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Low-Temperature Specific Heats of *Ag*Au Alloys*†

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The specific heats of solid solutions of up to 40 at.% Au in Ag have been measured between 2 and 4°K. The electronic specific heat coefficient γ decreases on adding Au to Ag at the initial rate of about -30% per unit concentration, reaching a minimum value at about 20% Au. This result disagrees sharply with scattering theories proposed to account for the increase of γ upon alloying noble metals with *b*-subgroup solutes. In view of other evidence that wave functions for both pure Au and Ag have the same symmetry near the necks of the Fermi suface, our result disagrees with either "rigid" or "soft" band-structure interpretations. The Debye temperatures of the alloys are slightly greater than those expected from linear interpolation between those of the pure metals.

INTRODUCTION

As a result of recent experimental work, it is becoming possible to discern certain regularities in the curious behavior of the electronic specific heat coefficient γ of the noble metals upon alloying with polyvalent nontransition metals. The hope, a naive one perhaps, in doing such an experiment is to trace out the density of states of the pure metal as a function of energy or, more directly, as a function of the spatial density of conduction electrons. Thus one expects the measured coefficient γ to be a single-valued function of the number e/a of conduction electrons per atom, regardless of the solute introduced, insofar as the band structure of the solvent can be regarded as unaffected by the alloying. The theoretician, upon being presented with this idea, is apt to view such an expectation with scorn, since it is based in theory upon nothing more extensive than a first-order perturbation calculation[1] starting from a free-electron model of the pure metal. Nevertheless, this "rigid band" model for alloys has had considerable success in explaining properties of transition metal alloys,[2] in which the density of states (*d* band) is about 10 times greater than it is in the noble metals (*s* band). In the noble metals, too, the value of e/a largely determines the value of γ to be observed, but with the disturbing feature that where one expects a decreasing density of states, one finds an increasing electronic specific-heat coefficient.

The history of this problem is an interesting one. The first experiments of this kind were done by Rayne[3] in 1956 and 1957, before it was known that the Fermi surface of copper was indeed in contact with the boundary of the first Brillouin zone. Rayne found a sharp increase in γ upon adding a few percent of Zn to Cu, and concluded that contact was lacking in the pure metal. After Shoenberg found the de Haas–van Alphen oscillations due to neck orbits in copper,[4] it became clear that a mystery had been found. Rayne investigated the *Cu*Ge system[5] (italics indicate the majority constituent—it is understood that we limit the discussion to alpha-phase solid solutions) again with the result that γ increases upon alloying. The puzzle created by these findings was discussed in several review articles,[6–8] in which some hypotheses were put forth. But it is clear that more experimental information was needed to determine whether the effect were peculiar to copper or not, and to explore the dependence of the effect upon the properties of the solute.

No more experimental information was published until 1963, when Montgomery and Pells[9] announced their results on the system *Ag*Cd. They found again that γ increases upon alloying. Then, Green and Culbert[10] investigated *Ag*Sn and found γ to increase quite linearly with Sn concentration up to $e/a=1.25$, and that the rate of increase is closely the same as that in *Ag*Cd when compared on an e/a basis. (The governing role of e/a was suggested by Rayne's *Cu*Zn and *Cu*Ge results, but the nonlinearity of the increase and the scatter in the data did not inspire confidence in this conclusion. Veal and Rayne[11] repeated the *Cu*Zn study with careful attention to the exclusion of paramagnetic impurities, and found a much less violent increase in γ upon alloying.)

Gold has only recently been investigated. Preliminary measurements by Will and Green[12] of the *Au*Sn system show that γ increases in gold-based alloys as well. Thus the phenomenon seems to be a universal property of the noble metals.

We must confess that the above view of the experi-

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mental evidence is controversial. The work of Isaacs and Massalski[13] in *Cu*Zn and *Ag*Sn and more recently in *Cu*Sn does not agree with the results cited above. Particularly in the copper-based alloy systems, they find an initial decrease in γ with solute concentration out to $e/a=1.03$. Clune and Green have independently examined both *Cu*Zn and *Cu*Sn with results closely verifying the initial increase Veal and Rayne find in *Cu*Zn. We know of no explanation for the disagreement. Sample purity is unlikely to be at fault, since all workers report less than 5 ppm of paramagnetic impurities. If the negative slopes are correct, then the discussion below must be disregarded.

