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Low-Temperature Specific Heats of Alloys Based on the Noble Metals, Cu, Ag, and Au: α-Phase Ag-Sn Alloys*

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Heat-capacity measurements have been made below 4.2°K on a series of silver-tin alloys. The alloys covered the entire range of α-phase solid solutions. The density of states at the Fermi surface is found to have a maximum. The data are interpreted in terms of possible models involving interaction of electrons with the Brillouin zone.

I. INTRODUCTION

During the last three decades the studies of the properties of alloys based on the noble metals and their possible interpretation have been the subject of many papers. The face-centered cubic primary solid solutions, i.e., the α phases, formed by the monovalent Ag and Cu with the polyvalent *B*-subgroup elements of the periodic table have received most attention. Of these, the α phases based on silver are of special interest because they show most clearly the striking relationship between the maximum solid solubility and the electron concentration, hereafter called *e/a*.[1,2] This relationship is illustrated in Fig. 1. Interpretation of the nearly constant value of *e/a* at the termination of solid solubility has been proposed in terms of simple electronic theories that involve the interaction between the Fermi surface of the conduction electrons and the Brillouin zone for the fcc structure. A specific feature of such theories is the relationship between *e/a* and the trend in the density of states.[3,4]

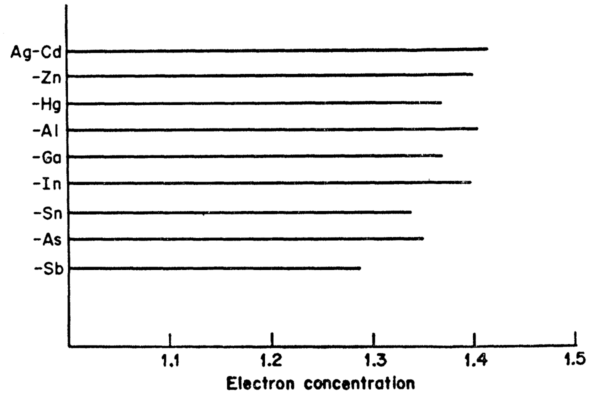

FIG. 1. Maximum solid solubility of α-phase silver-based alloys as a function of electron concentration.

Renewed interest in the α-phase alloys follows from the experimental determinations of the topography of the Fermi surface in Cu, Ag, and Au, which shows that the Fermi surface is already in contact with the {111} zone faces in these metals.[5,6] In the case of silver the degree of contact appears to be the smallest so that its Fermi surface most nearly approximates the free-electron sphere but is distorted in the [111] directions. Measurements of the electronic specific heat of silver[7,8] and of the changes in a number of other properties in its alloys, such as the Hall effect,[9] the lattice spacings,[10] and the various transport properties,[11] also suggest a nearly free-electron behavior in the alloys.

The theoretically estimated value of the band gap at the centers of the {111} Brillouin zone faces in silver is of the order of 3.5 eV.[12] Furthermore, the *d* band in silver lies about 1 eV further below the Fermi level than it does in copper or gold[4] so that relatively little additional contribution to the valence may be expected from the *s-d* hybridization both in the pure silver and in the alloys of silver. The chemical valence of silver and its color support this view.[13]

Interest in the relationship between the topography of the Fermi surface in pure noble metals and its possible forms in the alloys has been stimulated by measurements of the electronic specific heat in a number of alloys based on copper.[14] Such experiments provide a direct measure of the density of states at the Fermi level and hence are related to the possible forms of the Fermi surface. Following the work by the present authors on the α-phase alloys in the Cu-Zn system[15] the

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[1] W. Hume-Rothery, *The Structure of Metals and Alloys* (Institute of Metals Monograph and Report Series, No. 1, London 1936).

