

## Size Effect on Phonon Drag in Platinum\*

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Thermoelectric measurements with thermocouples consisting of thin platinum foils and 0.254-mm-diam platinum wire have been carried out between 4.2 and 310°K. The thickness of the foils was  $1.6 \times 10^{-8}$  to  $8 \times 10^{-8}$  mm. The difference  $\Delta S$  between the thermoelectric power of the foils and the wire was separated into the electronic component  $\Delta S^e$ , caused by the electron scattering at the crystal surface, and the phonon-drag component  $\Delta S^g$ , resulting from the phonon scattering at the crystal surface. From the phonon-drag component  $\Delta S^g$  the phonon mean free path  $\lambda_0$  in the bulk material was determined as a function of the temperature. Above 60°K (approximately the temperature of the phonon-drag peak) the relation  $\lambda_0 = (1.1 \times 10^{-5}) e^{64^\circ\text{K}/T}$  mm was found, in agreement with the expectation that in this temperature range  $\lambda_0$  is mainly limited by phonon-phonon umklapp processes. The pre-exponential factor in  $\lambda_0$  is within a factor of two in agreement with the value calculated from Klemens's theory. From the electronic component  $\Delta S^e$ , the derivative of the electron mean free path  $l$  with respect to the electron energy  $E$  was found to be  $\{\partial l / \partial E\}_{EF} = 3.4 \pm 0.8$  (eV)<sup>-1</sup>. Measurements of the electrical-resistivity difference between the foils and the wire yielded for the electron mean free path in platinum the value  $l = (6.4 \pm 1.0) \times 10^{-7}$  cm at 296°K.

## I. INTRODUCTION

THE thermoelectric power of thin specimens differs from the bulk value because of the scattering of electrons and phonons at the crystal surface. The electron scattering at the crystal surface causes a change in the electronic component of the thermoelectric power. From measurements of the size effect on the electronic component of the thermoelectric power, information on the dependence of the electron mean free path on the electron energy can be obtained. The thermoelectric size effect has been investigated in the past by numerous authors<sup>1-10</sup> in a series of metals. In all but the last of these papers the specimens consisted of thin films deposited on a substrate by evaporation. The thickness of these films ranged from 50 to  $5 \times 10^4$  Å. In these experiments with thin evaporated films<sup>1-9</sup> the electron mean-free-path effect<sup>1,3,10</sup> was disturbed to a large extent because of the following reasons. Since the films could not be annealed at sufficiently high temperatures after deposition, they contained apparently regions of local strain and large concentrations of lattice defects which contributed to the thermoelectric power.<sup>6,10</sup> On the other hand, in the extremely thin films, as obtained by evaporation, the electronic structure may have been different from that in the bulk material.<sup>2,6</sup> Because of these difficulties most of the studies with thin evaporated films<sup>1-9</sup> did not yield quantitative information on the variation of the electron mean free path with electron

energy. From this point of view a technique in which the thermoelectric power of annealed foils versus annealed wire of the same material is measured, seems to be more promising. Using this technique, the size effect on the electron-diffusion thermoelectric power has been investigated recently in gold.<sup>10</sup>

The phonon scattering at the crystal surface causes a change in the phonon-drag component of the thermoelectric power. The size effect on the phonon-drag component of the thermoelectric power has been observed for the first time by Geballe and Hull<sup>11</sup> in germanium. These authors have found that the phonon-drag component of the thermoelectric power in germanium is reduced due to the phonon scattering at the crystal surface. A reduction of the phonon-drag component of the thermoelectric power due to the phonon scattering at the specimen surface has also been observed recently<sup>12</sup> in evaporated gold films.

Quantitative studies of the size effect on the phonon-drag component of the thermoelectric power are particularly interesting since they provide information on the average phonon mean free path in the bulk material. In the present investigation the difference between the thermoelectric power of thin platinum foils and 0.254-mm-diam. platinum wire is measured between 4.2 and 310°K. The thermoelectric size effect is separated into the electronic component and the phonon-drag component. From the size effect on the electronic component of the thermoelectric power, the dependence of the electron mean free path on the electron energy is obtained. From the size effect on the phonon-drag component of the thermoelectric power the average phonon mean free path in the bulk material is found as a function of temperature. Preliminary results of the present investigation were reported earlier.<sup>13,14</sup>

<sup>11</sup> T. H. Geballe and G. W. Hull, *Conference de Physique des Basses Températures* (Paris, 1955), Nr. 86.

<sup>12</sup> W. Worobey, P. Lindenfeld, and B. Serin, *Phys. Letters* **16**, 15 (1965).

<sup>13</sup> R. P. Huebener, *Phys. Letters* **15**, 105 (1965).

<sup>14</sup> R. P. Huebener and R. E. Govednik, *Phys. Letters* **17**, 99 (1965).

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<sup>1</sup> E. Justi, M. Kohler, and G. Lautz, *Naturwiss.* **38**, 475 (1951).

<sup>2</sup> E. Justi, M. Kohler, and G. Lautz, *Z. Naturforsch.* **6a**, 456 (1951).

<sup>3</sup> E. Justi, M. Kohler, and G. Lautz, *Z. Naturforsch.* **6a**, 544 (1951).

<sup>4</sup> J. Savornin and G. Couchet, *Compt. Rend.* **234**, 1608 (1952).

<sup>5</sup> J. Savornin and F. Savornin, *J. Phys. Radium* **17**, 283 (1956).

<sup>6</sup> L. Reimer, *Z. Naturforsch.* **12a**, 525 (1957).

<sup>7</sup> F. Savornin, *Ann. Phys. (Paris)* **5**, 1355 (1960).

<sup>8</sup> F. Savornin, J. Savornin, and A. Donnadieu, *Compt. Rend.* **254**, 3348 (1962).

<sup>9</sup> R. Nossek, *Z. Naturforsch.* **16a**, 1162 (1961).

<sup>10</sup> R. P. Huebener, *Phys. Rev.* **136**, A1740 (1964).

In Sec. II the theory of the size effect on the electronic component and on the phonon-drag component of the thermoelectric power is outlined. It is shown that measurements of the size effect on the phonon-drag component of the thermoelectric power provide information on the average phonon mean free path in the bulk material. The method used for obtaining the electronic component and the phonon-drag component of the thermoelectric size effect separately is summarized. Sections III and IV give a description of the experiments and the results. In Sec. V the variation of the electron mean free path with electron energy, found experimentally, is discussed. The bulk phonon mean free path  $\lambda_0$  obtained from the results in the temperature range where  $\lambda_0$  is mainly limited by phonon-phonon umklapp processes is compared with theoretical estimates by Klemens.

## II. THEORY

The absolute thermoelectric power  $S_0$  of a pure metal consists of a contribution  $S_0^e$ , arising from the nonequilibrium distribution of the conduction electrons, and a contribution  $S_0^g$ , caused by the interaction between the conduction electrons and the phonon current present in a temperature gradient:

$$S_0 = S_0^e + S_0^g. \quad (1)$$

$S_0^e$  and  $S_0^g$  are usually called electronic thermoelectric power and phonon-drag thermoelectric power, respectively. The subscript 0 in Eq. (1), and hereafter, refers to the bulk value of a pure specimen. The change  $\Delta S$  in the thermoelectric power due to lattice defects (point defects, dislocations, crystal surface, etc.), which scatter the electrons and the phonons, is according to Eq. (1)

$$\Delta S = \Delta S^e + \Delta S^g. \quad (2)$$

Here  $\Delta S^e$  and  $\Delta S^g$  are the change in the electronic and the phonon-drag thermoelectric power, respectively.