How can we understand this increase of γ upon alloying? Consider the following two hypotheses which have been discussed: (1) We might expect that the atomic disorder of the alloy, which has been ignored above, should surely affect any property governed by the presence of a Brillouin-zone boundary, such as the expected decrease in γ. After all, the existence of the boundary depends on the existence of translational symmetry in the metal. Jones[14] has calculated that the scattering of conduction electrons should lead to a change in the observed value of γ proportional in strength to the residual resistance produced in the solvent by the solute. (2) Another factor which clearly should be examined is the change in band structure due to the difference in the core potentials of the solvent and solute. It has been suggested by Cohen and Heine[6,8] that the effect of alloying the noble metals may be accounted for roughly by (a) supposing that only the (111) Fourier component V_{111} of the potential need be considered (since it determines the extent of contact) and (b) assuming that this quantity is a weighted mean value of V_{111} for the solvent and some quantity appropriate to the solute. In the case of alloys of silver and gold, which form solid solutions in all proportions and which have the same crystal structure with almost the same lattice constant, we might expect to average V_{111} for pure silver with V_{111} for pure gold. Ziman[7] has analyzed the effect of changes in V_{111} on the band structure of a noble metal. He finds that an increase in V_{111} corresponds to an increase in density of states, in spite of an increase in the area of contact. This is consistent with the fact that gold has a larger neck than silver and also a larger electronic specific heat (neglecting all other differences).

A possibly crucial experiment for these theories is to examine the system *Ag*Au, which we have done. In this system, there should be no change in electron concentration, and no volume effects, since Ag and Au have the same valence and the same atomic size (to within 1%). The variation of lattice parameter with composition shows very small negative deviation from Vegard's law (linear proportion). Furthermore, McAlister, Stern, and McGroddy[15] have found that the size of the necks in the Fermi surfaces of AgAu alloys varies linearly with composition, establishing that the wave functions of the pure metals have the same symmetry at the necks, and that the pseudopotential for the alloys may indeed be approximated by the weighted mean of those of the pure metals. We might reasonably expect that γ should increase as we add Au to Ag either (1) because of the effect of scattering or (2) because of the averaging of potentials, since the γ for Au is greater than that for Ag. Our result *contradicts* this expectation. We find that γ decreases initially at the rate of about -30% per unit concentration.

EXPERIMENTAL METHOD

The specimens were prepared from 99.9999% silver (Cominco) and 99.999% gold (American Smelting and Refining Company) by melting the weighed constituents in silica envelopes under vacuum. The melted metals were mixed by tipping the tubes back and forth. They were cooled by air blast to black heat from just above the liquidus temperature. The 20% and 30% samples were homogenized at about 800°C for 44 h and then quenched in water. The other samples were homogenized for only 24 h and cooled by air blast. Since this drastic difference in treatment produced no evident features in the results, we believe the differences to be irrelevant. The samples were machined flat on one end, drilled for mounting, and etched. In final form, the specimens were cylinders 2.5 cm in diam and about 5 cm long, being about 1.5 moles each.

Spectrographic analysis showed less than 1 ppm of any of the following elements: Fe, Mn, Co, Ni, Cr, Si, Cu, Al, in any of the samples with the single exception that 3 ppm of Al was found in the 4 at. % alloy.

The specific heats were measured in the calorimeter developed by Green and Culbert[10] using essentially the same method. This method is somewhat unusual in that thermal isolation of the sample is sacrificed in favor of rigid support. The sample is in contact with a cold reservoir (about 1.5°K) through three No. 4 nylon screws about 2 cm long. Its temperature is established at the desired temperature of measurement by adjusting power in an auxiliary heater, which balances the heat lost through the supports. The sample is then cooled sufficiently below the equilibrium temperature by a mechanical heat switch, heat is supplied by the "differential heater" at a separately measured rate, and the time is measured which the sample requires to warm through a preset temperature interval ΔT symmetrically disposed about the equilibrium temperature T. For each of the seven T's, $\Delta T \simeq T/20$.

