

## Heat Capacity of $\alpha$ Brasses below 4.2°K

JOHN A. RAYNE

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received October 4, 1956; revised manuscript received June 6, 1957)

Heat capacity measurements below 4.2°K have been made on a series of  $\alpha$  brasses with compositions ranging up to thirty-four weight percent zinc. The variation of density of electronic states as a function of zinc composition suggests that the Fermi surface in copper deviates appreciably from sphericity. A comparison with theory and other experimental data concerning the shape of the Fermi surface in copper is given.

### I. INTRODUCTION

RECENT work<sup>1,2</sup> has indicated the need for direct information concerning the band structure of copper. Such information can be obtained, in principle, from electronic heat capacity measurements on a series of binary alloys of copper and a multivalent solute element forming a fairly extensive primary solid solution with it. If one assumes that the solute contributes its valence electrons to the collective 4s band, thereby altering the extent to which it is filled without changing its shape,<sup>3</sup> it is clear that the resulting variation of electronic heat capacity with solute concentration is simply related to the band shape of copper in the vicinity of the Fermi level.

To date, no such experiments have been made on a suitable alloy series. An extensive program has been undertaken to remedy the situation and in this paper the results of heat capacity measurements below 4.2°K on alloys of the  $\alpha$  phase in the copper-zinc system are described.

### II. EXPERIMENTAL

The experiments were carried out in a modified form of the calorimeter employed by Corak *et al.*<sup>4</sup> in their work on the heat capacities of the noble metals. Measuring techniques were substantially unaltered except that the carbon resistance thermometer was calibrated against the 1955 vapor pressure-temperature scale of Clement, Logan, and Gaffney.<sup>5</sup> The specimens employed were 1 in. in diameter, 1 $\frac{5}{8}$  in. in length, and weighed approximately 180 grams. They were produced by induction melting of appropriate quantities of high-purity copper and zinc under an argon atmosphere, care being taken to ensure good mixing of the components. In no case did subsequent chemical analysis of the ends of each ingot reveal a macroscopic inhomogeneity exceeding 0.05% zinc. Qualitative spectroscopic analysis of each specimen

revealed a component purity of the order of 99.99%. The ingots were hot worked to remove segregation, turned to size and finally annealed for one hour at 700°C in an argon atmosphere prior to use.

### III. RESULTS AND DISCUSSION

In all cases it was possible to obtain a good straight line fit to the heat capacity data when plotted as  $C/T$  versus  $T^2$ , a typical graph being shown in Fig. 1. The heat capacity is thus of the usual form

$$C = \gamma T + A(T/\Theta)^3, \quad (1)$$

these terms representing the electronic and lattice contributions, respectively. A least-squares analysis of the results yields the values of  $\gamma$  and  $\Theta$  shown in Table I. The representative uncertainties quoted in this table represent both systematic and random errors, the former being estimated to be about  $\frac{1}{2}\%$ . The variation of  $\gamma$  and  $\Theta$  with zinc composition is shown in Figs. 2 and 3.

According to the collective electron theory,  $\gamma$  is related to the density of states at the Fermi surface,  $N(E_0)$ , by the equation

$$\gamma = \frac{1}{3}\pi^2 k^2 N(E_0). \quad (2)$$

From Fig. 2, it is thus apparent that, with increasing zinc concentration, the density of states for the  $\alpha$  brasses rises quite sharply at first and then remains substantially constant\*. If these results are interpreted from

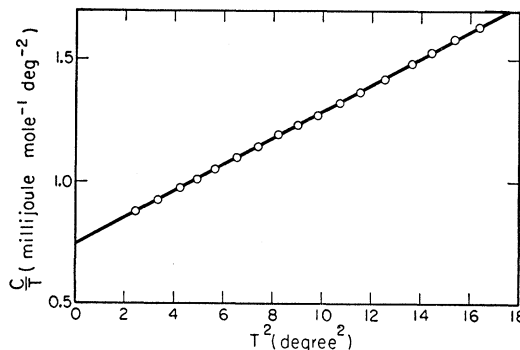


FIG. 1. Heat capacity of copper—20% zinc alloy.