### A. Size Effect on the Electronic Component of the Thermoelectric Power

The electronic thermoelectric power  $S^e$  of a thin specimen differs from the bulk value  $S_0^e$  by  $\Delta S^e$  because of the electron scattering at the crystal surface. The difference  $\Delta S^e$  is given by<sup>15</sup>

$$\Delta S^e = S^e - S_0^e = \frac{S_0^e}{(W_0^e/\Delta W^e) + 1} \left( \frac{S_i^e}{S_0^e} - 1 \right). \quad (3)$$

Here  $W_0^e$  is the electronic thermal resistivity of the bulk material and  $\Delta W^e$  the change in the electronic thermal resistivity due to the electron scattering at the crystal surface.  $S_i^e$  is the electronic thermoelectric power associated with the electron scattering at the crystal

surface. In the derivation of Eq. (3) the following assumptions are required:

(1) The electron scattering at the crystal surface, which causes the increase  $\Delta W^e$  in the electronic thermal resistivity, and all other electron scattering processes in the bulk material are independent of each other (Matthiessen's rule).

(2) The heat which is transported by the conduction electrons is independent of the heat transported by the phonons. This assumption is valid, since the electronic heat conductivity is not affected by the nonequilibrium distribution of the phonon system.<sup>16-18</sup>

If, in addition to the validity of the requirements (1) and (2), the electrical conductivity and the electronic component of the heat conductivity are determined by the same relaxation time (Wiedemann-Franz law), the ratio  $W_0^e/\Delta W^e$  in Eq. (3) can be replaced by  $\rho_0/\Delta\rho$ . Here  $\rho_0$  is the bulk electrical resistivity and  $\Delta\rho$  the electrical resistivity change due to the electron scattering at the crystal surface. The electronic thermoelectric power of a pure metal is then given by<sup>19</sup>

$$S_0^e = \frac{\pi^2 k_B^2 T}{3e} \left\{ \frac{\partial \ln \rho_0(E)}{\partial E} \right\}_{E_F}. \quad (4)$$

Here  $k_B$  is Boltzmann's constant,  $T$  the absolute temperature, and  $e$  the absolute value of the elementary charge.  $E$  is the energy of the conduction electrons and  $E_F$  the Fermi energy. The change in the electronic component of the thermoelectric power due to additional electron scattering events in the bulk material, which cause a resistivity increase  $\Delta\rho$ , can then be written as<sup>15</sup>

$$\Delta S^e = \frac{S_0^e}{(\rho_0/\Delta\rho) + 1} \left\{ \frac{\partial \ln \Delta\rho/\partial E}{\partial \ln \rho_0/\partial E} - 1 \right\}_{E_F}. \quad (5)$$

For calculating the size effect on the electronic thermoelectric power from Eq. (5), the size effect on the electrical resistivity must be known. We refer now, and hereafter, to the case of the present experiment, in which thin foils are compared with comparatively thick wire of the same material. The electrical resistivity difference between a foil of the thickness  $a_1$  and a cylindrical wire of the diameter  $a_2$ , caused by the electron scattering at the surface, is<sup>20</sup>

$$\Delta\rho \equiv \rho_{\text{foil}} - \rho_{\text{wire}} = \frac{3}{4} \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) \rho_0 l. \quad (6)$$

Here  $l$  is the average value over the Fermi surface of the electron mean free path. In Eq. (6) it is assumed that

<sup>16</sup> A. Sommerfeld and H. Bethe, *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Julius Springer Verlag, Berlin, 1933), Vol. XXIV, Part 2, p. 333.

<sup>17</sup> R. E. B. Makinson, Proc. Cambridge Phil. Soc. 34, 474 (1938).

<sup>18</sup> I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) A239, 247 (1957).

<sup>19</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953).

<sup>20</sup> E. H. Sondheimer, Advan. Phys. 1, 1 (1952).

<sup>15</sup> R. P. Huebener, Phys. Rev. 135, A1281 (1964).

TABLE I. Temperature dependence of the Wiedemann-Franz ratio  $\rho_0/W_0^e T$  for platinum.  $L_0$  is the Lorentz number:  $L_0=2.45 \times 10^{-8}$  (V/deg)<sup>2</sup>. Up to 100°K the values are obtained from the data on the electrical and thermal resistivity of platinum given in Ref. 21. Above 100°K the values are taken from Ref. 22.

$T$ (°K)	20	25	30	40	50	60	75	100	150	200	250	300
$\frac{\rho_0}{W_0^e T L_0}$	0.40	0.45	0.51	0.62	0.71	0.73	0.75	0.89	0.91	0.97	1.01	1.04

$l/a_1 \ll 1$  and  $l/a_2 \ll 1$  and that the electrons are scattered diffusely at the crystal surface.

At high temperatures the Wiedemann-Franz law is valid. Inserting Eq. (6) into Eq. (5) and with the relation  $\Delta\rho \ll \rho_0$  the difference between the electronic thermoelectric power of a foil of thickness  $a_1$  and a wire of diameter  $a_2$  is found to be

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

As seen from Eq. (7) measurements of the size effect on the electronic component of the thermoelectric power yield information on the quantity  $\left\{ \frac{\partial \ln l}{\partial E} \right\}_{E_F}$ .

At temperatures below the Debye temperature appreciable deviations from the Wiedemann-Franz law occur because of the inelasticity of the electron scattering by the lattice vibrations. In Table I the Wiedemann-Franz ratio  $\rho_0/W_0^e T$  is shown for platinum as a function of the temperature. Up to 100°K the ratio  $\rho_0/W_0^e T$  was calculated from the data of White and Woods<sup>21</sup> on the electrical and thermal resistivity of platinum. Above 100°K the ratio  $\rho_0/W_0^e \cdot T$  was taken from Slack.<sup>22</sup> As seen from Table I, below about 100°K the ratio  $\rho_0/W_0^e \cdot T$  decreases appreciably with decreasing temperature. Above about 100°K the ratio  $\rho_0/W_0^e \cdot T$  is close to the theoretical value given by the Lorentz number,  $L_0 = 2.45 \times 10^{-8}$  V<sup>2</sup>/deg<sup>2</sup>, which is calculated under the assumption that the conduction electrons are scattered elastically by the lattice vibrations. Because of the deviations from the Wiedemann-Franz law, the ratio  $W_0^e/\Delta W^e$  in Eq. (3) cannot be replaced by  $\rho_0/\Delta\rho$  at low temperatures. However, the scattering of the conduction electrons by the crystal surface is expected to be elastic and to follow the Wiedemann-Franz law. Therefore, the quantity  $\Delta W^e$  in Eq. (3) can be replaced by the electrical resistivity change  $\Delta\rho$  using the relation

$$\Delta W^e = \frac{\Delta\rho}{T L_0}. \quad (8)$$

From Eqs. (3) and (8) we obtain

$$\Delta S^e = \frac{S_0^e}{(W_0^e T L_0 / \Delta\rho) + 1} \left( \frac{S_1^e}{S_0^e} - 1 \right). \quad (9)$$

## B. Size Effect on the Phonon-Drag Component of the Thermoelectric Power

The phonon-drag thermoelectric power  $S^g$  of thin specimens differs from the bulk value  $S_0^g$  by  $\Delta S^g$  because of the phonon scattering at the crystal surface. In a rigorous treatment  $\Delta S^g$  must be calculated by integration over the entire frequency spectrum of the phonons. We write the phonon-drag thermoelectric power of the bulk material as

$$S_0^g = \sum_j \int s_g(\mathbf{q}, j) d^3q. \quad (10)$$

Here  $j$  is the polarization and  $\mathbf{q}$  the wave vector of the phonon. The quantity  $s_g(\mathbf{q}, j)$ , as defined by Eq. (10), is a sum over all possible electron transitions, in which the emission or absorption of a phonon  $\mathbf{q}, j$  is involved.<sup>23,24,15</sup>  $s_g(\mathbf{q}, j)$  depends on the velocity of the electrons and the phonons and on the electron-phonon interaction. The change of the phonon-drag thermoelectric power due to the phonon scattering at the crystal surface is given by<sup>15</sup>

$$\Delta S^g = S^g - S_0^g = - \sum_j \int \frac{s_g(\mathbf{q}, j)}{\lambda_B/\lambda_0(\mathbf{q}, j) + 1} d^3q. \quad (11)$$

Here  $\lambda_B$  is the phonon mean free path for boundary scattering.  $\lambda_0(\mathbf{q}, j)$  is the phonon mean free path in the bulk material. In the derivation of Eq. (11) the following assumptions are required:

(1) The phonon scattering at the crystal surface and all other phonon scattering events in the bulk material are independent of each other (Matthiessen's rule).

