Heat Capacity of α-CuZn Alloys below 4.2°K

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Heat capacity measurements below 4.2°K have been made on a series of high-purity alloys covering the entire α phase of the copper-zinc system. The density-of-states at the Fermi surface is found to rise initially with increasing zinc concentration in qualitative agreement with previous data. This behavior is not consistent with the rigid band model nor with the model proposed by Cohen and Heine. Alternative explanations of the alloying behavior are considered. The variation of the Debye temperature with solute concentration is in good agreement with that found from low-temperature elastic data.

I. INTRODUCTION

THE band structure of the primary solutions of the simple binary alloys involving the noble metals, and in particular copper, has attracted considerable theoretical and experimental interest.[1] Of crucial importance in this regard is the behavior of the density-of-states at the Fermi surface upon alloying. Since the Fermi surface of copper has substantial contact with the {111} faces of the Brillouin zone,[2-4] its density-of-states curve must be a decreasing function of energy beyond the Fermi level. Thus the original rigid band model of Jones would predict that the density of states for the alloys would be a decreasing function of solute concentration. Previous heat-capacity data[5,6] have shown, however, that the density-of-states actually increases with increasing solute concentration. On the basis of these results, Cohen and Heine[1] proposed that the energy gap across the {111} faces of the zone *decreased* on alloying. They assumed that this change in the energy gap would be sufficient to counteract the effect of increasing electron concentration. Ziman,[7] using a fairly general model, showed that this was not correct; in fact, the Cohen and Heine model gives a greater decrease of the density of states with solute concentration than does the rigid band model. Thus the behavior of the electronic specific heat becomes rather more difficult to understand and it has been suggested[8] that the results are not characteristic of the alloys but rather denote the presence of small amounts of ferromagnetic impurities in the samples. Heat-capacity measurements on dilute copper-iron,[9] copper-manganese[10] and copper-cobalt[11] alloys have, indeed, shown that quite small concentrations of ferromagnetic impurities can give large apparent linear contributions to the specific heat at low temperatures. It is thus of considerable importance to establish whether or not these effects were present in the original heat capacity measurements on the Cu-Zn and Cu-Ge primary solid solutions.

For this reason, the present series of measurements on the primary phase of the Cu-Zn system was instituted; particular care was taken to use high-purity specimens free from any trace of ferromagnetic impurities. In general, the results are in reasonable qualitative agreement with the previous data and establish unequivocally that the density of states in this system *does*, in fact, increase with increasing zinc concentration. Various explanations of this effect are advanced. Good agreement is found between the lattice heat capacities obtained calorimetrically and those calculated from the low-temperature elastic constants.

II. EXPERIMENTAL

Heat-capacity measurements were made in the temperature range 1.4 to 4.2°K using the apparatus and techniques described in a previous paper.[5] Approximately 35 data points were taken for each specimen. The samples were cyclinders 1 in. in diam and approximately $1\frac{1}{2}$ in. long and covered almost completely the composition range of the α phase of the Cu-Zn system. Particular care was taken to avoid the presence of ferromagnetic impurities in the specimens. Spectroscopically pure starting materials were used. The copper was 99.999+% pure metal obtained from the American

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[9] J. P. Franck, F. D. Manchester, and D. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).
[10] J. E. Zimmerman and F. Hoare, J. Phys. Chem. Solids **17**, 52 (1960).
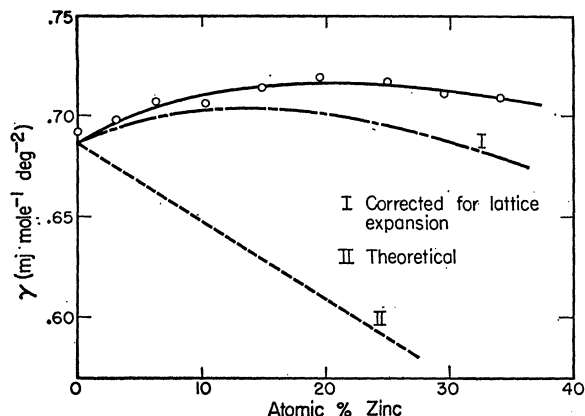[11] L. T. Crane and J. E. Zimmerman, Phys. Rev. **123**, 1 (1961).

TABLE I. Results of chemical and spectrographic analyses of specimens used in this work.