<sup>1</sup> J. A. Rayne, *Australian J. Phys.* **9**, 189 (1956).  
<sup>2</sup> J. A. Rayne and W. R. G. Kemp, *Australian J. Phys.* **9**, 569 (1956).  
<sup>3</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 171.  
<sup>4</sup> Corak, Garfunkel, Satterthwaite, and Wexler, *Phys. Rev.* **98**, 1699 (1955).  
<sup>5</sup> Clement, Logan, and Gaffney, *Phys. Rev.* **100**, 743 (1955).

\* Note added in proof.—Recently Jones [*Proc. Roy. Soc. (London)* A240, 321 (1957)] has considered the effect of electron-

the standpoint of the rigid-band theory<sup>3</sup> of binary alloys, this sharp initial rise is not consistent with the assumption of a parabolic form for the density of states curve for copper. Thus, for an alloy with a concentration  $c$  of impurities with a valence  $Z$  relative to the solvent, we have in the first-order approximation<sup>6</sup>

$$\frac{\Delta N(E_0)}{N(E_0)} = \frac{cZ}{3p}, \quad (3)$$

it being assumed that the solvent contributes  $p$  electrons per atom to the parabolic conduction band. In the case of solutions of zinc in copper for which  $Z=1$ ,  $p=1$ , we find that a 3% zinc concentration should produce a 1% change in  $\gamma$ . This figure is clearly much too low.

Such a discrepancy can be explained by assuming that the Fermi surface in copper departs appreciably from a spherical shape. Since the density of states is

TABLE I. Values of  $\gamma$  and  $\Theta$  in the relation  $C = \gamma T^3 + A(T/\Theta)^3$  for  $\alpha$  brasses.

Composition (atomic percent zinc)	$\gamma$ (millijoule mole <sup>-1</sup> deg <sup>-2</sup> )	$\Theta$ (deg K)
0	0.687 ± 0.012	344.5 ± 3 <sup>a,b</sup>
1.49	0.708	343.6
3.15	0.735	343.3
5.98	0.742	343.6
7.80	0.731	342.6
8.18	0.750	341.6
9.76	0.743	341.3
15.07	0.740	335.6
19.97	0.745	329.9
24.50	0.746	325.9
29.19	0.752	320.9
32.98	0.733	315.3

<sup>a</sup> Mean values of  $\gamma$  and  $\Theta$ . See references 1 and 3.

<sup>b</sup> Random error estimated from plot of  $C/T$  versus  $T^2$  at 99% confidence level. Systematic error assumed to be ½%.

given by the relation

$$N(E_0) = 2V \iint \frac{dS}{|\text{grad}_k E|}, \quad (4)$$

the integral being taken over the Fermi surface,  $N(E_0)$  will increase more rapidly than in the free electron case when  $|\text{grad}_k E|$  is small. Such a situation occurs when the Fermi surface deviates from sphericity, as will be the case when it approaches any set of faces of the Brillouin zone relating to the outermost electrons of the metal. In the case of copper, which has a face-centered cubic structure, the first Brillouin zone has the form shown in Fig. 4. For the point  $A$  on the  $\{111\}$  face we have  $ka=0.866$ , while for the radius of the

lattice interaction on the apparent  $\gamma$  values for the  $\alpha$  brasses. He concludes that the curve of Fig. 2 should exhibit an anomaly at the zinc composition for which the Fermi surface just touches the zinc boundary. From the experimental data it would appear that no such behavior is observed and that the effect of the interaction is not as large as predicted theoretically.

<sup>6</sup> J. Friedel, *Phil. Mag.* **3**, 465 (1954).

