

Heat Capacity of Copper-Germanium Alloys below 4.2°K

JOHN A. RAYNE

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received January 6, 1958)

Heat capacity measurements below 4.2°K have been made on a series of alloys in the primary phase of the copper-germanium system. When corrected for lattice expansion, the resulting change in the electronic specific heat for low electron/atom ratios is found to be the same as that for the copper-zinc system. In neither case is the variation consistent with that expected for a parabolic valence band, thereby lending support to the previously advanced hypothesis that the Fermi surface in copper departs appreciably from sphericity. Both systems exhibit the same variation of Debye temperature with electron concentration, when appropriate corrections are made for the differences in the atomic mass and volume of the two alloy series. This supports the idea that the variation of the elastic constants in these alloys is influenced principally by the proximity of the Fermi surface to the boundaries of the first Brillouin zone. The variation of elastic constants with solute concentration, as deduced from the present work, is compared with that obtained from ultrasonic pulse measurements at room temperature.

I. INTRODUCTION

CONSIDERABLE interest attaches to the behavior of the primary solid solutions of copper when alloyed with elements directly to its right in the same row of the periodic table. According to the rigid-band model of Hume-Rothery and Jones,¹ the character of these alloys is determined principally by the valence-electron concentration. It is assumed that each solute atom contributes its valence electrons to the collective 4s band of the alloy, thereby altering the Fermi level of the system without changing the band shape from that of pure copper. As Mott² and more recently Friedel³ have pointed out, this picture cannot be correct, since the additional electrons contributed by the solute are localized near the solute atoms in such a way as to screen out their additional nuclear charge. Leaving aside the question of whether or not these screening charges occupy bound states, it is clear that, in dilute alloys at least, the majority of copper atoms see the same potential as in the pure metal, since the screening radius is of the order of 1 Å. This means that the Fermi level in the alloy must be the *same* as that in parent metal, contrary to the situation envisaged in the rigid-band model.

Using the Thomas-Fermi model of a metal, however, Friedel⁴ has been able to show that, in the first-order approximation, the rigid-band model correctly predicts the *effects* of alloying on the density of electronic states, even though it is incorrect conceptually. It thus follows that, insofar as the Friedel theory correctly describes such systems, measurements of the electronic heat capacity of alloys of copper with zinc, etc., should give the band shape in copper.

The present work describes experiments to determine the variation of electronic heat capacity with solute

concentration in the primary phase of the copper-germanium system. These measurements were undertaken to obtain a comparison with the previously determined electronic properties of the copper-zinc alloys. The degree of correspondence between the two systems is, of course, a direct measure of the correctness of the Friedel theory, and also an indication of how far the density-of-states curve for the α -brasses may be taken as representing that in pure copper.

II. EXPERIMENTAL

The calorimeter and techniques used in the present work have been described in an earlier paper⁵ and do not need further elaboration. As in the previous experiments, the specimens were in the form of cylinders, 1 in. in diameter and 1 $\frac{5}{8}$ in. in length, weighing approximately 180 grams. They were prepared by the induction melting of appropriate quantities of high-purity copper and germanium 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% germanium. The ingots were hot-worked, and then maintained at 900°C for about 14 hours to remove coring and to assist in their homogenization. After being turned to size, they were finally annealed for 1 hour at 700°C in an argon atmosphere and furnace-cooled, except for the last specimen. This sample was heated to 800°C and water-quenched to ensure that only the α -phase was present in it.

III. RESULTS

In all cases it was possible to obtain a good straight-line fit to the heat-capacity data when plotted as C/T vs T^2 . The specific heat 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

¹ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 171.

² N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

³ J. Friedel, J. phys. Radium **14**, 561 (1953).

⁴ J. Friedel, *Advances in Physics* (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 465.

⁵ J. A. Rayne, Phys. Rev. **108**, 22 (1957).

results yields the values of γ and Θ shown in Table I. In this table, the representative uncertainties represent both systematic and random errors, the former being estimated to be about $\frac{1}{2}\%$. The variation of γ and Θ with germanium concentration is shown in Figs. 1 and 2.

