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Thermoelectric Power in Silver-Gold and Silver-Germanium Alloys*

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The thermoelectric powers of dilute silver-gold and silver-germanium alloys are determined from 78 to 300°K. Nordheim–Gorter plots are made for these alloy systems at 273 and 295°K, and the characteristic thermopowers S_e^1 and S_e^0, due to solute and solvent, respectively, are determined at these temperatures. Calculated values of S_e^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.%. The Ag-Ge data, however, deviate from the expected linearity predicted by the Nordheim–Gorter relation at approximately 0.5 at.%. A detailed comparison of the present Ag-Au data with previous results for Cu-Ag and Cu-Au is carried out, using a Nordheim-Gorter type relation for ΔS, the difference in thermopower between the pure metal and alloy.

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, and they have the same crystal structure, nearly the same atomic radii, and similar Fermi energies.[1] The relative simplicity of this alloy system has facilitated detailed studies of change in the Fermi surface 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.[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 general shape, varying linearly as a function of alloy concentration.[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 {111} zone faces. Defining the distance from the origin to the {111} faces of the Brillouin zone as p, the neck radius is $0.13p$ in silver and $0.16p$ in gold.[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 which is particularly sensitive to changes in Fermi-surface geometry. However, since gold and silver are monovalent, one would not, in the light of the PRFE results,[2] expect any large or unusual change in diffusion thermopower in silver-gold alloys containing on the order of 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.[3,4] On the other hand, previous thermopower measurements on the silver-gold alloy system[5] indicate a larger thermopower change with alloying than in the experimental results for the copper alloys.[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 than for copper and gold.[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.

From mass-difference considerations, one expects a relatively large attenuation of phonon-drag thermopower in dilute silver-gold alloys.[4,7] To minimize the complicating effects of phonon-drag thermopower, it thus 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,[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,[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, the maximum gold concentration being 1.5 at.%. One objective lies in the 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.[3,4] At the

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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 to Ag-Au, the Ag-Ge alloys present a relatively large difference in number of valence electrons between solute and solvent. Hence, one can anticipate a larger alteration in electronic structure, for a given germanium concentration, than for the same concentration of gold in silver. In this case, the use of thermoelectric power in the detection of possible electronic changes associated with alloying 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[10,11]

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

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.[10] In the case of dilute alloys, an extension of Eq. (1) is obtained using Matthiessen's rule,

$$\rho = \rho_0 + \Delta\rho, \tag{2}$$

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

$$S_e = S_e^1 + (\rho_0/\rho)(S_e^0 - S_e^1), \tag{3}$$

with

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

and

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

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. Equation (3) is a special case of the Nordheim-Gorter relation[12]

$$S_e = (\textstyle\sum_i S_e^i \rho^i)/\rho, \tag{6}$$

where S_e^i and ρ^i are the characteristic diffusion thermopower and electrical resistivity due to the ith 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), the following conditions must be satisfied for Eq. (6), and hence Eq. (3), to be valid:

1. The addition of impurities does not alter the Fermi surface.
2. Conduction in the alloy is describable in terms of a single homogeneous group of conduction electrons.
3. The scattering of electrons by an impurity, and all other electron scattering events are independent of each other.

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

$$S_e^0 = S^0, \tag{7}$$

where S_e^0 is obtained from the Nordheim-Gorter plot and S^0 is the thermopower of the pure metal. In writing the previous equation, it is further assumed that the plot of Eq. (3) to fit the data results in the correct value for S_e^0. In this respect, the agreement with 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.[13,14] References to several other applications of this rule are found in MacDonald[15] and in Pearson.[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

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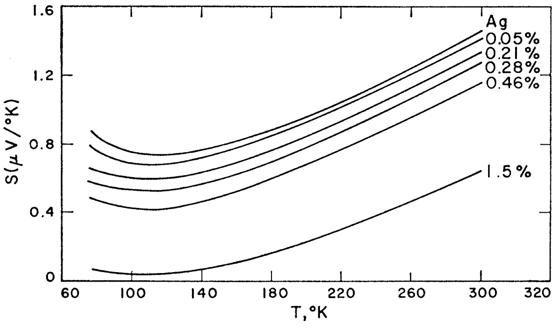

FIG. 1. Thermoelectric power of silver and dilute silver-gold alloys from 78 to 300°K. Percentages are gold concentrations in atomic percent.

expressions. Limitations with respect to carrying out reliable calculations of the characteristic thermopowers are discussed in Sec. IV.

