

and D are probably caused by the same effect for both centers.

CONCLUSIONS

The electron spin resonance and optical absorption spectra were studied for divalent vanadium ions in NaCl. The ESR signal shows that there are two types of centers with tetragonal or orthorhombic symmetry. These centers are fairly stable and probably are V^{2+} ions associated with positive ion vacancies.

The three weak-optical absorption bands between Stark levels are located at 8190, 12 800 and 20 250 cm^{-1} which are assigned to transitions from the ground state 4A_2 to 4T_2 , ${}^4T_1(a)$, and ${}^4T_1(b)$, respectively. They yield a crystalline field strength $\Delta=8190 \text{ cm}^{-1}$ and a Racah parameter $B=559 \text{ cm}^{-1}$. One strong electron

transfer band is also found at 42 300 cm^{-1} . 4T_2 and ${}^4T_1(a)$ states have some structure, probably due to splitting by a low symmetry field while no structure is found in the ${}^4T_1(b)$ state.

The g shift and zero-field splitting may be explained by assuming that the d orbitals are considerably distorted by covalency which causes the ground state $\pm(3/2)$ level to lie below the $\pm(1/2)$ level.

ACKNOWLEDGMENTS

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Thermopowers and Resistivities of Silver-Palladium and Copper-Nickel Alloys*

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The absolute thermopowers and electrical resistivities of Ag-Pd and Cu-Ni have been measured as a function of temperature between 4.2 and 300°K for concentrations up to 20 at. %. The two systems behave differently in many respects. Matthiessen's rule is obeyed well for Ag-Pd but very poorly for Cu-Ni alloys. The phonon-drag peak is completely suppressed by the addition of less than 1 at. % Ni to Cu but persists to greater than 6 at. % Pd in Ag. Nordheim-Gorter plots are curved for both alloys, but related plots for fixed concentrations are linear, indicating that any given concentration the thermopower can be considered as arising from two nearly independent scattering mechanisms, both of which have characteristic thermopowers proportional to temperature. The results in general are consistent with a rather rapid initial change in the Fermi surface up to about 0.5 at.% followed by a more gradual modification. No marked anomalies which might coincide with the departure of the Fermi surface from the zone boundary have been observed.

1. INTRODUCTION

IN this work we describe measurements of the thermoelectric power and the resistivity of silver-palladium and copper-nickel alloys. Other measurements have been made on these alloys at selected temperatures.¹⁻⁴ The present measurements are made as a function of temperature between 4.2 and 300°K for concentrations up to 20 at.% palladium and 17 at.% Ni. These have permitted (a) the study of both the diffusion and phonon-drag thermoelectric phenomena, which occur in the concentration region where the Fermi surface is expected to become detached from the zone boundary, (b) finding the temperature dependence of parameters occurring in the diffusion thermopower, (c) a com-

parison with the results of Henry and Schroeder⁵ for the Cu-Zn system.

The existence of a phonon-drag contribution to the thermopower of pure copper and silver has been established by Blatt and Kropschot,⁶ Pearson,⁷ Gold *et al.*,⁸ and Blatt *et al.*⁹ In these metals the phonon-drag thermopower is positive indicating that the contribution from umklapp processes predominates over the contribution from normal scattering processes below 100°K. Blatt and Kropschot⁶ have shown that the phonon-drag peak in copper disappears on the addition of 1% of elements (Cd, In, Sn, and Sb) which are considerably displaced from copper in the periodic system. It is

* Supported by the National Science Foundation.

¹ B. R. Coles, Proc. Phys. Soc. (London) **B65**, 221 (1952).

² J. C. Taylor and B. R. Coles, Phys. Rev. **102**, 27 (1956).

³ B. R. Coles and J. C. Taylor, Proc. Roy. Soc. (London) **267**, 139 (1962).

⁴ W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, Proc. Roy. Soc. (London) **A233**, 480 (1956).

⁵ W. G. Henry and P. A. Schroeder, Can. J. Phys. **41**, 1076 (1963).

⁶ F. J. Blatt and R. H. Kropschott, Phys. Rev. **118**, 480 (1960).

⁷ W. B. Pearson, Phys. Rev. **119**, 549 (1960).

⁸ A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. **5**, 765 (1960).