(2) The heat which is transported by the phonons is independent of the heat transported by the electrons. This assumption is valid, since the phonon distribution is independent of the distribution of the electrons.<sup>16-18</sup>

The boundary scattering of phonons is analogous to the boundary scattering of electrons. Therefore, the theory developed for the boundary scattering of electrons<sup>20</sup> can be used directly to describe the boundary scattering of phonons. In this way we find the phonon mean free path for the boundary scattering in a foil of thickness  $a_1$ ,

$$\lambda_{B, \text{foil}} = 8a_1/3, \quad (12)$$

<sup>21</sup> G. K. White and S. B. Woods, Can. J. Phys. **35**, 248 (1957).

<sup>22</sup> G. A. Slack, J. Appl. Phys. **35**, 339 (1964).

<sup>23</sup> M. Bailyn, Phil. Mag. **5**, 1059 (1960).

<sup>24</sup> M. Bailyn, Phys. Rev. **120**, 381 (1960).

and the phonon mean free path for the boundary scattering in a cylindrical wire of diameter  $a_2$ ,

$$\lambda_{B, \text{wire}} = 4a_2/3. \quad (13)$$

In Eqs. (12) and (13) it is assumed, that  $\lambda_B \gg \lambda_0$  and that the phonons are scattered diffusely at the crystal surface.

According to Eqs. (12) and (13)  $\lambda_B$  is independent of the wave vector and the polarization of the phonon. Since the bulk phonon mean free path is a function of  $\mathbf{q}$  and  $j$ , in a rigorous treatment,  $\Delta S^\sigma$  must be represented by an integral over  $\mathbf{q}$  and a sum over  $j$ , as indicated in Eq. (11). The calculation of  $\Delta S^\sigma$  may be simplified by dropping the differentiation between phonons with different polarization and by replacing the sum over  $j$  by the factor of 3. In the integration over all phonons the phonon frequency spectrum may be cut off at the Debye frequency. Further, dispersion may be neglected. With these approximations Eq. (11), in combination with Eqs. (12) and (13), allows us in principle to calculate the bulk phonon mean free path  $\lambda_0(\mathbf{q})$  from the experimentally obtained quantity  $\Delta S^\sigma$ , if the function  $s_\sigma(\mathbf{q})$  is known. The function  $s_\sigma(\mathbf{q})$  may be obtained from Baily's theory<sup>23,24</sup> on the phonon-drag thermoelectric power  $S_0^\sigma$ . The term in the theoretically obtained function  $s_\sigma(\mathbf{q})$  which contains the electron-phonon interaction and which is difficult to evaluate may be treated as an adjustable parameter determined from an experimentally obtained value of  $S_0^\sigma$ .<sup>15</sup>

Whereas an analysis of the quantity  $\Delta S^\sigma$  along the lines given above is desirable, it is rather difficult, mainly because of uncertainties in the determination of the function  $s_\sigma(\mathbf{q})$ . On the other hand, the bulk phonon mean free path  $\lambda_0$  may not depend very strongly on the phonon wave vector.<sup>25</sup> Therefore, we simplify the treatment further by replacing the phonon frequency spectrum by an average frequency around which the phonon distribution is concentrated at any given temperature. According to Eq. (11) the change of the phonon-drag thermoelectric power due to the phonon scattering at the crystal surface is then given by

$$\Delta S^\sigma = -\frac{S_0^\sigma}{(\lambda_B/\lambda_0) + 1}. \quad (14)$$

We refer now, and hereafter, to the case of the present experiment, in which thin foils are compared with relatively thick wire of the same material. Using Eq. (14) in combination with Eqs. (12) and (13), the difference between the phonon-drag thermoelectric power of a foil of the thickness  $a_1$  and a wire of the diameter  $a_2$  is found to be

$$\Delta S^\sigma \equiv S_{\text{foil}}^\sigma - S_{\text{wire}}^\sigma = -S_0^\sigma \left[ \frac{1}{(8a_1/3\lambda_0) + 1} - \frac{1}{(4a_2/3\lambda_0) + 1} \right]. \quad (15)$$

<sup>25</sup> P. G. Klemens, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 50.

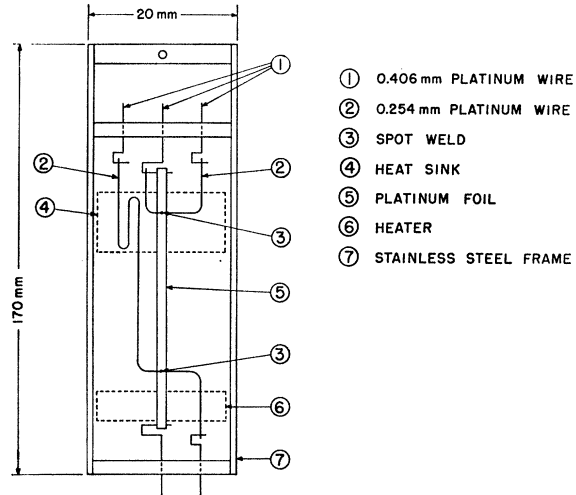


FIG. 1. Scheme of the specimen.

With the relation  $\lambda_B \gg \lambda_0$ , which was assumed in the derivation of Eqs. (12) and (13), we obtain

$$-\frac{\Delta S^\sigma}{S_0^\sigma} = \frac{3}{4} \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) \lambda_0. \quad (16)$$

As seen from Eqs. (14) and (16), measurements of the size effect on the phonon-drag component of the thermoelectric power yield information on the mean free path  $\lambda_0$  of the dominant phonon mode in the bulk material.

Presumably, above the temperature of the phonon-drag peak  $\lambda_0$  is mainly limited by phonon-phonon umklapp-processes. If phonon-phonon umklapp-processes are the main source of the lattice thermal resistivity,  $\lambda_0$  has the form<sup>25</sup>

$$\lambda_0 = A e^{T^*/T} \quad (17)$$

below the Debye temperature. Here  $T^*$  is about half the Debye temperature. The quantity  $\Delta S^\sigma$  is then given by

$$-\frac{\Delta S^\sigma}{S_0^\sigma} = \frac{3}{4} \left( \frac{1}{2a_1} - \frac{1}{a_2} \right) A e^{T^*/T}. \quad (18)$$

In platinum the temperature of the phonon-drag peak is about 65°K. Therefore, Eq. (18) should be valid in platinum between about 65°K and the Debye temperature. Below the temperature of the phonon-drag peak  $\lambda_0$  is mainly limited by phonon-electron collisions.