IV. DISCUSSION

(a) Electronic Heat Capacity

Reference to Fig. 1 shows that the γ value, and hence the corresponding density of states, for the copper-germanium system rises quite rapidly at low solute concentrations and then tends to flatten out. This behavior is roughly similar to that found for the copper-zinc alloys.

To achieve a more detailed comparison, it is necessary to make allowances for the differences of lattice expansion in the two systems. As in the previous paper,⁵ it is assumed that the effect of a change in the lattice parameter can be computed with sufficient accuracy

TABLE I. Values of γ and Θ in the relation $C = \gamma T + A(T/\Theta)^3$ for copper-germanium alloys.

Composition (atomic percent germanium)	γ (millijoule mole ⁻¹ deg ⁻²)	Θ (°K)
0	0.687 ± 0.012	344.5 ± 3 ^{a,b}
0.44	0.709	345.0
0.84	0.722	344.5
1.82	0.722	343.6
2.63	0.731	342.0
4.38	0.742	337.9
6.54	0.746	329.6
8.55	0.750	321.2
10.93	0.765	315.2

^a Mean values of γ and Θ . See Corak, Garfunkel, Satterthwaite, and Wexler, *Phys. Rev.* **98**, 1699 (1955), and J. A. Rayne, *Australian J. Phys.* **9**, 189 (1956).

^b Random error estimated from least-squares analyses of C/T vs T^2 at 99% confidence level. Systematic error assumed to be $\frac{1}{2}\%$.

from the formula obtaining for free electrons. In this case it is readily shown that the density of states at the Fermi surface $N(E_0)$ is related to the total number of electrons \mathcal{N} by the formula

$$N(E_0) = \frac{3m}{2h^2} \left(\frac{8\pi}{3} \right)^{\frac{2}{3}} \mathcal{N}^{\frac{2}{3}} V^{\frac{1}{3}}, \quad (2)$$

where V is the molar volume. Thus, if a is the cubic-lattice parameter, we have for a fixed total number of electrons

$$N(E_0) = \frac{3m}{2h^2} \left(\frac{8\pi}{3} \right)^{\frac{2}{3}} \mathcal{N}^{\frac{2}{3}} a^2 \propto a^2. \quad (3)$$

With the known data for the lattice parameters of the Cu-Zn and Cu-Ge systems,⁶ Eq. (3) can be used to

⁶ W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (Institute of Metals, London, 1954), third edition, p. 170.

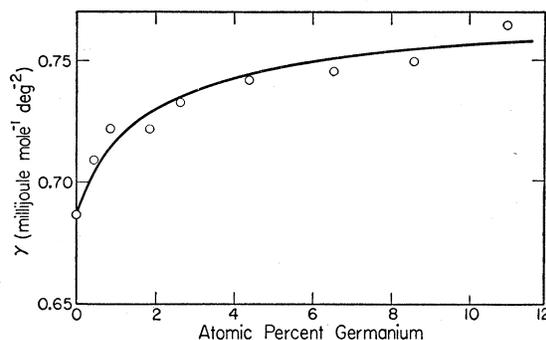


FIG. 1. Variation with solute concentration of electronic heat capacity for Cu-Ge alloys.

reduce the density-of-states data to a common lattice parameter, *viz.*, $a = 3.608$ kx, corresponding to that for pure copper. The two sets of reduced data are shown in Fig. 3 plotted as a function of electron/atom ratio, it being assumed that each zinc atom contributes one and each germanium atom three additional valence electrons to the alloy. It will be seen that, to within experimental error, the two sets of corrected data are coincident for low electron concentrations but that there is an increasing divergence between them for higher concentrations.

Using the Thomas-Fermi model, Friedel⁴ has demonstrated that the density of states in an alloy is related to that of the pure solvent after the manner shown in Fig. 4. In the first-order approximation, the band is shifted back *without* change of shape by an amount

$$E_1 = \frac{1}{V} \int V_P d\tau, \quad (4)$$

and the Fermi level is altered by an amount ΔE_0 . The additional levels at the bottom of the band may be subtracted therefrom to form bound states, but this question need not concern us here.

