Thermoelectric Power of Annealed and Quenched Gold-Platinum Alloys*

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The absolute thermoelectric power of dilute gold-platinum alloys, containing 0.11, 0.50, 1.03, and 4.99 at.% Pt, has been measured between 4.2 and 300°K. Also, the change in the thermoelectric power of the alloys due to quenched-in lattice vacancies has been determined. The alloys containing 1 at.% Pt or less show clearly a positive phonon-drag component S^g of the thermopower below about 150°K. The positive values of S^g become smaller with increasing platinum concentration. At 20 to 30°K, S^g in these alloys changes its sign and is negative at very low temperatures. It is suggested that the appearance of a negative phonon-drag thermopower in the dilute Au-Pt alloys at very low temperatures is based on the anisotropy of the relaxation times for electron scattering. Quenched-in lattice vacancies cause a reduction of S^g in the alloys containing 1 at.% Pt or less. The reduction of $|S^g|$ due to vacancies is very pronounced at low temperatures, where S^g in the annealed alloys is negative. This is explained by the anisotropy of the electron scattering by vacancies, which apparently is opposite to the anisotropy of the electron scattering by the platinum ions, thus leading to an enhancement, due to vacancies, of the positive contribution to S^g at low temperatures.

I. INTRODUCTION

IN the present paper we report measurements of the absolute thermoelectric power of gold alloyed with small concentrations of platinum. Also, measurements on the influence of quenched-in lattice vacancies on the thermoelectric power of dilute gold-platinum alloys are reported. The platinum concentration in the alloys investigated ranged between 0.1 and 5 at. %. The experiments were mainly carried out to study the phonon-drag component of the thermoelectric power in dilute gold-platinum alloys as a function of the platinum concentration, and to investigate the change in the phonon-drag thermopower of dilute gold-platinum alloys caused by quenched-in lattice vacancies.

Thermoelectric measurements of noble metals alloyed with small concentrations of the metal next down in the periodic system have been carried out with copper-nickel alloys[1] and silver-palladium alloys.[1-3] The influence of quenched-in lattice vacancies on the thermoelectric power has been studied by one of the authors in pure gold[4] and platinum.[5] The experiments with quenched platinum[5] indicated that the reduction in the phonon-drag thermopower caused by lattice vacancies is particularly strong at low temperatures. The magnitude of the phonon-drag thermopower in quenched platinum at low temperatures has been explained by a resonance in the phonon-scattering cross section of vacancies.[5] The present study of the thermoelectric power in quenched gold-platinum alloys was stimulated by the desire to measure the change in the low-temperature thermopower caused by lattice vacancies in another system. In "pure" gold the thermopower at very low temperatures is strongly affected by very small traces of magnetic impurities, such as iron, present in solid solution.[4] Because of this reason the experiments with quenched gold[4] did not yield reliable results below about 20°K. The iron-impurity effect can be eliminated by alloying gold with a sufficient amount of another solute, which then determines the electronic thermopower of the alloy at low temperatures. The solute metal must have approximately the same mass as gold in order to minimize the reduction in the phonon-drag thermopower due to alloying. On the other hand, one requires a high electric resistivity and a high partial thermopower of the solute in order to eliminate effectively the iron influence. Because of these arguments, we carried out thermoelectric measurements with annealed and quenched gold-platinum alloys.

The thermoelectric measurements with the annealed gold-platinum alloys were generally carried out between 4.2 and 300°K. The measurements with the quenched alloys covered the temperature range between 4.2 and 220°K. Preliminary results of the present investigation were reported earlier.[6,7]

II. EXPERIMENTAL PROCEDURE

The specimen material was polycrystalline alloy wire of 0.010-in. diam.[8] Four alloy specimens, obtained from Engelhard, contained 0.11, 0.50, 1.03, and 4.99 at. % Pt. They were made from 99.999% pure Au and 99.999%

[1] P. A. Schroeder, R. Wolf, and J. A. Woollam, Phys. Rev. 138, A105 (1965).
[2] P. R. F. Simon, in *Proceedings of the 9th International Conference on Low Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 1045.
[3] C. van Baarle, thesis, Leiden, 1965 (unpublished).
[4] R. P. Huebener, Phys. Rev. 135, A1281 (1964).
[5] R. P. Huebener, Phys. Rev. 146, 490 (1966).
[6] R. P. Huebener and C. van Baarle, Phys. Letters 23, 189 (1966).
[7] R. P. Huebener and C. van Baarle, in Proceedings of the 10th International Conference on Low Temperature Physics (to be published).
[8] Obtained from Engelhard Industries, Inc., Newark, New Jersey, and from Cominco American, Inc., Spokane, Washington.

pure Pt. One specimen, containing 1.06 at. % Pt, was made by Cominco from 99.9999% pure Au and 99.999% pure Pt. The specimens were mounted on a sample holder and placed in a cryostat for the thermoelectric measurements. The specimen arrangement was similar to that described elsewhere.[4,5] Before mounting the specimen wires on the sample holder, they 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 for 20–30 h at about 850°C by passing direct current through them, and were gradually cooled to room temperature.