### C. Separation of the Electronic Component and the Phonon-Drag Component of $\Delta S$

The electronic component and the phonon-drag component of  $\Delta S$  can be obtained separately in the following way.<sup>15</sup> At high temperatures,  $S_0^\sigma$  and  $\Delta S^\sigma$  become negligible because of the dominant influence of phonon-scattering processes which do not involve

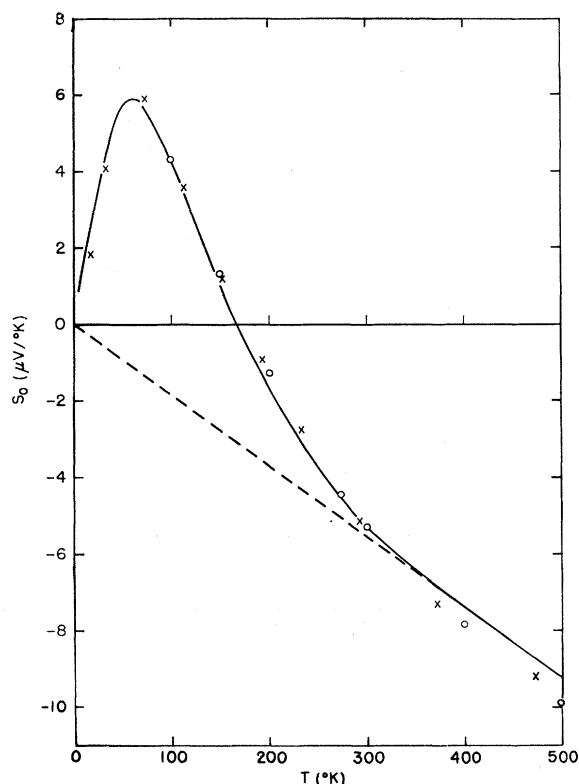


FIG. 2. Absolute thermoelectric power of platinum versus temperature. The circles and the crosses indicate the values given in Refs. 30 and 31, respectively.

electrons. Usually the vanishing of the phonon-drag thermoelectric power at high temperatures can be seen from the fact, that at high temperatures  $S_0$  is linearly proportional to the absolute temperature [Eq. (4)]. Therefore, the value of  $\Delta S$  at high temperatures is equal to  $\Delta S^e$ . In combination with Eq. (9), it can be used to calculate  $\Delta S^e$  as a function of the temperature. In the calculation of  $\Delta S^e(T)$  the quantity  $S_0^e/S_0^e$  in Eq. (9) is assumed to be independent of the temperature.  $S_0^e$  is assumed to be proportional to the absolute temperature. The proportionality factor  $S_0^e/T$  may be obtained from the values of  $S_0$  at high temperatures, where the phonon-drag thermoelectric power vanishes. The function  $\Delta S^e(T)$  is obtained finally from the experimentally determined function  $\Delta S(T)$  using Eq. (2).

### III. EXPERIMENTAL PROCEDURE

The specimen material was polycrystalline 99.999% pure platinum wire of 0.254 mm diameter.<sup>26</sup> Foils with a thickness of  $1.6 \times 10^{-3}$  to  $8 \times 10^{-3}$  mm were manufactured from this wire by cold rolling. The wire was cold-rolled between stainless steel foils. To check for possible contamination of the specimen during the

<sup>26</sup> Obtained from the Sigmund Cohn Corporation, Mount Vernon, New York.

manufacturing of the foil, several foils were made by rolling the platinum wire between sheets of platinum. The specimens, shown in Fig. 1, consisted of a thermocouple made from a foil and two 0.254-mm diam wires. They were mounted on a stainless steel sample holder. The specimen wires and the foil were spot-welded to short pieces of 0.406-mm-diam platinum wire which were attached to the sample holder. The lower specimen wire was bent as indicated in Fig. 1 to obtain a good thermal contact with the heat sink inside the cryostat. Before mounting, the specimen wires and foils were placed for about 30 min in hydrochloric acid and nitric acid, respectively, and were rinsed with distilled water. After mounting, the foil and the wires of the specimen were rinsed in acetone and methyl alcohol. Then they were annealed in air by passing direct current through them. The wires were annealed for 15 min at 1500°C and for 4 h at 1400°C and were cooled within several hours to room temperature. The foils were annealed for 15-20 h at 800°C and were cooled within about 0.5 h to room temperature. After annealing, the wires were spot-welded to the foil to obtain the thermocouple consisting of both. The annealed specimens were handled carefully to introduce as little cold work as possible. The length of the foils between the hot and the cold junction was about 6 cm. The width of the foils was about 3 mm.

To perform the thermoelectric measurements the specimens were mounted in a cryostat. The cold junction of the specimen was in close thermal contact with the heat sink inside the cryostat and could be kept at the temperature of the temperature bath (liquid helium, liquid nitrogen, ice water, and room temperature). The temperature of the hot junction was raised continuously above the temperature of the cold junction using a heater attached to the sample holder. A description of the cryostat is given elsewhere.<sup>15</sup> The area of the heat sink and of the heater is shown in Fig. 1 by a dashed line. The annealed specimen wires were spot-welded to extensions of annealed 99.999% pure platinum wire<sup>26</sup> leading out of the cryostat into a thermally shielded oil bath kept at room temperature. Within the oil bath the platinum wire was connected to copper wire leading to the potentiometer.

During the thermoelectric measurements the cryostat was evacuated to less than  $10^{-5}$  mm Hg. The thermoelectric measurements were carried out using a Rubicon model 2768 microvolt potentiometer and a Rubicon model 3550 photoelectric galvanometer. With this equipment voltage changes of  $0.01 \mu\text{V}$  could be detected. The thermoelectric voltage was measured as a function of the temperature of the hot junction keeping the cold junction at the temperature of the temperature bath. For the measurements in the temperature interval between 4.2 and 80°K the cryostat was placed in liquid helium. During the measurements in the temperature range between 77.3 and 260°K the cryostat was immersed in liquid nitrogen. For obtaining the data above 273°K the

TABLE II. Phonon-drag thermoelectric power of platinum for various temperatures. The values of  $S_0^p$  are the difference between the curve  $S_0(T)$  and the straight line shown in Fig. 2.

$T(^{\circ}\text{K})$	20	25	30	40	50	60	75	100	150	200
$S_0^p(\mu\text{V}/^{\circ}\text{K})$	3.14	3.91	4.64	5.86	6.62	6.97	6.95	6.18	3.79	2.07

cryostat was placed in a mixture of distilled water and ice. For efficient cooling of the cold junction the ice water was pumped into the open tube attached to the heat sink in the cryostat.<sup>15</sup> Further measurements were carried out, in which the cold junction was kept at room temperature by blowing air of the laboratory into the open tube attached to the heat sink in the cryostat. Below 80°K the temperature of the hot junction of the sample was raised by 0.2°K per minute or slower. Above 80°K the temperature of the hot junction was raised by 0.3°K per minute or slower. The data were taken at temperature intervals of 0.5–1°K at temperatures below 80°K and at intervals of 1–2°K at higher temperatures.

After plotting the thermoelectric voltage versus the temperature of the hot junction, a smooth curve was drawn through the points. The thermoelectric power was obtained by differentiating graphically the voltage-temperature curves. Around 80°K the thermoelectric power obtained in the liquid-helium bath agreed within  $3 \times 10^{-3} \mu\text{V}/^{\circ}\text{K}$  or better with the thermoelectric power obtained in the liquid-nitrogen bath.

After the specimen was assembled in the cryostat the electrical resistance of the specimen foil was measured at room temperature and at 4.2°K. During the resistance measurements the cryostat was filled with helium gas. After the thermoelectric measurements the specimen was taken from the cryostat and the electrical resistance of the lower specimen wire was measured at room temperature and at 4.2°K. For this purpose an additional potential lead was spot-welded to the lower specimen wire. The resistance measurements were carried out with a conventional potentiometric technique.

