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Phonon Scattering by Lattice Vacancies in Platinum*

R. P. Huebener
Argonne National Laboratory, Argonne, Illinois

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The change ΔS of the thermoelectric power of high-purity platinum wire due to quenched-in lattice vacancies was measured between 4.2 and 400°K and was separated into the electronic component ΔS^e and the phonon-drag component ΔS^g. The vacancy concentration ranged from about 1×10^{-2} to 6×10^{-2} at.%. Vacancies were found to increase the electronic part and to reduce the phonon-drag part of the thermoelectric power in platinum. From the $\Delta S^g(T)$ curves the phonon-scattering cross section σ of vacancies in platinum was estimated. The experimental $\Delta S^g(T)$ curves could not be fitted using for σ a pure Rayleigh-type scattering law. However, a good fit could be obtained, using for σ the expression which is valid for resonance scattering of phonons by point defects. The experiments suggest that in the phonon scattering by vacancies in platinum a resonance occurs at about one-third of the Debye frequency.

I. INTRODUCTION

The absolute thermoelectric power in a metal containing small concentrations of point defects differs from the value in the pure material because of the scattering of electrons and phonons by the imperfections. The electron scattering by lattice defects causes a change in the electronic component of the thermoelectric power. From the change in the electronic component of the thermoelectric power the derivative of the electrical resistivity of the lattice defects with respect to the electron energy can be obtained. The phonon scattering by point defects causes a change in the phonon-drag component of the thermoelectric power. From the change in the phonon-drag component of the thermoelectric power, information on the phonon-scattering properties of the imperfections can be derived. In electrical insulators the phonon-scattering cross section of lattice defects can be deduced from thermal-conductivity measurements. Because of the dominant thermal conductivity of the conduction electrons, thermal-conductivity measurements are not suited for determining the phonon-scattering cross section of small concentrations of lattice defects in relatively pure metals. The phonon-drag component of the thermoelectric power is caused by the phonon current, present in a temperature gradient, and its interaction with the conduction electrons. This close relation between the phonon-drag thermoelectric power and the phonon current is the reason why in pure metals phonon-scattering properties of lattice defects can be deduced from thermoelectric measurements in a similar way as they are found in electrical insulators from thermal-conductivity experiments. The fact that the phonon-drag component of the thermoelectric power cannot be obtained directly from experiment but only after subtracting the electronic component is a disadvantage one has to bear in metals.

The influence of point defects on the thermoelectric power of a pure metal has been measured with dilute alloys of a series of metals.[1–8] From these measurements the phonon-scattering cross section of the chemical impurities investigated can be estimated. Recently[9] the phonon-scattering cross section of lattice vacancies in gold has been determined from thermoelectric measurements. Measurements of the size effect on the phonon-drag thermoelectric power have been used to determine the phonon mean free path in platinum.[10,11]

In the present investigation the change ΔS of the thermoelectric power of high-purity platinum wire due to quenched-in lattice vacancies is measured between 4.2 and 400°K. The change in the thermoelectric power is separated into the electronic component and the phonon-drag component. In Sec. II the theoretical treatment of the influence of point defects on the thermoelectric power is briefly summarized. A more detailed description of the theory may be obtained from Refs. 9 and 11. The experiments and the experimental results are presented in Secs. III and IV. In Sec. V the relaxation time for phonon scattering by lattice vacancies in platinum is estimated from the phonon-drag component of ΔS.

II. ELECTRONIC AND PHONON-DRAG THERMOELECTRIC POWER

The absolute thermoelectric power S_0 of a pure metal is a sum of the electronic component S_0^e and the phonon-drag component S_0^g

$$S_0=S_0^e+S_0^g. \tag{1}$$

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

[1] F. J. Blatt and R. H. Kropschot, Phys. Rev. **118**, 480 (1960).
[2] F. J. Blatt, M. Garber, and B. W. Scott, Phys. Rev. **136**, A729 (1964).
[3] A. M. Guénault and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A264**, 41 (1961).
[4] A. M. Guénault and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A274**, 154 (1963).
[5] W. G. Henry and P. A. Schroeder, Can. J. Phys. **41**, 1076 (1963).
[6] R. S. Crisp, W. G. Henry, and P. A. Schroeder, Phil. Mag. **10**, 553 (1964).
[7] P. A. Schroeder, R. Wolf, and J. A. Woollam, Phys. Rev. **138**, A105 (1965).
[8] I. Weinberg, Phys. Rev. **139**, A838 (1965).
[9] R. P. Huebener, Phys. Rev. **135**, A1281 (1964).
[10] R. P. Huebener, Phys. Letters **15**, 105 (1965).
[11] R. P. Huebener, Phys. Rev. **140**, A1834 (1965).

The subscript 0 in Eq. (1), and hereafter, refers to a pure specimen. According to Eq. (1) the change ΔS in the thermoelectric power due to point defects, which scatter electrons and phonons, is given by the sum

$$\Delta S = \Delta S^e + \Delta S^g. \tag{2}$$

Here ΔS^e and ΔS^g are the change in the electronic and the phonon-drag thermoelectric power, respectively. The electronic thermoelectric power S^e of a specimen containing small concentrations of point defects differs from the value in the pure material by ΔS^e because of the electron scattering by the lattice defects. The difference ΔS^e is given by

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

Here $W_0{}^e$ is the electronic thermal resistivity of the pure material and ΔW^e the change in the electronic thermal resistivity due to the electron scattering by the impurities. $S_i{}^e$ is the electronic thermoelectric power associated with the electron scattering by the lattice defects. In the derivation of Eq. (3) it is assumed that the electron scattering by the imperfections and all other electron-scattering processes in the material are independent of each other (Matthiessen's rule). If, in addition to the validity of Matthiessen's rule, 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 ρ_0 is the electrical resistivity of the pure material and $\Delta\rho$ the electrical resistivity change due to the electron scattering by the impurities. The electronic thermoelectric power of the pure metal is then given by

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

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 the additional electron-scattering events in the material, which cause the resistivity increase $\Delta\rho$, can then be written as

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

TABLE I. Temperature dependence of the Wiedemann-Franz ratio $\rho_0/W_0{}^eT$ for platinum. L_0 is the Lorentz number: $L_0 = 2.45 \times 10^{-8}$ (V/deg)^2. Up to 100°K the values are obtained from the data on the electrical and thermal resistivity of platinum given in Ref. 12. Above 100°K the values are taken from Ref. 13.

T(°K)	$\dfrac{\rho_0}{W_0{}^eTL_0}$
20	0.40
25	0.45
30	0.51
40	0.62
50	0.71
60	0.73
75	0.75
100	0.89
150	0.91
200	0.97
250	1.01
300	1.04
350	1.07
400	1.09
450	1.10

At temperatures above the Debye temperature the electron-phonon collisions are practically elastic and the Wiedemann-Franz law is valid. 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 $\rho_0/W_0{}^eT$ is shown for platinum as a function of the temperature. Up to 100°K the ratio $\rho_0/W_0{}^eT$ was calculated from the data of White and Woods[12] on the electrical and thermal resistivity of platinum. Above 100°K the ratio $\rho_0/W_0{}^eT$ was taken from Slack.[13] As seen from Table I, below about 100°K the ratio $\rho_0/W_0{}^eT$ decreases appreciably with decreasing temperature. Above about 100°K the ratio $\rho_0/W_0{}^eT$ is close to the theoretical value given by the Lorentz number, $L_0 = 2.45 \times 10^{-8}$ V^2/deg^2, 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. The scattering of the conduction electrons by the point defects is expected to be elastic and to follow the Wiedemann-Franz law. Therefore, the quantity ΔW^e in Eq. (3) can be replaced by the electrical-resistivity change $\Delta\rho$ using the relation

$$\Delta W^e = \frac{\Delta\rho}{TL_0}. \tag{6}$$

From Eqs. (3) and (6) we obtain

$$\Delta S^e = \frac{S_0{}^e}{W_0{}^eTL_0/\Delta\rho + 1}\left\{\frac{S_i{}^e}{S_0{}^e} - 1\right\}. \tag{7}$$

The phonon-drag thermoelectric power S^g of a specimen containing small concentrations of lattice defects differs from the value in the pure material by ΔS^g because of the phonon scattering by the imperfections. ΔS^g must be calculated by integrating over the entire frequency spectrum of the phonons. We write the phonon-drag thermoelectric power of the pure

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[12] G. K. White and S. B. Woods, Can. J. Phys. 35, 248 (1957).