⁹ F. J. Blatt, M. Garber, R. H. Kropschott, and B. Scott, Australian J. Phys. **13**, 223 (1960).

comparatively unaffected by the addition of 1% of an element close by in the periodic system (Zn, Ge). Crisp, Henry, and Schroeder,¹⁰ and confirmed this by showing that the phonon-drag peak persists in the α -phase alloys of zinc, gallium, germanium, and arsenic in copper for concentrations up to the phase boundary (i.e., 37 at.% for copper-zinc alloys). Indeed, far from becoming small, the peak first diminishes and resurges at higher concentrations. This is particularly marked in the copper-zinc system where the phonon-drag contribution in a 35.32 at.% alloy is about the same magnitude as that in pure copper.

Blatt and Kropschot attribute the decrease in the phonon-drag thermopower on the addition of Cd, In, Sn, and Sb to the scattering of phonons, which otherwise would have contributed to the phonon-drag process, by the solute atoms of markedly different mass from the solvent atoms. If we write the phonon-drag thermopower

$$S_d \propto \bar{p}_0 / (\bar{p}_0 + \bar{p}_e),$$

where \bar{p}_e is the phonon relaxation time for phonon-electron collisions giving rise to phonon drag, and \bar{p}_0 is an average relaxation time for all other phonon interactions, then Blatt and Kropschot effectively say that $\bar{p}_0 \ll \bar{p}_e$ when solute atoms of different mass are added, and S_d becomes small.

There are two ways in which the phonon-drag thermopower will be diminished, besides the mechanism suggested by Blatt and Kropschot, and it is generally not easy to determine which mechanism will be most effective. These are:

(a) The phonons are scattered at the region of distortion about the solute atom. Kemp *et al.*,¹¹ suggest that the distortion about a Zn atom in α brass is about 5%, and that this will be the main cause of phonon scattering by the Zn atoms. Distortion about a nickel atom in copper is about one-half of this, as measured by lattice parameter changes, and the distortion about a palladium atom in silver is still smaller. However, lattice parameter measurements are not necessarily a good indication of local distortions.

(b) The phonons are scattered by the difference from the normal values of inter-ionic force constants in the vicinity of the solute atom.

In the copper-nickel and silver-palladium systems we assume each of these three scattering mechanisms to have about the same effect as in the copper-zinc system though this is difficult to justify for the last mechanism. We might therefore expect to find the phonon-drag peak persisting to high-solute concentrations, but steadily decreasing with concentration. However, as in the copper-zinc system, this conclusion must be modified by effects arising from changes in the Fermi surface.

¹⁰ S. Crisp, W. G. Henry, and P. A. Schroeder, *Phil. Mag.* (to be published).

¹¹ W. R. G. Kemp, P. G. Klemens, R. J. Tainsh, and G. K. White, *Acta Met.* 5, 303 (1957).

\bar{p}_e , in particular, is very dependent on the shape of the Fermi surface, and it is the variation of this parameter to which Henry and Schroeder implicitly ascribe the resurgence of the phonon-drag peak in the α -phase copper-based alloys. At any temperature both normal and umklapp processes contribute to the phonon-drag process. In the noble metals and in the α -phase solutions of Sn, Ga, Ge, and As in Cu, the phonon-drag peak is positive, indicating the domination of the umklapp process contribution. Henry and Schroeder assumed that the umklapp contribution would be greatest when there are portions of the Fermi surface close to or just in contact with the Brillouin zone boundary. It follows that the positive phonon-drag contribution would increase as the Fermi surface approaches the {100} faces of the zone boundary, and this is consistent with the experimental observations.

Presumably when nickel is added to copper, or palladium to silver, the number of conduction electrons per unit cell decreases, and the Fermi surface shrinks in volume. At some point it will break away from the zone boundary and become roughly spherical. At higher concentrations the phonon-drag contribution may be expected to decrease rapidly with concentration and a negative phonon-drag dip caused by the predominance of normal scattering processes might appear.

At high temperatures, 150–300°K, where the phonon-drag contribution is apparently small for the alloys, the Nordheim Gorter¹² relation

$$S_d = \sum \rho_i S_i / \sum \rho_i \quad (1)$$

is a useful basis for analysis of diffusion thermopower results. Here S_d is the measured absolute diffusion thermopower, ρ_i is the contribution to the resistivity of the i th scattering mechanism, assuming that it is independent of other scattering mechanisms, and S_i is the characteristic thermopower associated with the same mechanism. For the present work, we write

$$S_d = (\rho_{th} S_{th} / \rho_t) + (\rho_{imp} S_{imp} / \rho_t), \quad (2)$$

where the subscripts refer to thermal scattering by phonons, and impurity (nickel or palladium) scattering, and ρ_t is the total resistivity.

