

the 300°K given by Mador. The simple interpretation of a stability radius made by Faraday *et al.* seems inadequate to explain the complex behavior shown here. We propose kinetic effects involving labile forms, using lifetimes, capture probabilities, etc. Since the experimental data are inadequate for this problem, the subject is left to the interested reader.

Also, since the conclusion of this work, Wiegand¹² has reported that significant lattice parameter changes are associated with color center formation and the concomitant volume expansion. Such a result would indicate that the ratio of the expansion per color center to the molecular volume as reported here does not have the simple physical explanation offered earlier.³ Wiegand

¹² D. A. Wiegand, Phys. Rev. Letters 9, 201 (1962).

did not observe a contribution of centers other than F centers to his volume expansions, a contribution which should have been significant since his lowest concentrations appear to be in the range of our highest ones. Additional work will be required to clarify these problems.

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Heat Capacity of γ -CuZn Alloys below 4.2°K

BOYD W. VEAL AND JOHN A. RAYNE

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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Low-temperature heat capacity measurements have been made on a series of high-purity specimens covering the entire γ phase of the Cu-Zn system. The electronic heat capacity decreases rapidly with increasing zinc concentration, thereby lending support to the hypothesis that the γ brasses are electron compounds. An excellent fit to the data may be obtained by assuming that the Fermi surface of these alloys is spherical and makes contact with the large Brillouin zone of the γ -brass structure. The Debye temperature of the alloys is 433°K and is approximately independent of zinc concentration.

I. INTRODUCTION

It was first pointed out by Hume-Rothery¹ that certain alloy structures, with narrow stability ranges, occur at a definite electron-atom ratio. The γ structure, which occurs at the ratio of 21/13, is perhaps the best known example of such an electron compound. Jones^{2,3} has considered the so-called large Brillouin zone associated with the γ -brass structure. This zone is *not* the true zone containing two electrons/atom, but is the complex polyhedron formed by those planes having a large structure factor,⁴ in this case {330} and {411}. The large zone contains 90 states per unit cell or 1.73 states per atom, so that for an electron concentration of 21/13 (=1.615) it is almost completely full. On this basis, one would expect substantial contact between the associated Fermi surface and the zone faces. Furthermore, the density of states would decrease rapidly as a function of electron to atom ratio, thereby accounting

for the narrow range of stability for the γ phase.⁵

Jones has calculated the expected form of the density-of-states curve for the γ -brass structure, assuming a spherical Fermi surface. He has also considered the possible effects resulting from the incompleteness of the large Brillouin zone, and also from the possibly different gaps across the different faces. It thus is of considerable interest to test these predictions experimentally. For this reason, the present measurements on the γ phase of the copper-zinc system were initiated. The results indicate that the coefficient of the electronic heat capacity, and hence the density of states, is indeed a rapidly decreasing function of electron concentration. It also appears that it is possible to obtain a very good fit to the data, assuming a spherical Fermi surface and an effective mass at the bottom of the band equal to the free-electron mass. The possible theoretical consequences of this fit are discussed.

II. EXPERIMENTAL

Heat capacity measurements were made from 1.4 to 4.2°K using the same calorimeter described previously.⁶

⁵ See for example, W. Hume-Rothery and G. V. Raynor, in *The Structure of Metals and Alloys* (Institute of Metals, London, 1954), p. 206.

⁶ J. A. Rayne, Phys. Rev. 108, 22 (1957).

¹ W. Hume-Rothery, *The Metallic State* (Oxford University Press, New York, 1931), p. 328.

² H. Jones, Proc. Roy. Soc. (London), A144, 225 (1934).

³ H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960), p. 173.

⁴ A. J. Bradley and J. Thewliss, Proc. Roy. Soc. (London), A112, 678 (1926).

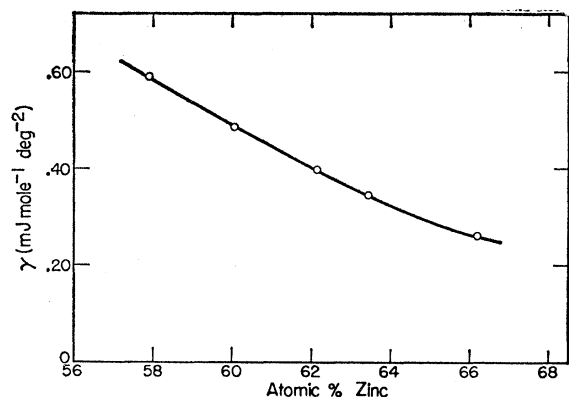


FIG. 1. Variation with zinc concentration of the coefficient of the electronic heat capacity for the γ brasses.