[13] G. A. Slack, J. Appl. Phys. 35, 339 (1964).

material as

$$S_0{}^g=\sum_j \int s_g(\mathbf{q},j)d^3q\,, \tag{8}$$

where $\mathbf{q}$ is the wave vector and j the polarization of the phonon. The quantity $s_g(\mathbf{q},j)$, as defined in Eq. (8), contains the relative probability for the phonon $\mathbf{q}$, j to interact with an electron. A more detailed description of the function $s_g(\mathbf{q},j)$ is given in Sec. V. The change of the phonon-drag thermoelectric power due to the phonon scattering by lattice defects is given by

$$\Delta S^g \equiv S^g - S_0{}^g = -\sum_j \int \frac{s_g(\mathbf{q},j)}{1+\tau_i(\mathbf{q},j)/\tau_0(\mathbf{q},j)} d^3q\,. \tag{9}$$

Here $\tau_i(\mathbf{q},j)$ is the relaxation time for phonon scattering by the defects. $\tau_0(\mathbf{q},j)$ is the relaxation time for phonon scattering in the pure material. In the derivation of Eq. (9) it is assumed that the phonon scattering by the imperfections and all other phonon scattering events in the metal are independent of each other (Matthiessen's rule). It is seen from Eq. (9) that measurements of the quantity ΔS^g yield information on the relaxation time τ_i if the functions s_g and τ_0 are known.

The separation of the quantity ΔS into the electronic component ΔS^e and the phonon-drag component ΔS^g can be achieved in the following way. At high temperatures $S_0{}^g$ and ΔS^g become negligible because of the dominant influence of phonon-scattering processes which do not involve electrons. Therefore, the value of ΔS at high temperatures is equal to ΔS^e. In combination with Eq. (7) the high-temperature value of ΔS can be used to calculate ΔS^e as a function of the temperature. In the calculation of $\Delta S^e(T)$ the quantity $S_i{}^e/S_0{}^e$ in Eq. (7) is assumed to be independent of the temperature. $S_0{}^e$ is assumed to be proportional to the absolute temperature [see Eq. (4)]. 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 and where S_0 is usually proportional to the absolute temperature. The function $\Delta S^g(T)$ is obtained from the experimentally determined function $\Delta S(T)$ and from the calculated function $\Delta S^e(T)$ with Eq. (2).

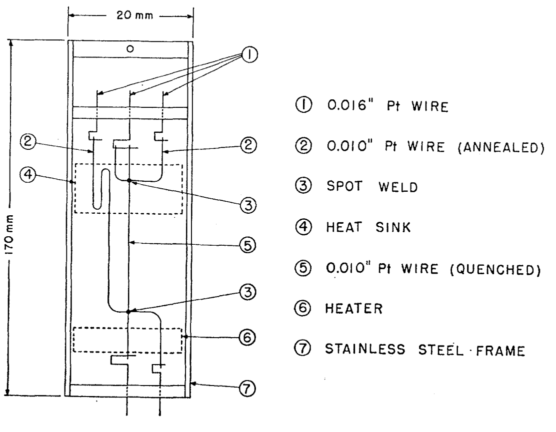

FIG. 1. Scheme of the specimen.

III. EXPERIMENTAL PROCEDURE

A. Specimen

The specimen material was polycrystalline 99.999% pure platinum wire of 0.010-in. diameter.[14] The specimen, shown in Fig. 1, consisted of a center wire and two potential lead wires mounted on a stainless-steel sample holder. The specimen wires were spot welded to short pieces of 0.016-in.-diam platinum wire which were attached to the sample holder. The center wire was electrically connected with both potential lead wires by two platinum wires of 0.002-in. diameter and of about 0.5-cm length. The lower potential lead wire was bent as indicated in Fig. 1 to obtain a good thermal contact with the heat sink inside the cryostat. The length of the center wire between the potential lead wires was about 6 cm. All platinum wires used in assembling the specimen were 99.999% pure.[14] Before mounting, the specimen wires were placed for about 30 min in hydrochloric acid and nitric acid, respectively, and were rinsed with distilled water. After mounting, the specimen wires were rinsed in acetone and methyl alcohol. Then they were annealed in air by passing direct current through them. All 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. After annealing, the electrical resistance of the part of the center wire between the 0.002-in.-diam wire connections to both potential leads was measured at room temperature and in a liquid-helium bath. The resistance measurements were carried out using a conventional potentiometric technique.

For quenching the center wire, the method described earlier[9] was used. The experiments were carried out with quench temperatures between 1300 and 1600°C. Optical pyrometry indicated that before quenching the temperature of the heated wire was uniform within ±5°C over the length between both potential leads. The recording oscillograph, used for measuring the electrical resistance of the center wire during quenching, indicated that the temperature of the heated wire dropped about linearly with time to the temperature of the ice water bath used as the quench medium. A summary of the specimens including the quench temperatures and the time required for cooling the specimen wire is given in Table II. The quench temperatures given in Table II were obtained by optical pyrometery. The quench temperatures and the cooling times of Table II correspond to quench rates of about 3×10^4 to 4×10^4 °C/sec.

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[14] Obtained from the Sigmund Cohn Corporation, Mount Vernon, New York.

TABLE II. Summary of the specimens.

Specimen number	$\left\{\frac{\rho(296°\mathrm{K})}{\rho(4.2°\mathrm{K})}\right\}$ center wire, before quench	$\left\{\frac{\rho(296°\mathrm{K})}{\rho(4.2°\mathrm{K})}\right\}$ center wire, after quench	$\left\{\frac{\rho(296°\mathrm{K})}{\rho(4.2°\mathrm{K})}\right\}$ lead wire	Quench temperature (°C)	Cooling time (10^{-2} sec)
1	7610	212.8	6307	1370	3.3
2	7087	201.6	5954	1330	5.1
3	5671	160.5	5924	1330	4.4
4	7188	110.8	5540	1500	3.7
5	6846	73.6	7089	1600	5.2
6	7412	71.4	5596	1570	4.2
7	5799	48.1	6413	1600	5.2

After quenching, the specimen was rinsed with methyl alcohol. The 0.002-in.-diam platinum wires connecting the center wire and the potential lead wires were cut off. Both potential lead wires were spot welded to the center wire at the crossing points. The electrical resistance of the quenched wire was measured again at room temperature and in a liquid-helium bath. Then the specimen was mounted in the cryostat used for the thermoelectric measurements and was cooled to 77.3°K. The specimens were kept at room temperature for less than 1 h after quenching. After completion of the thermoelectric measurements the specimen was taken from the cryostat and the electrical resistance of the lower potential lead wire was measured at room temperature and in a liquid-helium bath. For this purpose an additional potential lead was spot welded to this wire. The electrical resistivity ratios obtained for the various specimens are given in Table II.

