\rho_3 S_0$  from Eq. (13) we have tried to interpret them in terms of the concentration of unoxidized magnetic impurity. Using values of  $S_0$  from the literature we can obtain a value of  $\rho_3$ . For dilute alloys  $\rho_3$  can be assumed to be proportional to the concentration of impurity present. Resistivity data in the literature can then be used to deduce the impurity concentration. Since it is generally agreed that iron is the main cause of the low-temperature anomalies in the thermo-electric power and resistance of the noble metals,

the values of  $S_0$  and the proportionality constant between resistivity and concentration were taken from dilute-alloy studies of iron in the noble metals.

This yielded estimates of the concentrations from 0.06 to 0.30 ppm. This is in fair agreement with the results of analysis of a number of samples, before and after annealing, by atomic absorption spectroscopy.

## V. DISCUSSION AND CONCLUSIONS

The negative values of  $U$  given in Table I for gold and copper show the decrease in electron mean free path with increasing energy as suggested by Ziman,<sup>3</sup> Blatt,<sup>5</sup> and Robinson<sup>6</sup> and in strong disagreement with the free-electron value of 2.0. The value of  $U$  for gold agrees well with the value obtained by Huebener,<sup>9</sup> Lin and Leonard,<sup>22</sup> and Worobey *et al.*,<sup>23</sup> as seen in Table I. The values of  $U$  for gold and copper agree in sign with Robinson's<sup>6</sup> theoretical estimates of  $-0.63$  and  $-1.67$  for gold and copper, respectively. It has been suggested by Huebener<sup>9</sup> and Lin and Leonard<sup>22</sup> that the positive values of  $U$  obtained by Angus and Dalglish<sup>21</sup> and Gouault<sup>18</sup> were in error because the thin films could not be annealed at sufficiently high temperatures after deposition, and as a result are probably masked by the presence of large concentrations of lattice defects within the films.

The values of  $V$  for gold and copper given in Table I are in agreement in that they indicate that the area of Fermi surface decreases with increasing energy. This is in disagreement with Ziman's<sup>3</sup> value of 0.5 and Robinson's<sup>6</sup> assumption of the free-electron value of 1.0.

It is concluded for gold and silver that neither  $U$

nor  $V$  is separately responsible for the positive sign of the electronic thermoelectric power, but in fact both terms contribute.

A surprising result of this experiment is the positive value for  $U$  in the case of silver. While this agrees in sign with the value obtained by Angus and Dalglish<sup>21</sup> we have already noted that their results are in question. It also disagrees with Robinson's<sup>6</sup> theoretical estimate of  $-0.62$ . The positive value of  $U$  for silver shows that in this case the mean free path is increasing with increasing energy in disagreement with Ziman,<sup>3</sup> Blatt,<sup>5</sup> and Robinson.<sup>6</sup> The positive sign, in fact, is more characteristic of the free-electron prediction. As with gold and copper, the value of  $V$  is negative for silver. In the case of silver,  $V$  is the dominant term, giving rise to a positive thermoelectric power.

It is apparent that Robinson's<sup>6</sup> theory does not explain the sign anomaly of the electronic thermoelectric power in silver. In all of the noble metals existing theories are unable to explain the negative sign of  $V$ .

With the extremely accurate knowledge of the detailed shape of the Fermi surfaces of the noble metals now available from de Haas-Van Alphen studies, it would seem that a new theoretical calculation of the change in the area of the Fermi surface with energy  $V$  would be feasible and a valuable aid in

clearing up the problem of the negative values of  $V$  found in this experiment.

A successful experiment on evaporated films of copper and silver similar to those of Lin and Leonard,<sup>22</sup> and Worobey *et al.*<sup>23</sup> on gold would be useful to verify the results of this work.

The original purpose of the low-temperature measurements was to determine the size effect on the phonon-drag thermoelectric power. While there are some indications of such an effect, it was obvious that another, much larger, effect was predominant. Examination of the results in terms of magnetic-impurity scattering and size effect has led to some rather surprising results.

The peak height due to iron has given us a value for  $\rho_3 S_0$  which is a measure of the unoxidized magnetic impurity present in the sample. As is seen in Eq. (13) our results depend only upon the resistivity of the wire and foil and the absolute temperature. Using published data on the thermoelectric power and the concentration of iron as a function of residual resistivity from dilute-alloy studies of iron in the noble metals, we can obtain an estimate of the concentration of unoxidized magnetic impurity, mainly iron, that is present in the samples. This has exciting possibilities as a tool with which to determine low-level iron concentrations in the noble metals.

\*Based on a thesis submitted by R. F. M. to the University of Oklahoma in partial fulfillment of the requirement for the Ph.D. degree.

†Work supported by the Atomic Energy Commission under Contract No. AT-(40-1) 3940. A grant from the Research Corporation made preliminary work on this project possible.

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