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Heat Capacity of β-CuZn below 4.2°K

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The specific heat of a series of high-purity β brasses has been measured below 4.2°K. Because of the possibility of large contributions to the specific heat from small amounts of ferromagnetic impurities, each specimen was examined spectroscopically and was found to contain less than 1 part per million of Fe, Mn, and Co. The data were fitted by the method of least squares to a curve of the form $C/T=\gamma+\beta T^2+\delta T^4$, the δT^4 term being included to account for the apparently large phonon dispersion. All of the coefficients showed a marked decrease with increasing electron-atom ratio. The variation of electronic density of states as a function of electron-atom ratio is compared to the theoretical relation based on the nearly free electron approximation. For the specimen of approximately 50 at. % copper and zinc, γ was found to be 0.699 mJ mole^{-1} deg^{-2} and the Debye temperature 291 ± 2°K. This compares favorably with the value of 288 ± 3°K, obtained from low-temperature elastic-constant measurements on an alloy of similar composition.

I. INTRODUCTION

THEORIES have been advanced by Jones[1] and, more recently, Ziman,[2] to explain the transport properties of noble metals and their alloys and the Hume-Rothery rules governing phase formation. These theories are based on the nearly free electron approximation and the assumption of rigid bands. For noble metals alloyed with multivalent solutes, the rigid-band hypothesis assumes that the valence electrons of the solute are contributed to the collective conduction band of the alloy without changing the band shape. The important parameter from each of these calculations is the density of the states which is given as a function of electron concentration. Thus, an experimental determination of the density of states for an alloy series is needed in order to see if one is justified in using the assumption of rigid bands. Since the electronic specific heat gives a direct measure of the density of states, it would seem that a series of measurements of the specific heat for a number of Cu-Zn alloys over a suitable composition range should provide a good test of the rigid band theory.

The heat capacity has previously been measured for the α phase[3] of the copper-zinc system as well as for certain other primary phase alloy systems[4-6] and agreement between theory and experiment has generally been found to be very poor. This experiment was undertaken in order to investigate the validity of the theory for the β-phase alloys.

The low-temperature specific heat has been measured for a series of Cu-Zn alloys representing the entire composition range of the β phase. The data are compared to the predictions made by the theories of Jones and Ziman. By making use of experimental evidence from other sources, possible alternative comparisons between the specific-heat data and the theories are discussed.

II. EXPERIMENTAL

The measurements were carried out using the techniques as described in a previous paper[3] incorporating a slightly modified calorimeter. The heat capacity specimens were ingots approximately 1½ in. long that weighed about 150 g. They were prepared from 99.999+% pure copper supplied by American Smelting and Refining Company, and 99.999+% pure zinc supplied by Cominco, Inc., by induction melting the appropriate quantities of each under an argon atmosphere. The metals were melted in a graphite crucible and were stirred with a graphite rod to insure adequate mixing.

β-brass is a brittle material, so that none of the specimens could be cold worked. The two alloys nearest the two phase regions were annealed and quenched into salt water to insure the presence of the β phase. The 49.9 at. % zinc specimen was twice quenched from 810°C. It had, in each case, been annealed for approximately 20 min. The 42.5 at. % zinc specimen received similar treatment except that it was annealed at 830°C. Polished surfaces from both specimens were examined microscopically in order to see if the alloys contained any α- or γ-phase material. No α phase was observed in the 42.5 at. % zinc specimen and only a trace of γ phase was seen in the 49.9 at. % zinc alloy. Chemical analyses of the ends of the ingots showed no detectable composition inhomogeneity.

Because small quantities of ferromagnetic impurities give a large contribution to the low-temperature specific heat,[7-9] each specimen was spectroscopically analyzed for iron, manganese, and cobalt impurities. No manganese or cobalt was detectable in any of the specimens, while iron appeared in the amount of only 2 parts per million (ppm) in the 42.5 at. % zinc alloy and 5 ppm in the 49.9 at. % zinc alloy. No iron was detected in any of the other alloys. These impurity concentrations should affect the results by less than 1%.