By quenching, lattice defects, which are thermally generated at the high temperature, are trapped within the crystal. In fcc metals like platinum the lattice defects in thermal equilibrium with the perfect crystal at high temperatures are predominantly monovacancies. The quenching technique has been used for studying the formation energy and the migration energy of vacancies in platinum. An extensive investigation of point defects in quenched platinum has been carried out recently by Jackson.[15] Using quench temperatures and quench rates similar to those of the present experiments Jackson found that in quenched platinum no annealing occurs at temperatures below about 150°C. The annealing of defects in quenched platinum is characterized by a single annealing stage regardless of the initial vacancy concentration. Less than 0.1% of the quenched-in electrical resistivity remains after long isothermal anneals carried out at a temperature at which annealing just starts with an appreciable rate. The isothermal annealing curves obtained with quenched platinum have not the S-like structure found in gold quenched from above 800°C.[16] From his results Jackson concluded that during annealing of quenched platinum point defects diffuse to sinks which become less efficient with time. During the time necessary to cool the specimen monovacancies, which are predominant under equilibrium at high temperatures, may coagulate to some extent, forming small vacancy clusters. An estimate of the formation of small vacancy clusters during quenching is quite complicated. It depends sensitively on parameters, like the binding energy between individual vacancies, which are difficult to evaluate with high accuracy. Theoretical estimates regarding the formation of polyvacancies during quenching were carried out in the past mainly for gold.[17–19] These calculations seem to indicate that in gold predominantly monovacancies are obtained by quenching with a cooling time similar to that achieved in the present experiments with platinum.

B. Thermoelectric Measurements

For performing the thermoelectric measurements the specimens were mounted in a cryostat. The cold junction of the specimen was in good thermal contact with the heat sink inside the cryostat and could be kept at the temperature of the temperature bath (liquid helium, liquid nitrogen, and ice water). 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.[9] The area of the heat sink and of the heater is shown in Fig. 1 by a dashed line. The potential lead wires of the specimen were spot welded to extensions of annealed 99.999% pure platinum wire[14] leading out of the cryostat into a thermally shielded oil bath kept at room temperature. Within the oil bath the

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[15] J. J. Jackson, in *Proceedings of the International Conference on Lattice Defects in Quenched Metals* (Academic Press Inc., New York, 1965), p. 467. References regarding the earlier studies of lattice vacancies in quenched platinum may be obtained from this paper.

[16] M. De Jong and J. S. Koehler, Phys. Rev. **129**, 49 (1963).

[17] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

[18] H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, Acta. Met. **7**, 145 (1959).

[19] R. M. J. Cotterill, in *Proceedings of the International Conference on Lattice Defects in Quenched Metals* (Academic Press Inc., New York, 1965), p. 97.

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 μV 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 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.[9] Below 80°K the temperature of the hot junction of the sample was raised by 0.2°K/min or slower. Above 80°K the temperature of the hot junction was raised by 0.3°K/min 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. The gold 2.1% cobalt versus copper thermocouple[14] used for measuring the temperature difference between the hot and the cold junction of the specimen in conjunction with the data of Powell *et al.*[20] was checked at the temperatures of liquid helium, liquid nitrogen, and ice water. The thermoelectric voltage was found to deviate by less than 0.2% from the values obtained from the table of Powell *et al.*[20] for these temperatures. The gold 2.1% cobalt versus copper thermocouple was also compared with a germanium resistance thermometer from Minneapolis-Honeywell in the temperature range between 4.2 and 80°K. The germanium resistance thermometer, which has been calibrated by Minneapolis-Honeywell, agreed better than within 1% with the gold 2.1% cobalt versus copper thermocouple.

The thermoelectric power was obtained by differentiating the voltage-temperature curves with respect to the temperature using a CDC 3600 computer. A quadratic function was fitted by the method of least squares to six neighboring points with the condition that the function obtained for the total range of a set of data and its first and second derivative were continuous. Around 80°K the thermoelectric power obtained in the liquid-helium bath agreed within 1×10^{-2} μV/°K with the thermoelectric power obtained in the liquid-nitrogen bath.

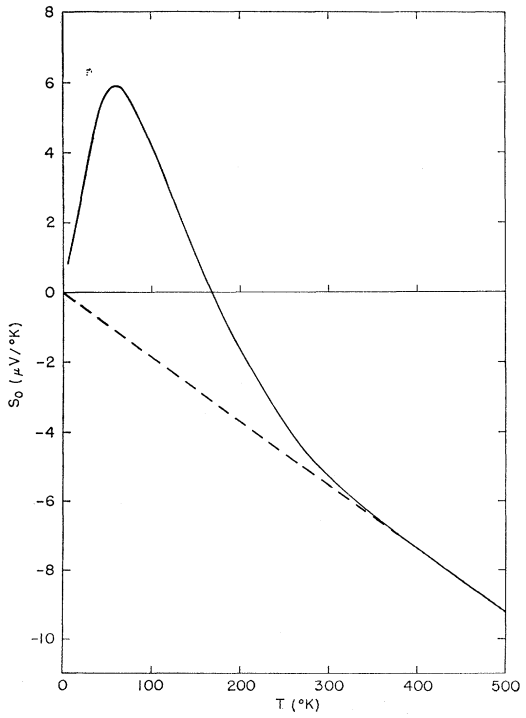

FIG. 2. Absolute thermoelectric power of platinum versus temperature.

IV. EXPERIMENTAL RESULTS

The absolute thermoelectric power of the annealed platinum wire is shown in Fig. 2 as a function of the temperature. Below 300°K the curve shown in Fig. 2 was obtained from measurements against lead[11]; above 300°K the data were deduced from measurements against gold.[11] 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^g 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 $S_0^g(T)$. Values of S_0^g obtained in this way from the curve shown in Fig. 2 are tabulated in Ref. 11 for various temperatures. From the high-temperature branch of the function $S_0(T)$ given in Fig. 2 the relation

$$S_0^e/T=-1.84\times10^{-2}\,\mu\text{V}/°\text{K}^2 \tag{10}$$

is obtained for platinum.

The difference ΔS between the thermoelectric power of the quenched and the annealed platinum wire is shown in Fig. 3 as a function of the temperature for three specimens and for temperatures above 20°K. Typical curves $\Delta S(T)$ obtained below 20°K are shown in Fig. 4. At the lowest temperatures studied ΔS has

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[20] R. L. Powell, M. D. Bunch, and R. J. Corrucini, Cryogenics **1**, 1 (1961).

small positive values. ΔS changes its sign at about 5°K and rises with increasing temperature to large negative values. At about 12°K $|\Delta S|$ passes through a maximum. Above about 12°K $|\Delta S|$ decreases rapidly with increasing temperature. $|\Delta S|$ passes through a minimum at about 40°K and a maximum at about 60°K. At 170 to 190°K ΔS changes its sign. ΔS increases with increasing temperature at higher temperatures and reaches a constant positive value at about 360°K.

