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

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Heat-capacity measurements between 1.6 and 4.2°K were made on a series of copper-zinc alloys covering the entire range of the face-centered cubic phase. The density of states at the Fermi surface is found to decrease initially with alloying rather than to increase. Alternative explanations of the data are considered, and a possible model involving overlapping of electrons into the second Brillouin zone is suggested.

INTRODUCTION

THE binary face-centered cubic α solid solutions of copper and silver with the B-subgroup elements of the periodic table have been for a number of years a testing ground for simple electronic theories of alloys.[1] In recent years renewed interest has been stimulated in this field by new experimental data and discussion of optical absorption,[2] magnetic susceptibility,[3] various transport properties,[4] and, in particular, by measurements of electronic specific heat.[5] It is clear that the band structure and the energies and the behavior of the conduction electrons in these alloys play a prominent role.

Additional interest in alloys of the noble metals follows from the determination by means of a number of new techniques of the topography of the Fermi surfaces in copper, silver and gold.[6] In particular, it has been established[7] that in all three cases the $\{111\}$ discontinuities in the Brillouin zone are contacted by the Fermi surface. One would therefore expect the density of states at the Fermi level to decrease initially upon alloying with elements whose valence is greater than one, such as the B-subgroup elements.

Because of the increased scattering caused by introduction of alloying elements into pure metals the mean free path of electrons in alloys is substantially reduced when compared with the pure metals. For this reason, the techniques such as, for example, the de Haas–van Alphen measurements, cannot be applied to the alloys unless they are highly ordered.[8] With this limitation the measurement of other properties, such as the electronic specific heat, takes on a special significance because this technique yields a direct measure of the density of states at the Fermi level. Interest in the relationship between the possible forms of the Fermi surface in alloys and the density of states has been stimulated by earlier measurements of the electronic specific heat in two alloy systems, Cu-Zn[9,10] and Cu-Ge.[11] The present paper describes results of a new measurement of specific heats at low temperatures in the α phase of the Cu-Zn system.

EXPERIMENTAL DETAILS

A helium-4 cryostat employing a mechanical heat switch similar to that described by Ramanathan and Srinivasan[12] was used. The sample is inserted into a copper-beryllium clamping ring. On the ring a carbon resistor, which serves as the temperature sensor, and a heater resistor are mounted. The heat capacity of the ring assembly is determined in a separate experiment and amounts to approximately 2.5% of the total heat capacity of the sample.

Energy inputs to the sample result from Joule heating. The energy inputs ranging from 0.1 to 2 mJ are measured with a potentiometer and electronic timer.

The resistance of the carbon resistor is determined by means of an ac Wheatstone Bridge, operated at 35 cps and similar to that described by Blake.[13] The calibration curve for the thermometer is obtained by a least-squares fitting of the expression,

$$[\ln R/T]^{1/2}=\sum_{0}^{2} a_i(\ln R)^i \ . \tag{1}$$

By this technique the calibration values are reproduced to within half a mdeg. The calculated temperatures are based on the 1958 He^4 scale.[14] A separate calibration curve was obtained for each thermal cycling of the system to room temperature.

The Cu-Zn alloys studied in this investigation have

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been prepared with great care that the initially very pure materials did not become contaminated during sample preparation. It has been shown that small quantities of ferromagnetic elements, of the order of several ppm, will influence the low-temperature specific-heat measurements appreciably.[15] For the case of Cu-Zn alloys possible contamination with iron has been shown to lead to considerably different results.[10] In the present investigation 99.999+% pure copper and zinc were obtained from the American Smelting and Refining Company as the base materials. They were melted together under reduced atmosphere of helium in sealed, clean, quartz tubes. The molten material was vigorously stirred before chill-casting into iced brine. The details of the subsequent heat treatment are given in Table I.

TABLE I. Descriptive characterization of the alloys investigated.

