If $\mathbf{E}'(0)$ is the electric field in vacuum, we have the boundary conditions at $x_2=0$:

$$E_2'-\frac{E_2'(0)}{\kappa}=\frac{4\pi}{\kappa}\epsilon_s,\quad E_3'=\frac{E_3'(0)}{\kappa}. \tag{83}$$

Here κ is the "dielectric constant" of Eq. (26). Since κ is assumed to be a large number, we neglect $E_2'(0)$ in Eq. (83). We may now eliminate ϵ_s between Eqs. (82) and (83) and express E_2' in terms of $\mathbf{a}$ using Eq. (79). This, combined with $\nabla\cdot\mathbf{E}'=0$ and Eq. (81) leads to

$$\Omega^2=gk_3, \tag{84}$$

and

$$-ik_2\equiv k\simeq k_3. \tag{85}$$

This is the Kruskal-Schwarzschild instability rate.

To solve the same problem with the virial (44), we note that

$$\mathbf{j}_g'\simeq\hat{e}_3\frac{gC}{B_0}M_i[-\nabla\cdot(\xi n_0)], \tag{86}$$

and that Eqs. (43) and (44) are modified to read

$$\rho_0\frac{\partial^2\xi}{\partial t^2}=-\nabla\cdot\mathbf{p}_T'+\frac{1}{B_0{}^2}[\mathbf{B}_0\cdot\nabla\times(\xi\times B_0)]\frac{(\mathbf{j}_1{}^0\times\mathbf{B}_0)}{C} \\ -\frac{1}{4\pi}\mathbf{B}_0\times\{\nabla\times[\nabla\times(\xi\times B_0)]\}t\hat{e}_2g\nabla\cdot(\xi\rho_0), \tag{87}$$

$$\int\rho_0\xi\cdot\frac{\partial^2\xi}{\partial t^2}d\tau=-\int\left\{\frac{1}{4\pi}[\nabla\times(\xi\times\mathbf{B}_0)]^2-\mathbf{j}_1{}^0\cdot\xi\right. \\ \left.\times[\nabla\times(\xi\times\mathbf{B}_0)]-(\nabla\xi):\mathbf{p}_T'-g\xi_2\nabla\cdot[\xi\rho_0]\right\}d\tau. \tag{88}$$

To make the right-hand side of Eq. (88) as large as possible, we must take $\nabla\times(\xi\times\mathbf{B}_0)\simeq0$. This is true for our solution (84) and (83). Also $\mathbf{p}_T'$ is small when $\beta\ll1$, so Eq. (88) reduces to

$$\int\rho_0\xi\cdot\frac{\partial^2\xi}{\partial t^2}d\tau=\int g\xi_2\nabla\cdot[\xi\rho_0]d\tau\simeq\int g\xi_2{}^2\rho_0d\Sigma, \tag{89}$$

where $d\tau=dx_2d\Sigma$, $d\Sigma$ is an element of area on the surface of the plasma, and the contribution to $\int dx_2$ comes from the discontinuity at the boundary. To evaluate the left-hand side, we have $|\xi_2|\simeq|\xi_3|\simeq e^{-kx_2}$. Thus, Eq. (89) becomes

$$\Omega^2\int d\Sigma\frac{\rho_0}{k}\xi_2{}^2=\int g\xi_2{}^2\rho_0d\Sigma. \tag{90}$$

Because of the uniformity of the plasma, we have

$$\Omega^2=gk, \tag{91}$$

which is equivalent to Eq. (84).

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Thermoelectric Powers in Palladium-Silver and Palladium-Rhodium Alloys*

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Thermoelectric powers have been measured in the temperature range 77°K to 273°K in the alloys of palladium with silver. The absolute thermoelectric power is found to be highly sensitive to the presence of unoccupied *d*-band states, and a marked variation with composition is also found in alloys with more than 90% of either element. This latter behavior is ascribed to a departure of the Fermi surface from an accurately spherical form as the *s*-electron concentration increases above 0.9 per atom in the silver-rich alloys, and to a contribution to conduction from *d*-band holes in the palladium-rich alloys. The values of thermoelectric power obtained for the pure metals by extrapolation from the results for alloys where these effects are absent are in good agreement with estimates made on the basis of simple theoretical models. Results of measurements on some palladium-rich palladium-rhodium alloys are also presented and discussed briefly.