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 of 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, in 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. and then drawn through diamond dies to the final diameter of 0.010 in. The material was etched frequently, during the swaging and drawing process, using 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 h. 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 I.

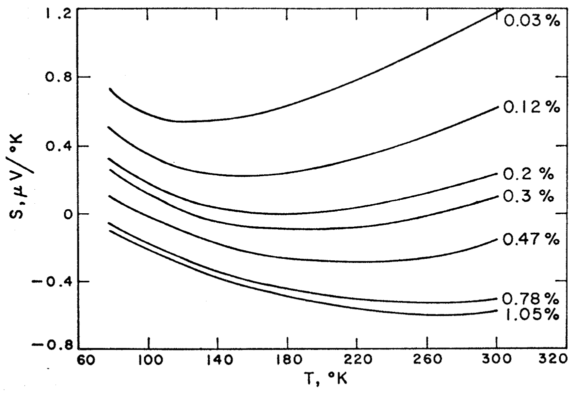

FIG. 2. Thermoelectric power of dilute silver-germanium alloys from 78 to 300°K. Percentages are germanium concentrations in atomic percent.

B. Determination of Resistivity and Thermoelectric Power

The thermoelectric powers were determined by first forming a thermocouple between 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 being contained within a brass can 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 can. 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 emfs generated by the thermocouples were measured at 2° intervals using a Rubicon "thermofree" potentiometer. Temperatures were determined by means of a copper-Constantan thermocouple and a Leeds and Northrup Type K-3 potentiometer. The difference in thermopowers between the alloys and pure lead was determined by taking the derivatives with respect to temperature of the thermal emf data. The derivatives were determined using a program based on the method outlined by Henry and Schroeder.[13] Numerical computations were carried out with an IBM 1620 computer. Absolute thermopowers were than determined by use

TABLE I. Solute concentrations and resistivities for dilute silver-gold and silver-germanium alloys.

Solute	Solute concentration Atomic %	$\rho_{4.2}$ μΩ cm	$\rho_{77.3}$ μΩ cm	ρ_{273} μΩ cm	ρ_{295} μΩ cm
Au	0.05	0.02	0.29	1.48	1.61
Au	0.21	0.07	0.35	1.52	1.65
Au	0.28	0.10	0.38	1.54	1.67
Au	0.46	0.16	0.44	1.62	1.76
Au	1.5	0.50	0.81	1.99	2.13
Ge	0.03	0.22	0.51	1.69	1.83
Ge	0.12	0.72	1.01	2.18	2.32
Ge	0.20	1.28	1.57	2.73	2.86
Ge	0.30	1.59	1.89	3.07	3.20
Ge	0.47	2.44	2.74	3.93	4.05
Ge	0.78	4.54	4.85	6.10	6.20
Ge	1.05	5.61	6.34	7.17	7.30
Pure silver	···	0.003	0.27	1.47	1.60

of the calibrated absolute thermopowers of pure lead.[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 0.01 μV, while temperatures are accurate to 0.1 deg. Resistivities were determined at 4.2, 77.3, 273, and 295°K. A standard four-point technique was used, the voltage drop across the sample being measured by the Rubicon thermofree potentiometer, while current was determined by means of the voltage drop across a 1-Ω standard resistance placed in series with the current through the sample. Voltage drops across the standard resistance were determined with the Type K3 potentiometer.

IV. ANALYSIS AND DISCUSSION

A. The Nordheim-Gorter Plots

Since the Debye temperature of silver is approximately 220°K,[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 $S=S_e$, where S is the measured thermopower of the alloy. Plots of S versus $1/\rho$, at $T=273$ and 295°K, are shown in Figs. 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 deviate 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[2] this alloy concentration corresponds to a change in Fermi-surface neck radius of approximately 0.0045p.