Composition (At. % Zn)	Heat treatment Temp. (°C)	Time (h)	Ferromagnetic impurity content (ppm)
0	Air Cooling		<2
1.1	880	65	<2
2.3	880	65	<2
3.2	880	65	3
4.2	880	65	3
5.1	880	65	4
7.5	880	65	3
10.5	880	65	3
15.2	880	65	8
18.9	880	70	2
25.2	880	65	13
33.3	700	65	21
38.4	450	500	4

Test specimens, 0.937 in. in diameter and approximately 2 in. long, were cut from the ingots using diamond-edged tool bits. Before and after machining, samples were etched with dilute nitric acid solution to remove possible surface contamination. Sections adjacent to the specimen ends were used for metallographic, x-ray and spectroscopic examinations. Metallographic work has shown all specimens to be single α-phase alloys. Compositions were determined by x rays using the parametric method.[16] Both ends of each sample were examined for this purpose and the results agreed to better than 0.1 at.% zinc. The final compositions and the spectroscopic results on all alloys are also included in Table I.

The following technique was employed in the spectroscopic work. A series of standards containing 2 to 100 ppm of iron in copper were obtained from Johnson and Matthey Company, Ltd. Both the standards and the samples were cut with a diamond-studded copper wheel and adjusted in size to give a total of 35 mg by weight of sample in the arc. The metal was burned in a 12-A dc arc and the spectra recorded photographically. Spectral lines for iron at 3020.5 Å and copper at 3030.3 Å were used with background correction for an analytical line pair.

As may be seen from Table I, the total content of ferromagnetic impurities in the alloys that cover the range of the first ten atomic percent is particularly low, amounting to less than four parts per million, and only in two alloys of higher zinc content does the total ferromagnetic impurity content exceed ten parts per million. Even these amounts do not seem to indicate any noticeable change in the trend of the results.

RESULTS

In order to obtain a large number of experimental points two sets of heating cycles were followed for each alloy in the temperature range between approximately 1.6–4.2°K. Following the experimental runs data were evaluated with the help of a computer program. The results are shown in Fig. 1 in the form of C/T versus T^2 curves. In the temperature range under investigation the data points satisfy the simple relationship $C/T=\gamma+AT^2$, where C is the measured heat capacity per mole of material, γ the electronic specific heat coefficient, and A is related to the characteristic limiting Debye temperature θ_0 by the relation $A=12/5\pi^4(1/\theta_0)^3$, where N is Avogadro's number. γ and A were evaluated for each alloy by a least-squares procedure. The values of the parameters γ and θ_0 are given in Table II for each alloy composition. In Fig. 2(a) θ_0 is plotted as a function of zinc concentration. The results are in good agreement with previous calorimetric work[9,10] and with θ_0 values calculated from data on elastic constants.[17]

The random error in the data γ coefficients as calculated from the standard deviations is approximately 0.5%. It is estimated that the systematic errors are not

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

Composition	γ (mJ mole^{-1} deg^{-2})	A (mJ mole^{-1} deg^{-4})	θ_0(°K)
0	0.698±0.002	0.0485±0.0003	342.3
1.1	0.692±0.005	0.0488±0.0006	341.6
2.3	0.683±0.002	0.0500±0.0003	338.7
3.2	0.675±0.004	0.0487±0.0004	341.7
4.2	0.678±0.003	0.0491±0.0004	340.9
5.1	0.681±0.002	0.0494±0.0003	340.1
7.5	0.686±0.002	0.0540±0.0003	330.1
10.5	0.696±0.003	0.0496±0.0004	339.8
15.2	0.698±0.002	0.0534±0.0002	331.5
18.9	0.696±0.003	0.0575±0.0003	323.3
25.2	0.695±0.003	0.0581±0.0004	321.9
33.3	0.690±0.003	0.0682±0.0003	305.0
38.4	0.689±0.003	0.0706±0.0004	301.9