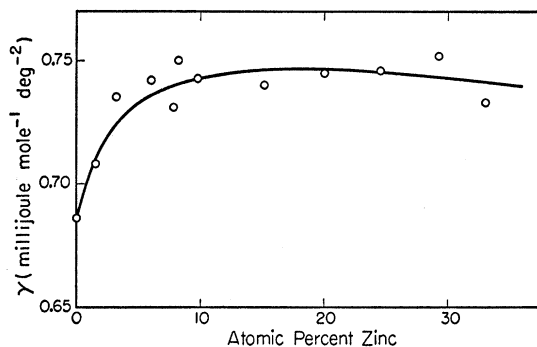


FIG. 2. Variation with zinc concentration of electronic heat capacity for  $\alpha$  brasses.

sphere containing one electron per atom we have  $ka=0.782$ . Thus the Fermi surface must come quite close to the  $\{111\}$  faces of the zone and it is not unreasonable to suppose that in actual fact it almost touches the zone boundaries at points such as  $A$ . The sharp initial rise in  $\gamma$  would then be due to approaching contact at these points. It is of interest that Klemens<sup>7</sup> and Jones<sup>8</sup> have also invoked the concept of a non-spherical Fermi surface in copper to explain the behavior of certain of its transport properties.

The accuracy of the present experiment is not sufficient to determine unequivocally whether there is a shallow maximum in the curve of Fig. 2. According to Jones<sup>9</sup> the density-of-states curve for copper should rise sharply to a cusp at a relatively low electron/atom ratio and then decrease linearly as shown in Fig. 5. In comparing this curve with Fig. 2, on the assumption that the zinc contributes both its conduction electrons to the conduction band of the alloy, one must take into account the expansion of the copper lattice caused by the addition of zinc. As a first approximation, this effect can be calculated by treating the metal as a

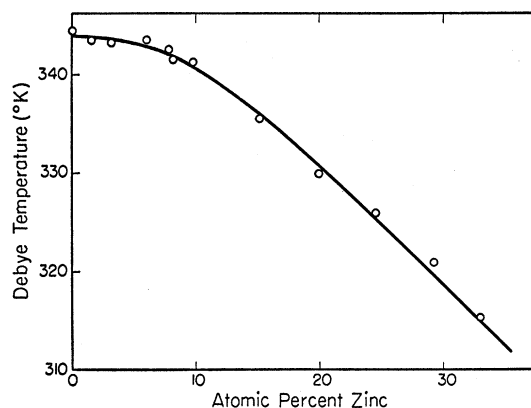


FIG. 3. Variation with zinc concentration of Debye temperature for  $\alpha$  brasses.

<sup>7</sup> P. G. Klemens, *Australian J. Phys.* **7**, 70 (1954).

<sup>8</sup> H. Jones, *Proc. Phys. Soc. (London)* **68**, 1191 (1955).

<sup>9</sup> H. Jones, *Proc. Phys. Soc. (London)* **49**, 250 (1937).

free electron gas. Thus, we have

$$N(E_0) \propto 1/E_0, \quad (5)$$

where the Fermi energy is given by

$$E_0 = \frac{\hbar^2}{2m} \left( \frac{3n}{8\pi} \right)^{\frac{2}{3}} \propto \frac{1}{a^2}, \quad (6)$$

$n$  being the electron density and  $a$  the cubic lattice spacing. Hence

$$N(E_0) \propto a^2, \quad (7)$$

and so for a given total number of electrons the density of states increases as the square of the lattice parameter. Using the lattice parameters for copper,  $a = 3.608 \text{ kX}$ , for the limit of the  $\alpha$  phase  $a = 3.693 \text{ kX}$  and assuming Vegard's law to hold, one thus obtains for the variation of  $N(E_0)$  with lattice expansion the straight line of Fig. 6. Subtracting this from the experimental curve, the dotted curve representing the variation of density of states with electron/atom ratio for a fixed lattice spacing is obtained. In view of the approximations

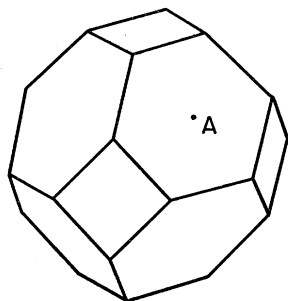


FIG. 4. First Brillouin zone for copper.

made in Jones' theory and the difficulty of obtaining the exact variation of  $\gamma$  for low zinc concentrations, the agreement between Figs. 5 and 6 must be considered to be reasonably satisfactory.