INTRODUCTION

In the metallic state palladium has about 0.6 unoccupied states per atom in the band derived from the 4*d* levels of the free atoms.[1] In its alloys with silver, which form a continuous series of solid solutions, these empty states or *d*-band holes are gradually filled, pure silver having a full *d*-band and one electron per atom in the 5*s*-band. The magnetic properties of the alloys give a clear indication of the general character of the change in electronic structure produced in traversing the system, and the most recent susceptibility measurements[2] suggest that *d*-band holes are present only when the silver content is less than about 60%.[3] The present

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[†] On leave of absence at Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

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[3] Concentrations are expressed in atomic percentages throughout.

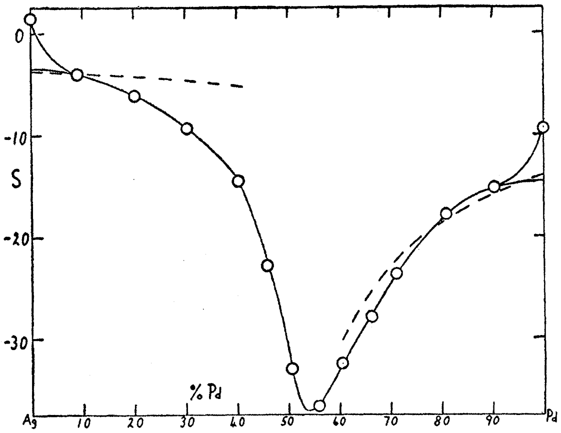

FIG. 1. Absolute thermoelectric power (S) in μv per degree as a function of composition for the palladium-silver alloys at 273°K. The broken curves show the values given by theoretical expressions.

investigation forms part of a series of studies[4,5] of the physical properties of this interesting system. Additions of rhodium to palladium decrease the total number of outer electrons and increase the number of empty d-band states. The effect on the details of the electronic structure is not yet understood, and more experimental results are required.

Previous measurements of the thermoelectric force of palladium-silver alloys against platinum have been made by Giebel[6] in the temperature range 0 to 900°C. The measurements were not of high accuracy and were made on alloys the compositions of which were not obtained by chemical analysis, but the results suggested that more interest might attach to measurements made at lower temperatures and on alloys more closely spaced in composition. Other measurements, made by Sedström against copper at room temperature, are quoted by Borelius.[7]

MATERIALS AND METHODS

The alloys used in this investigation were kindly loaned by the Mond Nickel Company (Precious Metals Division). They were prepared by induction furnace melting of high-purity materials, the specimens for these measurements being forged, drawn into wire form, and annealed.

The wires were spot-welded to pure platinum wires and the junctions were tied with platinum wire to the junction of a copper-constantan couple which provided the means of temperature measurement. A triple junction employing a platinum-rhodium wire could not be used, since the thermoelectric power of a platinum/platinum-rhodium couple becomes very small at low temperatures and restricts the accuracy of the temperature measurements. For each sample, preliminary measurements were made in constant temperature baths and these provided checks on the calibration curve of the copper-constantan couple; the baths employed were liquid nitrogen and liquid oxygen boiling at atmospheric pressure, isopentane, normal pentane, alcohol, acetone, carbon tetrachloride, and ice at their melting points, and solid carbon dioxide in equilibrium with its vapor. The temperature of the fourfold junction was then allowed to rise slowly from 77°K, and alternate readings of the copper-constantan emf and that of the specimen with respect to the platinum were made. Both voltages were measured on a low-resistance Tinsley Diesselhorst potentiometer, thus ensuring that no current greater than 1/100 μa was drawn from either thermocouple.

