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Thermoelectric Power in Silver-Gold and Silver-Germanium Alloys

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*Thermoelectric Power in Silver-Gold and
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Abstract

The thermoelectric powers of dilute silver-gold and silver-germanium alloys are determined from 78 to 300°K. Nordheim-Gorter plots are carried out for these alloy systems at 273 and 295°K; and the characteristic thermopowers S_p^1 and S_p^0 , attributed to solute and solvent, respectively, are determined at these temperatures. Calculated values of S_p^1 , for both alloy systems, agree in sign and approximate numerical value with the experimental values. For Ag-Au, small or negligible Fermi surface changes are indicated up to the maximum gold concentration of 1.5 at.%. This is in agreement with recent conclusions based on polar-reflection Faraday experiments in Ag-Au. The Ag-Ge data, however, deviate from the expected linearity predicted by the Nordheim-Gorter relation at approximately 0.5 at.%. The deviation in the Ag-Ge case is attributed to Fermi surface changes as a result of alloying. A detailed comparison of the current Ag-Au data with previous results for Cu-Ag and Cu-Au is carried out by use of a Nordheim-Gorter type relation for the difference in thermopower ΔS between the pure metal and alloy. It is found that, for a given solute concentration, ΔS is greatest in Ag-Au, decreases in Cu-Au, and is still less in Cu-Ag. It is concluded that the observed ΔS differences are attributable to a possible combination of small Fermi surface changes and slight differences in electronic charge associated with the solute atoms when compared to the host atom in these alloys.

Thermoelectric Power in Silver-Gold and Silver-Germanium Alloys

I. Introduction

The silver-gold alloy system is a relatively simple one for comparison between theory and experiment. Silver and gold form solid solutions in all proportions, with negligible variation in lattice constant from pure silver to pure gold. In addition, silver and gold are both monovalent, have the same crystal structure, nearly the same atomic radii, and similar Fermi energies (Ref. 1). The relative simplicity of this alloy system has facilitated detailed studies of the Fermi surface change with alloying.

In particular, measurements of the polar reflection Faraday effect (PRFE) have yielded direct information on the Fermi surface geometry for nondilute solutions of gold in silver (Ref. 2). Specifically, the PRFE results for these alloys indicate a well defined Fermi surface of the noble metal type, with neck radius of contact with the Brillouin zone, and a general shape that varies linearly as a function of alloy concentration (Ref. 2). It follows, then, that estimates of the Fermi surface change with alloying can be obtained from values of the neck radius, a measure of Fermi surface contact with the $\langle 111 \rangle$ zone faces. If p is the distance from the origin to the $\langle 111 \rangle$ faces of the Brillouin zone, the neck radius is $0.13 p$ in silver and $0.16 p$ in gold (Ref. 1). Thus, for

1 at.% gold in silver, a negligible change in neck radius and, indeed in the Fermi surface as a whole, is indicated.

The thermoelectric power is a transport property that is particularly sensitive to changes in Fermi surface geometry. However, because of the monovalent character of gold and silver and the PRFE results (Ref. 2) one would not expect any large or unusual change in diffusion thermopower in silver-gold alloys with approximately 1 at.% gold. This expectation receives partial support from the results obtained for the changes in diffusion thermopower observed for dilute alloys of the homovalent impurities silver and gold in copper (Refs. 3, 4). On the other hand, previous thermopower measurements on the silver-gold alloy system (Ref. 5), indicate a larger thermopower change with alloying as compared with the experimental results for the copper alloys (Refs. 3, 4). Furthermore, the difference in behavior for Ag-Au is held to be consistent with the smaller area of contact with the Brillouin zone for silver, as compared with that for copper and gold (Ref. 6). The implication that Fermi surface changes may be responsible for the relatively large changes in diffusion thermopower previously observed for dilute Ag-Au alloys warrants a detailed examination of the thermoelectric power in this

alloy system. The current work takes on added significance in view of the recent experimental results with respect to the Fermi surface in these alloys (Ref. 2).