To check the experimental procedure, a specimen was quenched from about 1540°C yielding a resistivity increment of $\Delta\rho = 134\times10^{-9}$ Ω cm. By keeping the specimen for 65 h at 350°C, 97.6% of the quenched-in electrical resistivity was then annealed out. Between 10 and 270°K the annealed specimen produced a thermoelectric voltage corresponding to the thermoelectric power $|\Delta S| \leqslant 5\times10^{-3}$ μV/°K. Below 10°K the thermoelectric power obtained with the annealed sample was somewhat larger.

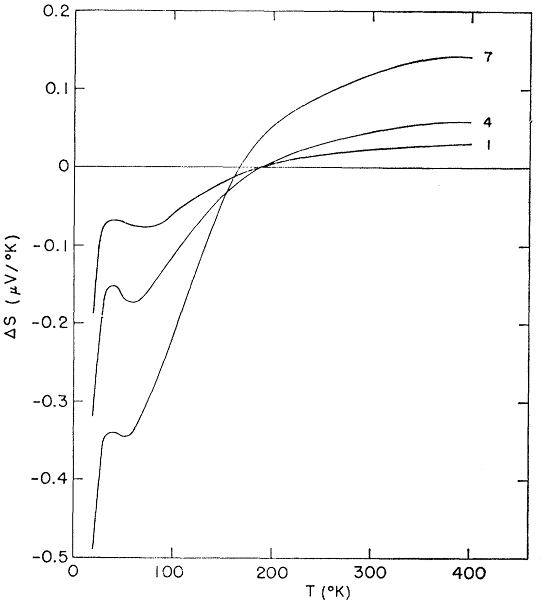

FIG. 3. Difference ΔS between the thermoelectric power of the quenched and the annealed platinum wire versus temperature. The number at each curve indicates the specimen according to Table II.

The total difference ΔS between the thermoelectric power of the quenched and the annealed wire was separated into ΔS^e and ΔS^g using the method outlined in Sec. II. 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 above 300°K. Therefore, above 300°K ΔS approaches closely the value of ΔS^e. From the value of ΔS at 400°K the function $\Delta S^e(T)$ was calculated with Eqs. (7) and (10). The function $W_0{}^e(T)$ in Eq. (7) was obtained from the data of White and Woods[12] 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 $\rho(296°\text{K})/\rho(77.3°\text{K})$ calculated from the data of White and Woods[12] agrees within 1% with the value obtained for the annealed platinum wire in the present experiment. The resistivity difference $\Delta\rho$ was calculated in the way described elsewhere[11] from the resistance measurements at 4.2°K and room temperature using the value $\rho_0(296°\text{K}) = 10.6\times10^{-6}$ Ω cm. The $\Delta\rho$ value obtained in this way was used at all temperatures for calculating the function $\Delta S^e(T)$. The assumed temperature independence of $\Delta\rho$ was checked by measuring the quenched-in electrical resistance of several specimens at 4.2, 77.3, 194.6, and 273.2°K. At the temperatures above 4.2°K $\Delta\rho$ was slightly larger than at 4.2°K. The maximum deviation from the $\Delta\rho$ value at 4.2°K was found to be about 20%.

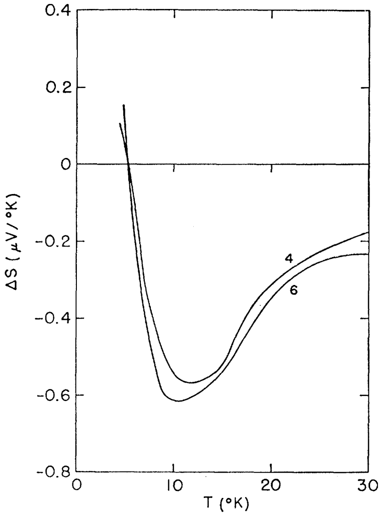

FIG. 4. Difference ΔS between the thermoelectric power of the quenched and the annealed platinum wire versus temperature for specimens No. 4 and No. 6.

At very low temperatures the quantity ΔS^e is difficult to evaluate since here the thermal resistivity $W_0{}^e$ in Eq. (7) 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 quantities ΔS^e and ΔS^g calculated in the way mentioned above from the measured ΔS values are shown in Figs. 5 and 6, respectively, as a function of the temperature. ΔS^e decreases with increasing temperature above 20°K and is almost temperature independent above about 100°K. From Eq. (7) we can see qualitatively the behavior of the function $\Delta S^e(T)$ below 20°K. We assume that $S_0{}^e/T$ and $S_i{}^e/S_0{}^e$ are strictly constants down to $T = 0$°K. In the temperature range,

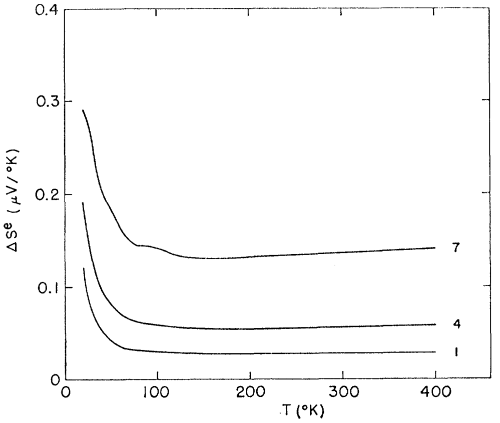

FIG. 5. Difference ΔS^e between the electronic thermoelectric power of the quenched and the annealed platinum wire versus temperature. The number at each curve indicates the specimen according to Table II.

where $\Delta\rho \gg W_0{}^eTL_0$, ΔS^e should then be proportional to the absolute temperature. At higher temperatures, where $\Delta\rho \ll W_0{}^eTL_0$ and where $W_0{}^eT$ increases more rapidly than linearly with T, ΔS^e should decrease with increasing temperature, as seen in Fig. 5. The function $\Delta S^e(T)$ should, therefore, pass through a maximum below 20°K. As seen from Fig. 6, the phonon-drag component ΔS^g becomes appreciable below about 250°*K*. $|\Delta S^g|$ increases with decreasing temperature. It exceeds the change of the electronic component below about 180°K. Near the temperature of the phonon-drag peak in pure platinum the $|\Delta S^g|$ curves show in some cases a slight maximum. According to Fig. 6 $|\Delta S^g|$ increases with decreasing T even below the temperature of the phonon-drag peak. Since ΔS^g is zero for $T=0$°K the curves $|\Delta S^g(T)|$ will pass at least through one maximum below 20°K.

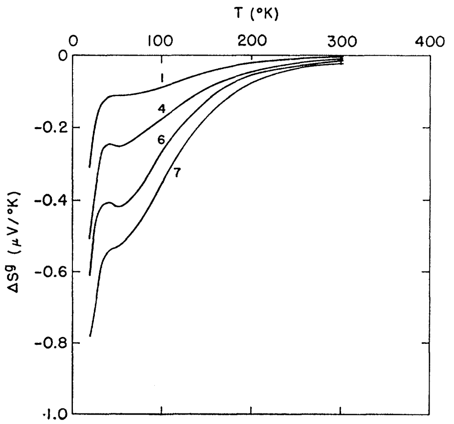

FIG. 6. Difference ΔS^g between the phonon-drag thermoelectric power of the quenched and the annealed platinum wire versus temperature. The number at each curve indicates the specimen according to Table II.