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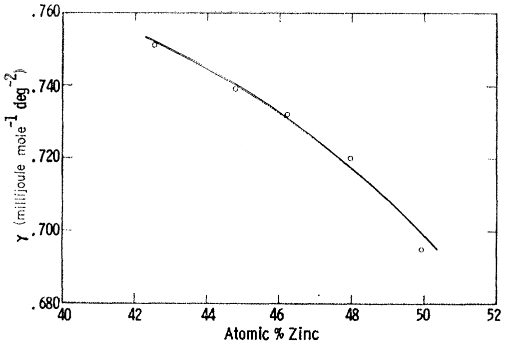

FIG. 1. Variation with zinc concentration of electronic heat capacity for β-brasses.

To check out the apparatus, the heat capacity of pure copper was remeasured. Table I lists the measured values of γ and θ and estimated uncertainties along with the best measurements made by other experimenters. It is felt that these measurements are in satisfactory agreement.

III. RESULTS

It was not possible to obtain a good straight-line fit to the heat-capacity data when plotted in the usual way, as C_v/T vs T^2. Hence, the data were fitted by the least-squares method to a curve of the form $C_v/T=\gamma+\beta T^2+\delta T^4$.[10] The first term in this equation represents the electronic contribution to the specific heat, the second term is the lattice contribution, and the third term apparently is an additional lattice contribution coming from phonon dispersion. The measured values of γ, θ, and δ and the estimated uncertainties are listed in Table II. The uncertainties include both systematic and random errors, the former estimated to be about $\frac{1}{2}\%$. The uncertainties in the measurements from the two alloys nearest the phase boundaries might be slightly larger as a result of the small ferromagnetic impurity content and possible small amounts of second phase material. The variations of γ, θ, and δ with zinc concentration are shown in Figs. 1–3.

TABLE I. Values of γ and θ in the relation $C_v=\gamma T+\beta T^3$ for copper.

	γ (mJ mole^{-1} deg^{-2})	θ (°K)
This work	0.692±0.007	342.7±3
Corak *et al.*[a]	0.688±0.002	343.8±3[c]
Rayne[b]	0.686±0.005	345.1±3[c]

[a] See W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, Phys. Rev. 98, 1699 (1955).

[b] See J. A. Rayne, Australian J. Phys. 9, 189 (1956).

[c] The error estimates of θ for the work of Corak *et al.* and Rayne are revised to include random and systematic errors.

TABLE II. Values of γ, θ, and δ for β-CuZn in the relation $C_v=\gamma+\beta T^3+\delta T^5$.

Composition (at. % Zn)	γ (mJ mole^{-1} deg^{-2})	θ (°K)	δ (mJ mole^{-1} deg^{-6})
42.54	0.751±0.007	271.1±3	0.00104
44.78	0.739	278.6	0.00095
46.20	0.732	282.3	0.00083
47.94	0.720	287.1	0.00082
49.92	0.699	291.2	0.00070

IV. DISCUSSION

A. Electronic Heat Capacity

Reference to Fig. 1 shows that γ and hence the density of states drops off sharply with increasing electron concentration. This suggests that the Fermi surface makes contact with the Brillouin zone boundaries for the entire β phase, a result which agrees qualitatively with the predictions made by Jones. The ratio of the thermal effective mass m_t to the optical effective mass m_a also supports this conclusion. The parameter m_t can be calculated from the heat capacity data for each specimen [see Appendix, Eq. (A5)], while m_a can be determined for alloys having the same electron concentrations [see Appendix, Eq. (A6)] using experimental measurements of (k/λ) taken by Schulz.[11] Table III lists the effective masses calculated for each specimen by assuming that zinc contributes two conduction electrons to the alloy, while Table IV shows the effective masses one obtains by assuming the electron-atom ratio for the alloys is one. In either case m_t/m_a is less than unity. Cohen[12] has shown that this ratio should be less than one when the Fermi surface makes appreciable contact with the zone faces.