$$S_{th} = \frac{\pi^2 k^2 T}{3e} \left(\frac{\partial \ln \rho_{th}}{\partial E} \right)_{E=\eta}, \quad (3)$$

$$S_{imp} = \frac{\pi^2 k^2 T}{3e} \left(\frac{\partial \ln \rho_{imp}}{\partial E} \right)_{E=\eta}.$$

For η expressed in electron volts, S_{imp} and S_{th} calculated for a free-electron model are

$$S_{imp} = (\pi^2 k^2 T / 3e) = -(2.45 \times 10^{-2} / \eta) T \mu V / ^\circ K, \quad (4)$$

$$S_{th} = (\pi^2 k^2 T / e) = -(7.35 \times 10^{-2} / \eta) T \mu V / ^\circ K.$$

¹² L. Nordheim and C. J. Gorter, *Physica* 2, 383 (1935).

Equations (1), (2), and (3) are easily derived from the Mott equation

$$S_d = -\frac{\pi^2 k^2 T}{3e} \left(\frac{\partial \ln \rho(E)}{\partial (E)} \right)_{E=\eta} \quad (5)$$

assuming Matthiessen's rule

$$\rho_t = \rho_{th} + \rho_{imp}, \quad (6)$$

where ρ_{imp} is independent of temperature and ρ_{th} is independent of concentration. The conditions under which Eq. (2) holds with S_{th} and S_{imp} constant are therefore the same as the conditions under which these relations are true. These are as follows. (a) The Wiedeman-Franz law is used in the derivation of (5), and this is obeyed for thermal scattering when $T \gtrsim \Theta_D$. According to the experimental results of White and Woods,¹³ for copper and silver the law is obeyed for $T > \Theta_D/2$, that is $T > 170^\circ\text{K}$ for copper and 110°K for silver. (b) The differential in Eq. (5) is evaluated at the Fermi surface, and in the derivation of (2) it is assumed that η and therefore the Fermi surface does not change on alloying. Invariably the Fermi surface will change, but the relation will hold if such changes are small, or if the relaxation times, density of states, and Fermi velocities inherent in ρ_{th} and ρ_{imp} are insensitive to small changes in the Fermi surface. (c) S_d is the diffusion thermopower and Eqs. (1)–(5) only hold in the absence of phonon drag. For pure copper the phonon-drag contribution may not be negligible at room temperatures, though it is negligible for the copper-nickel alloys. Once again silver is better in this respect since its phonon drag peak occurs at a much lower temperature (30°K) than that for copper (60°K). Using Matthiessen's rule, Eq. (2) may be written

$$S_d = S_{imp} + (\rho_{th}/\rho_t)(S_{th} - S_{imp}). \quad (7)$$

For low-concentration alloys the only variable with respect to concentration in the second term is ρ_t . Hence, a plot of S_d versus $1/\rho_t$ for constant temperature should be a straight line with intercept S_{imp} . In the systems of Zn, Ga, Ge, and As in Cu, the S_d versus $1/\rho_t$ curves at room temperature are linear up to a concentration corresponding to a valency electron per atom ratio of 1.1. In these alloys presumably the Fermi surface—or the electron relaxation times—are not changing drastically with concentration, since contact has already been made with the zone boundary. In the copper-nickel and silver-palladium systems however, the recession of the Fermi surface from the zone boundary may be accompanied by comparatively major changes in the Fermi surface and the relaxation times resulting in a nonlinearity of the S_d versus $1/\rho_t$ plots.

Instead of eliminating ρ_{imp} from (2) using Matthies-

sen's rule, ρ_{th} may be eliminated, and Eq. (2) then becomes

$$S_d = S_{th} + (\rho_{imp}/\rho_t)(S_{imp} - S_{th}). \quad (8)$$

In this expression both ρ_{imp} and ρ_t vary with concentration. Hence for a linear plot at constant temperature, S_d must be plotted against ρ_{imp}/ρ_t . It is more convenient, however, to use Eq. (8) as the basis for a plot at constant concentration in which case ρ_{imp} will be a constant. If we assume that Eq. (3) can be written

$$S_{th} = cT, \quad \text{and} \quad S_{imp} = bT, \quad (9)$$

where c and b are constants, then (8) becomes

$$S_d/T = c + (\rho_{imp}/\rho_t)(b - c). \quad (10)$$

Hence a plot of S_d/T versus $1/\rho_t$ at constant concentration, rather than at constant temperature, should yield a straight line. The conditions for this are less stringent than those required for the linearity of the S_d versus $1/\rho_t$ plots, since the linearity is preserved even when b and c vary with concentration. In the derivation of (10) this corresponds with relaxing the condition that ρ_{th} in (6) is independent of concentration. The differential in Eq. (5) is evaluated at the Fermi surface of the alloy, which may now be different from that for the pure metal. S_{th} will not be the same as S_{th} for the pure metal. The linearity of the plots is essentially a test of the assumptions of Eq. (9).