From mass-difference considerations, one expects a relatively large attenuation of phonon-drag thermopower in dilute silver-gold alloys (Refs. 4, 7). Thus, to minimize the complicating effects of phonon-drag thermopower, it becomes necessary to work in a temperature region where diffusion thermopower is the predominant contribution to the total thermopower. Since the phonon-drag peak in silver occurs at approximately 30°K (Refs. 5, 6, 8), we exclude this region from consideration by taking measurements from 78 to 300°K. Since the Debye temperature of silver is approximately 220°K (Ref. 9), the assumption of negligible phonon drag effects appears to have greater validity in the vicinity of room temperature. The current work is thus concerned with the diffusion thermopower of dilute silver-gold alloys with a maximum gold concentration of 1.5 at.%. An objective lies in use of thermoelectric power as a probe in exploring for possible Fermi surface changes in dilute silver-gold alloys. An additional objective lies, in comparison and analysis of the current work, with some previous results on similar alloy systems (Refs. 3, 4). At the same time, data and analysis are presented for a series of dilute silver-germanium alloys with maximum germanium concentrations of approximately 1 at.%. In comparison with Ag-Au, the Ag-Ge alloys present a relatively large difference in number of valence electrons between solute and solvent. Assuming that the excess germanium electrons enter the conduction band, one expects a relatively larger alteration of the Fermi surface for a given concentration of germanium as compared with the same concentration of gold in silver. In this case, use of thermoelectric power in detection of possible Fermi surface changes should be facilitated by comparison with the relatively well known properties of the Ag-Au system.

II. Theory

For a restricted range of temperatures, the diffusion thermopower of a metal is given by the well known relation (Refs. 10, 11),

$$S_e = - \frac{\pi^2 k^2 T}{3 |e|} \left[\frac{\partial \ln \sigma(E)}{\partial E} \right]_{E_F} \quad (1)$$

where S_e is the diffusion thermopower, k is Boltzmann's constant, T is the temperature, $|e|$ is the absolute value of the electronic charge, $\sigma(E)$ is the electrical conductivity at energy E and E_F is the Fermi energy. Equation

(1) applies when electron scattering is describable by a single relaxation time: i.e., in general, for $T > \theta_D$ or $T \ll \theta_D$, where θ_D is the Debye temperature. Additionally, for Eq. (1) to be valid in the low temperature region, the residual resistance must be large compared with the resistance due to thermal motion of atoms (Ref. 10). In the case of dilute alloys an extension of Eq. (1) is obtained using Mattheissen's rule:

$$\rho = \rho_0 + \Delta\rho \quad (2)$$

where ρ is the total electrical resistivity, ρ_0 the intrinsic resistivity of the pure metal, and $\Delta\rho$ is the electrical resistivity due to impurities in the otherwise pure metal. ρ_0 is a temperature-dependent quantity while $\Delta\rho$ is assumed independent of temperature. Substituting Eq. (2) into Eq. (1), one obtains, for a single impurity in an otherwise pure metal, the result

$$S_e = S_e^1 + \frac{\rho_0}{\rho} (S_e^0 - S_e^1) \quad (3)$$

with

$$S_e^1 = \frac{\pi^2 k^2 T}{3 |e|} \left[\frac{\partial \ln \Delta\rho(E)}{\partial E} \right]_{E_F} \quad (4)$$

and

$$S_e^0 = \frac{\pi^2 k^2 T}{3 |e|} \left[\frac{\partial \ln \rho_0(E)}{\partial E} \right]_{E_F} \quad (5)$$

where S_e^1 is defined as the characteristic thermopower of the impurity in the alloy and S_e^0 is the diffusion thermopower of the metal in the absence of impurities. Eq. (3) is a special case of the Nordheim-Gorter relation (Ref. 12)

$$S_e = \frac{\sum_i S_e^i \rho^i}{\rho} \quad (6)$$

where S_e^i and ρ^i are the characteristic diffusion thermopower and electrical resistivity due to the i th electron scattering agent in the metal.

The current data will be interpreted using the Nordheim-Gorter relation in the form shown in Eq. (3). In this respect the assumptions limiting the validity of the Nordheim-Gorter rule are of special importance. In

addition to the temperature restrictions mentioned in connection with Eq. (1), Eq. (6) and, hence, Eq. (3), are valid under the following conditions.

First, the addition of impurities does not alter the Fermi surface.

Second, conduction in the alloy is describable in terms of a single homogeneous group of conduction electrons.

Third, the scattering of electrons by an impurity and all other electron scattering events are independent of each other.

Fourth, the lattice heat conductivity is negligible—i.e., all of the effective heat transport should be by conduction electrons.