A more detailed discussion of the theories advanced by Jones and Ziman and subsequent comparison with experiment follows.

Using the nearly free electron model of a metal, it can be shown[13] that the Fermi energy in the neighbor-

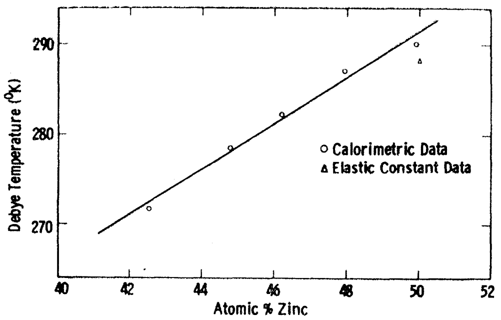

FIG. 2. Variation with zinc concentration of Debye temperature for β-brasses.

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[10] The constant β is related to the Debye temperature θ by the equation $\beta=(12\pi^4/5)R/\theta^3$, where R is the molar gas constant.

[11] L. G. Schulz (private communication).

[12] M. H. Cohen, Phil. Mag. 3, 762 (1958).

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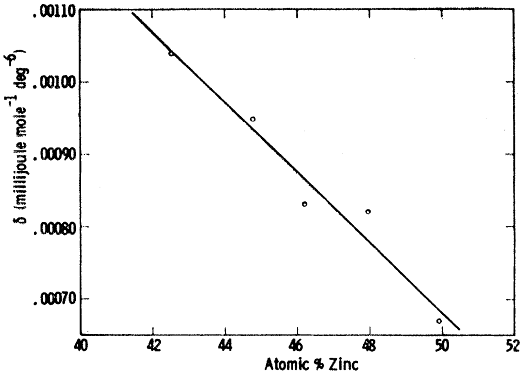

FIG. 3. Variation with zinc concentration of coefficient δ for β-brasses.

hood of the Brillouin zone boundary is

$$E=(h^2/2m^*)[k_x^2+k_y^2+k_0^2+\alpha(k_z-k_0)^2]-\tfrac{1}{2}\Delta E, \quad (1)$$

where $\alpha=1-4E_0/\Delta E$ and ΔE is the energy gap across the zone boundaries. Equation (A2) of Appendix A shows a modified expression[1] which should serve as a good description of the energy surface in a metal, since it reduces to Eq. (1) for large values of k and to the free electron expression for energy surfaces near the origin. The density of states is defined as

$$N(E)=2V\int\frac{dS}{\mathrm{grad}E}, \quad (2)$$

the integral being taken over the Fermi surface. To obtain $N(E)$, Jones sectioned the Brillouin zone[14] (a regular dodecahedron for the bcc structure) into 12 prisms, one of which is shown as *OABCD* in Fig. 4. For the purposes of simplifying the calculations, the prisms were then approximated by cones of solid angle $\pi/3$. Figure 5 shows how the filled portion of a cone will look. A direct calculation yields, for the bcc structure,

$$N(E)=(48\pi m\Omega/h^2)[k_{z(\max)}-k_{z(\min)}], \quad (3)$$

where Ω is the atomic volume, $k_{z(\max)}$ is the largest value of k_z within the cone, and $k_{z(\min)}$ is the smallest value. Equations (A3) and (A4) of the Appendix give E vs $k_{z(\min)}$ and $k_{z(\max)}$ vs E, both relations being readily derived from Eq. (A2). Using these expressions and Eq. (3), one can obtain a graph of $N(E)$ vs E. Numerical integration of the density of states curve, i.e.,

$$n=\int_0^{E_F}N(E)dE, \quad (4)$$

gives the electron-atom ratio n. Hence, one is able to obtain a plot of $N(E)$ vs n. The mean value of 12.77×10^{-24} cm^3/atom for the atomic volume was used in the β-phase calculations since the variation of Ω across the phase is very small. The data were not corrected for lattice expansion because the composition range is very narrow and corrections will be small.