2. EXPERIMENTAL

The apparatus was similar to that described by Henry and Schroeder.⁵ The samples were made by melting the components in an alumina crucible by induction heating, and chill casting. Thereafter, the ingots were drawn down to wires of 0.2 mm diameter for the thermopower and resistivity measurements, and annealed in vacuum at 680°C . The cross-sectional areas were determined from weight-per-unit-length measurements and the densities given by the supplier for the pure material. For the alloys these densities were modified, if necessary, to allow for changes of lattice parameter on alloying, and for the different atomic mass of the solute atoms. The copper was purchased from the American Smelting and Refining Company. The resistance ratio $R_{273}/R_{4.2}$ for a sample annealed in vacuum was 1080. Similar samples of silver wire produced from Cominco 59 grade silver had a resistance ratio of 640. Both the nickel and palladium were in the form of sponge obtained from Johnson, Matthey, and Company. The main impurity in the nickel was iron with a concentration estimated by Johnson, Matthey to be 8 parts per million (ppm). Further chemical analyses indicated the presence of 3 ± 3 ppm of iron in the silver and 15 ± 10 ppm in an alloy containing 10% Pd. These iron concentrations are of some importance in the interpretation of the low-temperature results.

The thermopower results for the copper-nickel and silver-palladium alloys are shown in Figs. 1 and 2. The

¹³ G. K. White and S. B. Woods, Phil. Trans. Roy. Soc. London 251A, 293 (1959).

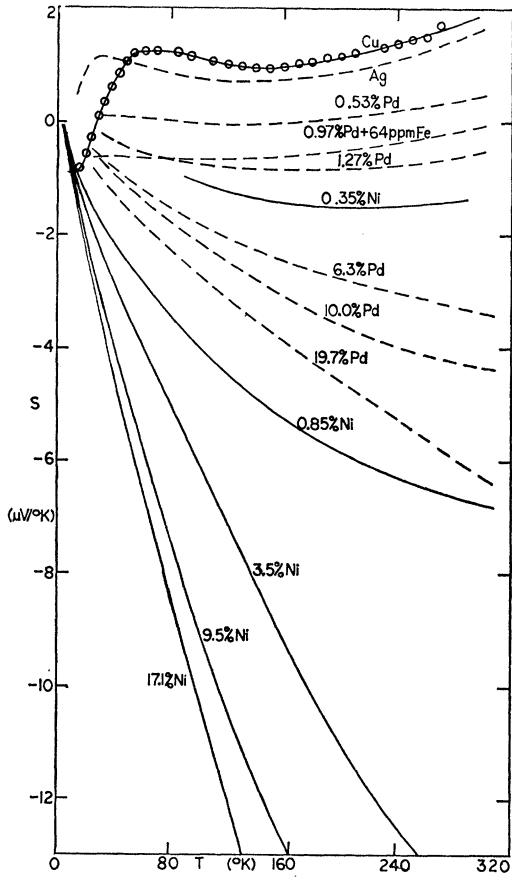


FIG. 1. The absolute thermopowers of Cu-Ni and Ag-Pd alloys, from 4.2-300°K.

corresponding resistivity results are given in Figs. 3 and 4. The concentrations given in the figures are in atomic percent throughout.

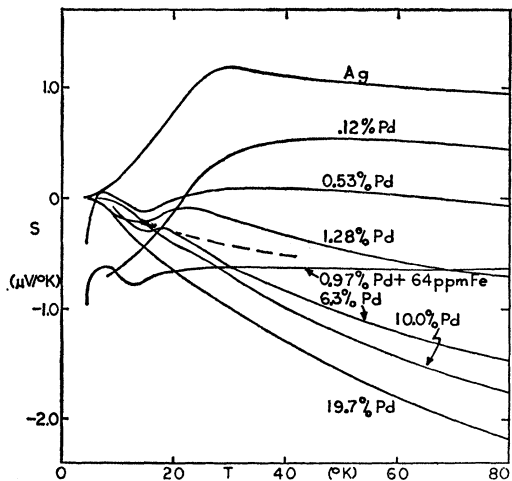


FIG. 2. The absolute thermopowers of Ag-Pd alloys from 4.2-80°K. --- Calculated diffusion thermopower for 1.28 at.% Pd sample.