TABLE II. Values of the characteristic thermopowers S_e^1 and S_e^0 obtained from the Nordheim-Gorter plots at 273 and 295°K. S^0 is the measured thermopower of silver at these temperatures.

Alloy	T °K	S_e^1 μV/°K	S_e^0 μV/°K	S^0 μV/°K	S_e^0/T μV/(°K)^2	S_e^1/T μV/(°K)^2
Ag-Au	273	−1.64	1.29	1.31	4.73×10^{-3}	-6.01×10^{-3}
Ag-Au	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}
Ag-Ge	295	−1.35	1.50	1.44	5.08×10^{-3}	-4.58×10^{-3}

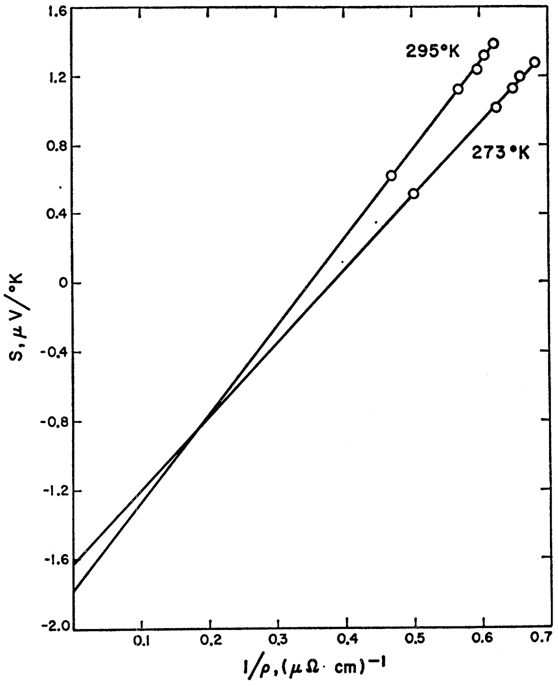

FIG. 3. Thermoelectric power versus reciprocal of electrical resistivity for Ag-Au alloys at 273 and 295°K.

From the intercepts of the straight lines in Figs. 3 and 4 with the S axis, we obtain the values of the characteristic thermopowers S_e^1 listed in Table II. From the slopes and the values of S_e^1 the values of S_e^0, also shown in Table II, are obtained. Also listed in the table are values of S_e^1/T, S_e^0/T, and the measured thermoelectric power S^0 of silver at the two temperatures. From Table II, it is concluded that, to a first approximation, the characteristic thermopower due to impurities and that in the pure metal are separately proportional to temperature. We make the assumption here that this approximately linear behavior will be manifest between the two temperatures investigated. Comparison between S_e^0 and S^0 indicates that Eq. (7) is reasonably satisfied for the silver-gold alloys. For

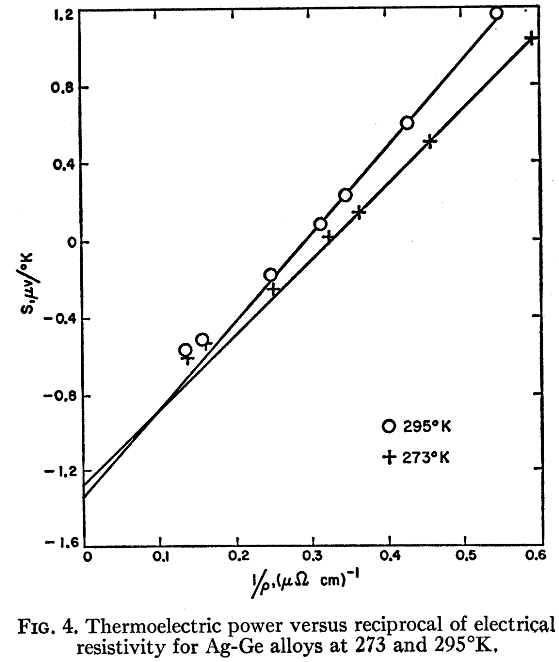

FIG. 4. Thermoelectric power versus reciprocal of electrical resistivity for Ag-Ge alloys at 273 and 295°K.