Composition (at.% Zn)	Impurity concentrations (ppm)		
	Fe	Co	Mn
Pure Cu	<1	<1	<1
3.03	<1	<1	<1
6.28	<1	<1	<1
10.23	<1	<1	<1
14.80	<1	<1	<1
19.45	2	<1	<1
23.93	1	<1	<1
29.45	1	<1	<1
34.05	1	<1	<1

FIG. 1. Variation with zinc concentration of the electronic specific heat for α brasses.

Smelting and Refining Company, and the zinc was 99.9999% pure metal obtained from the Consolidated Mining Company of Canada. Careful spectrographic analysis of the copper revealed an iron content of less than 2 parts per million (ppm) and a negligible amount of manganese and cobalt.

The ingots were induction melted in reactor grade carbon crucibles under an argon atmosphere. During the melting process, the mixture was continuously stirred with a graphite rod to insure good mixing of the components. After this process the ingots were heavily cold-worked, etched, then annealed for 4 h at 720°C to homogenize them. They were then turned to size and etched lightly. Samples of each ingot, adjacent to the section used for the calorimetric measurements, were taken for chemical and spectrographic analysis. Both ends of each ingot were analyzed chemically and no composition inhomogeneities were detected. The spectrographic analysis was performed against the copper starting material as standard, under identical arc conditions. A tabulation of the results of these analyses is shown in Table I, which shows that the *maximum* concentration of ferromagnetic impurities in any specimen was 2 ppm. Thus, there should be no question of spurious effects due to ferromagnetic impurities in the present data.

TABLE II. Values of γ and θ in relation $C/T = \gamma + \beta T^2$ for α phase of Cu-Zn system. It is to be noted that $\beta = (12\pi^4/5)(1/\theta^3)$.

Composition (at.% Zn)	γ (mJ mole^{-1} deg^{-2})	θ (°K)
Pure Cu	0.692	342.7
3.03	0.698	342.1
6.28	0.707	340.2
10.23	0.706	336.4
14.80	0.714	332.4
19.45	0.719	329.6
23.93	0.717	325.6
29.45	0.711	319.3
34.05	0.709	310.9

III. RESULTS

The heat-capacity data were initially fitted by a machine least-squares calculation to an expression of the form

$$C/T = \gamma + \beta T^2 + \delta T^4, \qquad (1)$$

the last term taking into account the possibility of phonon dispersion. It was found, however, that the term δ was very small and varied randomly from positive to negative values without significantly changing the coefficients γ, β. For this reason, all data were subsequently fitted assuming the coefficient $\delta = 0$. The resulting values of γ and Debye temperature θ $[\beta = (12/5)(\pi^4/\theta^3)]$ are given in Table II and in Figs. 1 and 2. It should be noted that curve I of Fig. 1 is the electronic specific heat when corrected for lattice expansion (see reference 5).

IV. DISCUSSION

A. Electronic Heat Capacity

Reference to Fig. 1 shows that γ, and hence the density-of-states at the Fermi level, increases with increasing solute concentration. This behavior is in qualitative agreement with the behavior previously reported. At lower solute concentrations, however, the old data are significantly higher than those obtained here and the scatter is considerably larger. It must therefore be concluded that there were traces of ferromagnetic impurities in the original specimens and that the scatter results, in fact, from variations in the amount of this impurity. It is quite apparent, however, that the actual behavior of γ is in marked contrast with that to be expected from the simple rigid band model. Curve II of Fig. 1 represents the theoretical behavior, using the density-of-states curve for copper given by Ziman.[7] Clearly, there is violent disagreement which, as he has shown, cannot be resolved by the assumption of a decreasing energy gap with increasing solute concentration.
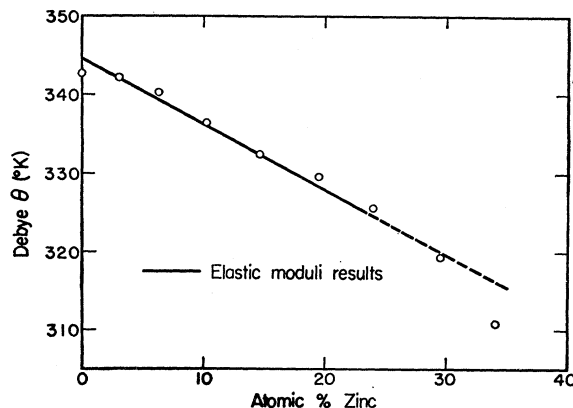