The absolute thermoelectric power of the annealed alloys was obtained from measurements versus 99.9999% pure lead.[9] For the absolute thermoelectric power of lead, the data of Borelius et al.[10] and of Christian et al.[11] were used. In addition, the alloy Au+1.03 at. % Pt was measured versus NbSn[12] below 16°K. The Pb wire and the NbSn strip were in the position of the "center wire" in the adopted specimen arrangement.[4,5]

In addition to the absolute thermoelectric power of the annealed alloys, the change in the thermoelectric power due to quenched-in lattice vacancies was determined. For this purpose the thermoelectric power of a quenched alloy wire was measured versus the annealed wire of the same alloy. For quenching, the same technique as described earlier[4,5] was employed. The center wires in the specimen arrangement were quenched from about 970°C to ice-water temperature within 4×10^{-2} sec, corresponding to quench rates of about 25000°C/sec. Approximately 25 to 35 min after quenching the specimens were mounted in the cryostat and placed in liquid nitrogen. The measurements on the influence of quenched-in vacancies were carried out for the alloys containing 0.11, 0.50, and 1.03 at. % Pt and were performed with two independent specimens.

The potential lead wires of the specimens were spot-welded to extensions of annealed wires from the same alloy leading out of the cryostat into a thermally shielded oil bath at room temperature. Within the oil bath the alloy wire was connected to copper wire leading to the potentiometer. Below 77°K a superconducting switch[13] was used to eliminate the spurious thermoelectric voltages in the potential leads. The switch was immersed in liquid helium outside the vacuum can of the cryostat. The tantalum coil of the switch was connected to the sample wires within the vacuum can of the cryostat via short pieces of niobium

wire. The spot-welds of these niobium wires to the sample wires were in close contact with the surface of the heat sink, which keeps the cold junction at the temperature of the cooling bath. In the nonsuperconducting state, the switch has an electrical resistance of about 45Ω at 4.2°K. This resistance is by more than a factor of 10^3 larger than the maximum output impedance encountered below 77°K in the thermocouples investigated. In the superconducting state the resistance of the superconducting shunt, including the pieces of niobium wire leading to the sample, was about 1×10^{-5} Ω. This resistance is by a factor of about 30 smaller than the output impedance of the thermocouple Au+0.11 at. % Pt versus Pb at the lowest temperature studied. In the measurements above 77°K the superconducting switch was disconnected.

The technique of the thermoelectric measurements was similar to that described elsewhere.[4,5] However, below 77°K the temperature of the hot junction of the specimens was measured with a germanium resistance thermometer[14] [attached to the small copper plate which carried the hot junction of the (Au 2.1% Co)-versus-Cu thermocouple]. The data were taken at temperature intervals of approximately 0.3°K below 10°K, 1°K between 10 and 80°K, and 1–2°K above 80°K.

The thermoelectric power was obtained by differentiating the emf-versus-temperature curves with respect to the temperature, using a CDC 3600 computer. A second-order polynomial was fitted by the method of least squares to either 5, 7, or 9 neighboring points. Then the derivative was calculated for the center point. By shifting the cluster of neighboring points one step at a time, the thermopower was obtained as a function of temperature.

III. DATA ANALYSIS

In the temperature range investigated, the total thermoelectric power S of the gold-platinum alloys is the sum of the electronic component and the phonon-drag component. The separation into both components can be achieved using the following arguments. The electronic component of the thermopower in the alloys is in first approximation given by[15]

$$S^e = cT + [(W_{ph}/W_{Pt})+1]^{-1}(b-c)T. \qquad (1)$$

Here T is the absolute temperature. W_{ph} and W_{Pt} are the electronic thermal resistivity associated with the scattering by phonons and by the platinum ions, respectively. The constants c and b are defined by

$$S_{ph}^e = cT \qquad (2)$$

and

$$S_{Pt}^e = bT, \qquad (3)$$

[9] Obtained from Cominco American, Inc., Spokane, Washington.
[10] G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, Proc. Acad. Sci. Amsterdam **35**, 10 (1932).
[11] J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).
[12] The material used was RCA niobium-tin superconductive ribbon, kindly supplied by C. Laverick.
[13] R. P. Huebener and R. E. Govednik, Rev. Sci. Instr. **37**, 1675 (1966).
[14] Obtained from Honeywell, Inc., Philadelphia, Pennsylvania.
[15] M. Kohler, Z. Physik **126**, 481 (1949).