TABLE III. Thermal and optical effective masses for β-CuZn, assuming that zinc contributes two conduction electrons/atom to the alloy. (Masses are in units of free electron mass.)

At. % Zn	n	m_a (exp)	m_t (exp)	m_t/m_a (exp)
42.54	1.425	2.759	1.259	0.456
44.78	1.448	2.790	1.228	0.440
46.20	1.462	2.808	1.210	0.431
47.94	1.479	2.831	1.183	0.418
49.92	1.499	2.857	1.132	0.397

TABLE IV. Thermal and optical effective masses for β-CuZn assuming $n=1$. (Masses are in units of free electron mass.)

At. % Zn	n	m_a (exp)	m_t (exp)	m_t/m_a (exp)
42.54	1.00	1.936	1.416	0.731
44.78	1.00	1.937	1.389	0.721
46.20	1.00	1.921	1.373	0.715
47.94	1.00	1.914	1.347	0.704
49.92	1.00	1.906	1.296	0.680

If the energy gap is chosen to be 4.7 eV, very close agreement is found to exist between theory and experiment (see Fig. 6). This value, however, is quite different from the 2.25-eV energy gap obtained from optical absorption measurements.[15] The energy gap value of 2.25 eV can be used in fitting the data if one adjusts

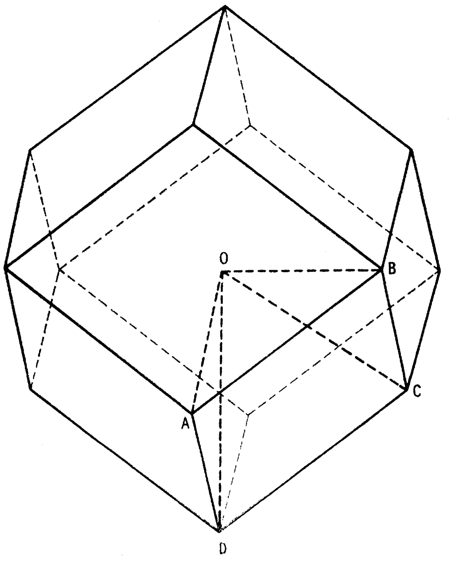

FIG. 4. First Brillouin zone for the bcc structure.

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[14] In both Jones treatment and the following, we ignore the subzones due to the fact that β Cu-Zn is an ordered structure. This procedure is justified since the associated energy gaps are presumably quite small.

[15] The absorption edge believed to be associated with the electron transitions from the Fermi level to the second zone appears at about 0.55 μ (see reference 11) or 2.25 eV.

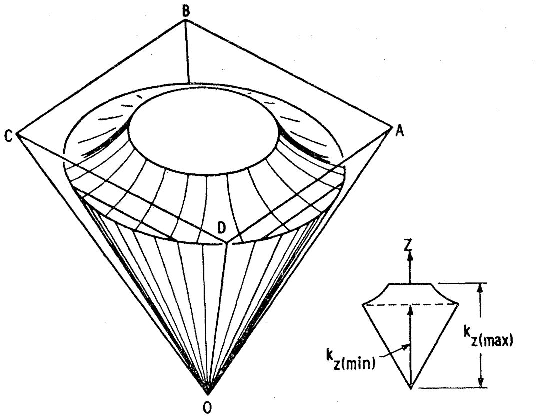

FIG. 5. A section of the Brillouin zone showing one cone of the approximate Fermi surface.

the magnitude of m^*, the effective mass at the bottom of the band. Appendix B gives the results of this calculation. Agreement with the optical data is obtained for $m^*=1.2m$, m being the free electron mass.