If the preceding assumptions are valid in a binary alloy, then it follows from Eq. (3) that a plot of S_e vs $1/\rho$, at constant temperature, should yield a straight line. The intercept of the resultant straight line with the S_e axis then results in a numerical value of S_e^1 while S_e^0 can be evaluated from the slope of the straight line. If one selects a temperature where the effects of phonon drag and the effects of any trace impurities in the pure metal are negligible, then

$$S_e^0 = S^0 \quad (7)$$

where S_e^0 is obtained from the Nordheim-Gorter plot, and S^0 is the thermopower of the pure metal. In addition, at temperatures high enough to ensure the validity of Eq. (7), $S^0 = S_e^{th}$, where S_e^{th} is the thermal component of the diffusion thermopower in the pure metal. In writing Eq. (7) it is further assumed that the data plot of Eq. (3) results in the correct value for S_e^0 . In this respect, satisfaction of Eq. (7) is another check on the validity of the Nordheim-Gorter relation for a specific alloy system.

The Nordheim-Gorter relation has recently been applied to a series of copper alloys (Refs. 13, 14). References to several other copper applications of this rule are found in the book by MacDonald (Ref. 15) and in the review article by Pearson (Ref. 16). The utility of Eq. (3) as a tool in exploring the electronic structure of disordered alloys would be considerably enhanced if S_e^1 and S_e^0 could be calculated from the correct theoretical expressions. Limitations with respect to carrying out reliable calculations of the characteristic thermopowers are discussed in Section IV of the current work.

III. Experimental

A. Preparation of Samples

Measurements were carried out with the alloys and pure silver in the form of annealed 0.010-in.-diam wires. The starting materials and their stated purities were: Cominco silver, 99.999% purity; American Smelting and Refining Co., gold of 99.999% purity; and Dow-Corning semiconductor grade germanium. During the melting operation, the alloy constituents were contained in previously outgassed, high-purity, graphite crucibles. Melting was carried out, at a dynamic vacuum of 10^{-6} torr, by means of an induction heater, the melt being shaken vigorously over a period of one hour. Following solidification, the billets were inverted and a similar melting cycle repeated. All billets were then given a homogenizing anneal at 600°C for 6 days under a dynamic vacuum of 10^{-6} torr. The resulting $\frac{3}{8}$ -in.-diam billets were swaged to 0.070 in., then drawn through diamond dies to the final diameter of 0.010 in. During the swaging and drawing processes, the material was etched frequently by use of a mixture of ammonium hydroxide and hydrogen peroxide. Following the drawing process, the wires were given a final vacuum anneal at 680°C for 24 hr. Fabrication of the pure silver wires was carried out by first vacuum melting in graphite crucibles. The swaging and drawing operations as well as the final anneal were identical to those used for the alloys. Solute concentrations determined by chemical analysis, together with resistivities measured at several convenient temperatures, are listed in Table 1.

Table 1. Solute concentrations and resistivities for dilute silver-gold and silver-germanium alloys

Solute	Solute concentration at. %	Electrical resistivity ρ , $\mu \Omega$ -cm			
		4.2°K	77.3°K	273°K	295°K
Silver-gold	0.05	0.02	0.29	1.48	1.61
	0.21	0.07	0.35	1.52	1.65
	0.28	0.10	0.38	1.54	1.67
	0.46	0.16	0.44	1.62	1.76
	1.5	0.50	0.81	1.99	2.13
Silver-germanium	0.03	0.22	0.51	1.69	1.83
	0.12	0.72	1.01	2.18	2.32
	0.20	1.28	1.57	2.73	2.86
	0.30	1.59	1.89	3.07	3.20
	0.47	2.44	2.74	3.93	4.05
	0.78	4.54	4.85	6.10	6.20
	1.05	5.61	6.34	7.17	7.30
Pure silver	—	0.003	0.27	1.47	1.60

B. Determination of Resistivity and Thermoelectric Power

The thermoelectric powers were determined by first forming a thermocouple between either the alloy or silver wires, and similar wires of high-purity lead. The hot junction of the thermocouple was placed in good thermal contact with a heater; both thermocouple and heater were contained within a brass vessel maintained at a dynamic vacuum of 10^{-5} torr. The thermocouple reference junctions were immersed directly in liquid nitrogen by means of a vacuum feed-through located in the bottom of the container. Measurements were carried out from liquid-nitrogen temperature to 300°K , the entire assembly being completely immersed in liquid nitrogen for the duration of each run. Thermal electromotive forces generated by the thermocouples were measured at 2°K intervals by a Rubicon, *thermofree* potentiometer. Temperatures were determined by means of a copper-constantan thermocouple and a Leeds and Northrop type K-3 potentiometer. The difference in thermopowers, between the alloys and pure lead, was determined with respect to temperature by taking the derivatives of the thermal emf data. The derivatives were determined by use of a program based on the method outlined by Henry and Schroeder (Ref. 13). Numerical computations were carried out with an IBM 1620 computer. Absolute thermopowers were then determined by use of the calibrated absolute thermopowers of pure lead (Ref. 17). The thermopowers of silver and the silver-gold alloys are shown in Fig. 1. Thermopowers of the silver-germanium alloys are shown in Fig. 2. Voltage measurements are accurate to within $0.01\ \mu\text{V}$, while temperatures are accurate to within 0.1°K . Resistivities were determined at 4.2,