The perturbing potential due to alloying, V_P , satisfies

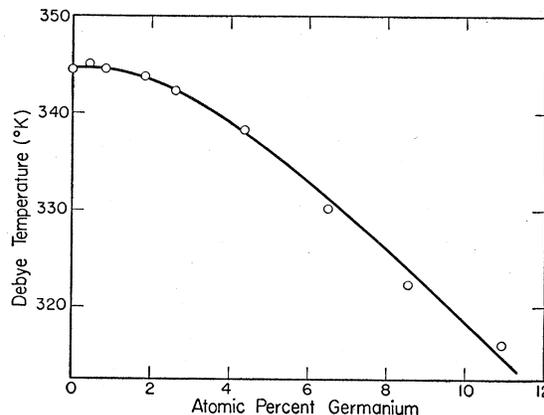


FIG. 2. Variation with solute concentration of Debye temperature for Cu-Ge alloys.

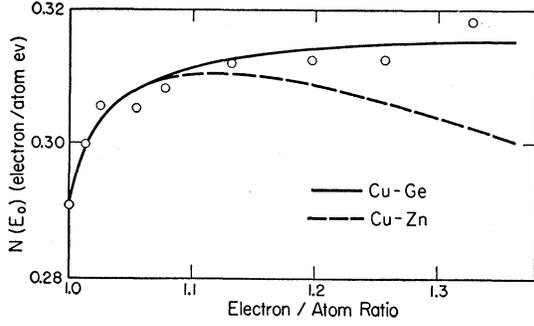


FIG. 3. Variation with electron/atom ratio of corrected density of states for Cu-Ge and Cu-Zn alloys.

the equation

$$\nabla^2 V_P = 4\pi N(E_0)(V_P - \Delta E_0), \quad (5)$$

subject to the boundary condition that it vanishes on the surface of a sphere of radius R . This is defined, in terms of the radius of the atomic sphere r_s , by the equation

$$1/R^3 = c/r_s^3, \quad (6)$$

where c is the concentration of solute.

The first-order solution of Eq. (5) is found to be

$$V_P = \Delta E_0 - \frac{Z q R \cosh[q(R-r)] - \sinh[q(R-r)]}{r q R \cosh q R - \sinh q R}, \quad (7)$$

where

$$\Delta E_0 = Zq/qR \cosh qR - \sinh qR. \quad (8)$$

The screening parameter q is given by the expression

$$q^2 = 4\pi N(E_0), \quad (9)$$

which equation gives a screening distance q^{-1} of the order of 1 Å for copper. For low solute concentrations ($R \gg r_s$), it is easily shown that (7) and (8) reduce to

$$V_P = -(Z/r)e^{-qr}; \quad \Delta E_0 = 0. \quad (10)$$

Thus the potential due to the solute atoms is screened out in a distance of about 1 Å and the Fermi level of the alloy is the same as that of the solvent.

By using (7), (8), and (9), it is easily shown that, providing second-order effects are small,

$$\Delta E_0 - \frac{1}{V} \int V_P d\tau = \frac{4\pi cZ}{q^2 v} = \frac{cZ}{vN(E_0)}, \quad (11)$$

Z being the valence of the solute relative to the solvent and v being the atomic volume. Hence, for the density of states in the alloy, we have

$$N'(E_0 + \Delta E_0) = N\left(E_0 + \Delta E_0 - \frac{1}{V} \int V_P d\tau\right),$$

whence, by (11),

$$N'(E_0 + \Delta E_0) = N\left(E_0 + \frac{cZ}{vN(E_0)}\right). \quad (12)$$

This is precisely the result computed from the rigid-band model, assuming that the Fermi level shifts by an amount corresponding to the change in electron concentration.