The ratio of the electrical resistance of the annealed 0.254-mm-diam platinum wire at 296°K to that at 4.2°K was 5000 to 7000. The difference in the electrical resistivity of the platinum foils and the 0.254-mm-diam platinum wire was determined from the ratios of their resistance at 296°K to that at 4.2°K in the following way. With

$$\{\rho(296^{\circ}\text{K})/\rho(4.2^{\circ}\text{K})\}_{\text{foil}} \equiv B_1 \quad (19)$$

and

$$\{\rho(296^{\circ}\text{K})/\rho(4.2^{\circ}\text{K})\}_{\text{wire}} \equiv B_2 \quad (20)$$

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

$$\Delta\rho = \rho_{\text{foil}} - \rho_{\text{wire}} = \rho_{\text{wire}}(296^{\circ}\text{K}) \times (1 - B_1/B_2)/(B_1 - 1), \quad (21)$$

assuming that  $\Delta\rho$  is independent of the temperature. The resistivity difference  $\Delta\rho$  was calculated with Eq.

(21) using the value

$$\rho_{\text{wire}}(296^{\circ}\text{K}) = 10.6 \times 10^{-6} \Omega \text{ cm}. \quad (22)$$

After completion of the electrical measurements, the foil was cut off, and the length and the width of the foil were measured with a micrometer microscope. The thickness of the foil was then determined from its weight using 21.45 g/cm<sup>3</sup> for the density of platinum.

The separation of  $\Delta S$  into the electronic component  $\Delta S^e$  and the phonon-drag component  $\Delta S^p$  requires the knowledge of the absolute thermoelectric power of the annealed specimen wire. Therefore, the thermoelectric power of the annealed platinum wire was measured versus 99.9999% pure lead wire<sup>27</sup> between 4.2 and 300°K. In the temperature range between 300 and 500°K the thermoelectric power of the annealed platinum wire was measured relative to annealed 0.254-mm-diam gold wire (99.999% pure).

#### IV. EXPERIMENTAL RESULTS

Figure 2 shows the absolute thermoelectric power of the annealed platinum wire as a function of the temperature. Below 300°K the absolute thermoelectric power of the platinum wire was obtained from the measurements against lead using the data of Borelius *et al.*,<sup>28</sup> and of Christian *et al.*,<sup>29</sup> on the absolute thermoelectric power of lead. The data between 300 and 500°K, shown in Fig. 2, were obtained from the measurements against gold using for the absolute thermoelectric power of gold the relation<sup>15</sup>  $S_0/T = +7.05 \times 10^{-3} \mu\text{V}/^{\circ}\text{K}^2$  in this temperature range. As seen from Fig. 2, the absolute thermoelectric power  $S_0$  of platinum reaches a maximum at about 60°K. At about 165°K,  $S_0$  reverses its sign, and above about 300°K  $S_0$  approaches a straight line which has a negative slope and which extrapolates to the origin. Since  $S_0^e$  is proportional to the absolute temperature according to Eq. (4) and since  $S_0^p$  vanishes at high temperatures, the curve obtained by extrapolating the high-temperature branch of  $S_0(T)$  linearly to the origin is interpreted as the electronic component  $S_0^e(T)$ . The difference between this linear curve and  $S_0(T)$  is interpreted as the phonon-drag component  $S_0^p(T)$ . The values of  $S_0^p$  obtained in this way from the data shown in Fig. 2 are given in Table II for various temperatures. From the high-temperature branch of

<sup>27</sup> Obtained from Cominco Products, Incorporated, Spokane, Washington.

<sup>28</sup> G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, Proc. Acad. Sci. (Amsterdam) **35**, 10 (1932).

<sup>29</sup> J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).

TABLE III. Summary of the specimens. The last column indicates the material between which the platinum wire was sandwiched during the manufacturing of the foil.

Specimen No.	Foil thickness (10 <sup>-3</sup> mm)	$\left(\frac{\rho(296^\circ\text{K})}{\rho(4.2^\circ\text{K})}\right)_{\text{wire}}$	$\left(\frac{\rho(296^\circ\text{K})}{\rho(4.2^\circ\text{K})}\right)_{\text{foil}}$	Material of the sandwich
1	8.03	5500	1897	Platinum
2	5.49	6300	1544	Platinum
3	5.45	5233	1979	Stainless steel
4	4.34	5900	1409	Stainless steel
5	3.92	5315	1524	Stainless steel
6	2.71	5899	983	Platinum
7	2.35	6629	801	Platinum
8	1.84	5030	744	Stainless steel
9	1.62	5265	532	Stainless steel
10	1.58	6938	680	Stainless steel

the function  $S_0(T)$  presented in Fig. 2 the relation

$$S_0^e/T = -1.84 \times 10^{-2} \mu\text{V}/^\circ\text{K}^2 \quad (23)$$

was obtained for platinum.

The function  $S_0(T)$  for platinum shown in Fig. 2 is in reasonable agreement with the data which are given in the literature<sup>30,31</sup> and which are also presented in Fig. 2. The absolute value of  $S_0^e/T$  given in Eq. (23) is by 5% smaller than the value obtained from the data given in Refs. 30 and 31 for the temperature range between 400 and 600°K.

A summary of the specimens used in the experiments is given in Table III.

The electrical resistivity difference  $\Delta\rho$  between the platinum foils and the 0.254-mm-diam platinum wire, as calculated from Eq. (21), is shown in Fig. 3 as a function of the geometric quantity  $(1/2a_1 - 1/a_2)$ . As

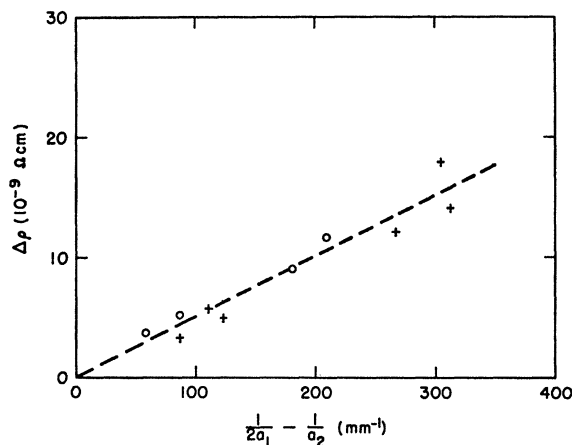


FIG. 3. Difference between the electrical resistivity of platinum foil of thickness  $a_1$  and platinum wire of diameter  $a_2 = 0.254$  mm, as calculated from Eq. (21), versus the quantity  $(1/2a_1 - 1/a_2)$ . The circles and crosses indicate the specimens in which the foils were manufactured by rolling between sheets of platinum and by rolling between stainless steel foils, respectively.

<sup>30</sup> N. Cusack and P. Kendall, Proc. Phys. Soc. (London) **72**, 898 (1958).

<sup>31</sup> Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer Verlag, Berlin, 1959), Vol. II, p. 931.

seen from Fig. 3,  $\Delta\rho$  increases proportional to  $(1/2a_1 - 1/a_2)$ , as expected from Eq. (6). The platinum foils rolled between sheets of platinum and the platinum foils manufactured by rolling between stainless steel foils yield the same relation between  $\Delta\rho$  and the quantity  $(1/2a_1 - 1/a_2)$ . This indicates, that the  $\Delta\rho$  values of the foils obtained by rolling between stainless steel sheets are not affected by contamination of the specimen during the manufacturing of the foil. From the data of Fig. 3 the relation

$$l\rho_0 = (6.8 \pm 1.1) \times 10^{-12} \Omega \text{ cm}^2 \quad (24)$$

is calculated using Eq. (6). With the value  $\rho_0(296^\circ\text{K}) \approx \rho_{\text{wire}}(296^\circ\text{K})$  given in Eq. (22) we obtain from Eq. (24)

$$l(296^\circ\text{K}) = (6.4 \pm 1.0) \times 10^{-7} \text{ cm}. \quad (25)$$

Equation (6), which is used for calculating the electron mean free path  $l$  from the experimentally determined values of  $\Delta\rho$ , is strictly valid in the temperature range in which  $l \ll a_1$  and  $l \ll a_2$ . The experimental values of  $\Delta\rho$  were obtained essentially from the resistivity measurements at 4.2°K. From the electron mean free