The method used in the present work differs in some details from that previously reported. Whereas formerly

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random heat input was the principal source of scatter in the measurements, such scatter has now been reduced from about 0.15% to less than 0.1%, sometimes considerably less. We regard random error in thermometer calibration to be the principal source of scatter in the present experiment. Thus we increased the number of measurement temperatures from three to seven, equally spaced in T^2. The number of repetitions of heats at each temperature was reduced from ten to four or five. In the data reduction, 0.1% random error was allowed as an estimate of the uncertainty due to thermometer calibration. The thermometer was a 0.1-W, 47-Ω, Ohmite resistor, mounted with the heaters in a 20-g copper support, to which the sample was screwed. The thermometer was calibrated after each run against the 1958 He^4 scale, as before. Its calibration was stable to 1 mdeg over more than 15 cooling cycles. The heating times were determined using an electronic zero-crossing detector and simple logic circuits gating an electric clock with least count 0.01 sec driven by a 60 cps tuning fork power supply. Measurement times were in the range from 30 to 70 sec.

RESULTS

The specific heat of all samples is adequately represented by the usual relation

$$C=\gamma T+\alpha T^3.$$

A T^5 coefficient as large as 0.0003 mJ mol^{-1} °K^{-6} would have easily been detected. Table I gives the value of γ and of the Debye temperature Θ_D for each alloy, and Table II gives the experimental values of C/T and T^2 for the seven temperatures corresponding to each sample measured. Figure 1 shows the behavior graphically and shows the curves expected on the basis of the two theories mentioned in the Introduction and discussed below. It is clear that the initial change in γ is negative. A quadratic fit to the γ data gives

$$\gamma=0.654-0.21c+0.50c^2$$

in mJ mol^{-1} °K^{-2}, where c, the atomic fraction of gold, ranges from 0 to 0.4. The initial slope is

$$d(\ln\gamma)/dc=-0.32.$$

TABLE I. γ and Θ_D for several Ag-Au alloys.

Gold concentration (at. %)	γ mJ/mole °K^2	Θ_D (°K)
0.00	0.654±0.002[a]	225.8±0.1
3.97	0.645±0.002	223.9±0.1
3.97[b]	0.648±0.002	224.1±0.1
12.90	0.634±0.003	218.9±0.1
20.00	0.635±0.002	215.5±0.1
30.00	0.633±0.002	210.5±0.1
40.00	0.650±0.003	204.7±0.1

[a] Errors shown are one standard deviation.
[b] Same sample remeasured.

TABLE II. Experimental values of C/T and T^2 for alloys of the Ag-Au system.

Gold concentration (at. %)	[C/T mJ/mole °K^2]	T^2 (°K)^2
0.00	1.319	3.928
	1.658	5.944
	1.981	7.857
	2.325	9.872
	2.651	11.799
	2.983	13.764
	3.311	15.753
3.97	1.326	3.928
	1.673	5.944
	2.007	7.857
	2.356	9.878
	2.694	11.813
	3.033	13.779
	3.376	15.769
3.97[a]	1.324	3.928
	1.679	5.944
	2.007	7.857
	2.353	9.872
	2.688	11.806
	3.025	13.764
	3.366	15.745
12.90	1.363	3.928
	1.732	5.939
	2.091	7.851
	2.460	9.872
	2.826	11.813
	3.187	13.779
	3.553	15.769
20.00	1.399	3.928
	1.789	5.944
	2.163	7.857
	2.555	9.878
	2.932	11.813
	3.315	13.779
	3.696	15.769
30.00	1.452	3.928
	1.870	5.939
	2.273	7.851
	2.692	9.872
	3.099	11.813
	3.506	13.779
	3.918	15.769
40.00	1.541	3.928
	1.997	5.944
	2.433	7.862
	2.892	9.878
	3.328	11.820
	3.778	13.786

[a] Same sample.