As discussed previously, it is helpful to know the ratio m^*/m_a. From Ziman's work, we have a direct calculation of m^*/m_a for the face-centered cubic alloys. Using a similar method for the bcc structure, assuming the Fermi surface makes contact with the zone faces, one can derive for $n=1.5$,

$$\frac{m^*}{m_a}=\frac{16\pi}{9\sqrt{2}}\left[2\epsilon(1-z_1)+2u^2\ln\left(\frac{(1-z_1)+[u^2+(1-z_1)^2]^{\frac{1}{2}}}{u}\right)-u\tan^{-1}\left(\frac{1-z_1}{u}\right)\right]. \quad (5)$$

Here $z_1=k_{z(\min)}/k_0$, $u=1/(1-\alpha)$, and ϵ is the normalized energy parameter $\epsilon=Em^*/\hbar^2k_0^2$, E being the energy at the Fermi surface. Using $m^*=m$, or $m^*=1.12m$, one is thus able to calculate m_a for $n=1.5$. The results are summarized in Table V.

The neck radius of the Fermi surface at the zone boundary is given by[2]

$$r=k_0(2u+2\epsilon-1)^{\frac{1}{2}}. \quad (6)$$

One finds that $r=0.843\times10^7$ cm^{-1} at $n=1.5$ when the data are fitted by assuming $\Delta E=4.7$ eV and $m^*=m$. On the other hand, if one fits the data by adjusting m^* and using Schulz's value of ΔE, it is seen that $r=0.718\times10^7$ cm^{-1}. This means that the Fermi surface makes contact with the zone boundaries over an appreciable area forming a circle of radius about half the radius of the largest circle that can be inscribed in one of the faces of the Brillouin zone (see Fig. 5). A more direct measure of the neck radius by means of de Haas-van Alphen experiments on a crystal of ordered β-brass should be possible and would provide a valuable cross check of the rigid-band theory.

TABLE V. Comparison of theoretical and experimental effective masses for β-CuZn at $n=1.5$. (Masses are in units of free electron mass.)

	(m^*/m_a) Ziman theory	m^*	m_a (theor)	m_a (exp)
Data fitted by assuming $\Delta E=4.7$ eV	0.30	1.00	3.30	2.86
Data fitted by assuming $\Delta E=2.25$ eV	0.35	1.12	3.20	

In judging the validity of the nearly free electron approximation and the rigid-band hypothesis, it must be remembered that these theories are based on single-particle calculations. In the case of a real metal, however, one is confronted with a many particle problem involving interactions between electrons and the crystal lattice. Hence it is unlikely that one will be able to obtain more than qualitative agreement between theory and experiment.

B. Lattice Heat Capacity

The variation of the Debye temperature as a function of composition is shown in Fig. 2. The value of θ for the 49.9 at. % zinc specimen was found to be 291.2±3°K. This is to be compared with the value of 288.1±3°K obtained by McManus and Rayne[16] on a specimen of about the same composition by means of elastic constant measurements. Agreement is within the combined limits of uncertainty and is therefore considered to be satisfactory.

V. CONCLUSIONS

The low-temperature heat capacity measurements of the β phase of the Cu-Zn system indicate that the rigid-band model might be applicable for certain intermediate phases in alloy systems. Though there is uncertainty as to the magnitude of the energy gap in β-brass and the size of the effective-mass parameters, the agreement

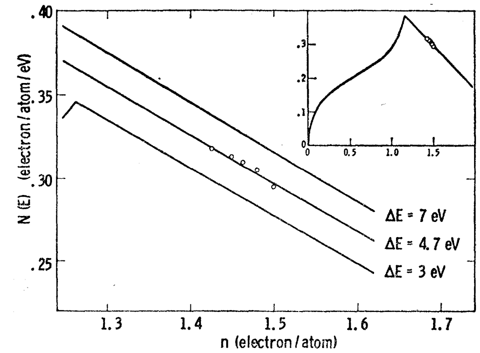

FIG. 6. Variation with electron concentration of the density of states for β-brasses. The inset is the theoretical curve for $\Delta E=4.7$ eV.