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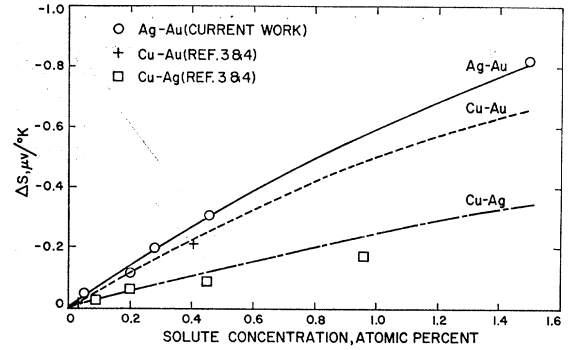

FIG. 5. Change in thermoelectric power, at 295°K, versus concentration for Ag-Au, Cu-Ag, and Cu-Au. The solid and broken curves are computed using Eqs. (13) and (14).

Ag-Ge, on the other hand, the agreement between S_e^0 and S^0, although fair, is not quite so good as in the silver-gold system. The discrepancy in the Ag-Ge case could be attributable to either the presence of a phonon-drag component and/or departures from the Nordheim-Gorter relation. The results for the Ag-Au alloys tend, however, to indicate the presence of a negligible phonon-drag component in the pure silver for $T \geqslant 273°\mathrm{K}$. Deviations from the linear behavior predicted by the Nordheim-Gorter rule can be attributed to any or all of the assumptions listed in Sec. II. Hence further experimental work is required before one can attribute the Ag-Ge deviation to a specific mechanism, or combination of mechanisms. In this respect, it would be significant to extend the present Ag-Ge data to higher germanium concentrations and at the same time observe the behavior of the phonon-drag component as a function of germanium concentration.[13,14]

B. The Characteristic Thermopowers

Various attempts have been made to arrive at a correct theoretical expression for S_e^0 in the noble metals.[1,18,19] To date, however, there exists no satisfactory theory which can account for both the sign and the numerical value of S_e^0 in copper, silver, or gold. Hence we include no numerical estimates of this quantity in the current work.

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 semi-empirical evaluation of the logarithmic derivative has been carried out by Huebener.[20] Strictly speaking, one needs to take into account the departure of the Fermi surface from the free-electron model.[1] This is accomplished for gold by means of data acquired from a size-effect experiment.[21] The cross section for electron scattering due to imperfections is then computed using the partial-wave method[22] and the Friedel sum rule,[23] a square-well potential being used in the free-electron approximation.[20] This is then combined with data from the size effect on thermoelectric power to obtain reasonable values for the logarithmic derivative.[20] 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.[14] Using Mott's simple expression for residual resistivity,[24] these authors calculate values for the characteristic thermopowers which agree in sign and magnitude with the observed values. In view of the previous results,[14] it is of interest to carry out numerical estimates of S_e^1 using Mott's theory of residual resistivity. According to Mott,[24]

$$\Delta\rho = N_a m v f A / N e^2, \tag{8}$$

with

$$A = 0.81\pi a^2[(E_0 - E^1)/E]^2, \tag{9}$$

where N_a is the number of atoms per unit volume, N is the number of conduction electrons per unit volume, f is the fraction of solute atoms present, m and v are, respectively, 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 (8) and (9) correctly predict that the residual resistivity per at. % of gold in silver is equal to the residual resistivity per at. % of silver in gold.[24] Substituting (8) and (9) into Eq. (4), one obtains[14]

$$S_e^1 = -(\pi^2 k^2 T)/2|e|E_F. \tag{10}$$

Although essentially a free-electron theory, the Mott theory is specifically intended for alloys such as Ag-Au.[24] In applying Eq. (10) 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.[14] Furthermore, in the case of polyvalent solutes, such as germanium, in silver, one must consider screening effects in obtaining theoretical expressions for $\Delta\rho$.[24,25] We thus expect Eq. (10) to give better results for the Ag-Au system. Evaluating Eq. (10), it is found that

$$S_e^1 = -1.82\ \mu\mathrm{V}/°\mathrm{K}; \quad T = 273°\mathrm{K} \tag{11}$$

and

$$S_e^1 = -1.97\ \mu\mathrm{V}/°\mathrm{K}; \quad T = 295°\mathrm{K}. \tag{12}$$

Comparison of these results with the data of Table II 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