3. HIGH-TEMPERATURE RESULTS

The behavior of the Ag-Pd and Cu-Ni systems varies in many ways. Much of the prior analysis will not be applicable to the Cu-Ni system because the departures from Matthiessen's rule in these alloys are large and much greater than the departures for the Ag-Pd system. This is illustrated by the data in Table I giving $(\rho_{240} - \rho_r)$ for the pure metals and alloys. ρ_{240} is the resistivity at 240°K and ρ_r is the residual resistivity. Considering that the Fermi surface of the silver-palladium alloys probably changes rapidly in the vicinity of the necks for low

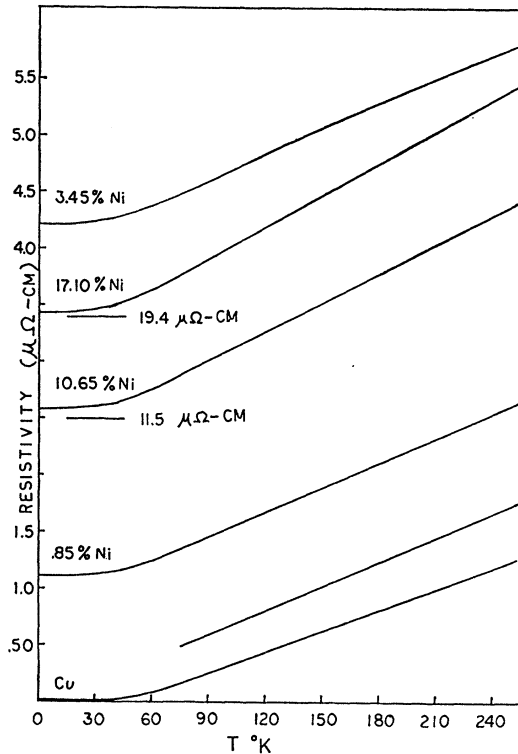


FIG. 3. The resistivity of Cu-Ni alloys from 4.2-250°K.

concentrations of Pd, the remarkable extent to which Matthiessen's rule is obeyed must indicate that the

TABLE I. $(\rho_{240} - \rho_r)$ for copper-nickel and silver-palladium alloys. ρ_{240} is the resistivity at 240°K and ρ_r is the residual resistivity. For Matthiessen's rule to apply, $(\rho_{240} - \rho_r)$ should be independent of concentration.

Specimen	$(\rho_{240} - \rho_r)$ (Ω -cm)
Cu	1.18
Cu+0.85 at.% Ni	1.44
Cu+3.45 at.% Ni	1.51
Cu+10.65 at.% Ni	1.73
Cu+17.10 at.% Ni	1.90
Ag	1.25
Ag+0.52 at.% Pd	1.29
Ag+1.28 at.% Pd	1.26
Ag+6.3 at.% Pd	1.31
Ag+10 at.% Pd	1.42

relaxation times of the neck electrons is much smaller than those for the belly electrons. This is consistent with the thermoelectric and magnetoresistive properties discussed by Ziman.¹⁴

The results for the 200 and 600 ppm Ag-Pd samples are not shown in Figs. 1 and 2, since above 100°K they are within the experimental error ($0.02 \mu\text{V}/^\circ\text{K}$) of the thermopower of pure silver. At temperatures less than 100°K, the 200 ppm sample has a phonon drag peak $0.1 \mu\text{V}/^\circ\text{K}$ less than pure silver, and the 600 ppm results are typical of a sample contaminated with iron. There are no anomalies of the type suggested by Ziman¹⁵ which should occur at the concentration where the Fermi surface leaves the zone boundary.

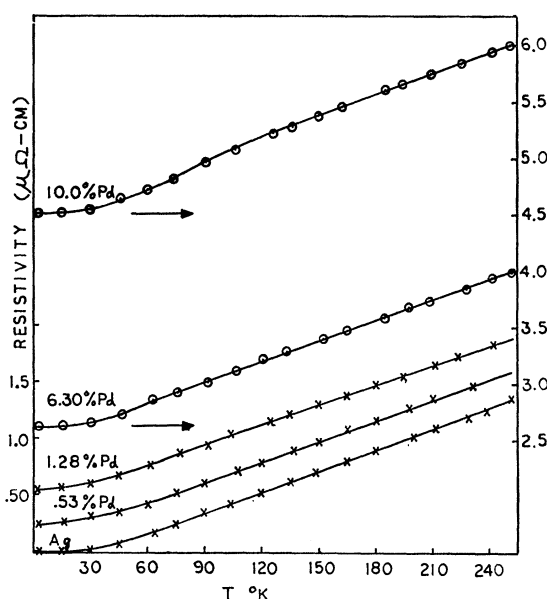


Fig. 4. The resistivity of Ag-Pd alloys from 4.2–250°K.