Figure 7 shows the quantity ΔS measured at 360°K versus the resistivity change $\Delta\rho$ due to quenching. ΔS is seen to increase linearly with $\Delta\rho$. The data shown in Fig. 7 yield the relation

$$\frac{\Delta S(360\text{°K})}{\Delta\rho} = (6.4\pm0.6)\times10^5 \frac{\mu\text{V}}{\text{°K}\,\Omega\,\text{cm}}. \tag{11}$$

The quantity ΔS^g is shown in Fig. 8 as a function of $\Delta\rho$ for different temperatures. The data given for 150°K yield the relation

$$\frac{\Delta S^g(150\text{°K})}{\Delta\rho} = -(9.2\pm0.5)\times10^5 \frac{\mu\text{V}}{\text{°K}\,\Omega\,\text{cm}} \tag{12}$$

for $\Delta\rho < 150\times10^{-9}$ Ω cm.

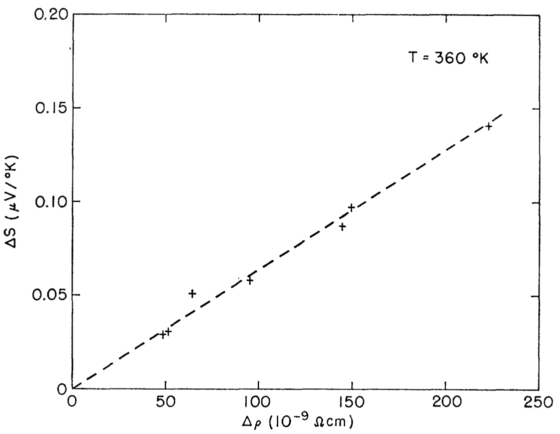

FIG. 7. Difference ΔS between the thermoelectric power of the quenched and the annealed platinum wire measured at 360°K versus the electrical resistivity change due to quenching.

The functions $\Delta S^e(T)$ and $\Delta S^g(T)$, which are shown in Figs. 5 and 6, depend, of course, critically on the way in which the measured function $\Delta S(T)$ is separated into both components. Perhaps the most striking feature in Figs. 3 and 6 is the fact that ΔS and ΔS^g fall with decreasing temperature to relatively large negative values even below the temperature of the phonon-drag peak. We will see in Sec. VB that the interpretation of the results depends strongly on the behavior of the function $\Delta S^g(T)$ around and below the temperature of the phonon-drag peak. If the dip in the $\Delta S(T)$ curves below about 50°K is caused by an anomaly in the function $\Delta S^e(T)$ at low temperatures, it cannot be ascribed, of course, to the phonon-drag component $\Delta S^g(T)$. From a comparison between Figs. 5 and 6 we see that, in order to get rid of the low temperature dip in the $\Delta S^g(T)$ curves, we must assume that the function $\Delta S^e(T)$ changes its sign somewhere above 20°K. However, such a drastic departure of the function $\Delta S^e(T)$ from its regular behavior is very unlikely. If the low-temperature dip in the function $\Delta S(T)$ would be associated with the electronic component $\Delta S^e(T)$, one would expect that the dip also occurs for various impurities added to the platinum. On the other hand, the variation of the phonon-scattering cross section of an imperfection with the phonon frequency depends critically on the nature of the lattice defect. Therefore, if the dip in the function $\Delta S(T)$ is associated with the phonon-drag component $\Delta S^g(T)$, one would expect that the appearance of the dip depends strongly on the nature of the lattice defect. To differentiate between both possibilities we measured the thermoelectric power of a platinum specimen containing 9 at. % rhodium[14] versus pure platinum. The result is shown in Fig. 9. Apparently the dip in the $\Delta S(T)$ curve at low temperatures does not occur in this system. The dashed line in Fig. 9 shows the electronic component $\Delta S^e(T)$. In the calculation of the function $\Delta S^e(T)$ for the alloy specimen the electrical resistivity of the alloy was obtained from the electrical resistance and the length and the cross-sectional area of the allow wire. The length of the alloy wire was measured with a micrometer microscope. The cross-sectional area was computed from the weight of a piece with known length. The density of the alloy was calculated from the mass and the concentration of rhodium and the lattice parameter of the alloy.[21]

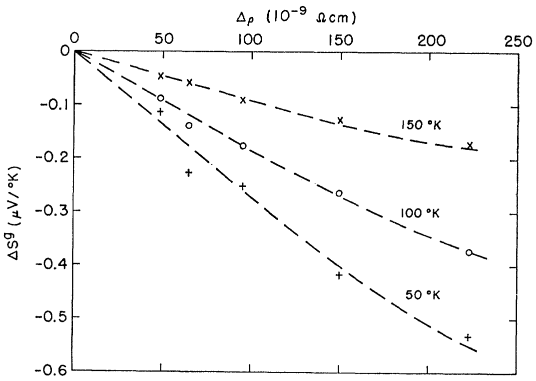

FIG. 8. Difference ΔS^g between the phonon-drag thermoelectric power of the quenched and the annealed platinum wire for different temperatures versus the electrical resistivity change due to quenching.

The arguments given above seem to indicate that the dip found in the $\Delta S(T)$ curves at low temperatures is associated with a dip in the phonon-drag component $\Delta S^g(T)$ as shown in Fig. 6. Such a dip in the $\Delta S^g(T)$ curves at low temperatures indicates that the phonon scattering by vacancies in platinum is particularly strong at low temperatures.

V. ANALYSIS AND DISCUSSION

A. Electronic Component of ΔS

As shown in Fig. 6 the phonon-drag component ΔS^g vanishes above about 300°K. Therefore, the result given in Eq. (11), in combination with Eq. (5), can be used for calculating the derivative $\{\partial \ln\Delta\rho/\partial E\}_{E_F}$. Table I indicates that around 360°K the deviation from the Wiedemann-Franz law, assumed in Eq. (5), is relatively small. From Eqs. (4) and (10) we calculate

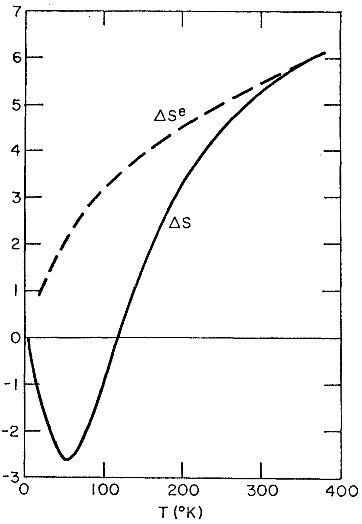

FIG. 9. Difference ΔS between the thermoelectric power of Pt-9 at. % Rh alloy and pure platinum versus temperature. The dashed line shows the electronic component of ΔS.

$$\{\partial \ln\rho_0(E)/\partial E\}_{E_F} = -0.75 \text{ (eV)}^{-1}. \tag{13}$$

From Eq. (5) in combination with Eqs. (10), (11), and (13) we then obtain

$$\{\partial \ln\Delta\rho/\partial E\}_{E_F} = 0.20 \pm 0.09 \text{ (eV)}^{-1}. \tag{14}$$

The value $\rho_0(360°\text{K}) = 13.2 \times 10^{-6}$ Ω cm used in the derivation of Eq. (14) was obtained by interpolating the data given by Slack.[13]

A quantitative discussion of the derivative $\{\partial \ln\Delta\rho/\partial E\}_{E_F}$ is difficult because of the complicated electronic band structure of platinum. The values given in Eqs. (13) and (14) may be understood qualitatively in the following way. The electrical resistivity of a metal is inversely proportional to the product of the density of the electron states, the electron velocity, and the electron mean free path l. Therefore, the logarithmic derivative of the electrical resistivity with respect to the electron energy is a sum of three terms, one of which has the form $\{-\partial \ln l/\partial E\}_{E_F}$. According to the model proposed by Mott[22] for the band structure of platinum the location of the Fermi energy 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. In the transition metals the electron mean free path associated with the scattering by lattice vibrations is mainly limited by 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

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[21] W. B. Pearson, *Handbook of Lattice Spacings and Structure of Metals* (Pergamon Press, Inc., New York, 1958).