where S_{ph}^e and S_{Pt}^e are the electronic thermopower associated with the scattering by phonons and by the platinum ions, respectively. Since the Wiedemann-Franz law is valid in good approximation for the electron scattering by the solute ions, we have

$$W_{Pt} = \rho_{Pt}/TL_0. \qquad (4)$$

Here ρ_{Pt} is the electrical resistivity of the solute ions, L_0 is the Lorentz number $(L_0 = 2.45 \times 10^{-8}~V^2/\text{deg}^2)$. Inserting Eq. (4) into Eq. (1) we obtain

$$S^e = cT + [(W_{ph}L_0T/\rho_{Pt}) + 1]^{-1}(b-c)T. \qquad (5)$$

In pure gold the phonon-drag component of the thermopower vanishes above about 180°K.[4] Therefore, above this temperature the total thermopower of the gold-platinum alloys is given by Eq. (5). Further, the temperature dependence of S above about 180°K can be used to calculate the constants b and c from Eq. (5). After determining b and c in this way, the function $S^e(T)$ can be calculated from (5) for the low-temperature range. The phonon-drag component S^g, present at low temperatures, is then given by the difference

$$S^g(T) = S(T) - S^e(T). \qquad (6)$$

The change ΔS in the thermoelectric power of the gold-platinum alloys due to quenched-in lattice vacancies is the sum of the change ΔS^e in the electronic component and the change ΔS^g in the phonon-drag component;

$$\Delta S = \Delta S^e + \Delta S^g. \qquad (7)$$

In first approximation the change ΔS^e is given by[4,5]

$$\Delta S^e = [S^e/(W_{alloy}/W_{vac} + 1)][S_{vac}^e/S^e - 1]. \qquad (8)$$

Here W_{alloy} is the electronic thermal resistivity of the annealed alloy, W_{vac} is the electronic thermal resistivity of the quenched-in vacancies, and S_{vac}^e is the electronic component of the thermopower associated with the quenched-in vacancies. (S^e is, as before, the electronic component of the thermopower of the annealed alloy.) The quantity W_{alloy} is given by

$$W_{alloy} = W_{ph} + W_{Pt}. \qquad (9)$$

Assuming again the Wiedemann-Franz law for the electron scattering by lattice vacancies, we have

$$W_{vac} = \rho_{vac}/TL_0, \qquad (10)$$

where ρ_{vac} is the electrical resistivity of the quenched-in vacancies. Inserting Eqs. (9), (10), and (4) into Eq. (8), we obtain

$$\Delta S^e = [S^e/(W_{ph}TL_0/\rho_{vac} + \rho_{Pt}/\rho_{vac} + 1)]$$
$$\times [S_{vac}^e/S^e - 1]. \qquad (11)$$

In first approximation S_{vac}^e is given by

$$S_{vac}^e = d \times T, \qquad (12)$$

where d is a constant.

At temperatures above about 180°K, where the phonon-drag thermopower vanishes in gold, the measured quantity ΔS is equal to ΔS^e. The ΔS values found in this temperature range can then be used to calculate the parameter d from Eq. (11). After determining d in this way, the function $\Delta S^e(T)$ can be calculated from (11) for the low-temperature range. The change $\Delta S^g(T)$ in the phonon-drag component caused by lattice vacancies is then given by Eq. (7).

IV. EXPERIMENTAL RESULTS

A. Annealed Alloys

The absolute thermopower of the four (annealed) alloys investigated is shown in Figs. 1–4 as a function of temperature. From the measured values of the thermopower at 200 and 300°K the constants b and c were calculated using Eq. (5). Using these values of b and c, the function $S^e(T)$ was then calculated for the low-temperature range from Eq. (5). The extrapolated function $S^e(T)$ obtained in this way is shown in Figs. 1–3 by a dashed line. In Fig. 4 the extrapolated values of $S^e(T)$ are indicated by crosses.

In the calculation of the function $S^e(T)$, the electronic thermal resistivity W_{ph} of the gold host lattice above 200°K can be obtained from the electrical resistivity of pure gold, since the Wiedemann-Franz law is well satisfied in this temperature range. Below
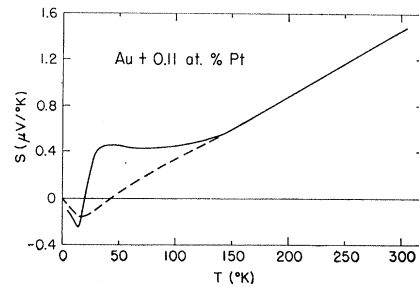

FIG. 1. Absolute thermoelectric power S of the annealed alloy Au+0.11 at. % Pt versus temperature. The dashed line indicates the electronic component of S.
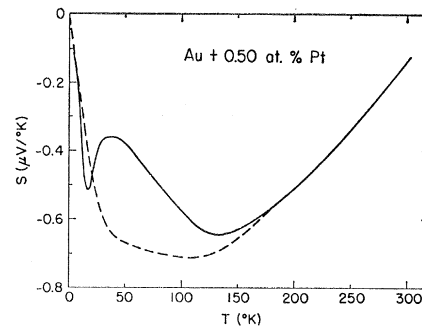

FIG. 2. Absolute thermoelectric power S of the annealed alloy Au+0.50 at. % Pt versus temperature. The dashed line indicates the electronic component of S.