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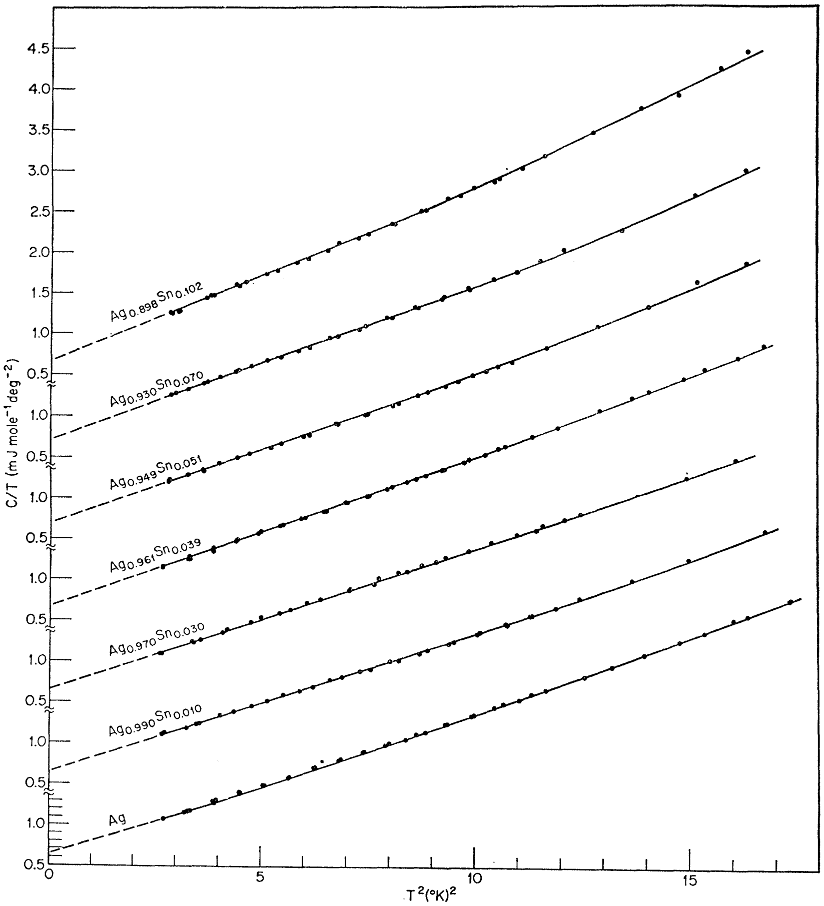

FIG. 2. The plots of C/T versus T^2 for pure silver and the α-phase Ag-Sn alloys.

present paper describes similar work on the α-phase alloys in the Ag-Sn system.

II. EXPERIMENTAL DETAILS AND RESULTS

The experimental technique and the apparatus were the same as in the previous paper by the authors on the electronic specific heats of the α-phase Cu-Zn alloys.[15] Similar procedures and precautions have been followed in the present work with regard to the preparation of the alloys. 99.9999+% purity silver and tin from the United Chemical and Mineral Corporation (New York) were used for the alloys. The elements in the required proportions were placed in quartz tubes which were evacuated at about 150°C for an extended time to remove oxygen and water vapor. Prior to sealing, helium gas was admitted. The melts were chill cast into iced brine, and the resulting ingots homogenized in vacuo for 14 days 75°C below the solidus temperature. The ingots were etched to remove surface contamination and test specimens 0.937 in. in diameter, and approximately 2 in. long, were machined using ceramic tool bits. Sections adjacent to the ends of the specimens were used to check the purity, homogeneity and composition. Compositions of the two ends of each specimen agreed in all cases to better than 0.1%. Careful spectroscopic examination revealed that ferromagnetic impurity content was less than 3 ppm in all cases.

In Fig. 2 the experimental data is displayed in the form of C/T versus T^2 curves. The data fitted well to the usual expression

$$C/T=\gamma+AT^2+BT^4+\cdots, \qquad (1)$$

where C is the measured specific heat per mole of material, T is the temperature, and γ, A, and B are constants.

γ, A, and B were derived by the least-squares fitting of the data to the above expression. In Table I the values of the constants for each alloy composition are given together with the calculated values of the limiting Debye characteristic temperature θ_0, which were obtained from the coefficients A in the usual manner.

The random error in the data as calculated from the standard deviations is approximately 1%. It is estimated that the systematic errors are not greater than about 1%. Therefore, the over-all accuracy is estimated as 2% of the measured values.

TABLE I. The values[a] of γ, A and B calculated from least-squares fitting of the expressions $C/T=\gamma+AT^2+BT^4$(mJ mole^{-1} deg^{-2}) and values of $\theta_0=(12\pi^4/5A)^{1/3}$.