It would thus be expected that the variation of the density of states as a function of the electron/atom ratio should be the same for different alloys systems. As Fig. 4 shows, this appears to be the case for Cu-Zn and Cu-Ge at low electron concentrations, and so one may reasonably expect that this part of the curve correctly represents the density-of-states curve for copper just beyond the Fermi level. Now, expanding (12), we find

$$\frac{\Delta N(E_0)}{N(E_0)} = \frac{cZ}{v} \frac{1}{N^2(E_0)} \left(\frac{dN}{dE}\right)_0. \quad (13)$$

For the case of a solvent having a parabolic valence band with p electrons per atom, this reduces to

$$\frac{\Delta\gamma}{\gamma} = \frac{\Delta N(E_0)}{N(E_0)} = \frac{cZ}{3p}, \quad (14)$$

since $\gamma = \frac{1}{3}\pi^2 k^2 N(E_0)$. In the present case $p=1$, so that for an electron/atom ratio of 1.03 ($cZ=0.03$) one would expect from (14) to find a one percent change in γ , a figure 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 given by the relation

$$N(E_0) = 2V \iint \frac{dS}{|\text{grad}_k E|}, \quad (15)$$

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. This situation occurs wherever there is distortion of the Fermi surface resulting from its approach to any set of faces of the Brillouin zone relating to the outermost electrons of the metal. In the case of copper, the sphere containing one electron per atom approaches quite close to the $\{111\}$ faces of the first zone, so that it is probable that the Fermi surface

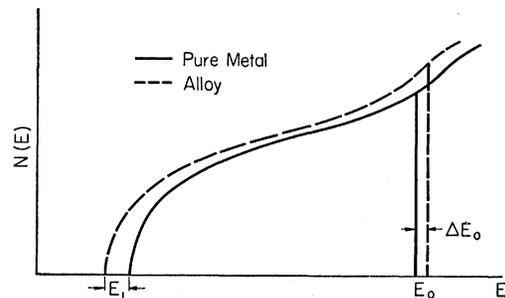


FIG. 4. Rigid-band model for an alloy according to Friedel (reference 4).

is quite distorted in their vicinity. The sharply rising density-of-states curve would then be due to the approaching contact between the Fermi surface and the {111} faces of the zone. It is of interest that Klemens⁷ and Jones⁸ have made similar proposals about the energy surface in copper to explain certain of its transport properties, *viz.*, the abnormal ratio of its ideal electrical and thermal resistances at low temperatures and the positive sign of its thermoelectric power.

Although susceptibility measurements on copper alloys,⁹ soft x-ray absorption data,¹⁰ and theoretical energy band calculations^{11,12} have been used to obtain information concerning the band shape in copper, the conclusions reached are not mutually consistent. As it is felt that the electronic heat capacity provides more direct information about the band structure than the above, the latter will not be considered further. The only other firm evidence regarding the shape of the Fermi surface is that obtained by Pippard,¹³ from measurements of the anomalous skin effect in copper at low temperatures.

It may be shown that the principal surface resistances of a planar single crystal are related to the principal curvatures of those parts of the associated Fermi surface with normals parallel to the plane of the crystal. By making measurements on copper single crystals of different orientations, Pippard found that the surface resistance and hence the curvature of the Fermi surface were markedly anisotropic, so that the latter must deviate appreciably from sphericity. With a suitable choice of an initial form for the surface, Pippard was able to correct its shape so that its curvature reproduced the experimentally observed anisotropy in surface resistance. The resulting Fermi surface, although agreeing in general with that proposed here, differs from it in that contact with the {111} faces of the zone has already occurred. As Pippard admits, however, this feature is not at all unequivocal, being based on somewhat uncertain theoretical grounds. It is thus possible that the Fermi surface is only *close* to the zone boundary. The present work favors this viewpoint, since zone contact would necessarily imply that the density of states decreases with increasing energy.

Recently, Jones¹⁴ has considered the effect of incipient contact between the Fermi surface and a set of zone faces on the distribution of lattice modes in a metal at low temperatures. He concludes that there is a resulting change, in what normally is the zero-point energy of the system, which yields a contribution to the heat capacity that is linear in temperature. This term in-

creases very rapidly as the surface approaches the zone boundary, becomes infinite at the onset of contact and then vanishes. It would thus be expected, that the apparent γ values, for the systems studied here, would have an anomaly at low solute concentrations. From the data, it would appear that the anomalies do not exist and that the theory overestimates the effect of the relevant phonon-electron interaction.