FIG. 2. Variation with zinc concentration of the Debye temperature for α brasses.
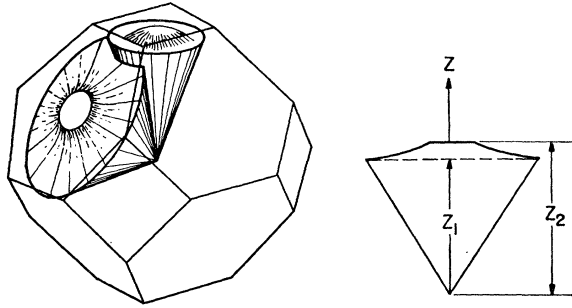
FIG. 3. Brillouin zone for fcc structures showing two of the 14 cones constructed for calculating the density of states. (Inset shows a cone cross section.)

A number of possible explanations of the observed behavior may be advanced. It has been suggested[12] that the limit of the α-phase for noble metal alloys results from contact of the Fermi surface with the {200} faces of the Brillouin zone. In this case the density of states for copper would differ from that shown in Fig. 1. This curve was obtained from a single orthogonalized plane wave calculation by sectioning the Brillouin zone into eight cones pointing in the $\langle 111 \rangle$ directions. The total solid angle of the cones is correctly 4π but they overlap in some places within the Brillouin zone and leave gaps elsewhere, notably in the vicinity of the {200} faces. Clearly this model does not correctly describe the regions of Fermi surface in the immediate vicinity of these faces, particularly in the event of incipient zone contact. In this case, one should rather divide the surface into two sets of cones, one set being associated with the hexagonal faces of the zone, while the other is associated with the square faces as shown in Fig. 3. The density-of-states curve would then have two cusps, resulting from contact at the {111} and {200} zone faces. Figure 4 shows the resulting behavior, assuming the energy gap across the {111} faces to be 7.0 eV, the magnitude obtained when the de Haas-van Alphen data is appropriately fitted.[7] In curve I, the energy gap across the {200} faces was taken to be 12 eV and in Curve II, 10 eV. From the former it is clear that the rigid band model *can* be used to explain the initial rise in the density of states. The magnitude of $N(E)$, the density-of-states at the Fermi level, may be lowered to match the experimental results by appropriate adjustment of the effective mass at the bottom of the conduction band or by adjusting the relative contributions to $N(E)$ from the {111} and {200} cones. It should be pointed out that z_1 (see Fig. 3) is not identical for the two types of cones at a given energy, as would be expected, so that the curves are only rough approximations to the true behavior of the density of states. A detailed calculation would hardly seem justified, however, in view of the rather unrealistic magnitudes of the energy gap across

the {200} faces.[13] It, thus, hardly seems possible to retain any form of rigid band model, at least in explaining the observed behavior of the α phase of the noble metal alloys.

In considering other possible theories, it is necessary to study the model of Ziman in more detail. Denoting by p the distance from the zone center to the center of a (111) face and taking this line to be the z axis, it is convenient to introduce dimensionless wave number coordinates x, y, z defined by $x = k_x/p$, etc. Energy is measured in terms of the dimensionless variable $\epsilon = (E_k)/(\hbar^2 p^2/m^*)$, m^* being an adjustable effective mass parameter. The energy surface is then assumed to be of the form

$$\epsilon = \tfrac{1}{2}(x^2 + y^2) + f(z), \qquad (2)$$

where $f(z)$ is a function of the gap across a (111) face and whose explicit form need not concern us here. It is then easily shown that $N(E)$ is given by

$$N(E) = (4/\pi^2)(m^* p/\hbar^2) \int_{z_1}^{z_2} dz, \qquad (3)$$

where z_1 and z_2 are the appropriate limits of z. Since

$$1/m^* = (1/\hbar^2)(\partial^2 E/\partial k^2), \qquad (4)$$

the effective masses for neck and belly orbits are, respectively,

$$m_{\text{neck}}^* = m^*, \quad m_{\text{belly}}^* = m^* z/f'(z), \qquad (5)$$

where for the belly orbits in question $0.8 < z < 0.9$.