Composition (At. % Sn)	e/a	γ(mJ mole^{-1} deg^{-2})	A (mJ mole^{-1} deg^{-4})	θ_0(°K)	B(mJ mole^{-1} deg^{-6})
0	1.00	0.645 ± 0.007	0.1622 ± 0.0017	228.9	0.0009 ± 0.0001
1.0	1.030	0.648 ± 0.007	0.1674 ± 0.0007	226.4	0.0004 ± 0.0001
3.0	1.090	0.654 ± 0.006	0.1727 ± 0.0008	224.1	0.0000 ± 0.0001
3.9	1.117	0.667 ± 0.005	0.1780 ± 0.0010	221.8	0.0003 ± 0.0001
5.1	1.153	0.693 ± 0.007	0.1790 ± 0.0010	221.0	0.0006 ± 0.0002
7.0	1.210	0.716 ± 0.006	0.1854 ± 0.0009	218.9	0.0005 ± 0.0002
10.2	1.306	0.676 ± 0.007	0.2016 ± 0.0010	212.9	0.0008 ± 0.0005

[a] The errors indicated are standard deviations calculated from the least-squares plots.

III. DISCUSSION

The changes with composition and e/a of the parameters θ_0 and γ are plotted in Fig. 3.[16] Because of the temperature range of the present measurements (1.6–4.2°K) Debye temperatures show considerable scatter as may be expected. Their trends with composition indicate a decrease in θ_0 as is the case in other α phases.

Of some interest is the presence of the T^5 term in the specific-heat equation, which is similar to the behavior of pure silver.[7] The data points in the present investigation were insufficient to evaluate the T^5 coefficients accurately.

As mentioned in Sec. I, the trend in the behavior of electronic specific heat on alloying may be expected to provide information about the relationship between the general features of the Fermi surface and the density of states. Since the contact between the Fermi surface and the {111} faces of the Brillouin zone exists already in the pure silver, one would expect an initial decrease on alloying in the measured γ values, as observed in Cu-Zn alloys.[15] Instead, practically no change of γ is observed in dilute Ag-Sn alloys and an increase is observed at higher tin contents with a broad maximum at $e/a=1.2$. In the light of the previous discussion of Cu-Zn alloys a plausible interpretation of the present data is that the observed trend in γ results from the existence of overlaps across the {111} faces of the Brillouin zone. Recently reported results on additional de Haas-van Alphen periods in silver[17] have been interpreted as possible evidence for overlaps already in the pure metal. Thus, it is likely that the {111} overlaps exist in the entire range of the α phase in the Ag-Sn system. Initially, electrons would fill both the holes in the first zone and the overlaps in the second zone with little resultant change in the measured γ. Beginning at about 1.1 electrons per atom, the γ values (density of states) show a measurable increase, presumably due to electrons entering mainly the overlap regions in the second zone.

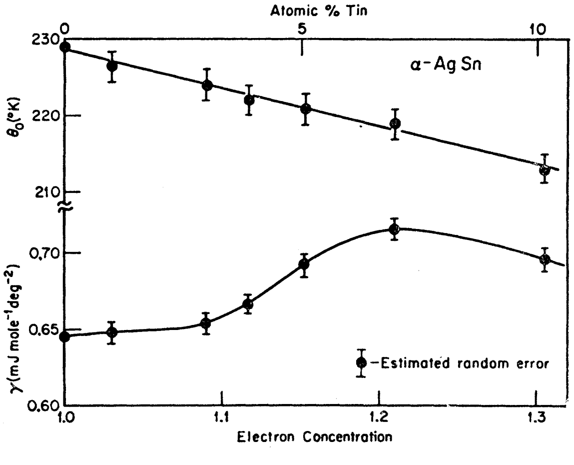

FIG. 3. The trend in the limiting Debye temperature (θ_0) and the electronic specific-heat coefficient (γ) plotted as a function of electron concentration.

Another parameter that is directly related to the density of states at the Fermi level is the magnetic susceptibility χ_e of the free-electron gas,

$$\chi_e=4/3\mu_B{}^2N(E_F)\,, \tag{2}$$

where μ_B is the Bohr magneton and $N(E_F)$ is the density of states at the Fermi level. In Fig. 4 the magnetic susceptibility data of Henry and Rogers[18] for several Ag-based systems, corrected for the diamagnetic susceptibility of the ionic cores,[2] are plotted together with the ratio γ/γ_F as a function of e/a.[19] γ_F represents the free electron value of the electronic specific heat for

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[16] Since the submission of this manuscript measurements on Ag-Sn alloys have been reported by H. V. Culbert and B. A. Green, Jr. [Bull. Am. Phys. Soc. **9**, 657 (1964)]. The experimental data are interpreted as consistent with a linear behavior between the density of states and the e/a. The scatter of the reported points permits a curve similar to the one given in Fig. 3 to be drawn through points up to 5 at.% Sn. For tin contents greater than 5 at.% the trend proposed by Culbert and Green differs from that shown in Fig. 3.