200°K the resistivity W_{ph} in pure gold was taken from the data of White.[16] The electrical resistivity ρ_{Pt} of the platinum admixture was calculated from the electrical resistivity ratios

$$A = [\rho(296°K)/\rho(4.2°K)]_{alloy}$$

and

$$B = [\rho(296°K)/\rho(4.2°K)]_{pure\ gold},$$

using the equation

$$\rho_{Pt} = \rho_{gold}(296°K)(1-A/B)/(A-1), \qquad (13)$$
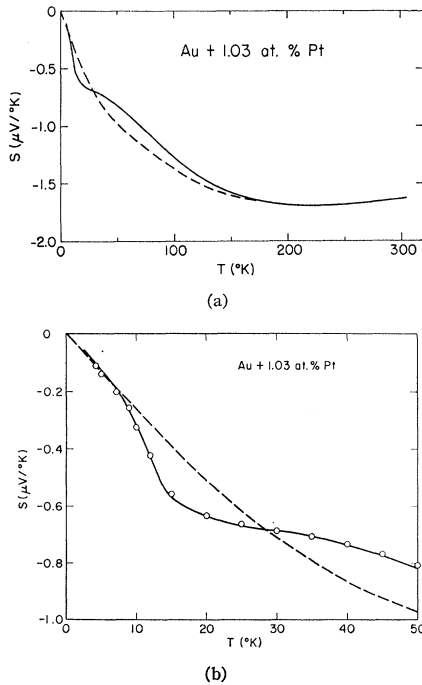

(a)

(b)

FIG. 3(a). Absolute thermoelectric power S of the annealed alloy Au+1.03 at. % Pt versus temperature. The dashed line indicates the electronic component of S. (b) Low-temperature part of Fig. 3(a) on an expanded scale. Solid curve represent thermoelectric power of the alloy Au+1.03 at. % Pt from Engelhard. Circles represent thermoelectric power of the alloy Au+1.06 at. % Pt from Cominco.
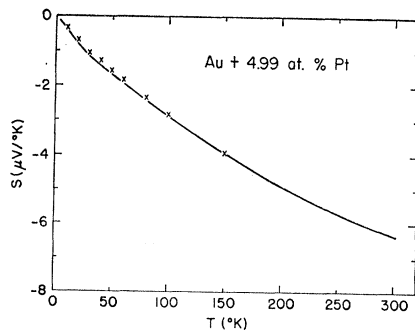

FIG. 4. Absolute thermoelectric power S of the annealed alloy Au+4.99 at. % Pt versus temperature. The crosses indicate calculated values of the electronic component of S.

[16] G. K. White, Proc. Phys. Soc. (London) **A66**, 559 (1953).

TABLE I. The constants c and b for the various platinum concentrations.

at. % Pt	c ($10^{-3}\mu V/°K^2$)	b ($10^{-2}\mu V/°K^2$)
0	7.05[a]	...
0.11	5.65	−1.13
0.50	4.61	−2.45
1.03	3.26	−2.65
4.99	2.81	−3.37

[a] Reference 4.

with the value $\rho_{gold}(296°K) = 22.25 \times 10^{-7}\Omega$ cm. For B the value $B = 2500$ was used.[17] In Eq. (13) it is assumed that Matthiessen's rule is valid for ρ_{Pt}.

The values of b and c are listed in Table I for the different alloys. Table II shows the electrical resistivity of platinum in gold for the various platinum concentrations.

As seen from Figs. 1–4, the alloys containing 1 at. % Pt or less show clearly a positive phonon-drag component of the thermopower below about 150°K. However, the positive phonon-drag thermopower in the alloys is reduced below the values found in pure gold,[4] the reduction becoming stronger with increasing platinum concentration. Apparently the phonon-drag thermopower in the alloys containing 1 at. % Pt or less changes its sign between about 17 and 28°K, and is negative at the lower temperatures. In Fig. 3(b) the thermoelectric power obtained with the Cominco specimen, which contains 1.06 at. % Pt, is indicated by circles. It is seen that the Cominco specimen gave the same results as the sample from Engelhard. In the alloy Au+4.99 at. % Pt the phonon-drag thermopower has practically vanished. Here the calculated curve $S^e(T)$ follows closely the measured curve $S(T)$ at low temperatures.

From Fig. 4 we note that in the alloy Au+5 at. % Pt the thermoelectric power can be described quite satisfactorily by Eq. (5) over the whole temperature range. As seen from Figs. 2 and 3, in the dilute alloys the electronic component calculated from Eq. (5) matches the experimentally determined thermopower very well at very low temperatures, where the phonon-drag component is expected to be negligible. It therefore appears that Eq. (5) describes the function $S^e(T)$ quite accurately over the whole temperature range in the alloys investigated.

TABLE II. Electrical resistivity of platinum in gold per unit platinum concentration c obtained for the different alloys.

at. % Pt	ρ_{Pt}/c ($10^{-6}\ \Omega$ cm/at. %)
0.11	1.00
0.50	0.95
1.03	0.91
4.99	0.89

[17] R. P. Huebener, Phys. Rev. **136**, A1740 (1964).