It is of interest that the results of the present work do not agree with those of Henry and Rogers<sup>10</sup> obtained from susceptibility measurements on  $\alpha$  brasses. According to these workers the Fermi surface in copper lies beyond the maximum in the density of states curve, the latter being a monotonic decreasing function of electron/atom ratio in the region of interest. In view of the uncertainties in the analysis of susceptibility data, particularly concerning corrections for the diamagnetism of the conduction electrons, the disagreement is not considered to be significant.

Although the hypothesis of an aspherical Fermi surface finds further experimental support in the work

<sup>10</sup> W. G. Henry and J. L. Rogers, *Phil. Mag.* **1**, 237 (1956).

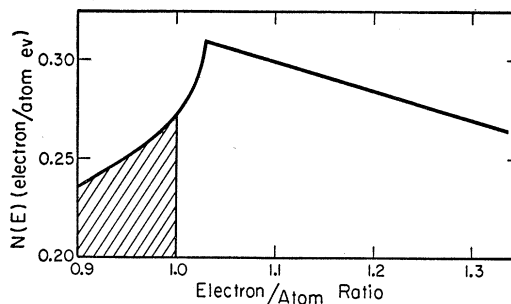


FIG. 5. Theoretical density of states curve for copper.<sup>9</sup>

of Pippard<sup>11</sup> on the anomalous skin effect in copper, it is to be noted that the detailed calculations of Krutter<sup>12</sup> and Howarth<sup>13</sup> give band shapes differing considerably from those found in the present work. Owing to the difficulties associated with such calculations, particularly as regards computing the effects of exchange, it is not certain just how much reliance can be placed upon them. Thus the discrepancies with the present results may not be as serious as they seem.

In principle the band shape of a metal beyond the Fermi surface can be obtained from its x-ray absorption spectrum. Cauchois<sup>14</sup> has measured the  $K$ - and  $L$ -absorption spectra of copper and concludes that the density of states is a monotonic increasing function of energy up to a point 3.5 eV beyond the Fermi surface. Now the absorption of a metal is given by the relation

$$\mu(E) \propto f(E)N(E), \quad (8)$$

$f(E)$  being the transition probability between the initial and final states and  $N(E)$  the final density of states. It is not easy to evaluate  $f(E)$  and variations of this quantity as a function of energy make it difficult

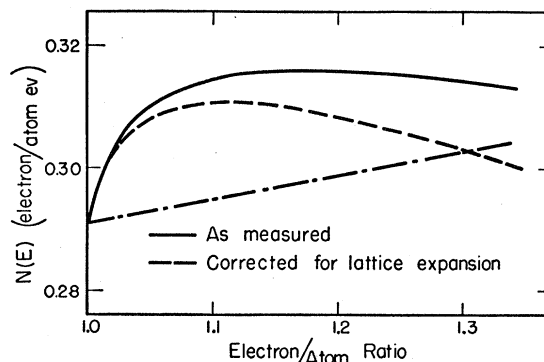


FIG. 6. Experimental density of states curve for copper.

<sup>11</sup> R. G. Chambers, "Proceedings of the international conference on electron transport in metals and solids," Ottawa, 1956, p. 1406 [*Suppl. Can. J. Phys.* **34**, No. 12A (1956)].

<sup>12</sup> H. M. Krutter, *Phys. Rev.* **48**, 664 (1935).

<sup>13</sup> D. J. Howarth, *Proc. Roy. Soc. (London)* **A220**, 513 (1953).

<sup>14</sup> Y. Cauchois, *Phil. Mag.* **44**, 173 (1953).

to evaluate  $N(E)$  from absorption data in an unequivocal way. Thus, again, the discrepancy with the present work may not be serious.

Further experiments are planned to investigate in more detail the effects of lattice distortion and also to extend the measurements to solute elements of valency greater than two.