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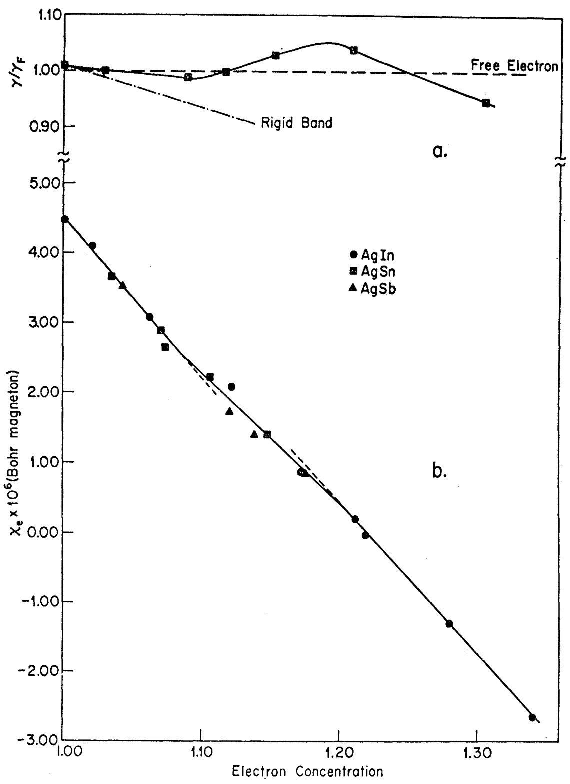

FIG. 4. (a) The thermal effective-mass ratio γ/γ_F; (b) the magnetic susceptibility χ_e of the electron gas plotted as functions of electron concentration.

each alloy. For face-centered cubic structures

$$\gamma_F = 3.848\times10^{11}a^2n^{1/3}(\text{mJ mole}^{-1}\text{ deg}^{-2})\,, \qquad (3)$$

where a is the lattice parameter at 0°K, and n is the electron concentration. The values of a at 0°K were estimated by assuming that the α-phase alloys have the same coefficient of expansion as that of pure silver. Hence, the ratio γ/γ_F provides a measure of the thermal effective mass and indicates the distortion of the Fermi surface from a sphere. It is of interest to note that a change in slope in both γ/γ_F and χ_e occurs at nearly the same value of e/a and that both suggest an increase in the density of states. Thus, magnetic susceptibility data and electronic specific heat data indicate similar behavior.

The general trend of the ratio γ/γ_F in the Ag-Sn system shows only small departures from unity, the value characteristic of free electrons (Fig. 4). Trends in the Hall coefficients in a number of Ag-based α phases[9] suggest a similar behavior.

It is possible to consider a number of other contributions to the measured density of states in an alloy system:

(i) An increase in the density of states may be expected from contact, or imminent contact, between the Fermi surface and the square {200} faces of the Brillouin zone.[20,21]

(ii) A virtual contribution to γ has been suggested[22] that should result from increased scattering of electrons by impurity atoms in alloys which possess a peak in the density of states just below the Fermi level.

(iii) Hybridization between s and d bands may give rise to increased density of states from the d-band electrons.[4,21]

Contribution from the d-band electrons seems unlikely in view of the position of the d level below the Fermi level in pure silver as mentioned earlier. In any case, any such contribution should diminish on alloying with the B-subgroup elements that have completely filled d shells and would thus tend to produce a decrease of γ, contrary to observation. The virtual contribution to γ should be particularly evident in the dilute alloys where the Fermi level is nearest the peak in the density of states and where the positive tin ions may be expected to be very effective scatterers. The present data, as well as the data on Cu-Zn alloys,[23] does not seem to indicate that this contribution is substantial.

Finally, in order to bring about possible contact between the Fermi surface and the {200} faces of the Brillouin zone in the range of the α phase $(1\leq e/a\leq 1.4)$, band gaps exceeding 10 eV are required.[20] This seems unlikely in view of the many indications of the nearly free-electron behavior.