B. Quenched Alloys

In Figs. 5–7 the difference $\Delta S = S_{\text{quenched}} - S_{\text{annealed}}$ caused by quenched-in lattice vacancies is shown for the alloys containing 1 at. % Pt or less. The two independent quench experiments carried out for each of these alloys always led to similar results. From the value of ΔS at 200°K, the constant d was calculated using Eqs. (11) and (12). Then the function $\Delta S^e(T)$ was calculated from Eq. (11) for the low-temperature
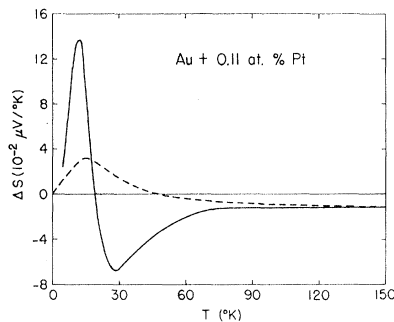

FIG. 5. Difference ΔS in the thermopower of the quenched and the annealed alloy Au+0.11 at. % Pt versus temperature (quenched-in resistivity $\rho_{\text{vac}} = 2.87 \times 10^{-8}$ Ω cm). The dashed line indicates the electronic component of ΔS.

FIG. 6. Difference ΔS in the thermopower of the quenched and the annealed alloy Au+0.50 at. % Pt versus temperature (quenched-in resistivity $\rho_{\text{vac}} = 6.89 \times 10^{-8}$ Ω cm). The dashed line indicates the electronic component of ΔS.
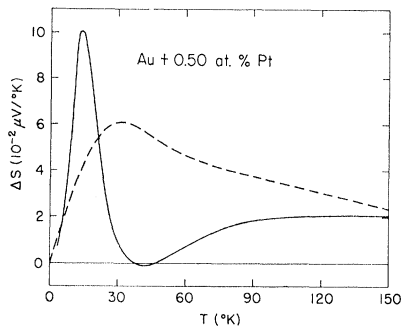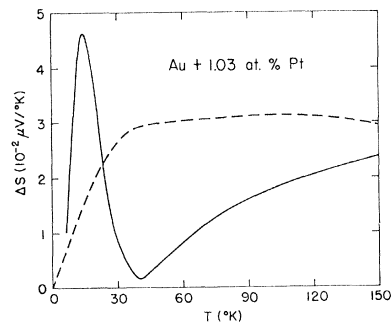

FIG. 7. Difference ΔS in the thermopower of the quenched and the annealed alloy Au+1.03 at. % Pt versus temperature (quenched-in resistivity $\rho_{\text{vac}} = 4.20 \times 10^{-8}$ Ω cm). The dashed line indicates the electronic component of ΔS.

range. The extrapolated function $\Delta S^e(T)$ is shown in Figs. 5–7 by a dashed line.

The electrical resistivity increment ρ_{vac} caused by quenching was calculated using the analog of Eq. (13). (In this case the quantities A and B are the corresponding resistivity ratios for the quenched and the annealed alloy, respectively.) The resistivity increment ρ_{vac} and the constant d for the different quench experiments are given in Table III. The d value obtained in the earlier experiments[4] with quenched pure gold is also given.

According to Figs. 5–7, above 15 to 25°K the phonon-drag component of ΔS is negative, indicating a reduction in the positive phonon-drag thermopower of the annealed alloys due to vacancies. Between 15 and 25°K the phonon-drag component of ΔS changes its sign and is positive at low temperatures, indicating here a reduction in the negative phonon-drag thermopower of the annealed alloys due to vacancies. The sign reversal of S^g and ΔS^g in each alloy occurs at approximately the same temperature.

As seen from Table III, the parameter d fluctuates appreciably between the two quench experiments carried out with the same alloy. The parameter d enters the function $\Delta S^e(T)$ through the quantity S_{vac}^e in Eq. (11). Since S_{vac}^e is small compared to S^e, except where $S^e(T)$ passes through zero, ΔS^e is rather insensitive to the parameter d. Therefore, the uncertainty in the parameter d indicated in Table III does not seriously affect the function $\Delta S^e(T)$.

V. DISCUSSION

A. Annealed Alloys

As seen from Table I, the parameter c, defined in Eq. (2), decreases with increasing platinum concentration. At 5 at. % Pt the value of c is 40% of the value for pure gold. A similar reduction of c with increasing solute concentration has been found in silver-palladium alloys[1] for palladium concentrations less than about 5 at. %. The parameter b, defined in Eq. (3), falls with increasing platinum concentration to larger negative values. A similar trend has been found in silver-palladium alloys.[1] The value of b given in Table I for

TABLE III. Electrical resistivity increment ρ_{vac} and the constant d from Eq. (12) for the different quench experiments.

at. % Pt	ρ_{vac} (10^{-8} Ω cm)	d (10^{-3} μV/°K^2)
0 (pure gold)	...	+0.32 ±0.14[a]
0.11 run 1	2.87	+0.72
0.11 run 2	2.89	+0.52
0.50 run 1	6.11	−1.02
0.50 run 2	6.89	−0.73
1.03 run 1	4.20	−1.16
1.03 run 2	3.74	−0.54

[a] See Refs. 4 and 36.