It is difficult to assign error limits to this slope. The random error in the specific-heat measurements is negligible. Any systematic error remaining constant between runs has no effect. Thermometer calibration changes between runs are probably negligible. The chief uncertainty in the results we believe is in the characterization of the samples, not in the specific heat measurements. There is a slight tendency in the AgAu

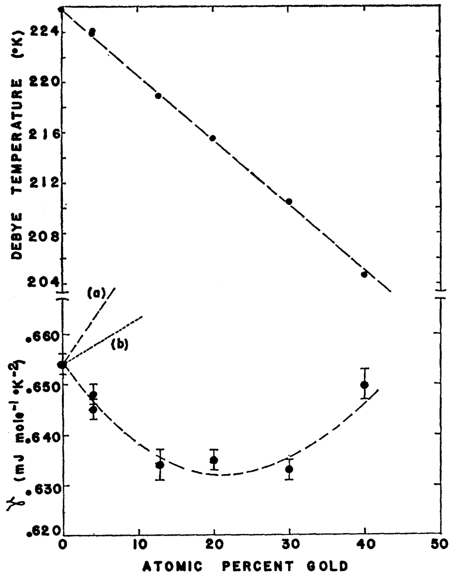

FIG. 1. γ and Θ_D versus concentration for the *Ag*-Au system. Line (a) is the prediction of the scattering theory and line (b) is the linear interpolation between the pure-metal values.

system to form short-range order. Norman and Warren[16] annealed an Ag_3Au specimen at 300°C for 4 weeks and found a mean of 9.45 Ag nearest neighbors per Au atom, compared with an expected number of 9 for no order and 12 for complete order. Our treatment, 800°C followed by cooling within minutes to room temperature, should produce considerably greater randomness. Although no meaningful estimate can be given until the factors influencing γ are better understood, from the internal consistency shown in Fig. 1, we may say perhaps that the initial slope for our samples is -32% $\pm 10\%$.

The Debye temperatures slightly exceed values interpolated between the established values of 226°K for Ag and 162°K for Au.[17] The observed values fit

$$\Theta_D = 225.8(1-c) + 173.8c$$

to within 0.3°K with no observable quadratic term in the range of concentration covered.

DISCUSSION

On the average potential theory, supported by the observation of linear neck-size behavior in this alloy system, one simply expects that the value of γ found in the alloys should be a weighted average of that found in the pure metals. This leads to a prediction that

$$d(\ln\gamma)/dc = +0.14,$$

where c is the atomic fraction of gold.

On the scattering-effect theory, one expects a positive contribution to γ proportional to the residual resistivity due to the dissolved gold. We may crudely estimate the predicted rate of change in γ in the present experiment as follows: In *Ag*Sn, we observe[10]

$$d(\ln\gamma)/dc = +0.66 \pm 0.18,$$

where c is the atomic fraction of Sn. If we take the band structure of silver near the Fermi surface as that of free electrons except that states are truncated from the sphere by contact with the (111) Brillouin zone faces, we find by a simple calculation

$$\begin{aligned} d(\ln N(E))/dc &= 3(-1) \\ &= -3, \end{aligned}$$

where the factor 3 comes from the excess valence of Sn over Ag. Thus scattering must account for 366% increase in γ per unit concentration. Linde[18] has found that Sn produces residual resistance in Ag at 11 times the rate Au does. Therefore, we predict that Au dissolved into Ag should cause γ to increase as follows:

$$d(\ln\gamma)/dc = +0.33.$$

Thus our result,

$$d(\ln\gamma)/dc = -0.32,$$

contradicts both expectations. We are left with no quantitative theory for what we observe.

One should keep in mind the scale of the observed effect. We are really dealing in pastels. Transition metal γ's are of the order of 10 mJ mol^{-1} $°\text{K}^{-2}$. The noble metals have less than one such unit. The changes in γ with which we are here concerned are of the order of hundredths of this unit. It may be that effects negligible in rigid-band treatments of transition metals may dominate the subtle behavior we are seeing. For example, the electron-phonon and electron-electron interactions may contribute to the electronic specific heat in a way affected by alloying. It has been suggested[19] that the electron-phonon interaction may double the electronic specific heat in lead, for example. If such a powerful mechanism were sensitive to alloying, it could easily control the observed behavior.