A qualitative interpretation of the present experimental data is that the band gaps of silver probably decrease further on alloying in accordance with the variable-band models discussed by Cohen and Heine[4] and by Ziman,[11] while at the same time filling of holes in the first zone and perhaps overlaps across the {111} faces into the second zone take place. The resultant density of states would then resemble the density of states trend proposed for the Cu-Zn alloys[15] except that overlap in the Ag-based alloys would have to occur at lower values of e/a.[23a] As in the case of Cu-Zn alloys the present model requires that the original model[3] proposed for the termination of α-phase solid solubility should be modified. Following Jones[24] and Blandin[25] the stability of the primary solid solutions is enhanced

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[23] However, in this respect the data on Cu-Zn alloys discussed in Ref. 15 is in disagreement with earlier work (Ref. 21).

[23a] *Note added in proof.* Following the earlier paper (Ref. 17) A. S. Joseph *et al.* [Bull. Am. Phys. Soc. **9**, 736 (1964)] suggest that the occurrence of the oscillatory term (P_e) in the dHvA effect in Ag is very unlikely to be associated with overlap of electrons into the second Brillouin zone. This makes the present proposal more tentative.

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[25] A. Blandin, in *Alloying Behavior and Effects in Concentrated Solid Solutions*, edited by T. B. Massalski (Gordon and Breach Science Publishers, Inc., New York, 1965, to be published).

when their total electronic energy is lowered following an increase in the density of states above the curve for the free electrons. However, the termination of solid solubility is governed by the balance between the free energies of the α phase and of the intermediate phase that follows it and is determined by the common tangent principle.

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Dispersion Curves and Lattice Frequency Distribution of Metals

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A lattice-dynamical 3-constant model for metals is presented. The treatment takes complete account of the symmetry requirements of the lattice. The influence of conduction electrons is considered through the screening of the long-range Coulomb interaction between ions. The theory is used to calculate dispersion curves, frequency spectra, and lattice specific heats of Li, Na, and K. For sodium, good agreement is found with the dispersion curves obtained from measurements of the inelastic scattering of slow neutrons.

INTRODUCTION

THE new method of deducing lattice-dynamical properties from the inelastic scattering of cold neutrons is able to give precise information on frequency spectra and frequency-versus-wave-vector dispersion relations in metals.[1] It is thus of interest to reconsider the theoretical side of this problem.[2] So far, fitting of experimental curves to theoretical models has met with only moderate success. With simple Born–von Karman models one needs, in general, more parameters than there are elastic constants. The fact that force constants even between more distant neighbors are not negligible points to the existence of long-range forces or to an inadequacy of the models used.

There is clear experimental evidence that the Cauchy relations are not fulfilled for metals. Fuchs has shown[3] that this might be explained by the presence of conduction electrons. Their influence on the lattice vibrations was taken into account by De Launay,[4] who constructed a phenomenological model which includes explicitly the effect of a compressible but shear-free electron gas. His model had some success,[5] but it violates symmetry requirements, as pointed out, for instance, by Lax.[6] In this respect also the new model of Sharma and Joshi[7] is unsatisfactory.

The same is true for Bhatia's theory,[8] which essentially considers the electronic effect via the screening of the Coulomb interaction between lattice ions. A theory which includes electronic terms and also takes proper account of the symmetry properties has been developed by Toya.[9] His model is based on Bardeen's quantum-mechanical calculation of the electron-phonon interaction.[10] Toya's theory is the most fundamental one, but contains a number of electronic parameters which are rather difficult to obtain with good precision. In the case of sodium, agreement between theoretical and experimental[11,12] dispersion curves is nevertheless quite satisfactory. However, larger discrepancies do appear in the [110] direction.[13] In the following we propose a theory which is simpler than Toya's and moreover shows good agreement with the experimental dispersion curves of sodium for all observed directions.

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[1] *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna 1960, Chalk River 1962* (International Atomic Energy Agency, Vienna, 1961, 1963).

[2] A preliminary account of this work has been given in Phys. Letters **10**, 12 (1964). Equation (1) of that note contains a typographical error in the term M_{xy}. For the correct expression see this paper, Eq. (4).

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[12] A. D. B. Woods, B. N. Brockhouse, R. H. March, and A. T. Stewart, Phys. Rev. **128**, 1112 (1962).

[13] The original calculations contain a numerical error, but even correcting for this [R. S. Srivastava and B. Dayal, Progr. Theoret. Phys. (Kyoto) **31**, 167 (1964)], there remains still a discrepancy of about 33%.