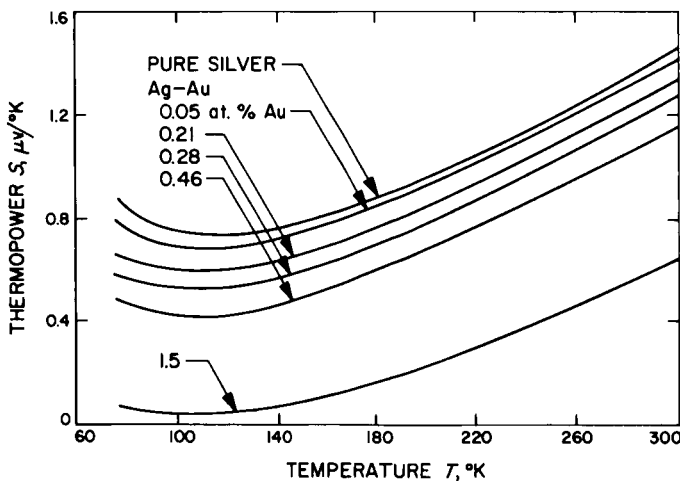


Fig. 1. Thermoelectric power of silver and dilute silver-gold alloys from 78 to 300°K

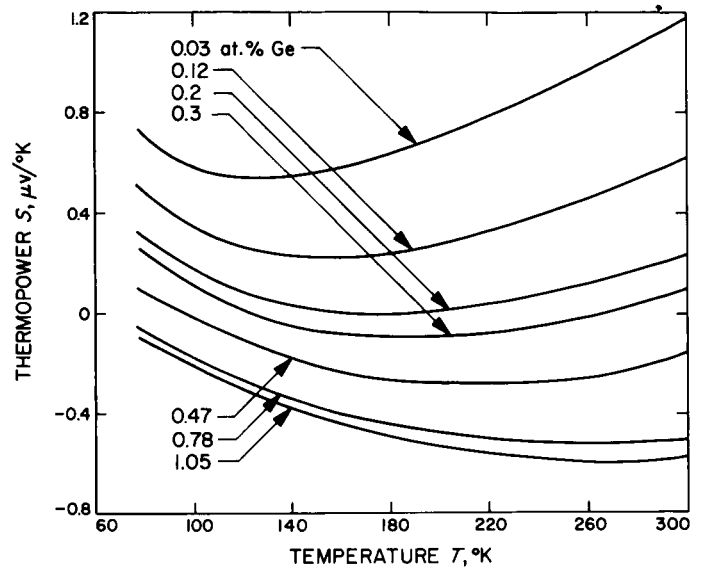


Fig. 2. Thermoelectric power of dilute silver-germanium alloys from 78 to 300°K

77.3 , 273 , and 295°K . A standard four-point technique was used, voltage drop across the sample being measured by the Rubicon *thermofree* potentiometer, while current was determined by means of the voltage drop across a one ohm standard resistance placed in series with the current through the sample. Voltage drops across the standard resistance were determined with the type K-3 potentiometer.

IV. Analysis and Discussion

A. Nordheim-Gorter Plots

Since the Debye temperature of silver is approximately 220°K (Ref. 9), it is reasonable to assume a negligible phonon drag component at the ice point. Hence, at and above 273°K , it is assumed that the total thermopower is very nearly equal to the diffusion thermopower. Thus, in Eq. (3) we set $S = S_e$, S being the measured thermopowers of the alloys. Plots of S vs $1/\rho$, at $T = 273$ and 295°K , are shown in Fig. 3 and 4. To the limit of gold concentrations employed, the Ag-Au data may be fitted by a straight line. On the other hand, the Ag-Ge data deviates from a straight line at a solute concentration somewhat lower than 1 at.%. From the figure, we estimate this deviation to occur at roughly 0.5 at. % germanium. The straight lines observed for Ag-Au indicate the lack of any appreciable Fermi surface changes up to 1.5 at. % gold. From the PRFE results (Ref. 2) this alloy concentration corresponds to a change in Fermi surface neck radius of approximately $0.0045\ \mu$. Deviations from