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

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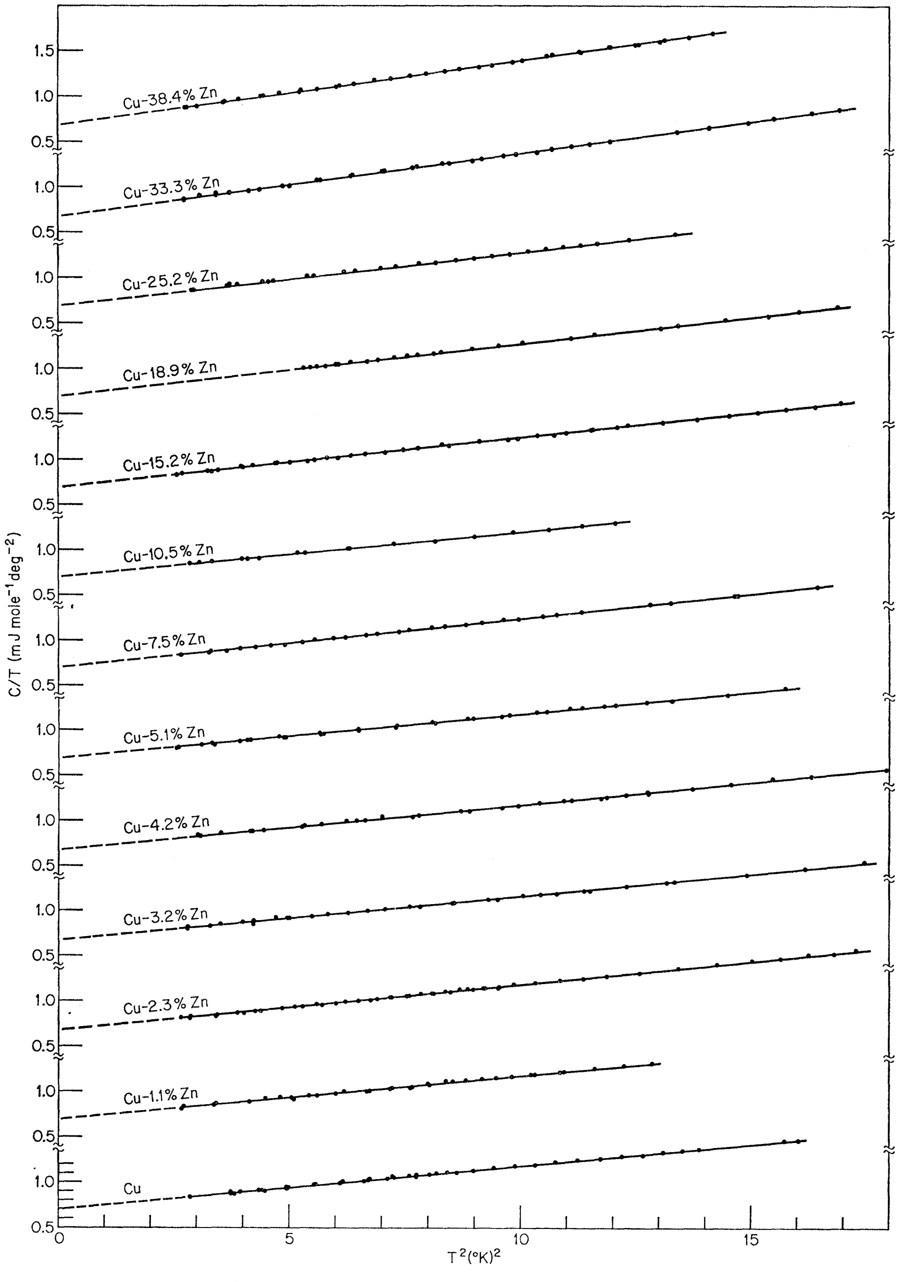

FIG. 1. The plots of C/T versus T^2 for pure copper and α-phase Cu-Zn alloys.

greater than about 1%. Therefore, the over-all accuracy is estimated as better than 2% of the measured values.

DISCUSSION

The heat capacity of a metal in the normal state at low temperatures may be expressed as a sum of the electronic and lattice contributions,

$$C_e(T)+C_l(T)=\gamma T+AT^3+BT^5+\cdots, \tag{2}$$

where T is the absolute temperature and γ, A and B are constants. The electronic specific heat constitutes the linear term in this expansion. Luttinger and Ward[18] have shown that the specific heat of a system of interacting electrons in the presence of a periodic potential at low temperatures is given by

$$C_e(T)=\gamma T=(\pi^2/3)K^2N(E_F)T, \tag{3}$$

where K = Boltzmann's constant and $N(E_F)$ is the density of states at the Fermi level. The density of states may be obtained by integrating over the Fermi surface (S_F) the expression $N(E_F)=1/(2\pi)^3\int dS_F/\text{grad}_{\mathbf{k}}E(\mathbf{k})$, where $E(\mathbf{k})$ is the energy of an electron. Therefore, a direct relationship exists between the density of states and the possible topography of the Fermi surface. For copper, in addition to experimental