From Eq. (5) it is readily seen that the ratio

$$m_{\text{belly}}^*/m_{\text{neck}}^* = z/f'(z) \qquad (6)$$

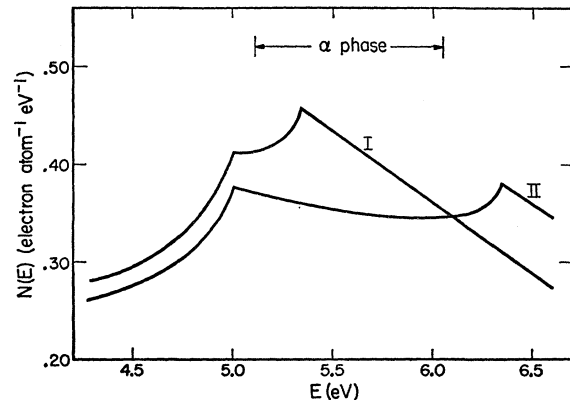is only a function of the energy gap. Thus, the model, as originally formulated, does not allow for the possibility

FIG. 4. Theoretical density-of-states curves calculated by dividing the Brillouin zone into two sets of intersecting cones.

[12] W. Hume-Rothery and D. Roaf, Phil. Mag. 6, 55 (1961).

[13] This conclusion is borne out by the recent band calculation of B. Segall [Phys. Rev. 125, 109 (1962)]. He finds that the band gap across the {200} faces in copper is 5.7 eV.

of a variation of this ratio once the gap has been fixed. It has been suggested that it is this feature of the model that produces disagreement with the observed behavior of the specific heat. As had been pointed out by Ziman,[14] however, it is easy to generalize Eq. (2) in the form

$$\epsilon = (\alpha/2)(x^2 + y^2) + f(z), \qquad (7)$$

where α is an adjustable constant. It is then readily shown that

$$m_{neck}^* = m^*/\alpha, \quad m_{belly}^* = m^* z / f'(z), \qquad (8)$$

so that the ratio of the two masses is an adjustable parameter. Equation (3) then becomes

$$N(E) = (4/\pi^2)(m^* p/\alpha \hbar^2) \int_{z_1}^{z_2} dz, \qquad (9)$$

from which it is clear that for any value of α there is only a *change of scale* in the density-of-states curve. Thus, if α is to remain a constant upon alloying, the present data are still unexplainable.

There is however another possibility, viz., that on alloying the constant α alters. If the ratio m_{belly}^*/m_{neck}^* decreases sufficiently upon alloying, then from (9) it may be seen that the density of states would in fact increase as required. This hypothesis does not *necessarily* imply a changing gap across the {111} faces. Since in copper $m_{belly}^*/m_{neck}^* \sim 2$, a decreasing ratio can be interpreted in a *restricted* sense as a type of sphericizing; for a spherical surface the ratio would be unity. Such behavior does not seem too implausible, because it is clear that it is the *s-d* hybridization which is responsible for the nonspherical Fermi surface in copper. The effect of alloying with zinc is presumably to reduce this *s-d* interaction, causing the alloy to behave more like a free electron system. It thus does not seem unreasonable to suppose that α does change in the manner postulated.

The foregoing considerations leave open the question as to whether or not the band gap remains constant on

alloying. For the β and γ phases of the Cu-Zn system,[15,16] it seems possible to explain the behavior of the density of states by assuming *constant* energy gaps across the phase, without invoking effects such as those described above, i.e., a rigid band model *does* appear to be satisfactory in these phases. The difference between the behavior of the primary and intermediate phases would thus appear to involve the initial effects of adding zinc on the hybridization of the *s-d* bands. At the moment it does not seem possible to ascertain whether or not the limits of the α phase are, in fact, determined by electron concentration effects. It does seem, however, that an explanation in terms of a rigid band model is fairly improbable.

B. Lattice Heat Capacity

The variation of Debye temperature as a function of solute concentration is shown in Fig. 2. As can be seen there is good agreement with that calculated from the low-temperature elastic data[17] except possibly for the highest zinc concentration. Due to the experimental difficulties associated with the determination of the elastic moduli for these alloys, such disagreement is not considered to be significant.

V. CONCLUSIONS

The low temperature heat capacity of the α phase for the Cu-Zn system has been measured using ultra-high purity specimens. Qualitative agreement is found with previous data, it being found that the density of states at the Fermi level increases with increasing solute concentration. Possible reasons for this behavior are discussed.

ACKNOWLEDGMENTS

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[16] B. W. Veal and J. A. Rayne (to be published).
[17] J. A. Rayne, Phys. Rev. **115**, 63 (1959).