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experimental values. The above results also indicate somewhat better agreement for the silver-gold system than for the silver-germanium.

C. Comparison with Previous Results

We concentrate on comparison of the Ag-Au results with recent data for dilute Cu-Ag and Cu-Au alloys.[3,4] Using Eq. (3) and assuming negligible phonon-drag effects, one obtains

$$\Delta S = (\Delta\rho/\rho)(S_e{}^1 - S_e{}^0)\,, \tag{13}$$

where ΔS is the difference in thermopower between the alloy and pure metal. A plot of ΔS, obtained using Eq. (13), is shown as the solid curve in Fig. 5. In computing ΔS, the value of $S_e{}^1$ is obtained from Table II, 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

$$\Delta\rho = C\alpha\,, \tag{14}$$

where C is the gold concentration in at. % and $\alpha = 0.36$ $\mu\Omega$ cm/at. %.[26] The figure shows, in addition, data taken from the present work, together with several recent results for the Cu-Au and Cu-Ag systems.[3,4] With respect to the Ag-Ge system, the present results are in essential agreement with the data presented by Blatt and his co-workers[27] for a single alloy containing 1 at. % germanium.

Referring to Eq. (14), we note that, for Ag in Cu, $\alpha = 0.14\,\mu\Omega$ cm/at. %, while for Au in Cu, $\alpha = 0.55$ $\mu\Omega$ cm/at. %.[26] Hence the term outside the brackets in Eq. (13) can contribute significantly to the observed variation in ΔS. Although Eq. (13) is useful in comparing ΔS values between alloy systems, use of the quantity $S_e{}^1$ is more appropriate in comparing related alloy systems. With respect to the characteristic thermopowers, insufficient data are available to carry out Nordheim-Gorter plots, and thus obtain reliable values of $S_e{}^1$, for Cu-Ag and Cu-Au. However, approximate values for $S_e{}^1$ are obtainable from Eq. (13). Using our previous data on Cu-Au and Cu-Ag,[4] we obtain $S_e{}^1 \approx -0.3\ \mu\text{V}/°\text{K}$ for Au in Cu and $S_e{}^1 \approx -1.5\ \mu\text{V}/°\text{K}$ for Ag in Cu at 295°K. Substituting these values in Eq. (13), and using Eq. (14), one obtains the additional curves shown in Fig. 5. Also, from Eq. (10), using $E_F = 7.04$ eV for copper, we obtain the calculated value $S_e{}^1 = -1.54\ \mu\text{V}/°\text{K}$. Considering, among other things, the use of a free-electron model in obtaining Eq. (10), the close agreement with respect to Cu-Ag is considered fortuitous.

With respect to the Ag-Au alloys, we are unable to find any evidence which would indicate that Fermi-surface changes are responsible for the relatively large observed values of ΔS in Fig. 5. In fact, for the silver-gold system, rather small Fermi-surface changes are indicated by the PRFE results.[2] This latter conclusion receives support in the results of de Haas–van Alphen experiments on dilute alloys of silver and gold.[28] Considering the limiting assumptions on the Nordheim-Gorter rule, one may conclude from the present work that there are no appreciable changes in Fermi surface up to 1.5 at. % gold. Alternatively, one may conclude that the Nordheim-Gorter plots are insensitive to the small Fermi-surface changes indicated by other experimental techniques.[2,28] Inasmuch, however, as no effects due to Fermi-surface changes are detected, the present results are in implicit agreement with the prediction of small, or negligible Fermi-surface changes in these dilute alloys.[2]

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