[22] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, New York, 1958).

would expect a large negative value[23] of the quantity $\{-\partial \ln l/\partial E\}_{E_F}$, yielding a negative value of $\{\partial \ln\rho_0/\partial E\}_{E_F}$. However, the probability for transitions from the s band into an unoccupied state of the d band through scattering by an impurity like a vacancy is very small, since the wave function of an empty d state has a very small amplitude within the range of the perturbing potential.[22] Therefore, the electron scattering by lattice defects in platinum is mainly determined by the s electrons. Because of this reason one would expect that the difference $\{\partial \ln\Delta\rho/\partial E\}_{E_F}-\{\partial \ln\rho_0/\partial E\}_{E_F}$ is positive, in agreement with Eqs. (13) and (14).

B. Phonon-Drag Component of ΔS

In the following the experimental results on the phonon-drag component ΔS^g are analyzed using Eq. (9). To simplify the calculation we drop the differentiation between phonons with different polarization j. Therefore, we omit hereafter the parameter j and replace sums over j by the factor of 3. In the integration over all phonons the phonon spectrum is cut off at the Debye frequency. Further, we neglect dispersion. Using these approximations we can estimate the relaxation time $\tau_i(\mathbf{q})$ from the experimentally obtained values of ΔS^g with Eq. (9) after specifying the functions $s_g(\mathbf{q})$ and $\tau_0(\mathbf{q})$.

The function $s_g(\mathbf{q})$ may be obtained from the expression for the phonon-drag thermoelectric power derived by Hanna and Sondheimer[24] with the approximations mentioned above:

$$S_0{}^g = AT^3\int_0^{\theta/T} dz\frac{z^4e^z}{(e^z-1)^2}\alpha(z). \tag{15}$$

Here A is a constant, θ the Debye temperature and $z=\hbar\omega/k_BT$ ($\hbar$ = Planck's constant divided by 2π, ω = phonon frequency). The function $\alpha(z)$ is the relative probability for the phonon with the frequency ω to interact with an electron. Neglecting phonon-impurity and phonon-boundary collisions, we have

$$\alpha=\frac{1}{1+\tau_{\text{pe}}/\tau_{\text{pp}}}, \tag{16}$$

where τ_{pe} and τ_{pp} are the relaxation times for the phonon-electron and phonon-phonon interaction, respectively. In their theory of the phonon-drag thermoelectric power Hanna and Sondheimer neglected phonon-electron Umklapp scattering. A theoretical treatment of the phonon-drag thermoelectric power which includes phonon-electron Umklapp scattering has been given by Bailyn.[25] However, for practical purposes Bailyn's formula must be simplified somewhat,[9] yielding the same expression as given in Eq. (15).

For the relaxation time τ_{pp}, which appears in Eq. (16), we assume the relation

$$\tau_{\text{pp}}{}^{-1}=b\omega^2Te^{-\beta/T}. \tag{17}$$

A relaxation time of this form has been used by Walker and Pohl[26] and by Walker[27] in an attempt to fit the thermal conductivity of the alkali halides in the temperature range where phonon-phonon scattering is dominant. The form of the relaxation time given in Eq. (17) has also been used to fit the lattice thermal conductivity of gold[9] and copper[8] above the temperature of the lattice thermal-conductivity maximum. For the temperature β in Eq. (17) we use the value $\beta=64°\text{K}$, which is suggested by recent measurements of the phonon mean free path in platinum through the size effect on the phonon-drag thermoelectric power.[11] The relaxation time τ_{pe} for phonon-electron collisions should be constant at high temperatures. From the size effect on the phonon-drag thermoelectric power of platinum[11] it appears that around the temperature of the phonon-drag peak τ_{pe} does not depend strongly on the temperature. Presumably, below the temperature of the phonon-drag peak we have $\tau_{\text{pe}}/\tau_{\text{pp}}\ll 1$. In this temperature range $S_0{}^g$ is apparently insensitive to the analytical form of τ_{pe}. Therefore, in the function $\alpha(z)$ we approximate τ_{pe} over the whole temperature range by a constant. The ratio $\tau_{\text{pe}}/\tau_{\text{pp}}$ in Eq. (16) is then

$$\tau_{\text{pe}}/\tau_{\text{pp}}\approx Be^{-64/T}z^2T^3, \tag{18}$$

where B is a constant. The constants A and B were found by integrating the expression for $S_0{}^g$ in Eq. (15) numerically and by adjusting the value of $S_0{}^g$ at 150°K and the temperature where $S_0{}^g$ has a maximum to the experimental values. In this way the expression

$$S_0{}^g=0.58\times10^{-5}T^3\int_0^{230/T}dz\frac{z^4e^z}{(e^z-1)^2}\times\frac{1}{1+2\times10^{-6}e^{-64/T}z^2T^3}\left[\frac{\mu\text{V}}{°\text{K}}\right] \tag{19}$$

was obtained, where T is measured in °K. The Debye temperature $\theta=230°\text{K}$ for platinum was taken from Feldman *et al.*[28] A rough estimate of the constant B in Eq. (18) can be obtained in the following way. From the size effect on the phonon-drag thermoelectric power of platinum[11] the phonon mean free path at 150°K, where phonon-phonon scattering is dominant, is found to be 1.7×10^{-5} mm. We can use this value for estimating the proportionality constant in the relation $\lambda_{\text{pp}}{}^{-1}\sim z^2T^3e^{-64/T}$, where λ_{pp} is the phonon mean free

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[23] Direct experimental evidence that $\{-\partial \ln l/\partial E\}_{E_F}$ has a large negative value in platinum has been obtained in Ref. 11.

[24] I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957).

[25] M. Bailyn, Phys. Rev. **112**, 1587 (1958); **120**, 381 (1960); Phil. Mag. **5**, 1059 (1960).

[26] C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

[27] C. T. Walker, Phys. Rev. **132**, 1963 (1963).

[28] J. L. Feldman and G. K. Horton, Phys. Rev. **137**, A1106 (1965).

path limited by phonon-phonon scattering. Setting $z=1$ in the comparison we obtain $\lambda_{\text{pp}}^{-1}=0.027z^2T^3e^{-64/T}$ mm^{-1}, where T is measured in °K. At 50°K the size effect measurements[11] yield a phonon mean free path in platinum of 4.0×10^{-5} mm. Presumably, around the temperature of the phonon-drag peak λ_{pp} and the phonon mean free path λ_{pe} limited by phonon-electron collisions are of similar magnitude. Therefore, at 50°K we have $\lambda_{\text{pe}}\approx8\times10^{-5}$ mm. At higher temperatures λ_{pe} will be somewhat smaller. With $\lambda_{\text{pe}}\approx6\times10^{-5}$ mm above the temperature of the phonon-drag peak we obtain $B\approx1.5\times10^{-6}$ °K^{-3}, which is close to the value $B=2\times10^{-6}$ °K^{-3} found by the numerical integration and given in Eq. (19). In the limit of $\tau_{\text{pe}}/\tau_{\text{pp}}\gg1$ the formula in Eq. (19) has the same form as the expression used earlier[9] for representing the phonon-drag thermoelectric power of gold. The theoretical curve for $S_0{}^g(T)$ calculated from Eq. (19) together with the experimental curve is shown in Fig. 10.