Because of the brittle nature of γ brass, it was not possible to machine the specimens on a lathe. They were accordingly ground to one-inch cylinders, the end sections being reduced to approximately $\frac{1}{2}$ -in. diameter. These were fitted into beryllium-copper collars, one of which contained the thermometer and heater assembly. The composite specimen could be supported by nylon threads in the usual manner. Corrections for the heat capacity of the addenda were determined in a separate experiment.

The specimens of γ brass were prepared from 99.999+% pure copper obtained from American Smelting and Refining Company and 99.9999% pure zinc obtained from Consolidated Smelting and Refining Company, Canada. These components were induction melted in graphite crucibles under an argon atmosphere. The resulting ingots were then annealed in helium at approximately 700°C for one week, after which they were ground to shape. No cold working to promote recrystallization was possible, due to the extreme brittleness of the specimens. Each ingot was analyzed spectroscopically for ferromagnetic impurities. In all cases there was less than one ppm iron, cobalt, and manganese in the specimens.

III. RESULTS AND DISCUSSION

The heat capacity data were fitted by least squares to an expression of the form

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

where δ takes into account the effects of phonon dispersion. Table I gives the resulting values of the coefficient of electronic heat capacity γ , the Debye temperature θ ($\beta = (12\pi^4/5)1/\theta^3$) and δ , together with the chemical analyses of the specimens. The dependence of γ on zinc concentration is shown in Fig. 1.

A. Electronic Heat Capacity

Reference to Fig. 1 shows that γ , and hence the density of states, for these alloys decreases rapidly with

TABLE I. Values of γ , θ , and δ in the relation $C/T = \gamma + \beta T^2 + \delta T^4$ ($\beta = (12\pi^4/5)1/\theta^3$) for γ -CuZn alloys.

Composition (at.% Zn)	γ (mJ mole ⁻¹ deg ⁻²)	θ (deg K)	δ (mJ mole ⁻¹ deg ⁻⁶)
57.88	0.591	437	0.0013
60.05	0.487	423	0.0007
62.14	0.398	428	0.0007
63.44	0.345	434	0.0006
66.21	0.262	446	0.0008

increasing zinc concentration. This behavior is precisely that predicted by Jones, on the assumption that contact between the Fermi surface and the large zone determines the range of electron concentration, over which the γ structure is stable.

As noted previously, the large zone is composed of those planes having a large structure factor, viz. {330} and {411}, and contains 90 states, i.e., 1.73 states/atom. The bounding polyhedron, which is shown in Fig. 2, has 36 faces all at the same distance $3\sqrt{2}\pi/a$ from the origin. This distance corresponds to the radius of the inscribed sphere, which is readily shown to contain 79.97 states, i.e., 1.537 states/atom. If it is assumed that the energy contours are all spheres or sections thereof, it is easy to compute the resulting density-of-states curve [see Fig. 3(a)]. Up to the point A, corresponding to contact of the spherical Fermi surface with the zone boundaries, the curve is simply that for an assembly of free electrons. Immediately beyond this point, the Fermi surface consists of a sphere from which 36 equal caps have been cut. It is readily shown³ that the density of states is given by

$$N(E)/N(E_0) = 18 - 17(E/E_0)^{1/2}, \quad E \geq E_0, \quad (2)$$

where E_0 is the Fermi energy corresponding to the wave vector $k_0 = 3\sqrt{2}\pi/a$. From (2), it is clear that $N(E)$ then decreases rapidly in a linear fashion, corresponding to the section AB of Fig. 3(a). For values of E greater than B, overlap will occur into regions beyond the zone, however great the energy gaps may be. Figure 3(b) illustrates a possible density-of-states curve in an actual metal having the γ -brass structure. As Jones points out, the only indisputable feature of the curve is the

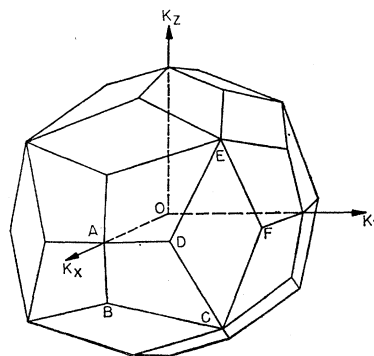


FIG. 2. Perspective view of the large Jones zone for γ -brass structure.

rapid drop from *C* to *D*. For a complete zone the curve shows a kink, like that at *F*, when overlap occurs. For an incomplete zone, however, this kink is absent and the curve should vary smoothly, as indicated by the full line *CDG*.