In Fig. 5 we show the thermopower at 270°K plotted as a function of concentration for Cu-Ni, Cu-Zn, and Ag-Pd alloys. These curves are a more detailed presentation of a part of the complete concentration range studied by Taylor and Coles.² Following Taylor and Coles, on the vertical axes we have inserted the theoretical values for S_{th} , $-3.55 \mu\text{V}/^\circ\text{K}$ for silver and $-2.82 \mu\text{V}/^\circ\text{K}$ for copper calculated from Eq. (4) which assumes a free-electron model. For the Ag-Pd alloys the high concentration points extrapolate back to this point. Taylor and Coles assume that the Fermi surface is spherical at the higher concentrations, and the extrapolated curve represents the thermopower which would be obtained if this sphericity were retained. Departures from the extrapolated curve are caused by the deviations of the Fermi surface from the ideally spherical form. On

¹⁴ J. M. Ziman, *Advan. Phys.* **10**, 1 (1961).

¹⁵ J. M. Ziman, *Proc. Roy. Soc. (London)* **A252**, 63 (1959).

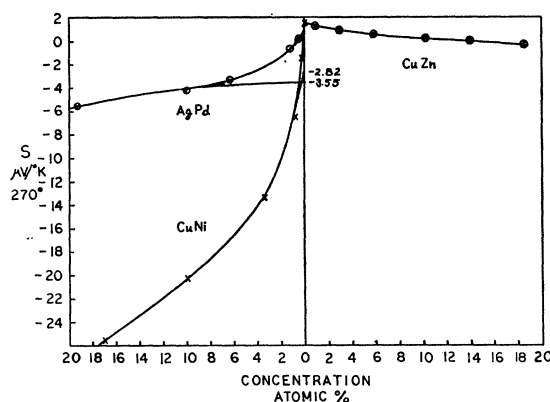


Fig. 5. The absolute thermopowers of Cu-Ni, Cu-Zn, and Ag-Pd alloys at 270°K.

this basis it would appear that there are substantial departures from sphericity for concentrations up to 10 at. % Pd.

The situation is not so clear with the Cu-Ni alloys. The shape of the curve is quite different and without foreknowledge of S_{th} for Cu it is not apparent how the high concentration results should extrapolate. If we perform the extrapolation to the theoretical value, and apply the above argument, then it would appear that the Fermi surface becomes approximately spherical at about 1.5 at. % Ni. Later, it will be seen that this is consistent with the phonon-drag results, but considering the many ways in which the Cu-Ni alloys differ from the Ag-Pd alloys,¹ this interpretation is highly questionable for the Cu-Ni alloys. The S_d versus T curves for neither the Cu-Ni nor the Ag-Pd alloys exhibit the degree of linearity of those for the Cu-Zn alloys. However the S/T versus $1/\rho_t$ curves, Figs. 6 and 7, are substantially linear. The departure from linearity for the pure metal and low concentration alloys at low values of ρ_t may be accounted for by the phonon-drag contribution which is beginning to be appreciable for these conditions.

Although these curves are linear the intercepts on

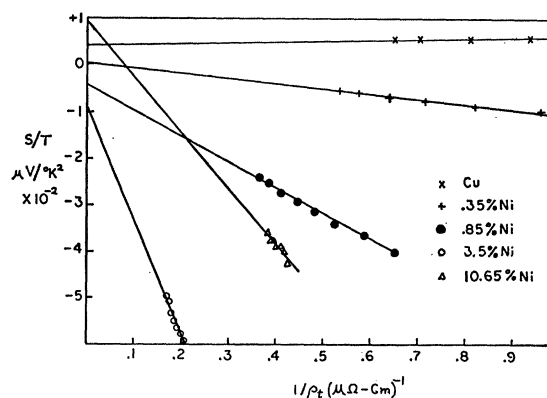


Fig. 6. S_d/T for Cu-Ni alloys plotted against $1/\rho_t$.