PALLADIUM-SILVER ALLOYS: EXPERIMENTAL RESULTS AND DISCUSSION

From plots of the emf (E) of the specimen/platinum couple against temperature, values of the thermoelectric power dE/dT have been obtained, and these have been converted to absolute thermoelectric powers (S) using the values of the absolute thermoelectric power of platinum given by Borelius.[8] The results are shown in Figs. 1 to 4; Figs. 1 and 2 show the variation of S with composition at temperatures of 273° and 83°K, respectively, and Figs. 3 and 4 the variation of S with temperature for the different specimens. In view of the large number of experimental points and the high accuracy to which each curve can be drawn through them, such points are not shown in the latter figures. The results shown in Fig. 1 are in good agreement with those of Sedström.[7]

Figure 2 shows that S is highly sensitive to the presence of d-band holes—more so, even, than the magnetic susceptibility—and the results place the composition at which d-band holes appear on adding palladium to

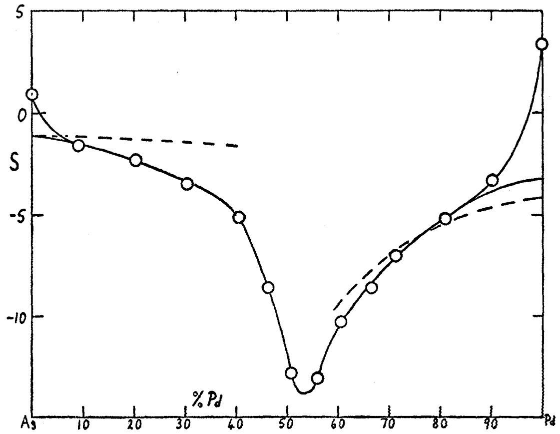

FIG. 2. Absolute thermoelectric power (S) in μv per degree as a function of composition for the palladium-silver alloys at 83°K. The broken curves show the values given by theoretical expressions.

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[4] B. R. Coles, Proc. Phys. Soc. (London) **B65**, 221 (1952).

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[6] W. Giebel, Z. anorg. u. allgem. Chem. **70**, 240 (1911).

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[8] G. Borelius, Proc. Koninkl. Akad. Wetenschap. Amsterdam **35**, 10, 25 (1932); **33**, 17 (1930); see also *Handbuch der Metallphysik*, edited by G. Masing (Akademische Verlagsgesellschaft Leipzig, 1935), p. 398.

silver very close to 40% palladium. It may be noted that this critical composition is that at which S decreases suddenly, and not that at which it takes its minimum value, as had been suggested previously.[9] The change of slope near 40% palladium is less marked at 273°K than at 83°K and this may be due to a variation with temperature of the number of d-band holes in alloys where this band is just or almost full. Such an effect has been considered by Wohlfarth[10] in his treatment of the closely related nickel-copper alloys, and may be responsible for the anomalous temperature dependence of S shown by the 40% palladium alloy.

The silver-rich alloys, having a full d-band and 0.6 to 1.0 electron per atom in the s-band, should be particularly amenable to theoretical discussion in fairly simple terms. It is well known that an ideal free-electron metal should have a thermoelectric power given by

$$S=-e\pi^2k^2T/\zeta, \tag{1}$$

where ζ is the Fermi energy, k is Boltzmann's constant, and $-e$ is the electronic charge; this being the form to which the more general expression

$$S=-\frac{e\pi^2k^2T}{3}\left[\frac{1}{n(\epsilon)}\frac{dn(\epsilon)}{d\epsilon}+\frac{1}{v^2}\frac{d(v^2)}{d\epsilon}+\frac{1}{\tau}\frac{d\tau}{d\epsilon}\right]_{\epsilon=\zeta} \tag{2}$$