It is of interest to compare the present data with the Jones model. From Eq. (2), it is easy to calculate the electron concentration n from the relations

$$n - n_0 = \int_{E_0}^E N(E) dE; \quad n_0 = \frac{2}{3} N(E_0) E_0. \quad (3)$$

A simple integration yields the result

$$\frac{n - n_0}{n_0} = 27 \left(\frac{E}{E_0} - 1 \right) - 17 \left\{ \left(\frac{E}{E_0} \right)^{3/2} - 1 \right\}, \quad (4)$$

from which one can readily compute $N(E)$ as a function of n . In Fig. 4 this has been done assuming an effective mass equal to the free-electron mass. As may be seen, there is a surprisingly good fit to the experimental data. Optical absorption measurements on the γ brasses⁷ indicate the presence of interband transitions in the infrared. If these transitions are associated with the excitation of electrons across the faces of the large zone, then the associated energy gaps must certainly be less than 0.5 eV. When the above calculations are modified to take account of these gaps, the resulting curve of $N(E)$ as a function of n is scarcely modified. Thus, it appears fruitless to attempt any inference about the band gaps from the present experiments.

By adjusting the value of the effective mass at the bottom of the band, it is possible to obtain a slightly better fit to the data. As noted previously, the Jones zone is not complete and this causes a considerable modification to the shape of the density-of-states curve. Thus, too literal a fit to the simple theory is quite misleading. It is interesting to note, however, that the deviation of the experimental points from the curve of Fig. 4 is in accord with the presence of overlap over the faces of the Jones zone for higher zinc concentration [cf. Fig. 3(b)]. In its essential features, then, this theory would appear to be correct, i.e., the γ phase of Cu-Zn is, in

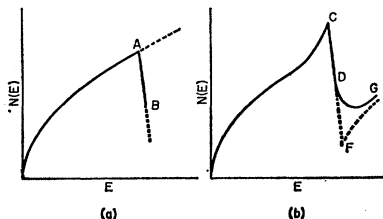


FIG. 3. Possible density-of-states curves for a metal having γ -brass structure.

⁷ L. G. Schulz (private communication).

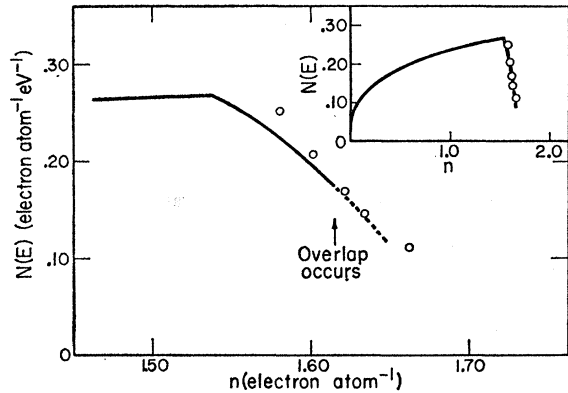


FIG. 4. Fit of experimental data to the theoretical curve for γ -brass structure assuming $\Delta E = 0$ across zone faces.

fact, an electron compound. There still remains the difficulty that the Jones zone is *not* the correct Brillouin zone for this system. The construction of the free-electron Fermi surface⁸ for a cubic metal containing 52 atoms/unit cell would, of course, offer considerable difficulty. From the present work it would appear, however, that there must be at least one set of the planes $\{330\}$ and $\{411\}$, which form part of the true zone and which overlap the Fermi surface in the manner postulated here.

B. Lattice Heat Capacity

From Table I it may be seen that the Debye temperature for the γ brasses is essentially constant, having a value $\theta = 433^\circ\text{K}$. There is some uncertainty in this figure, since the fit to the specific heat data is influenced considerably by the value of δ in Eq. (1). For this reason it is difficult to determine whether the trend of Table I, giving a shallow minimum on the curve of θ versus composition, is significant or not. Such behavior would not be unexpected, since the effects of zone overlap can give appreciable contributions to the elastic constants⁹ and, hence, to the Debye temperature of a metal. Measurements of the composition dependence of the elastic constants of γ brass would thus be of great value in settling this question.

IV. CONCLUSIONS

Low-temperature heat capacity measurements on the γ brasses confirm that these alloys are electron compounds. An excellent fit to the data can be obtained assuming that the Fermi surface of the alloys is spherical in shape and that overlap occurs across the faces of the large Jones zone for the γ -brass structure. The mean Debye temperature of the alloys is 433°K .

⁸ W. A. Harrison, Phys. Rev. **118**, 1190 (1960).

⁹ J. A. Rayne, Phys. Rev. **112**, 1125 (1958).