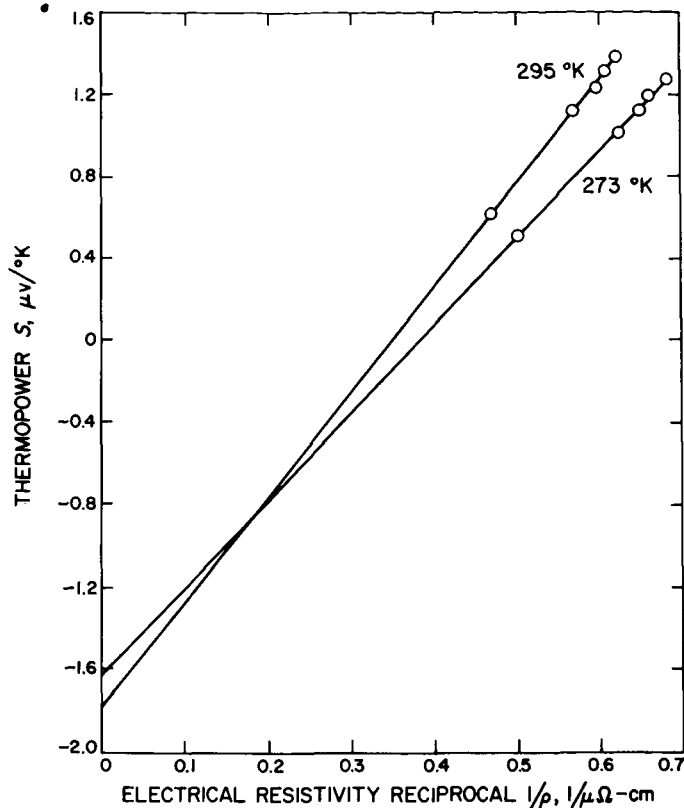


Fig. 3. Thermoelectric power vs reciprocal of electrical resistivity for Ag-Au alloys at 273 and 295°K

the straight-line plot for the Ag-Ge alloys can be attributed to Fermi surface changes resulting from the addition of electrons from the quadrivalent germanium. This addition of electronic charge should be compared to the decreased electron/atom contribution from monovalent gold in the Ag-Au alloys.

From the intercepts of the straight lines with the S_e axis in Figs. 3 and 4, we obtain values of the characteristic thermopowers, S_e^0 , listed in Table 2. From the slopes and

Table 2. Values of characteristic thermopowers S_e^1 and S_e^0 obtained from Nordheim-Gorter plots at 273 and 295°K

Alloy	Temp, °K	Thermopower, $\mu\text{V}/^\circ\text{K}$			Thermopower/deg, $\mu\text{V}/^\circ\text{K}^2$	
		S_e^1	S_e^0	S_e^a	S_e^0/T	S_e^1/T
Ag-Au	273	-1.64	1.29	1.31	4.73×10^{-3}	-6.01×10^{-3}
	295	-1.78	1.41	1.44	4.78×10^{-3}	-6.03×10^{-3}
Ag-Ge	273	-1.26	1.36	1.31	4.98×10^{-3}	-4.62×10^{-3}
	295	-1.35	1.50	1.44	5.08×10^{-3}	-4.58×10^{-3}

^a S_e^0 is the measured thermopower of silver at these temperatures.