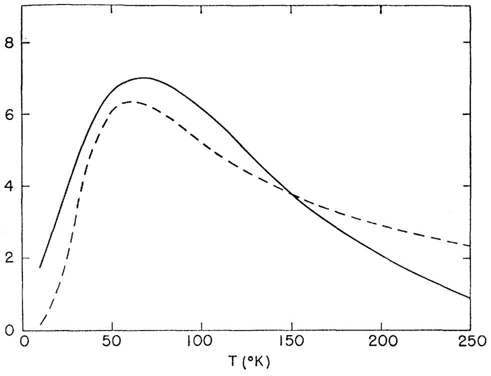

FIG. 10. Phonon-drag thermoelectric power of platinum versus temperature. Solid line: experimental curve; dashed line: theoretical curve calculated from Eq. (19).

In the analysis of the data on ΔS^g we assume that the relaxation time for phonon scattering by lattice vacancies is given by

$$\frac{1}{\tau_i}=\frac{a\omega^4}{(1-\epsilon(\omega^2/\omega_0{}^2))^2+(\pi^2/4)\epsilon^2(\omega^6/\omega_0{}^6)}. \tag{20}$$

Here ω_0 is the Debye frequency, a and ϵ are constants. The form of the inverse relaxation time given in Eq. (20) is characterized by a resonance in the scattering cross section at the frequency $\omega=\omega_0/\sqrt{\epsilon}$. The second term in the denominator acts as a damping for this resonance. The importance of resonances in the scattering of phonons by lattice defects has been pointed out in a series of theoretical papers.[29] Experimental evidence for such resonances has been obtained in the thermal-conductivity measurements by Klein,[30] Pohl,[31,26] and Walker.[27] The form for the inverse relaxation time given in Eq. (20) has been suggested by Krumhansl[32] for the scattering of phonons by vacancy-type defects. The model used by Krumhansl takes into account the change in the force constant at the vacant lattice site. It appears that the form of τ_i^{-1}, given in Eq. (20), has been used by Krumhansl and Walker for analyzing the low-temperature thermal conductivity of alkali halides containing F and U centers.[32] We see that, in the long-wavelength limit, Eq. (20) is identical with the Rayleigh scattering law $\tau_i^{-1}=a\omega^4$.

Inserting Eq. (20) into Eq. (9), using the relation

$$\tau_0^{-1}=\frac{1}{\tau_{\text{pe}}}\left(1+\frac{\tau_{\text{pe}}}{\tau_{\text{pp}}}\right) \tag{21}$$

together with Eq. (18), and taking the function $s_g(\mathbf{q})$ from Eq. (19) we find

$$\Delta S^g=-0.58\times10^{-5}T^3\int_0^{230/T}dz\frac{z^4e^z}{(e^z-1)^2}\{1+2\times10^{-6}e^{-64/T}z^2T^3\}^{-1}$$
$$\times\left\{1+\frac{1}{\tau_{\text{pe}}}(1+2\times10^{-6}e^{-64/T}z^2T^3)\frac{(1-\epsilon(z^2T^2/230^2))^2+(\pi^2/4)\epsilon^2(z^6T^6/230^6)}{aT^4(k_B/\hbar)^4z^4}\right\}^{-1}\left[\frac{\mu\text{V}}{°\text{K}}\right]. \tag{22}$$

In Eq. (22) again T is measured in °K. The integral in Eq. (22) was evaluated numerically for various values of ϵ. The scattering parameter a was determined with Eq. (22) from the experimental ΔS^g values measured at 150°K. Using this value of a, ΔS^g was then calculated as a function of temperature in temperature steps of 10°K. The numerical integrations in Eqs. (19) and (22) were performed on a CDC 3600 computer. In the calculation of the temperature dependence of ΔS^g it was assumed that τ_{pe}, which appears explicitly in Eq. (22), is independent of the temperature above 40°K. The fact that above 40°K, τ_{pe} varies only very slightly with temperature has been suggested by the measurements[11] of the size effect on the phonon-drag thermoelectric power of platinum. Below 40°K the size effect measurements[11] indicated that the phonon mean free path λ_0 in platinum increases appreciably with decreasing temperature. From these measurements the

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[29] References regarding the recent theoretical work on phonon scattering by lattice defects may be obtained from M. V. Klein, Phys. Rev. **141**, 716 (1966).

[30] M. V. Klein, Phys. Rev. **122**, 1393 (1961).

[31] R. O. Pohl, Phys. Rev. Letters **8**, 481 (1962).

[32] J. A. Krumhansl, *Proceedings of the 1963 International Conference on Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 523.

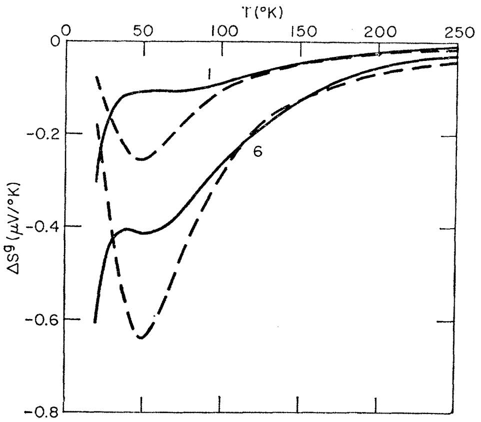

FIG. 11. Difference ΔS^g between the phonon-drag thermoelectric power of the quenched and the annealed platinum wire for specimens No. 1 and No. 6. Solid line: experimental curve; dashed line: theoretical curve calculated from Eq. (22) by adjustment to the experimental value of ΔS^g at 150°K for the case $\epsilon=0$ (pure Rayleigh scattering).

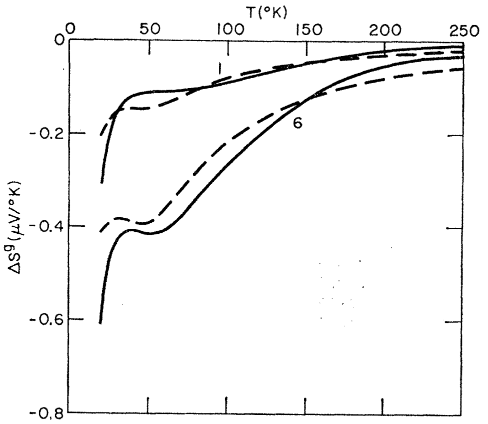

FIG. 12. Difference ΔS^g between the phonon-drag thermoelectric power of the quenched and the annealed platinum wire for specimens No. 1 and No. 6. Solid line: experimental curve; dashed line: theoretical curve calculated from Eq. (22) by adjustment to the experimental value of ΔS^g at 150°K for the case $\epsilon=12$.

ratios

$$\frac{\lambda_0(30°\mathrm{K})}{\lambda_0(40°\mathrm{K})}=1.3, \quad \text{and} \quad \frac{\lambda_0(20°\mathrm{K})}{\lambda_0(40°\mathrm{K})}=4.2 \tag{23}$$

are calculated. Presumably, below about 50°K the phonon mean free path in platinum is mainly limited by phonon-electron collisions. Therefore, the ratios given in Eq. (23) are close to the corresponding ratios of τ_{pe}. In the calculation of the function $\Delta S^g(T)$ below 40°K it was assumed that at 30°K and at 20°K τ_{pe} is larger than the value at higher temperatures by the factors given in Eq. (23).