Our observation that the Debye temperatures of the *Ag*Au alloys exceed the linear interpolation between the pure metal values agrees with the observation that the AgAu system has a negative entropy of mixing, as discussed by Kleppa.[20] The size of the excess in Θ_D is about $6\frac{1}{2}$°K at 50 at.% (extrapolated from 40%) compared with an excess of 9°K calculated by Kleppa from the estimated excess entropy of mixing of -0.3 cal mol^{-1} $°\text{K}^{-1}$ at high temperatures.

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CONCLUSION

In view of the direct confrontation of the neck-size experiment with our result, we are led to distrust the idea that the linear term in the specific heat of alloys is proportional to the density of states at the Fermi level, at least in any proportion which remains constant upon alloying. If this is correct, then this kind of experiment does not give direct information about the electronic band-structure in the alloys of noble metals to the precision available experimentally, in spite of its success in alloys of the transition metals and in intermediate alloy phases of the noble metals.

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Stress Field of a Dislocation

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A new method of calculating the stress field of an isolated dislocation, or the interaction energy between different dislocations, is presented. While continuum elasticity theory is utilized, account is taken of the finite number of degrees of freedom of real solids through the use of a Debye cutoff in momentum space. As a specific result of this model, it is shown that the stress field of a straight infinitely long dislocation in an elastically isotropic solid varies at large distances r as $[1-J_0(q_D r)]/r$, where q_D is the Debye radius in q space and $J_0(z)$ is the zero-order Bessel function of the first kind. Some physical consequences of this predicted behavior are discussed briefly.

I. INTRODUCTION

In this paper we present an alternative approach to problems involving stationary dislocations. The method is based upon a Hamiltonian formulation of the interaction between a dislocation and the lattice displacement field, using a slightly generalized version of the interaction Hamiltonian employed earlier by Eshelby[1] in another context. The method can be applied using either classical or quantum mechanics, it being a straightforward adaptation of Overhauser's method[2] of calculating the interaction between paramagnetic centers in an electron gas.[3,4] Thus, in the classical case, the displacement field associated with a dislocation is obtained by direct minimization of the energy; a procedure which can be generalized to yield the interaction energy between different dislocations of arbitrary geometry.

Were this method, in general, only to yield an integral representation for the displacement field comparable in simplicity to Burgers' method,[5] (which we believe is the case), the result might still be of interest. However, it has the additional feature that the effect of a finite number of degrees of freedom per unit volume can be incorporated in a natural manner through the use of a Debye cutoff in momentum space. Or stated in other terms, if the interaction between dislocations is regarded as arising from the exchange of virtual phonons, then the finite extent of the phonon spectrum is easily incorporated in the model. The effects of this cutoff in momentum space for straight, infinite dislocations are twofold (see Sec. II). First, all stresses are finite (tending to zero) at close approach to the dislocation, in contrast with the well-known r^{-1} divergence of continuum theory. And secondly, the stress field at large distances contains a decreasing oscillatory contribution, as illustrated in Fig. 1. Possible effects arising from this behavior are discussed in Sec. III.

In conclusion, we should point out the difference between the present approach and Peierls' approximation[6] for treating dislocations in discrete solids. The latter emphasizes the role of the discrete atomic nature

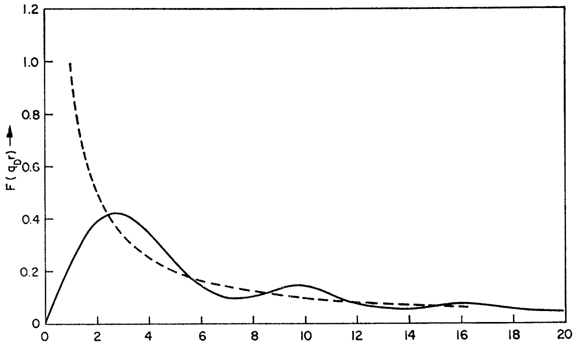

FIG. 1. Radial dependence of the stress field of a screw dislocation (full curve). The stress is expressed in units of $(Gbq_D/2\pi)$. The broken line is a plot of $F=(q_D r)^{-1}$ against $(q_D r)$.

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