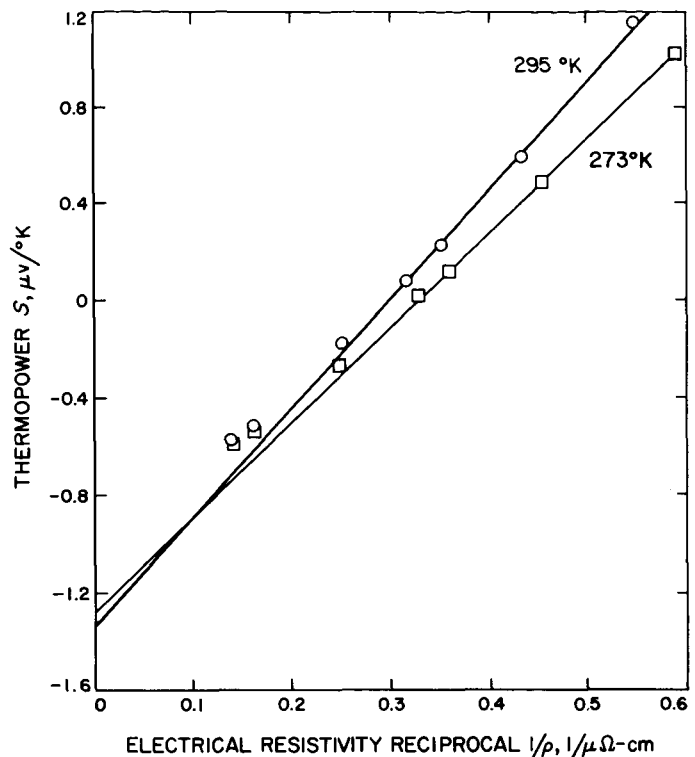


Fig. 4. Thermoelectric power vs reciprocal of electrical resistivity for Ag-Ge alloys

the preceding values of S_e^1 , the values of S_e^0 (also shown in Table 2) are obtained. Also listed in the table are values of S_e^1/T , S_e^0/T , and S_e^0 —the last named being the currently measured thermoelectric power of silver at the two temperatures. From Table 2 it is concluded that, to a first approximation, the respective characteristic thermopowers due to impurities, and the pure metal are proportional to temperature. We make the assumption here that this approximately linear behavior would be manifest between the two temperatures investigated. Comparison between S_e^0 and S_e^0 indicates that Eq. (7) is reasonably satisfied for the silver-gold alloys. For Ag-Ge, on the other hand, although the agreement between S_e^0 and S_e^0 is fair, it is not quite as good as in the silver-gold system. The discrepancy in the Ag-Ge case could be attributable either to the presence of a phonon-drag component or to departures from the Nordheim-Gorter relation, or to both conditions. The results for the Ag-Au alloys tend, however, to indicate the presence of a negligible phonon drag component in the pure silver for $T \geq 273^\circ\text{K}$.

B. Characteristic Thermopowers

The quantity S_e^0 is the characteristic thermopower due to scattering of electrons in the pure metal. At 273°K

electrons are thermally scattered in the pure metal, hence $S_e^0 = S_e^{\text{th}} = S^0$. From Eq. (5) one obtains, according to Wilson (Ref. 11),

$$S_e^0 = -\frac{\pi^2 k^2 T}{3|e|} \left[\frac{\partial \ln n(E)}{\partial E} + \frac{\partial \ln v^2(E)}{\partial E} + \frac{\partial \ln \tau(E)}{\partial E} \right]_{E_F} \quad (8)$$

where $n(E)$ is the electronic density of states, v an average electron velocity, and τ the electron relaxation time. Using the free electron approximation, Jones (Ref. 18) finds the bracketed term in Eq. (8) equal to $2.5/E_F$, while Wilson (Ref. 11) evaluates this term as numerically equal to $3/E_F$. Using Wilson's value, one obtains from Eq. (8)

$$S_e^0 = -\frac{7.3 \times 10^{-2} T}{E_F} \quad (9)$$

where the Fermi energy is expressed in electron volts, and S_e^0 has the units $\mu\text{V}/^\circ\text{K}$. If 5.51 eV is used for the Fermi energy of silver, Eq. (9) becomes

$$\frac{S_e^0}{T} = -1.32 \times 10^{-2} \mu\text{V}/^\circ\text{K}^2 \quad (10)$$

Comparison with Table 2 shows that the free-electron theory yields the incorrect sign and numerical value for the thermal component in the current alloys. Various attempts have been made to arrive at correct theoretical expression for S_e^0 in the noble metals (Refs. 1, 19, 20). To date, however, there exists no satisfactory theory that can account for both the sign and numerical value of S_e^0 in the noble metals.

To obtain numerical estimates of S_e^1 it is seen from Eq. (4) that one needs to evaluate the logarithmic derivative of $\Delta\rho$ with respect to energy. A semiempirical evaluation of the logarithmic derivative has been carried out by Huebener (Ref. 21). Strictly speaking, one needs to take into account the departure of the Fermi surface from the free electron model (Ref. 1). For gold, this is accomplished by means of data acquired from a size-effect experiment (Ref. 22). The cross section for electron scattering caused by imperfections is then computed using the partial wave method (Ref. 23) and the Friedel sum rule (Ref. 24); a square-well potential is used in the free-electron approximation (Ref. 21). These data are then combined with data from the size effect on thermoelectric power to obtain reasonable values for the logarithmic derivative (Ref. 21).