0.11 at. % Pt is close to the value obtained in silver-palladium alloys[1] for small palladium concentrations.

As mentioned above, the positive phonon-drag thermopower which appears in the dilute gold-platinum alloys above 20 to 30°K is reduced below the values found in pure gold. Between 40 and 80°K the phonon-drag thermopower of the alloy containing 0.50 at. % Pt is about 50% of the value in pure gold. We can compare this reduction in the phonon-drag thermopower caused by the platinum admixture with lattice-heat-conductivity data of Birch et al.[18] and White[19] for dilute gold-platinum alloys. The data of these authors indicate that above about 30°K the lattice heat conductivity in the alloy Au+0.5 at. % Pt is 84% of the value in pure gold. In general, the reduction in the phonon-drag thermopower due to alloying is somewhat stronger than the reduction in the lattice heat conductivity.[20] It therefore appears that our data on the phonon-drag thermopower in dilute gold-platinum alloys are in satisfactory agreement with the lattice-heat-conductivity data of Birch et al. and of White.

Perhaps the most striking feature in Figs. 1–3 is the appearance of a negative phonon-drag thermopower in the dilute alloys at low temperatures. In pure gold the phonon-drag thermopower has been found to be positive down to a temperature of 1.4°K.[21,22] It is tempting to explain the appearance of the negative phonon-drag thermopower at low temperatures with a change in the electronic band structure due to alloying, as suggested for silver-palladium alloys by Schroeder et al.[1] If the Fermi surface of gold becomes more free-electron-like because of alloying with platinum, one would expect that normal processes become more dominant in the electron-phonon interaction at low temperatures, thus leading to a negative phonon-drag thermopower. However, this interpretation appears to be inconsistent with recent measurements[23] of the de Haas–van Alphen effect in dilute gold-platinum alloys. An extrapolation of these measurements indicates that the neck size of the Fermi surface of gold decreases possibly by only 4% because of alloying with 1 at. % platinum.

Rather than relate the appearance of the negative phonon-drag thermopower in the Au-Pt alloys at low temperatures to a change in the electronic band structure due to alloying, we suggest a mechanism which is based on the anisotropy of the relaxation times for electron scattering. Van Baarle[3] reported recently an

increase at low temperatures in the positive phonon-drag thermopower of silver due to alloying with gold and antimony. He has shown[24] that this increase in S^g can be understood from the anisotropy in the relaxation times for electron scattering. Van Baarle's argument is based on the fact that, if the relaxation time for electron scattering by phonons and the relaxation time for electron scattering by impurities vary differently over the Fermi surface, then the contribution of the various parts of the Fermi surface to the phonon-drag thermopower in an alloy is weighted differently than in the pure metal. The effect of anisotropic relaxation times for electron scattering on the phonon-drag thermopower in dilute alloys has also been discussed recently in a similar way by Fletcher and Dugdale.[25]

The arguments given by van Baarle[24] can be summarized as follows. At low temperatures the phonon-drag contribution to the thermopower of a metal is, according to Ziman,[26] given by

$$S^g = -(U_L/TJ_1)P_{1L}/P_{LL}. \qquad (14)$$

Here U_L is the lattice thermal flux and J_1 is the generalized electron current. The scattering integrals P_{1L} and P_{LL} are defined by

$$P_{1L} = \frac{1}{k_B T} \int \int \int (\phi_k - \phi_{k'}) \phi_q P_{k,q}{}^{k'} dq dk' dk, \quad (15)$$

$$P_{LL} = \frac{1}{k_B T} \int \int \int (\phi_q)^2 P_{k,q}{}^{k'} dq dk' dk. \qquad (16)$$

Here $P_{k,q}{}^{k'}$ is the probability for an electron transition from state k to k' due to the interaction with a phonon of wave vector q. k_B is Boltzmann's constant. The functions ϕ represent the deviations from the equilibrium distribution in the electron and the phonon system. They are defined by

$$f_k = f_k{}^0 - \phi_k \partial f_k{}^0 / \partial E_k, \qquad (17)$$

$$n_q = n_q{}^0 - \phi_q \partial n_q{}^0 / \partial E_q. \qquad (18)$$

Here f_k and n_q are the electron and the phonon distribution, respectively; $f_k{}^0$ and $n_q{}^0$ are the equilibrium values. E_k and E_q are the electron and phonon energy, respectively. The trial function ϕ_k can be written as[27]

$$\phi_k \sim \tau(k)/\bar{\tau},$$

where $\tau(k)$ is the relaxation time for electrons in state k. $\bar{\tau}$ is an average relaxation time for electrons which normalizes the trial function ϕ_k properly. $\bar{\tau}$ is defined