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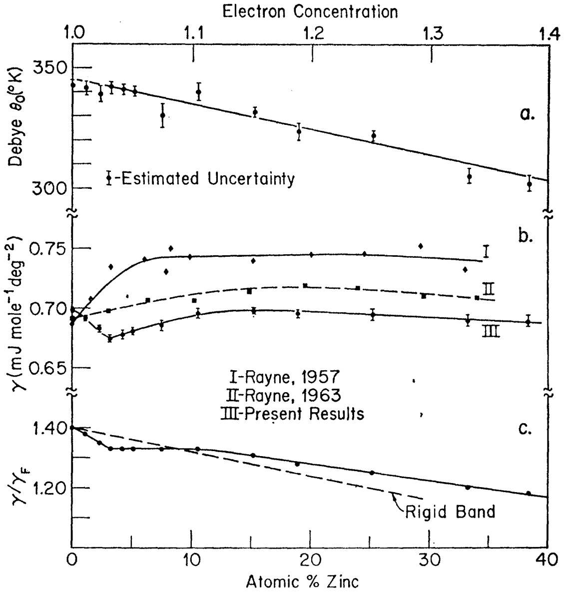

FIG. 2. (a) The trend in the limiting Debye temperature θ_0; (b) the trend in the electronic specific-heat coefficients γ from different experiments; and (c) the trend in the ratio γ/γ_F plotted against zinc concentration and electron concentration in α-phase Cu-Zn alloys.

work, band calculations using the Green's function method have been performed by Segall[19] and, using the augmented-plane-wave method (APW) by Burdick.[20] Both the experimental and theoretical work indicate contacts between the Fermi surface and the {111} discontinuities in the Brillouin zone.

In Cu-Zn α-phase alloys the electron concentration changes on alloying between one and about 1.4. The previous measurements[9,10] have suggested a small initial increase in the density of states on alloying which is difficult to explain in the light of the known topology of the Fermi surface in copper. The present results, although in general similar to the earlier data, differ in the significant detail that the initial trend in the density of states appears to decrease slightly upon alloying. All three measurements in the Cu-Zn system are shown in Fig. 2(b). As may be seen, the over-all measured change in γ coefficients in this system is very small indeed; alloys containing a large proportion of zinc possess nearly the same γ as that of pure copper. The minimum in the curve describing the present results [curve III in Fig. 2(b)] is reached at about 3 at.% zinc.[21] Since both the previous[10] and the presently studied samples contained only a very small amount of ferromagnetic impurities, it seems that the reason for the difference in the three sets of measurements must lie in some other unexplained source. In addition to the small initial discrepancy, the present results lie consistently below the previous data by Veal and Rayne.[10]

Since the {111} zone faces are contacted in copper, one would expect an initial decrease in the density of states to occur on alloying with polyvalent elements such as zinc as observed. This would be expected both for the case of a rigid-band model, in which the band gaps do not change on alloying, and for a variable-band model, in which the band gaps decrease. Ziman's phenomenological model for the noble metals and their alloys[4] considers a succession of rigid-band calculations in which the ratio γ/γ_0 varies with electron concentration for a number of assumed values of the band gaps. In this model γ corresponds to a calculated density of states for distorted Fermi surfaces and γ_0 refers to electrons of equivalent mass on a spherical Fermi surface. The calculated series of curves possess nearly identical slopes following the peak in the density of states due to contact between the Fermi surface and the {111} zone faces. This slope is indicated in Fig. 2(c) where the experimentally obtained γ values are divided by γ_F that correspond to the calculated free-electron values for each alloy.[22] This plot thus gives the variation of the thermal effective mass m_t in the α phase. Several points of interest may be noted.

(a) The initial slope of the experimental curve in Fig. 2(c) is steeper than that expected from the rigid-band model. This lends support to the suggestion of Cohen and Heine[23] that the band gaps decrease on alloying, since in a model with decreasing band gaps[4] one would expect at any constant value of the electron concentration to have a smaller $N(E)$ the smaller the band gaps.