In the present case, no size-effect data are available for silver. However, numerical estimates of the characteristic thermopower for several polyvalent solutes in copper have been obtained by Crisp, Henry, and Schroeder (Ref. 14). Using Mott's simple expression for residual resistivity (Ref. 25), these authors calculate values for the characteristic thermopowers that agree in sign and magnitude with the observed values. In view of the previous results (Ref. 14), it is of interest to carry out numerical estimates of S_e^1 using Mott's theory of residual resistivity. According to Mott (Ref. 25)

$$\Delta\rho = \frac{N_a m v f A}{N e^2} \quad (11)$$

with

$$A = 0.81 \pi a^2 \left[\frac{E_0 - E^1}{E} \right]^2 \quad (12)$$

where N_a is the number of atoms/unit volume, N is the number of conduction electrons/unit volume, f is the fraction of solute atoms present, m and v are the electron mass and velocity, a is the atomic radius, E is the energy of an electron evaluated at the Fermi surface, and $E_0 - E^1$ is the effective depth, in energy, of a square-well potential at the impurity atom site. Equations (11) and (12) correctly predict that the residual resistivity/at.% of gold in silver is equal to the residual resistivity/at.% of silver in gold (Ref. 25). Substituting Eqs. (11) and (12) into Eq. (4) one obtains (Ref. 14)

$$S_e^1 = -\frac{\pi^2 k^2 T}{2|e| E_F} \quad (13)$$

Although essentially a free-electron theory, the Mott theory is specifically intended for alloys such as Ag-Au (Ref. 25). In applying Eq. (13) to both Ag-Au and Ag-Ge, one makes the additional assumption that the form of the energy dependence for impurity scattering is independent of the nature of the solute (Ref. 14). Furthermore, in the case of such polyvalent solutes as germanium, in silver, one must consider screening effects in obtaining theoretical expressions for $\Delta\rho$ (Refs. 25, 26). We thus expect Eq. (13) to give better results for the Ag-Au system. From evaluation of Eq. (13), it is found that

$$S_e^1 = -1.82 \mu\text{V}/^\circ\text{K}, \quad T = 273^\circ\text{K} \quad (14)$$

and

$$S_e^1 = -1.97 \mu v / ^\circ K, \quad T = 295^\circ K \quad (15)$$

Comparison of these results with the data of Table 2 indicates rough agreement between the experimental and calculated values of S_e^1 for the Ag-Au alloys. The values obtained for the Ag-Ge system show agreement in sign and magnitude between the calculated and experimental values. The above results also indicate somewhat better agreement for the silver-gold system as compared with silver-germanium.

C. Comparison with Previous Results

In attempting to understand the mechanisms responsible for the change in diffusion thermopower with alloying, it is of interest to compare the current results for Ag-Au with those previously obtained for similar alloy systems. Since gold, silver, and copper are monovalent and have similarly shaped Fermi surfaces (Ref. 1), we concentrate on comparison with the most recent data for dilute Cu-Ag and Cu-Au alloys (Refs. 3, 4). In this respect, the quantity of interest is ΔS_e , the difference in diffusion thermopower between the pure metal and the alloy, where

$$\Delta S_e = S_e - S_e^0 \quad (16)$$

S_e is the diffusion thermopower of the alloy and S_e^0 is the diffusion thermopower of the pure metal. Using Eq. (3), and assuming negligible phonon drag effects, we obtain

$$\Delta S = \frac{\Delta \rho}{\rho} (S_e^1 - S_e^0) \quad (17)$$

where ΔS is the difference in thermopower between the pure metal and the alloy. A plot of ΔS obtained from Eq. (17) for the Ag-Au alloy system is shown as the solid curve of Fig. 5. In computing ΔS from Eq. (17), S_e^1 is obtained from Table 2, while the currently measured thermopower of silver at 295°K is used for S_e^0 . The quantity $\Delta \rho$ is obtained from the relation

$$\Delta \rho = C \alpha \quad (18)$$

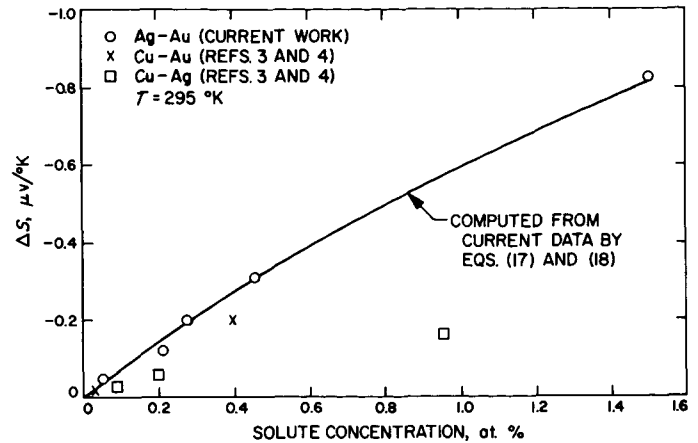


Fig. 5. Change in thermoelectric power at 295°K vs concentration for Ag-Au, Cu-Ag and Cu-Au