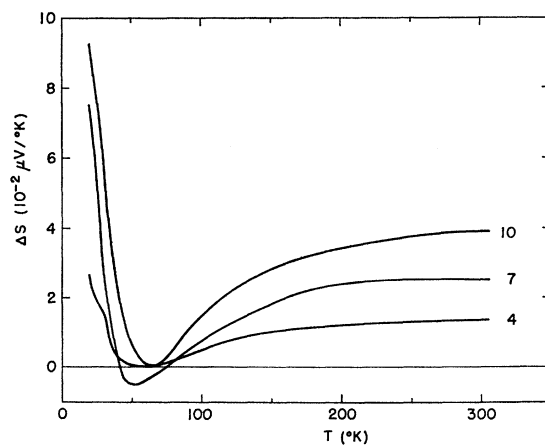
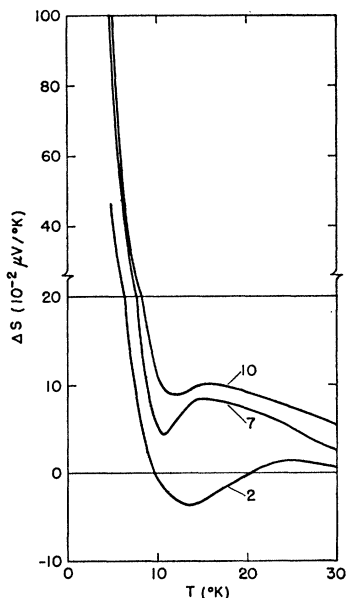


FIG. 4. Difference  $\Delta S$  between the thermoelectric power of the platinum foils and the 0.254-mm-diam platinum wire as a function of the temperature. The number at each curve indicates the specimen according to Table III.

FIG. 5. Difference  $\Delta S$  between the thermoelectric power of the platinum foils and the 0.254-mm-diam platinum wire versus temperature. The number at each curve indicates the specimen according to Table III.



path given in Eq. (25) and from the resistivity ratio  $\rho(296^\circ\text{K})/\rho(4.2^\circ\text{K})$  of 5000 to 7000 for the platinum wire a value of  $l \approx 1 \cdot 10^{-4}$  cm at  $4.2^\circ\text{K}$  is obtained. This value of  $l$  at  $4.2^\circ\text{K}$  is about equal to the thickness of the thinnest foils used in the experiments. Therefore, the validity of Eq. (6) for describing the resistivity difference between the specimen foils and the specimen wire at  $4.2^\circ\text{K}$  seems to be somewhat questionable. However, the theory of the electrical conductivity in a thin film<sup>20</sup> shows, that the additional resistivity in the film due to the electron scattering at the surface varies only by about 18% over the range  $0 < l/a_1 < 0.5$  ( $a_1$  = film thickness). This means, of course, that in the temperature range corresponding to this range of  $l/a_1$  Matthiessen's rule holds reasonably well for the elec-

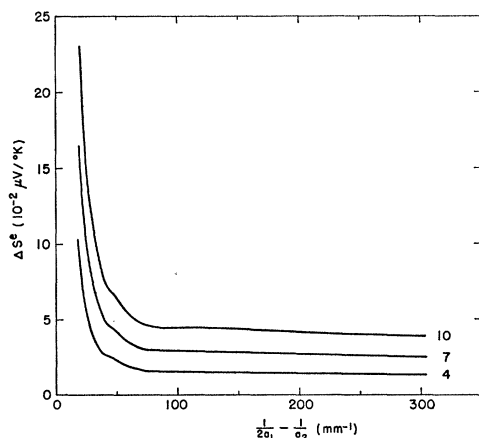


FIG. 6. Difference  $\Delta S^e$  between the electronic thermoelectric power of the platinum foils and the 0.254-mm-diam platinum wire as a function of the temperature. The number at each curve indicates the specimen according to Table III.

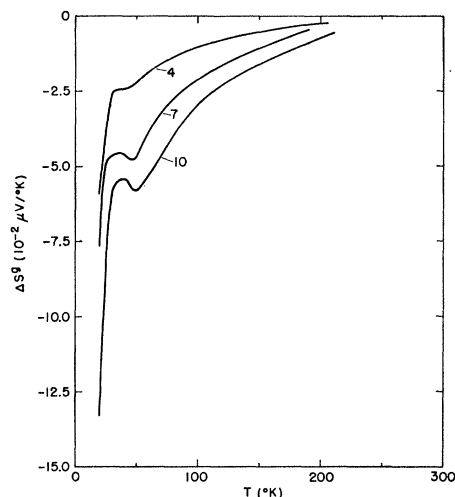


FIG. 7. Difference  $\Delta S^p$  between the phonon-drag thermoelectric power of the platinum foils and the 0.254-mm-diam platinum wire as a function of the temperature. The number at each curve indicates the specimen according to Table III.

tron scattering at the crystal surface. Therefore, errors in the calculation of the electron mean free path, due to deviations from Matthiessen's rule for the electron scattering at the crystal surface can be expected to be relatively small.

The difference  $\Delta S$  between the thermoelectric power of the platinum foils and the 0.254-mm-diam platinum wire is shown in Fig. 4 as a function of the temperature for different specimens and for temperatures above  $20^\circ\text{K}$ . Typical curves obtained for the function  $\Delta S(T)$  below  $20^\circ\text{K}$  are shown in Fig. 5 for three specimens. At low temperatures  $\Delta S$  decreases rapidly with increasing temperature. At about  $12^\circ\text{K}$   $\Delta S$  passes through a minimum, which is more pronounced for the specimens with the thicker foils. In the neighborhood of this

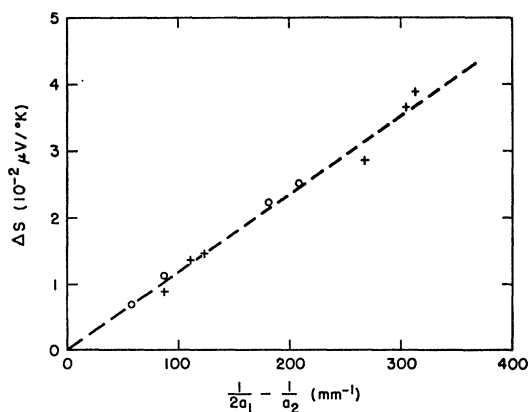


FIG. 8. Difference between the thermoelectric power of platinum foil of thickness  $a_1$  and platinum wire of diameter  $a_2=0.254$  mm, measured at  $300^\circ\text{K}$ , versus the quantity  $(1/2a_1-1/a_2)$ . The circles and crosses indicate the specimens in which the foils were made by rolling between sheets of platinum and by rolling between stainless steel foils, respectively.



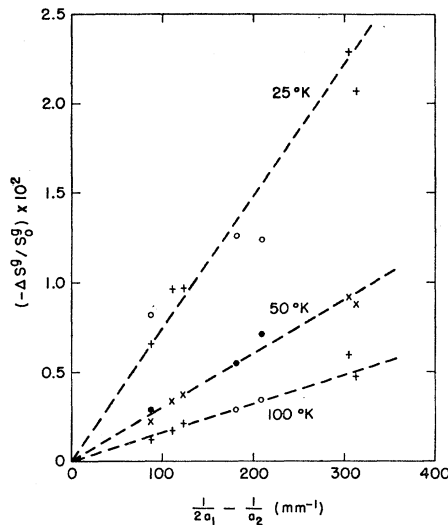


FIG. 9. Difference between the phonon-drag thermoelectric power of platinum foil of thickness  $a_1$  and platinum wire of diameter  $a_2=0.254$  mm versus  $(1/2a_1-1/a_2)$  for different temperatures. The circles and crosses indicate the specimens in which the foils were made by rolling between sheets of platinum and by rolling between stainless steel foils, respectively.

minimum  $\Delta S$  can reach small negative values. Above about 20°K  $\Delta S$  decreases again with increasing temperature. It passes through another minimum between 50 and 70°K. In the neighborhood of this minimum  $\Delta S$  can again reach small negative values. Above 50–70°K,  $\Delta S$  increases with increasing temperature up to about 280°K. Above 280°K  $\Delta S$  is independent of the temperature.