reduces[11] when the free-electron forms are assumed for the energy dependence of the density of states $n(\epsilon)$, the velocity v, and the relaxation time for lattice scattering τ. In Figs. 1 and 2, the broken curve on the silver-rich side of the diagram shows the values given by Eq. (1). It thus seems probable that the anomalously positive value of S for silver is due to the departure of the Fermi surface from the ideally spherical form, a departure that is removed when the number of electrons in the Brillouin zone is slightly reduced by additions of palladium; for the value obtained for silver by extrapolation from the values for such alloys agrees closely with the theoretical one. The Hall constant of pure silver differs by about 20% from the value predicted by the free-electron theory, but is of the correct sign; such behavior is further evidence for a dependence of electronic energy on the wave-vector different, at the Fermi surface, from the free-electron one. This difference is presumably associated with approach of the Fermi surface to certain of the Brillouin zone boundaries. The high sensitivity of S to such departures from a free-electron situation is also revealed by the positive value shown by lithium,[12] the Hall constant of which differs more from the free-electron value than does that of sodium, which has a negative thermoelectric power.

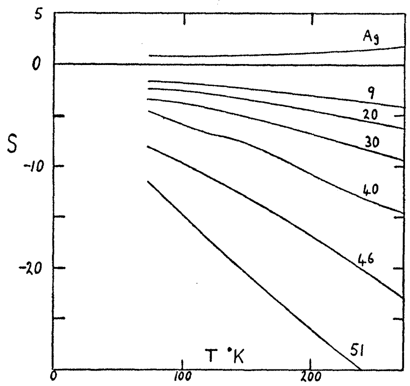

FIG. 3. Absolute thermoelectric powers (S) in μv per degree as a function of temperature for silver-rich palladium-silver alloys. The numbers with which the curves are labeled indicate the percentages of palladium in the alloys.

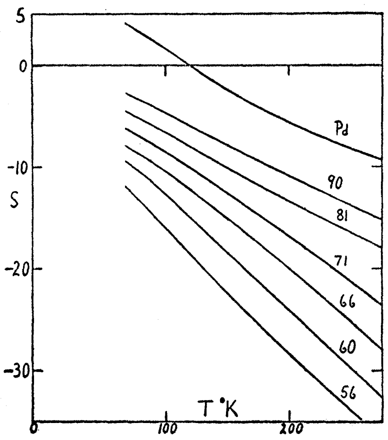

FIG. 4. Absolute thermoelectric powers (S) in μv per degree as a function of temperature for the palladium-rich palladium-silver alloys. The numbers with which the curves are labeled indicate the percentages of palladium in the alloys.

The marked variation of S with composition for alloys containing 0 to 10% palladium is confirmed by independent measurements on dilute alloys made by Otter.[13]

The assumption of free-electron forms for the dependence of $n(\epsilon)$ and v on the energy is probably quite justifiable for the silver-rich alloys, but the $\epsilon^{\frac{3}{2}}$ dependence assumed for τ cannot be appropriate for alloys since it was derived for scattering by lattice vibrations only. This point has been emphasized by Domenicali and Otter.[14] It is not, therefore, surprising that the theoretical curve agrees only with the extrapolated value for pure silver, and not with the values for the alloys, where scattering by solute atoms predominates.

At the palladium-rich end of the system a marked change of curvature is again found in plots of S against composition, and here also an extrapolation has been made to obtain a value for the pure metal with which theoretical predictions can be compared. In these alloys the number of s-electrons is close to 0.6 per atom; but it is probable that in pure palladium the contribution to conduction of the d-band holes is appreciable, although falling rapidly when these are

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[9] N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1936).

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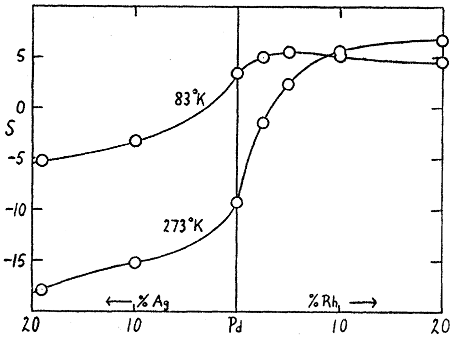

FIG. 5. Absolute thermoelectric powers (S) in μv per degree of palladium-rich palladium-silver and palladium-rhodium alloys at 273°K and 83°K.

reduced in number.[15] If it is assumed that the curves of extrapolation at the palladium-rich sides of Figs. 1 and 2 represent the behavior that would be shown by S in the absence of d-band conduction, we may compare with them the broken curves which have been derived theoretically. At first sight the greater curvature at high palladium contents shown by Fig. 2 would seem to imply that hole conduction plays a larger part at low temperatures, contrary to the implications of Hall effect data.[16] It should be remembered, however, that for pure metals Eq. (2) is appropriate only at temperatures greater than the Debye characteristic temperature, although it is valid at all temperatures when impurity scattering predominates.