(b) The initial value of the effective thermal mass m_t given by γ/γ_F ratio is 1.4. In the model of Ziman[4] the {111} band gap has been estimated as 7 eV on the basis of the experimentally established neck radius of the Fermi surface in contact with the {111} faces, assuming unity for the effective mass. If the present value of effective thermal mass $m_t = 1.4$, which averages over the whole Fermi surface, is used instead, the suggested band gaps become 5 eV which is in good agreement with the value suggested by optical data.[2]

(c) Following the initial slight minimum the present data suggest a reversal in the density of states with a broad maximum approximately between 3 and 25 at.% zinc. The magnitude of this maximum will be somewhat reduced if the data are corrected for the expansion of the lattice in Cu-Zn alloys, allowing for the fact that the

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[22] For face-centered cubic structures $\gamma_F = 3.848 \cdot 10^{11}\ a^2 n^{1/3}$ (mJ mole^{-1} deg^{-2}) where a is the lattice constant at 0°K and n is the electron concentration. The values of a were estimated by assuming that the α-phase alloys have the same coefficient of expansion as that of pure copper.

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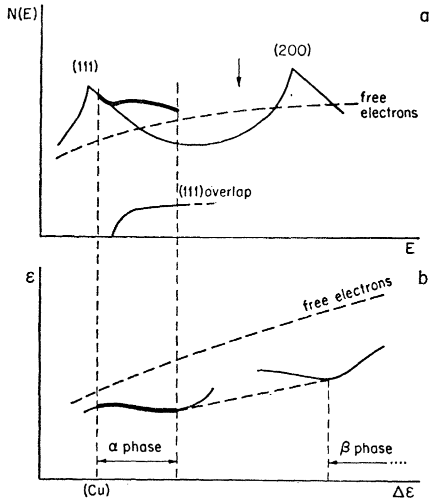

FIG. 3. (a) A diagramatic model of the trend in the density of states in the Cu-Zn alloys; and (b) illustration of the relationship between electronic energy and ranges of stability in Cu-Zn alloys.

density of states is proportional to the square of the lattice parameter. In that case the suggested density of states in the alloys will always be lower than that of pure copper.

It is tempting to speculate about the origin of the maximum. Qualitatively at least four possible contributions to electronic specific heat can be considered:

(a) The possible contribution from an upward trend in the density of states when the second (square) set of {200} faces in the Brillouin zone are approached or contacted by the Fermi surface. This region is indicated by an arrow in the diagramatic sketch of the density of states curve in Fig. 3(a). This contribution seems unlikely. In order to bring about possible contact between the Fermi surface and the {200} zone faces in the range of the α phase ($1\leq e/a\leq 1.4$), band gaps exceeding tion[19]10 eV are required.[10,24] Also the recent theoretical calculation[19] gives 5.7 eV as the band gap across the {200} faces in copper.

(b) A virtual contribution to γ has been suggested[25] 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, as would be the case in dilute copper alloys. Present data suggests that this contribution is not substantial, although in this respect it differs from the previous determinations.[9,10] On the other hand the steep increase in γ observed in Cu-Ge alloys[11] does lend support to this possibility.

(c) Hybridization between s and d bands may be expected in copper and copper alloys, giving rise to an additional contribution to the density of states. Influence of the d band is suggested by the occasional two-valent chemical behavior of copper, by its color, and by the relatively close position of the d band below the Fermi level.[23,26] Although this contribution is present in copper, alloying with elements containing full d bands should decrease it. Hence, the initially observed decrease in γ could be attributed to this effect but probably not the subsequent increase.

(d) On the other hand, if the existence of a variable band model is considered, it seems plausible that an overlap across the {111} zone faces into the second zone may occur somewhere within the range of the α-solid solution. The present data may be taken as a possible evidence of such overlapping in alloys whose zinc content exceeds about 3 at.%. Neglecting the possible contributions from the d band the qualitative trend in the density of states would then be as that illustrated in Fig. 3(a). This proposal does not invalidate the basic concept that the stability of the primary solid solutions based on the noble metals is related to the density of states.[27,28] The relationship between the density of states and the over-all energy of the electrons is illustrated in Fig. 3(b). The energy curve for the free electrons is shown by the dashed line, and the lowering of the energy due to the departure of the density of states from the free-electron parabola is shown as a full line. Stability is enhanced by the departure of the density of states curve above that for the free electrons, which makes the total energy lower for limited range of e/a, and is terminated when the energy of the conduction electrons in the phase that follows the primary solid solution makes the energy of the following phase lower. The actual extent of the solid solubility is determined by the common tangent principle.

ACKNOWLEDGMENTS

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