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[16] G. M. McManus and J. A. Rayne (to be published).

between theory and experiment is thought to be reasonably good.

APPENDIX A

Near the Brillouin zone boundaries, the energy at the Fermi surface is given in the nearly free electron theory by the approximate relation

$$E=\frac{h^2}{2m^*}[k_x^2+k_y^2+k_0^2+\alpha(k_z-k_0)^2]-\tfrac{1}{2}\Delta E. \qquad \text{(A1)}$$

For small energies, however, E approximates the energy of free electrons. An expression reducing to the proper relations for both large and small energies is

$$E=\frac{h^2}{2m^*}\left[k_x^2+k_y^2+(k_0-k_z)^2 -2k_0\left((k_0-k_z)^2+\frac{k_z^2}{(\alpha-1)^2}\right)^{\frac{1}{2}}\right]. \qquad \text{(A2)}$$

If the Brillouin zone is divided into prisms and the prisms are approximated by cones of solid angle $\pi/3$, Eq. (A2) can be related to $k_z(\text{min})$ for the bcc structure by

$$E=\frac{h^2}{2m^*}\left\{\frac{36}{25}k_{z(\text{min})}^2+2k_0\left[(k_0-k_{z(\text{min})}) -\left((k_0-k_{z(\text{min})})^2+\frac{k_0^2}{(\alpha-1)^2}\right)^{\frac{1}{2}}\right]\right\}. \qquad \text{(A3)}$$

The maximum value of k_z is readily derived from (A2) by assuming $k_x^2+k_y^2=0$ and is related to E by

$$\frac{k_{z(\text{max})}}{k_0}=1-\left[\frac{2m^*E}{h^2k_0^2}+1-2\left(\frac{2m^*E}{h^2k_0^2}+\frac{1}{(\alpha-1)^2}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}. \qquad \text{(A4)}$$

The experimental values of m_t are calculated from[17]

$$m_t=7.3(nV_m^2)^{\frac{1}{3}}\gamma, \qquad \text{(A5)}$$

where V_m is the molar volume in cm^3 and γ is given in millijoules mole^{-1} deg^{-2}. The experimental values of m_a are calculated from[18]

$$m_a=\frac{Ne^2}{\pi(k/\lambda)^2c^2}, \qquad \text{(A6)}$$

where N is the number of conduction electrons per unit volume and k is the extinction coefficient for light of wavelength λ.

APPENDIX B

The density of states for free electrons with a Fermi sphere of radius k_F is

$$N_0(E)=(8\pi m^*\Omega/h^2)k_F. \qquad \text{(B1)}$$

Since $N(E)=0.424\gamma$ mJ mole^{-1} deg^{-2}, we have from Eqs. (3) and (B1)

$$(\gamma/\gamma_0)_{\text{theo}}=N(E)/N_0(E)=6(k_{z(\text{max})}-k_{z(\text{min})})/k_F. \qquad \text{(B2)}$$

For an electron-atom ratio of 1.5, $\gamma_0=0.607m^*$ and $k_F=1.03k_0$. Now

$$\alpha=1-2h^2k_0^2/m^*\Delta E. \qquad \text{(B3)}$$

Thus we have

$$(\gamma/\gamma_0)_{\text{exp}}=\gamma\Delta E(1-\alpha)/21.04=0.0748(1-\alpha), \qquad \text{(B4)}$$

when use is made of the experimental value of γ and the energy gap value of 2.25 eV. If one plots $(\gamma/\gamma_0)_{\text{theo}}$ and $(\gamma/\gamma_0)_{\text{exp}}$, both vs α for $n=1.5$, the two curves intersect at $\alpha=12.81$ so that $m^*=1.12m$, where m is the free electron mass.

ACKNOWLEDGMENTS

We would like to thank A. J. Venturino, G. C. Cunningham, and Paul Hodder for valuable technical assistance and G. M. McManus for many helpful discussions.

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