The theoretical curves have been derived assuming s-electrons to be the only current carriers and, as proposed by Mott,[9] to have times of relaxation controlled mainly by the value of $n_d(\epsilon)$, the density of states in the d-band into which they may be scattered. Equation (2) then becomes

$$S=-e\frac{\pi^2k^2T}{3}\left[\frac{1}{n(\epsilon)}\frac{dn(\epsilon)}{d\epsilon}+\frac{1}{v^2}\frac{d(v^2)}{d\epsilon}-\frac{1}{n_d(\epsilon)}\frac{dn_d(\epsilon)}{d\epsilon}\right]_{\epsilon=\zeta}, \quad (3)$$

where the first two terms refer to the 0.6 electron in the s-band. This expression gives the value obtained for pure palladium by extrapolation from the alloys if the last term inside the brackets is taken as -2.0 ev^{-1}, in good agreement with the value derived from electrical resistance measurements made by the authors on these alloys. Specific heat measurements at liquid hydrogen temperatures[2] give a value of this term at pure palladium of about -20 ev^{-1}, which seems surprisingly large, but the extension of such measurements to liquid helium temperatures may cast some light on this discrepancy.

If the quantity $n_d(\epsilon)$ can be expressed in the form $A(\epsilon_0-\epsilon)^x$, where ϵ_0 is the energy of the top of the d-band, and there are 0.6 d-band holes in palladium, a value of -2.0 ev^{-1} for the term $[1/n_d(\epsilon)][dn_d(\epsilon)/d\epsilon]$ implies a value of x close to $\frac{1}{3}$. The theoretical curves for the palladium-rich alloys have been drawn taking x as $\frac{1}{3}$, and the agreement with experiment is very good for alloys containing up to 45% silver; at higher concentrations $n_d(\epsilon)$ becomes too small, relative to its value in pure palladium, for its energy dependence to be the only important factor governing that of the time of relaxation.

PALLADIUM-RHODIUM ALLOYS

In order to observe the effect of a reduction of the total number of electrons from that present in palladium, a number of palladium-rich palladium-rhodium alloys were also examined. Rhodium precedes palladium in the periodic table, and additions of it have, presumably, an effect opposite to that of silver additions—that is, they cause an increase in the number of d-band holes. The thermoelectric powers of these alloys are shown as a function of composition in Fig. 5, values for the palladium-rich palladium-silver alloys being included for comparison. No simple interpretation of these results is possible; although, if the sudden increase in the room-temperature value of S as the silver content is reduced to zero is correctly ascribed to an increase in a contribution of holes to conduction, initial additions of rhodium seem to give a further increase of this contribution. This behavior is in accord with expectation, but the smaller effect of larger additions is not. Magnetic susceptibility measurements on these alloys[17] also show effects for large rhodium additions different from those produced by smaller ones. At lower temperatures the situation is still more complicated, for anomalies in pure palladium arising from the inappropriateness of Eq. (2) at temperatures below the Debye temperature disappear as the proportion of impurity scattering increases. The tendency for S to return, as rhodium is added, to a negative value (such as is shown by palladium at higher temperatures in spite of the presence of some hole conduction) is opposed by the increase in the contribution of holes to the conduction, and the resultant variation of S with rhodium content is small.

Note added in proof.—Since this work was completed H. Jones has published a theoretical note[18] in which he shows that quite small distortions of the Fermi surface can give rise to a positive contribution to the thermoelectric power of a monovalent metal. He concludes, in agreement with the views expressed above, that such distortions are responsible for the positive values of S shown by copper, silver, and gold.

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