The total difference  $\Delta S$  between the thermoelectric power of the foils and the wire was separated into  $\Delta S^e$  and  $\Delta S^g$  using the method mentioned in Sec. IIC. From the temperature dependence of the absolute thermoelectric power of platinum, shown in Fig. 2, we can conclude that the phonon-drag component of the thermoelectric power of platinum vanishes at 300°K. Therefore, at 300°K  $\Delta S$  is equal to  $\Delta S^e$ . From the value  $\Delta S(300^\circ\text{K})$  the function  $\Delta S^e(T)$  was calculated using Eqs. (9) and (23). The function  $W_0^e(T)$  in Eq. (9) was obtained from the data of White and Woods<sup>21</sup> on the thermal conductivity of platinum. In addition to the thermal conductivity, White and Woods also measured the electrical resistivity of the same platinum specimen. The resistivity ratio  $\rho(296^\circ\text{K})/\rho(77.3^\circ\text{K})$  calculated from the data of White and Woods<sup>21</sup> is within 1% in agreement with the value obtained for the annealed platinum wire in the present experiment. The resistivity difference  $\Delta\rho$ , as calculated from Eq. (21), was used for all temperatures. It was pointed out above, that deviations from Matthiessen's rule in the quantity  $\Delta\rho$  can be expected to be relatively small.

At very low temperatures the quantity  $\Delta S^e$  is difficult to evaluate since here the thermal resistivity  $W_0^e$  in Eq. (9) depends sensitively on the purity of the

material. Furthermore, the assumption that  $S_0^e/T$  and  $S_i^e/S_0^e$  are independent of the temperature may not be satisfied at very low temperatures where the influence of lattice defects on the electron-scattering properties of the bulk material becomes appreciable. Because of these uncertainties, the function  $\Delta S^e(T)$  was not determined below 20°K.

The differences  $\Delta S^e$  and  $\Delta S^g$  calculated in the way mentioned above from the data of Fig. 4 are shown in Figs. 6 and 7, respectively, as a function of the temperature.  $\Delta S^e$  decreases rapidly with increasing temperature above 20°K and decreases only very slightly with increasing  $T$  above about 75°K. The qualitative behavior of the function  $\Delta S^e(T)$  below 20°K can be seen from Eq. (9). We assume that  $S_0^e/T$  and  $S_i^e/S_0^e$  are strictly constants down to  $T=0^\circ\text{K}$ . In the temperature range, where  $\Delta\rho \gg W_0^e T L_0$ ,  $\Delta S^e$  should then be proportional to the absolute temperature. At higher temperatures, where  $\Delta\rho \ll W_0^e T L_0$  and where  $W_0^e T$  increases more rapidly than linearly with  $T$ ,  $\Delta S^e$  should decrease with increasing temperature. Therefore, the function  $\Delta S^e(T)$  should pass through a maximum at low temperatures. As seen from Fig. 7, the phonon-drag component  $\Delta S^g$  becomes appreciable below about 250°K.  $|\Delta S^g|$  increases with decreasing temperature. Between 50 and 75°K  $|\Delta S^g|$  is about equal to  $\Delta S^e$ . Apparently the two minima in the curves for  $\Delta S(T)$  at about 12 and 60°K are due to the compensation between the electronic and the phonon-drag component of  $\Delta S$ .

Figure 8 shows the difference  $\Delta S$  measured at 300°K as a function of the geometric quantity  $(1/2a_1-1/a_2)$ . As mentioned above, at 300°K  $\Delta S$  is equal to  $\Delta S^e$ .  $\Delta S(300^\circ\text{K})$  is seen to increase proportional to  $(1/2a_1-1/a_2)$ , in agreement with Eq. (7). From the data given in Fig. 8 in combination with Eqs. (7) and (25) the derivative

$$\left\{ \frac{\partial \ln I}{\partial E} \right\}_{E_F} = 3.4 \pm 0.8 \text{ (eV)}^{-1} \quad (26)$$

was calculated. The value given in Eq. (26) is, of course, an average value over the Fermi surface.

In Fig. 9  $(-\Delta S^g/S_0^g)$  is plotted versus  $(1/2a_1-1/a_2)$  for different temperatures.  $(-\Delta S^g/S_0^g)$  is seen to increase proportional to  $(1/2a_1-1/a_2)$ , as expected from Eq. (16). According to Figs. 8 and 9, the same relation between the thermoelectric results and the quantity  $(1/2a_1-1/a_2)$  was found for the platinum foils rolled between sheets of platinum and the platinum foils made by rolling between stainless steel foils. In Fig. 10 the quantity  $(-\Delta S^g/S_0^g)$  is plotted logarithmically versus the reciprocal of the absolute temperature for different specimens.<sup>22</sup> It is seen that at temperatures above about 60°K the data on  $(-\Delta S^g/S_0^g)$  can be fitted reasonably

<sup>22</sup> The preliminary results on  $(-\Delta S^g/S_0^g)$  reported in Ref. 13 were obtained without correcting for the deviations from the Wiedemann-Franz law. Therefore, the values of  $(-\Delta S^g/S_0^g)$  given in Ref. 13 are somewhat too large at low temperatures.

well by the relation given in Eq. (18). This indicates that above about 60°K the mean free path  $\lambda_0$  of the dominant phonon mode in the bulk material has the form given in Eq. (17). This result is in agreement with the expectation that above the temperature of the phonon-drag peak (in platinum about 65°K)  $\lambda_0$  is mainly limited by phonon-phonon umklapp-processes. From the data shown in Fig. 10 for 60 and 100°K the values

$$\frac{(-\Delta S^g/S_0^g)_{60^\circ\text{K}}}{(1/2a_1) - (1/a_2)} = (2.48 \pm 0.10) 10^{-5} \text{ mm} \quad (27)$$

and

$$\frac{(-\Delta S^g/S_0^g)_{100^\circ\text{K}}}{(1/2a_1) - (1/a_2)} = (1.62 \pm 0.16) 10^{-5} \text{ mm} \quad (28)$$

were calculated. From the average values given in Eqs. (27) and (28), in combination with Eq. (18), the parameters

$$A = 1.1 \times 10^{-5} \text{ mm} \quad (29)$$

and

$$T^* = 64^\circ\text{K} \quad (30)$$

were obtained.

According to Fig. 10, the curves for the quantity  $(-\Delta S^g/S_0^g)$  follow the relation given in Eq. (18) down to approximately the temperature of the phonon-drag peak. Presumably, below the temperature of the phonon-drag peak  $\lambda_0$  is mainly limited by the interaction between phonons and electrons. The data in Fig. 10 indicate that between about 60 and 30°K the decrease of  $\lambda_0$  with increasing temperature is somewhat slower than at lower and at higher temperatures.

## V. DISCUSSION

### A. Electronic Component of $\Delta S$

The electron mean free path, given in Eq. (25), is by a factor of 7 to 12 smaller than the electron mean free path in the noble metals.<sup>10,33</sup> The relatively small electron mean free path found in platinum is in agreement with the fact that, in addition to the ordinary  $s$ - $s$  transitions, in the transition metals electrons can be scattered with high probability from the  $s$  band into an unoccupied state of the  $d$  band.