In Fig. 11 we show the theoretical curves $\Delta S^g(T)$ for two specimens calculated in the way mentioned above for the case $\epsilon=0$ (pure Rayleigh scattering). The experimental curves are also given in the figure. Apparently it is impossible to fit the experimental results using a pure Rayleigh-type scattering law for τ_i. The fact that a Rayleigh-type scattering law cannot reproduce the increase of $|\Delta S^g|$ with decreasing temperature found below the temperature of the phonon-drag peak may be seen just by looking at Eq. (9). In order to make $|\Delta S^g|$ rise with decreasing temperature below the temperature of the phonon-drag peak, where S_0^g decreases with decreasing T, the inverse relaxation time τ_0^{-1} must fall much faster with decreasing phonon frequency (and temperature) than the inverse relaxation time τ_i^{-1}. However, this is not possible if τ_i^{-1} falls as fast as with the fourth power of the phonon frequency.

A good fit of the experimental $\Delta S^g(T)$ curves can be obtained using the form of the relaxation time τ_i given in Eq. (20) for the case $\epsilon=12$. Figure 12 shows the theoretical curves $\Delta S^g(T)$ obtained for the case $\epsilon=12$ for two specimens together with the experimental data. The reasonable agreement between the theoretical and the experimental curves in Fig. 12 suggests that in the phonon scattering by vacancies in platinum a resonance occurs at a phonon frequency which is by a factor of about 3.5 smaller than the Debye frequency. This resonance frequency is not too far off Krumhansl's[32] estimate, which yields a resonance at $\omega=\omega_0/\sqrt{6}$ for vacancy-type defects.

Keeping in mind the approximations made in the determination of the function $s_g(\mathbf{q})$, a quantitative agreement between the theoretical and experimental $\Delta S^g(T)$ curves cannot be expected. There is definitely need for improving the analysis of phonon-drag thermopower measurements, in particular with respect to a better representation of the function $s_g(\mathbf{q})$ (see Fig. 9).

By adjusting the theoretical expression given in Eq. (22) for the case $\epsilon=12$ to the experimental ΔS^g values at 150°K the scattering parameter a was determined for the various specimens. In the calculation of the scattering parameter a the value of τ_{pe} (150°K) was obtained from the value $\lambda_{\mathrm{pe}}(150°\mathrm{K})\approx 6\times10^{-5}$ mm, suggested by the measurements of the size effect on the phonon-drag thermoelectric power,[11] and the sound velocity[33] $v=2.7\times10^5$ cm/sec. From the different values of a together with the electrical resistivity data the relation

$$a/\Delta\rho=(5.43\pm0.24)10^{-36}\ \mathrm{sec}^3/\Omega\ \mathrm{cm} \tag{24}$$

was obtained. In order to obtain the scattering parameter a per vacancy concentration, the electrical resistivity per vacancy in platinum must be known. In the absence of an experimental value we may estimate this quantity in the following way. Since platinum is a transition metal, one would expect that in platinum the resistivity per vacancy is somewhat larger than in the noble metals. The electrical resistivity of platinum

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[33] *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1929), Vol. VI, p. 465.

at its Debye temperature is by a factor of 7 larger than the electrical resistivity of gold at its Debye temperature, presumably because of the scattering of *s* electrons into unoccupied states of the *d* band. However, multiplying the electrical resistivity per vacancy, found in the noble metals, by a factor of 7, would result in a value for the vacancy resistivity in platinum which is too high since the probability for transitions from the *s* band into the *d* band through scattering by defects is much smaller than the probability for *s*-*d* transitions through the electron-phonon interaction.[22] The electrical resistivity of dilute concentrations of gold in platinum is, for example, larger by only a factor of 1.5 than the resistivity of dilute concentrations of platinum in gold.[22] With the electrical resistivity per vacancy in gold[34] of $\Delta\rho/c = 1.8\times10^{-6}\ \Omega$ cm/at. % we estimate the resistivity per vacancy in platinum to be about $\Delta\rho/c \approx 4\times10^{-6}\ \Omega$ cm/at. %. Using this value (which may be wrong by a factor of 2) we obtain from Eq. (24)

$$a/c \approx 22\times10^{-42}\ \mathrm{sec}^3/\mathrm{at.}\ \%. \tag{25}$$

It was pointed out above that in the long-wavelength limit the relaxation time given in Eq. (20) is identical with the Rayleigh scattering law. The phonon scattering by point defects in the limit of long wavelength has been treated theoretically by Klemens[35] and by Carruthers.[36] Klemens' theory takes into account the change in mass, the change in the elastic constants of the linkages, and the elastic strain field at a lattice point due to the presence of the point defect. For the relaxation time τ_i of phonon scattering by point defects Klemens obtained a Rayleigh-type scattering law with the scattering parameter

$$a = (3\Delta_0 c/\pi v^3)L^2, \tag{26}$$

where

$$L^2 = \frac{1}{12}\left(\frac{\Delta M}{M}\right)^2 + \left[\frac{1}{\sqrt{6}}\frac{\Delta F}{F} - (2/3)^{1/2} Q\gamma \frac{\Delta R}{R}\right]^2. \tag{27}$$

Here Δ_0 is the atomic volume of the crystal, c the mole fraction of the point defects, v the sound velocity, and γ the Grüneisen constant. M is the atomic mass of the crystal, F the force constant of a linkage, R the nearest-neighbor distance, and ΔM, ΔF, and ΔR are the changes in these quantities at the location of the point defect. The constant Q contains the influence from the strain in the lattice outside the six nearest neighbors of the point defect. In the case of a vacancy Klemens[35] obtained $Q = 3.2$.

In Carruthers's theory only the phonon scattering due to the strain field of point defects has been calculated. For the relaxation time of the phonon scattering by the strain field of point defects Carruthers also obtained a Rayleigh-type scattering law. According to Carruthers, the Rayleigh scattering parameter is given by Eq. (26) with

$$L^2 = 80\gamma^2(\Delta R/R)^2. \tag{28}$$

Apparently, Carruthers's theory yields a somewhat larger influence of the strain field than Klemens' theory.

With $\Delta M/M = -1$ and $\Delta F/F = -1$ for a vacancy the first two terms in Eq. (27) can immediately be calculated. Assuming that the term in Eq. (27) arising from the strain field is zero, the scattering parameter

$$a/c = 1.8\times10^{-42}\ \mathrm{sec}^3/\mathrm{at.}\ \% \tag{29}$$

is found from Eqs. (26) and (27). This value is by a factor of 12 smaller than the value given in Eq. (25). An estimate of the term in Eqs. (27) or (28) caused by the strain field is difficult, since the lattice relaxation around a vacancy in platinum is not known. However, from a comparison between Eqs. (29) and (25) it appears that the scattering parameter a is dominantly determined by the strain field around the vacancy in platinum. The importance of the strain field for the phonon scattering by point defects has also been revealed in recent measurements of the phonon scattering by vacancies in gold[9] and by F centers[27] and chemical impurities[37,26] in the alkali halides.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of R. E. Govednik during the experiments. The author is indebted to A. H. Lent for programming the calculations on the CDC 3600.

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[34] R P. Huebener and C. G. Homan, Phys. Rev. **129**, 1162 (1963).

[35] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[36] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[37] M. V. Klein, Phys. Rev. **123**, 1977 (1961).