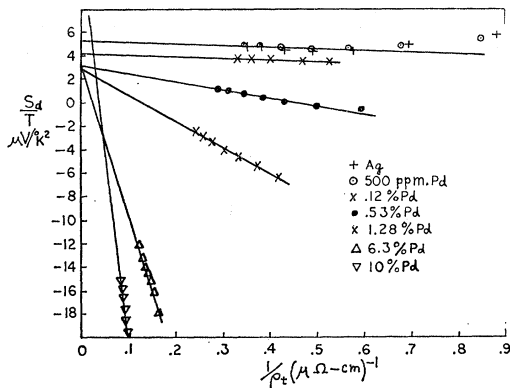


FIG. 7. S_d/T for Ag-Pd alloys plotted against $1/\rho_t$.

the vertical axis [parameter c in Eq. (9)] are not constant, first decreasing to a minimum and then rising rapidly for the 10 at.% Pd alloys. It would seem that for the alloys from $\frac{1}{2}$ to 6.3 at.% Pd, the intercept does not change appreciably, and corresponding with this the S_d versus $1/\rho_t$ plot for Ag-Pd is substantially linear over this range of concentration. In Fig. 8 the straight lines are drawn through these points. The intercepts of these lines vary linearly with temperature as shown in Fig. 9. In the same figure the intercepts of the tangents at zero concentration are also plotted. These are rather more difficult to define, but their intercepts also vary linearly with temperature within the experimental error.

The S/T versus $1/\rho_t$ plots are at constant concentrations. From their linearity we conclude that, for a given concentration alloy, the thermopower can be divided into two approximately independent contributions both of which are proportional to temperature over the range considered. The constants of proportionality however vary with concentration, but are roughly constant over the concentration range from $\frac{1}{2}$ to 6.3 at.% Pd.

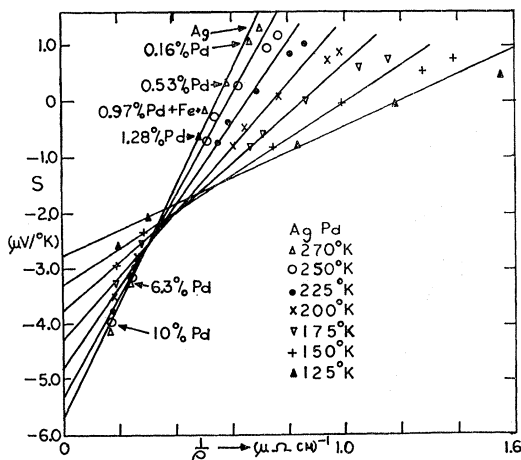


FIG. 8. Absolute thermopower for Ag-Pd alloys plotted as function of $1/\rho_t$. The straight lines are drawn through the points in the concentration range 0.53–6.3 at.% Pd.

4. LOW-TEMPERATURE RESULTS

The addition of 0.85 at.% Ni to Cu reduces the phonon-drag peak to an almost unobservable level (Fig. 1), and there is no sign of any resurgence similar to that in the Cu-Zn alloys.

With the Ag-Pd alloys (Fig. 2) on the other hand, although the initial decrease in the phonon-drag peak is very rapid, the phonon-drag peak is still plainly visible in the 6.3 at.% alloy.

Part of the reason for studying silver-palladium alloys in more detail was to avoid the effects of iron impurities, since iron has only a very small solubility in silver. In the pure silver sample the 600-ppm alloys and all alloys with concentration greater than 1.28 at.% Pd, there is no sign of the large negative thermopower typical of iron at low temperature. This is not true of the 200 ppm, 1200 ppm, and 0.53 at.% Pd, all of which

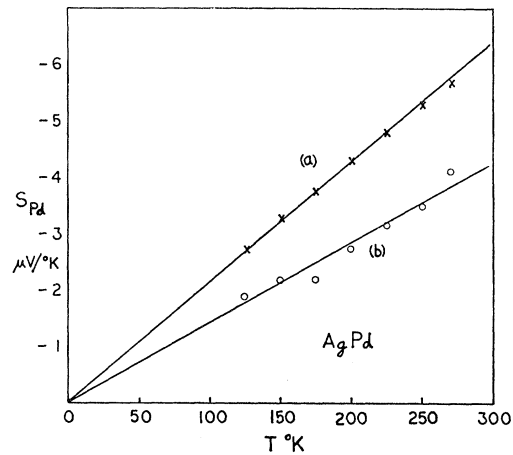


FIG. 9. (a) The intercepts on the vertical axis of Fig. 8 plotted against temperature. (b) The intercepts of the tangents at zero concentration of the Nordheim-Gorter plots for Ag-Pd.