[18] J. A. Birch, W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, Australian J. Phys. 12, 455 (1959).
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[20] F. J. Blatt, M. Garber, and B. W. Scott, Phys. Rev. 136, A729 (1964).
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[24] C. van Baarle, Bull. Am. Phys. Soc. 12, 22 (1966); C. van Baarle, Physica 33, 424 (1967).
[25] R. Fletcher and J. S. Dugdale, in Proceedings of the 10th International Conference on Low Temperature Physics (to be published).
[26] J. M. Ziman, Electrons and Phonons (Clarendon Press, Oxford, England, 1960).
[27] J. M. Ziman, Advan. Phys. 10, 1 (1961).

so that the kinetic equation

$$\sigma = ne^2\bar{\tau}/m$$

gives the actual electrical conductivity σ. (n is the number of electrons per volume, e is the elementary charge, and m is the electron mass.) In an alloy at low temperatures, where scattering by the impurity admixture with the relaxation time τ_i is dominant, we then have $\phi_k \sim \tau_i(\mathbf{k})/\bar{\tau}_i$. On the other hand, we have $P_{k,q}{}^{k'} \sim \tau_{ph}{}^{-1}$, where τ_{ph} is the relaxation time for electron scattering by phonons. Introducing the notation $\tau(\mathbf{k})/\bar{\tau} \equiv t(\mathbf{k})$, we have, for the product $\phi_k P_{k,q}{}^{k'}$ in Eq. (15) for an alloy at low temperatures, the relation

$$\phi_k P_{k,q}{}^{k'} \sim t_i/t_{ph}. \tag{19}$$

If t_i and t_{ph} vary differently over the Fermi surface, we see from Eqs. (14), (15), and (19) that the contributions to S^g from different parts of the Fermi surface are weighted differently because of the factor t_i/t_{ph}. In addition, if the anisotropy of one or both relaxation times is a function of temperature, this weighting factor is temperature-dependent.

In the case of the noble metals we can make the following qualitative and rather crude arguments. We differentiate between contributions from the neck and from the belly of the Fermi surface to the scattering integral P_{1L} and thereby to S^g. Approximating the weighting factor t_i/t_{ph} for the neck and for the belly region by a constant and taking it out of the integral we then obtain

$$P_{1L} = (t_i/t_{ph})_N I_N + (t_i/t_{ph})_B I_B. \tag{20}$$

The contribution to P_{1L} of the neck and of the belly area is indicated by the subscripts N and B, respectively. I_N and I_B are the rest of the contributions after the weighting factors have been taken out. We note that for the case of the pure host metal, Eq. (20) is reduced to $P_{1L} = I_N + I_B$. The negative contribution to S^g in general comes from the belly area of the Fermi surface. The enhancement of the negative contribution to S^g at low temperatures, observed in the dilute gold-platinum alloys, would then suggest the relation

$$(t_i/t_{ph})_B > (t_i/t_{ph})_N \tag{21a}$$

or

$$(t_i)_B/(t_i)_N > (t_{ph})_B/(t_{ph})_N \tag{21b}$$

for the scattering by platinum ions in gold.

The existence of an appreciable anisotropy in the relaxation times for electron scattering in metals and alloys has been suggested through the interpretation of available Hall-effect data.[27] The effect of anisotropy in the electron scattering on the Hall coefficient has been discussed recently by various authors.[28–32] Ziman[33]

and Taylor[34] calculated the anisotropy of τ_{ph} in the noble metals as a function of temperature. Ziman's estimate indicates that $(t_{ph})_B/(t_{ph})_N$ increases with decreasing temperature with a value of $(t_{ph})_B/(t_{ph})_N \approx 2.2$ at $\frac{1}{5}$ of the Debye temperature. There appears to be no independent estimate of the anisotropy of τ_i for scattering by platinum ions. Therefore, relation (21) is quite hypothetical. We will come back to relation (21) at the end of Sec. V B.

B. Influence of Lattice Vacancies

By comparing ΔS^g of the quenched specimens (Figs. 5–7) with S^g of the annealed specimens (Figs. 1–3) we see that, at the temperature where the *positive* branch of S^g has its maximum, the ratio $|\Delta S^g/S^g|$ for the quenched alloys is 15 to 20%. This value, in combination with the quenched-in resistivities ρ_{vac} given in Table III, is in reasonable agreement with the results obtained for annealed and quenched "pure" gold.[4] At $40°K$ and for the quenched-in resistivity $\rho_{vac} = 1.8 \times 10^{-8} \Omega$ cm, the relative reduction $|\Delta S^g/S^g|$ due to vacancies in pure gold has been found to be 12%.