where C is the gold concentration in at.%, and $\alpha = 0.36 \mu \Omega - \text{cm/at.}\%$ (Ref. 27). In addition, the figure shows data points taken from the current work, together with those representing recent results for the Cu-Au and Cu-Ag systems (Ref. 3, 4). It is seen from the figure that the curve obtained from Eq. (17) greatly facilitates a quantitative comparison between ΔS values, at a specific solute concentration, for the various alloy systems. With respect to the Ag-Ge system, the current work is in essential agreement with the data presented by Blatt and his coworkers for a single alloy containing 1 at.% germanium (Ref. 28). Since our interest lies in comparison of the Ag-Au results with similar alloys of the noble metals, no further comparison is made concerning the silver-germanium system. Returning to the noble metal alloys of Fig. 5, it is seen that, for the Cu-Ag system at a given concentration, the ΔS values are markedly less than those obtained for the current alloys. The data points shown indicate a slightly lower change in thermopower for the Cu-Au system when compared with the current data.

Several mechanisms require consideration in discussing the relative changes in diffusion thermopower observed for the various noble metal alloys shown in Fig. 5. Size effects do not appear to be significant, since one would expect the least contribution from this mechanism in the Ag-Au system. Another of the possible mechanisms lies in the effects of possible Fermi surface changes in contributing to the ΔS values for the various alloy systems. In the silver-gold system, PRFE results indicate rather small Fermi surface changes for the current dilute alloys.

Considering the limiting assumptions on the Nordheim-Gorter rule, one tends to conclude, from the present work, that there are no appreciable changes in Fermi surface up to 1.5 at.% gold concentration. Essentially, this means that, for the current dilute silver-gold alloys, the Nordheim-Gorter plots are insensitive to the small Fermi surface changes indicated by the PRFE data (Ref. 2). Inasmuch, however, as no effects due to Fermi surface changes are detected, the current data are in essential agreement with the PRFE results. Yet one cannot rule out the effects of small Fermi surface changes in contributing to the observed ΔS differences of Fig. 5. Another cause, of the observed ΔS differences, is found in the possibility that slight differences in electronic charge are associated with the solute atom when compared to the host atom in the alloy. In this respect, Mott (Ref. 25) concludes that, in dilute silver-gold alloys, gold with the larger ionization energy should present a more attractive potential than does silver to the conduction band electronic charge. In this connection, Stern (Refs. 29, 30) finds a small *charging* effect in the Ag-Au system. Charging, as defined by Stern, is the difference in amount of electronic charge deposited by an electron, in a given state, on each constituent of the alloy. It is found for Ag-Au that, although the charging effect is small, the gold atom has a slightly more negative charge associated with it as compared to the silver atom (Ref. 29). This conclusion receives support in the Mossbauer experiments of Roberts and his coworkers (Ref. 31). At present,

no numerical estimates are available for the charging effect (Ref. 29) in either Cu-Au or Cu-Ag. In this respect, however, it is of interest to examine the electronegativity (Ref. 32) values for the silver, gold, and copper atoms. The electronegativity value of an atom may be thought of as a rough measure of the power of the atom in a molecule to attract electrons to itself (Ref. 32). Strictly speaking, electronegativity values are computed for a particular atom in a diatomic molecule (Ref. 32); hence, one should use caution in applying the electronegativity concept to metals. Noting these limitations, the electronegativity values as given by Pauling (Ref. 32) for silver, gold, and copper are 1.9, 2.4 and 1.9, respectively. The electronegativity difference between solute and solvent is thus seen to be equal in the Cu-Au and Ag-Au alloys, with gold having the largest electronegativity value. For Cu-Ag, the electronegativity difference between solute and solvent is zero. Hence, the data of Fig. 5 is in qualitative agreement with the relative magnitude of possible contributions to the charging effects based on electronegativity values (Ref. 32). Thus, the possibility of electron scattering from electronic charge associated with the solute atom needs to be considered in detail, together with possible Fermi surface changes, as contributing to the observed ΔS differences. In this respect, numerical calculation of the charging effect in the Cu-Au and Cu-Ag systems would be of great value in any effort aimed at assessing the relative importance of the two mechanisms.

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