#### ACKNOWLEDGMENTS

Particular thanks are due to Mr. C. P. Mueller of the Technology Department of Westinghouse Research Laboratories for preparing the specimens used in this work. Thanks are also due to Dr. P. G. Klemens, Dr. C. B. Satterthwaite, and Dr. P. A. Flinn for their advice and interest in the experiments.

## Absorption of Light in Se near the Band Edge

W. J. CHOYKE AND LYLE PATRICK  
*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*  
 (Received June 19, 1957)

A photovoltaic method has been used to measure the relative absorption in hexagonal Se of photons of energy 1.6 ev to 2.0 ev in the temperature range 80°K to 440°K. The measurements show that the transitions are indirect at the band edge, requiring the absorption or emission of a phonon. The energy gap is found to be  $(1.79 \pm 0.01)$  ev at 300°K; above this temperature  $dE_g/dT = -9 \times 10^{-4}$  ev/degree. The absorption edge of hexagonal Se is compared with that of amorphous Se.

### I. INTRODUCTION

A NUMBER of investigators has reported values for the energy gap in hexagonal Se. These values of  $E_g$  scatter considerably, ranging from 1.7 ev to 2.3 ev. Some of the earlier work has been summarized by Moss.<sup>1</sup>

The results referred to above were obtained from optical transmission measurements. Electrical measurements in Se have not been carried into the intrinsic region because of the low melting point (217°C) of Se.

Much of the scatter in the values of  $E_g$  may be attributed to certain experimental difficulties in making direct optical (transmission) measurements of the fundamental absorption, *viz.*: (1) The good Se single crystals available have been so small that very accurate measurements of transmission were not feasible. (2) The impracticability of preparing good hexagonal Se surfaces prevents an accurate direct measurement of reflectivity. (3) It is difficult experimentally to separate the absorption due to free carriers and imperfections from the fundamental absorption.

In this paper we present values for the fundamental absorption in Se as deduced from photovoltaic measurements.<sup>2</sup> Only the relative absorption coefficient is determined in our work. To get the absorption coefficient of Se from our data, an absolute measurement at one wavelength would be required.

The photovoltaic method for determining the absorption coefficient in Se has advantages over the transmission method since it avoids the large reflectivity

correction. In addition, the results are simple to interpret in terms of the fundamental absorption, since free-carrier and impurity absorption do not contribute to the photovoltaic effect. We have found the photovoltaic method well suited for use with hexagonal Se.

The absorption near the band edge has been found to be of the form predicted for indirect transitions.<sup>3</sup> Accordingly, we have used a Macfarlane and Roberts plot<sup>4,5</sup> to determine values for  $E_g$  in Se. We have obtained in this way values of the energy gap accurate to 0.01 ev over a considerable temperature range.

An unusual feature of the results given here is that in fitting curves to our experimental points we find it necessary to use a phonon energy which varies with the temperature of measurement.

We have attempted to make similar measurements on amorphous Se cells in order to compare the absorption edges of amorphous and hexagonal Se. The results are somewhat ambiguous and we can interpret them only in part.

### II. PREPARATION OF SAMPLES

Because Se is known only as *p*-type, a foreign *n*-type material must be used to complete the junction. However, we wish to measure only Se absorption. We first made measurements on commercial Se photovoltaic cells, but found a large spurious response which we believe is due to hole-electron pair production in

<sup>1</sup> T. S. Moss, *Photoconductivity in the Elements* (Academic Press, Inc., New York, 1952), p. 192.

<sup>2</sup> W. J. Choyke and L. Patrick, *Phys. Rev.* **105**, 1721 (1957).

<sup>3</sup> Bardeen, Blatt, and Hall, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954* (John Wiley and Sons, Inc., New York, 1956), p. 146.

<sup>4</sup> C. G. Macfarlane and V. Roberts *Phys. Rev.* **97**, 1714 (1955).

<sup>5</sup> C. G. Macfarlane and V. Roberts *Phys. Rev.* **98**, 1865 (1955).