show the presence of iron impurity. The dip occurring in the 0.53, 1.28, and 6.3 at.% Pd alloys at about 15°K, however, is independent of the presence of iron, as evidenced by the presence of the same dip of more or less the same size in the 0.97 at.% Pd to which 64 ppm Fe were purposely added. It would appear that iron enters into solution much more readily in the ternary system Ag-Pd-Fe than into pure silver. Pearson and Templeton¹⁶ in studying the thermopower anomaly quenched their silver-iron alloys from a temperature near the melting point in order to keep the iron in solution.

The apparent dip at 15°K is not caused by a negative phonon-drag component. This can be seen by making a rough calculation of the diffusion thermopower using the Nordheim-Gorter relation [Eq. (2)] and assuming that at low temperature the contribution from S_{th} is

¹⁶ W. B. Pearson and I. M. Templeton, Can. J. Phys. 39, 1084 (1961).

negligible.

$$S_d = (\rho_{\text{imp}}/\rho_t)S_{\text{imp}}.$$

For S_{imp} we take the value from the slope of the lower line of Fig. 9.

$$S_{\text{imp}} = -0.014T \mu\text{V}/^\circ\text{K}.$$

The calculated curve for the 1.27 at.% Pd alloy is shown plotted in Fig. 4. The experimental curve lies on or above this line, and hence the negative phonon-drag contribution does not predominate, at least until temperatures less than 8°K where the present experimental results lack precision.

Using this curve as a basis, the phonon-drag peak for the 1.27 at.% Pd alloy is about 20% of the phonon-drag peak for pure silver. This contrasts with the copper-zinc alloys for which the phonon drag peak for a 0.92 at.% Zn alloy is about 90% of the pure-copper peak.

5. DISCUSSION

No marked anomalies coinciding with a possible departure of the Fermi surface from the zone boundary have been observed in either the diffusion thermopower or the phonon-drag thermopower. However, the following evidence is consistent with the view that in the Ag-Pd alloys there is an initial rapid change of the Fermi surface, possibly a departure from the zone boundary at less than 0.5 at.% Pd, followed by a gradual sphericization.

(1) According to the Taylor-Coles-type analysis the Fermi surface becomes spherical at a concentration of about 10 at.% Pd. Departures from the free-electron value of the thermopower become greater as the concentration decreases and vary more rapidly at the lowest concentrations.

(2) The phonon-drag peak disappears at approximately the same concentration at which the Fermi surface becomes spherical on the Taylor-Coles picture. Initially it decreases rapidly with concentration—much more rapidly than in the Cu-Zn alloys, and this is consistent with the Fermi surface receding from the

zone boundary. The persistence up to several at.% Pd may be due to a steady decrease in umklapps across the zone boundary combined with a steadily increasing impurity-phonon scattering, or it may be due to transitions across unfilled regions within the zone boundaries, which disappear when the Fermi surface becomes spherical.

(3) The S_d versus $1/\rho_t$ plots are substantially linear between $\frac{1}{2}$ and 6.3 at.% Pd, but curve appreciably at lower concentrations. Corresponding with this the intercepts of the S_d/T versus $1/\rho_t$ plots also vary rapidly with concentrations up to $\frac{1}{2}$ at.% and thereafter remain constant up to 6.3 at.%. At higher concentrations these same plots give a discrepancy in that in the Taylor-Coles picture we might expect to find the parameter c of Eq. (9) approaching the negative free-electron value, whereas it actually becomes strongly positive.

This system has not been the ideal system for studying the application of the Nordheim-Gorter relation at high temperatures because the Fermi surface apparently does change rapidly. Despite this, however, it does appear that at a given concentration the diffusion thermopower can be represented by a Nordheim-Gorter-type relation, in which both the characteristic thermopowers arising from thermal and impurity scattering vary linearly with temperature over the temperature range considered. It should be noted, however, that the diffusion thermopower of silver itself is not linear at higher temperatures.¹⁷

An interpretation of the Cu-Ni results in terms of Fermi surface changes is in a more precarious position, because of its rather anomalous physical properties including its paramagnetic behavior at low nickel concentrations.¹

ACKNOWLEDGMENT

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¹⁷ N. Cusack and P. Kendall, Proc. Phys. Soc. (London) **72**, 898 (1958).