At the temperature, where the *negative* branch of S^g has its maximum, the following values for $|\Delta S^g/S^g|$ are obtained: for the alloy containing 0.11 at. % Pt, $|\Delta S^g/S^g| \approx 100\%$; for the alloy containing 0.50 at. % Pt, $|\Delta S^g/S^g| \approx 60\%$; and for the alloy containing 1.03 at. % Pt, $|\Delta S^g/S^g| \approx 17\%$. In the very dilute Au-Pt alloys the relative reduction $|\Delta S^g/S^g|$ due to vacancies at very low temperatures (where S^g is negative) is clearly larger than at higher temperatures (where S^g is positive). The strong reduction of S^g in the alloys due to vacancies at low temperatures could lead one to believe that the phonon-scattering cross section of vacancies at long phonon wavelengths is much stronger than expected from a Rayleigh-scattering law. In the interpretation of the phonon-drag thermopower of platinum containing quenched-in vacancies it has been suggested[5] that in the phonon scattering by vacancies in platinum a resonance occurs at about $\frac{1}{3}$ of the Debye frequency. To check whether the large values of $|\Delta S^g/S^g|$ in the quenched gold-platinum alloys at low temperatures are caused by a resonant scattering state associated with a vacancy, lattice-heat-conductivity measurements on quenched and annealed specimens of the alloys Au+1.0 at. % Pt and Au+0.1 at. % Pt were carried out. The heat-conductivity experiments, the results of which will be published elsewhere,[35] did not indicate a strong reduction in the lattice heat conductivity below about $20°K$ due to vacancies. Because of this reason, an interpretation of the $\Delta S^g(T)$ curves in the quenched Au-Pt alloys at low temperatures with a large phonon-scattering cross section of vacancies at long phonon wavelengths appears to be invalid.

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Using the model, which is based on the anisotropy of the relaxation times for electron scattering and which was discussed in Sec. V A., we can interpret the large positive ΔS^g values observed in the quenched alloys at low temperatures as follows. Since vacancies apparently enhance the positive contribution to S^g at low temperatures, from the arguments given above we expect the relation

$$(t_i/t_{\text{ph}})_B < (t_i/t_{\text{ph}})_N \qquad (22\text{a})$$

or

$$(t_i)_B/(t_i)_N < (t_{\text{ph}})_B/(t_{\text{ph}})_N \qquad (22\text{b})$$

for the scattering by vacancies in gold.

Ziman[33] calculated the ratio $(t_i)_B/(t_i)_N$ for impurity scattering in the noble metals. He shows that $(t_i)_B/(t_i)_N$ can approximately be expressed as a function of the ratio of the phase shifts η_1/η_0. The phase shifts for lattice vacancies in gold have been calculated earlier,[36] using a repulsive square-well potential to represent the vacancy. The radius of the square well was taken as the atomic radius of gold. The height of the repulsive potential was obtained from the Friedel condition. The following phase-shift values were obtained: $\eta_0 = 0.75706$, $\eta_1 = 0.20871$, $\eta_2 = 0.02887$, $\eta_3 = 0.00199$, and $\eta_4 = 0.00008$. From these values in combination with Ziman's calculation,[33] one would expect for vacancies in gold the relation $(t_i)_B \approx (t_i)_N$. On the other hand, according to Ziman, at very low temperatures the ratio $(t_{\text{ph}})_B/(t_{\text{ph}})_N$ is appreciably larger than two. Thus, relation (22) is in agreement with Ziman's estimates.

The case indicated in relation (22) is precisely the same as that of dilute silver-gold alloys. Because of the strong localization of the scattering potential in silver-gold alloys, the electron scattering by the impurity is expected to be nearly isotropic. If the scattering is s like, we have $(t_i)_B/(t_i)_N \ll 1$, thus leading to a pronounced enhancement of the positive contribution to S^g at low temperatures. As mentioned above, in dilute alloys of silver with gold an enhancement of the positive contribution to S^g at low temperatures has recently been observed.[3]

Within the framework of our model, finally we can understand why vacancies reduce the negative phonon-drag thermopower in the alloys at low temperatures so effectively, although their contribution to the electrical resistivity is only a small fraction of the contribution of the platinum admixture. The relative contribution of vacancies to the resistivity is largest in the alloy specimens containing 0.11 at. % Pt, where it amounts to about 30% of the resistivity caused by the platinum admixture. We have concluded above that for the scattering by the platinum ions $(\tau_i)_B$ is several times longer than $(\tau_i)_N$, whereas for the scattering by vacancies we have $(\tau_i)_B \approx (\tau_i)_N$. Therefore, the introduction of vacancies will influence the relaxation time $(\tau_i)_B$ in the dilute Au-Pt alloys more effectively than the over-all low-temperature resistivity.

Note added in proof. A discussion of the phonon-drag thermopower in dilute noble metal alloys, similar to that presented here, has been published recently by Dugdale and Bailyn.[37] The discussion of these authors is based on an expression for the phonon-drag thermopower S^g, derived recently by Bailyn,[38] and in which S^g is separated into a sum of contributions from different parts of the Fermi surface, similar to our Eq. (20) together with Eq. (14). The treatment of Dugdale and Bailyn goes beyond the scope adopted in the present paper, since these authors considered *three* different sections of the Fermi surface: (1) the neck regions in the $\langle 111 \rangle$ directions, (2) the convex belly regions in the $\langle 100 \rangle$ directions, and (3) the concave belly regions around the $\langle 110 \rangle$ directions.

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