The result given in Eq. (26) indicates that the electron mean free path in platinum increases rapidly with increasing electron energy. The value of the quantity  $\{\partial \ln l / \partial E\}_{E_F}$  in platinum is of the opposite sign and larger by more than an order of magnitude than the value of about  $-0.1 \text{ (eV)}^{-1}$  measured recently in gold.<sup>10</sup> The result shown in Eq. (26) can be understood qualitatively from the model proposed by Mott<sup>34</sup> for the band

<sup>33</sup> D. K. C. MacDonald, *Encyclopedia of Physics*, edited by S. Flügge (Springer Verlag, Berlin, 1956), Vol. XIV, p. 188.

<sup>34</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, New York, 1958).

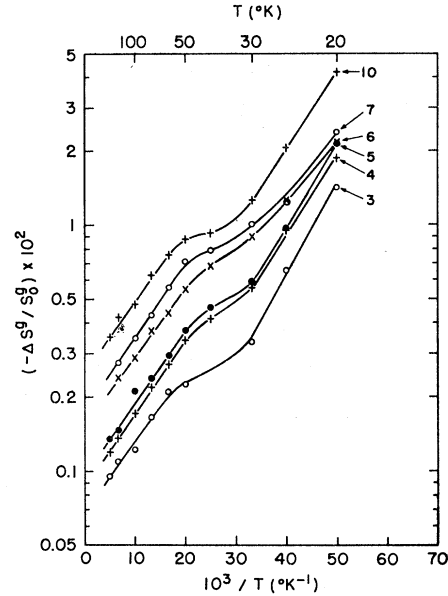


FIG. 10. Semilogarithmic plot of the quantity  $(-\Delta S^g/S_0^g)$  versus reciprocal of the absolute temperature. The number at each curve indicates the specimen according to Table III.

structure of platinum. According to this model the location of the Fermi energy in platinum is somewhere in the middle of the  $s$  band and slightly below the upper band edge of the  $d$  band, where the density of states in the  $d$  band decreases rapidly with increasing energy. The scattering processes mainly responsible for the electrical resistance in the transition metals are the  $s$ - $d$  transitions. The probability for such a transition is proportional to the density of states in the  $d$  band. Since the density of states in the  $d$  band decreases rapidly with increasing energy, one would expect a large positive value of the quantity  $\{\partial \ln l / \partial E\}_{E_F}$ , as indicated in Eq. (26).

### B. Phonon-Drag Component of $\Delta S$

In the temperature range in which the phonon mean free path  $\lambda_0$  is mainly limited by scattering processes not involving electrons, the phonon mean free path in a metal is determined by the same scattering processes as in an insulator. A theoretical treatment of the phonon mean free path in an insulator in the temperature range where phonon-phonon umklapp processes are dominant has been given by Leibfried and Schlömann<sup>35</sup> and by Klemens.<sup>25</sup> Apart from numerical constants, Leibfried and Schlömann and Klemens obtained the same expression for the phonon mean free path  $\lambda_0$ . According to these authors, below the Debye temperature  $\lambda_0$  follows the relation given in Eq. (17). An explicit expression for the constant  $A$  in Eq. (17) has been given by

<sup>35</sup> G. Leibfried and E. Schlömann, *Nachr. Adad. Wiss. Göttingen, II Math.-Physik. Kl. 2a*, 71 (1954).

Klemens,<sup>25</sup> who obtained

$$A \approx (Mv^2\alpha)/(8\gamma^2k_B\Theta). \quad (31)$$

Here  $M$  is the mass per atom,  $v$  the sound velocity,  $\alpha$  the lattice constant,  $\gamma$  the Grüneisen constant, and  $\Theta$  the Debye temperature. In Eq. (31) a factor  $\hbar\omega/k_B T$  ( $\omega$ =phonon frequency), which appears in Klemens's expression for  $A$ , was approximated by one. With the values  $v=2.7 \cdot 10^5$  cm/sec,<sup>36</sup>  $\alpha=3.92 \cdot 10^{-8}$  cm,<sup>37</sup>  $\gamma=2.5$ ,<sup>38</sup> and  $\Theta=230^\circ\text{K}$ <sup>39</sup> for platinum

$$A=0.59 \cdot 10^{-5} \text{ mm} \quad (32)$$

is calculated from Eq. (31). This value of  $A$  is within a factor of two in agreement with the experimentally obtained value given in Eq. (29).

Peierls<sup>40</sup> has estimated the temperature  $T^*$  in Eq. (17) as half the Debye temperature. An accurate calculation of the temperature  $T^*$ , which depends on the details of the zone structure and the dispersion of the lattice waves, is rather difficult. Berman, Simon, and Wilks<sup>41</sup> obtained the following values from thermal conductivity measurements at low temperatures:  $\Theta/T^*=2.6$  for diamond,  $\Theta/T^*=2.3$  for solid helium, and  $\Theta/T^*=2.1$  for sapphire. The value of  $T^*$  given in Eq. (30) corresponds to the ratio  $\Theta/T^*=3.6$ . This relatively large value of  $\Theta/T^*$  in platinum may be partly due to the fact that above  $60^\circ\text{K}$  collisions between phonons and electrons, besides phonon-phonon umklapp processes, still play a role in the limitation of the phonon mean free path. The collisions between phonons and electrons are strictly negligible compared to the phonon-phonon interaction only at high temperatures, where the phonon-drag thermoelectric power vanishes. Since the

<sup>36</sup> *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1929), Vol. VI, p. 465.

<sup>37</sup> C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952).

<sup>38</sup> J. G. Collins and G. K. White, *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV, p. 465.

<sup>39</sup> J. L. Feldman and G. K. Horton, *Phys. Rev.* **137**, A1106 (1965).

<sup>40</sup> R. Peierls, *Ann. Physik* **3**, 1055 (1929).

<sup>41</sup> R. Berman, F. Simon, and J. Wilks, *Nature* **168**, 277 (1951).

influence of the phonon-electron interaction on the limitation of the phonon mean free path increases with decreasing temperature, the phonon-electron collisions tend to reduce the apparent value of  $T^*$ .

Presumably, below the temperature of the phonon-drag peak the phonon mean free path is mainly limited by collisions between phonons and electrons. The phonon mean free path caused by the interaction between phonons and electrons has been calculated by Sommerfeld and Bethe<sup>16</sup> only for a spherical Fermi surface and for phonon-electron  $N$  processes. In the case when the phonons are scattered only by electrons these authors obtained  $\lambda_0=9\pi Mv^2(dE/dk)^2_{E_F}/2C^2\Omega_0k_{E_F}^2\hbar\omega$ . Here,  $C$  is the electron-phonon interaction constant.  $\Omega_0$  is the atomic volume of the crystal. This result of Sommerfeld and Bethe<sup>16</sup> indicates that at low temperatures, where the phonon frequency increases with  $T$ ,  $\lambda_0$  should decrease with increasing temperature. At higher temperatures, where  $\omega$  approaches the Debye frequency,  $\lambda_0$  should be independent of the temperature. According to Fig. 10, below  $50^\circ\text{K}$  the quantity  $(-\Delta S^o/S_0^o)$ , which is proportional to  $\lambda_0$ , shows qualitatively this temperature dependence expected from the Sommerfeld-Bethe relation. At very low temperatures, where  $\Delta S^o$  is varying very strongly with temperature (Fig. 6), a complication can arise from the fact that here the separation of  $\Delta S$  into the electronic component and the phonon-drag component may be somewhat uncertain.

A quantitative discussion of the phonon mean free path in platinum in the temperature range, where phonon-electron collisions are dominant, would require a theoretical treatment, which includes phonon-electron umklapp processes and an electronic band structure consisting of two overlapping bands. Such a theory is, at present, not available.

#### ACKNOWLEDGMENTS

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