In view of the discrepancy between the two curves of Fig. 3, there is considerable doubt as to the form of the experimental density-of-states curve for copper at higher electron concentrations. Comparison with Jones' theoretical curve¹⁵ would thus hardly seem justified. It is believed, however, that contact between the Fermi surface and the zone boundary certainly takes place before the electron/atom ratio reaches 1.1, so that the energy separation between them does not exceed 0.3 eV. No definite reason for the difference in the behavior of the two alloy series can be advanced, although it is entirely possible that, at larger solute concentrations, higher order corrections to the theory outlined above have to be considered. Friedel has treated this problem, but the complexity of the solution makes an evaluation in the present case rather intractable. In addition, it is quite possible that additional factors, arising from the rather different natures of the solute atoms, also affect the density-of-states curve.

(b) Lattice Heat Capacity

Reference to Fig. 2 shows that the Debye temperature for the copper-germanium alloys remains relatively constant for low solute concentrations and then decreases quite rapidly. As in the case of the copper-zinc alloys, this behavior is not at all consistent with the Kopp-Neumann relation. Thus, for an alloy with a concentration x of solute having a Debye temperature Θ_2 , we should expect that

$$\frac{1}{\Theta^3} = \frac{1-x}{\Theta_1^3} + \frac{x}{\Theta_2^3}, \quad (16)$$

where Θ and Θ_1 are the Debye temperatures of the alloy and solvent, respectively. For germanium $\Theta_2 = 366^\circ\text{K}$,¹⁶ so that Eq. (16) predicts that the Debye temperature should increase with increasing concentration of germanium, whereas the opposite actually happens.

Although a general analysis of the lattice dynamics of a disordered cubic array is not available, it is still possible to make some predictions about its behavior at low temperatures. Here we are dealing only with long-wavelength phonons, which presumably are unaffected by such fine details of structure as short-range order, etc. It may therefore be expected that the alloy behaves like an anisotropic cubic metal, with the same values of density and elastic constants.

⁷ P. G. Klemens, Australian J. Phys. **7**, 70 (1954).

⁸ H. Jones, Proc. Phys. Soc. (London) **68**, 1191 (1955).

⁹ W. G. Henry and J. L. Rogers, Phil. Mag. **1**, 237 (1956).

¹⁰ Y. Cauchois, Phil. Mag. **44**, 173 (1953).

¹¹ H. M. Krutter, Phys. Rev. **48**, 664 (1935).

¹² D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).

¹³ A. B. Pippard, Phil. Trans. Roy. Soc. (London) **250**, 325 (1957).

¹⁴ H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).

¹⁵ H. Jones, Proc. Phys. Soc. (London) **49**, 250 (1937).

¹⁶ P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1347 (1953).

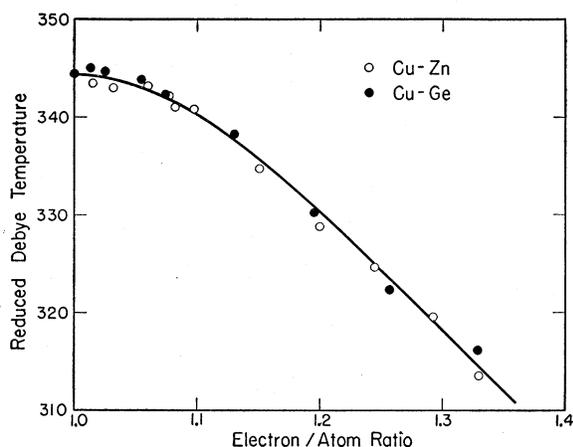


FIG. 5. Variation with electron/atom ratio of reduced Debye temperature for Cu-Ge and Cu-Zn alloys.

DeLaunay¹⁷ has investigated the vibrational spectrum of cubic metals in some detail, using a central-force model with electron participation to take into account deviations from the Cauchy relation. At low temperatures, he derives a general expression for the Debye temperature of a cubic metal in terms of its elastic constants, *viz.*,

$$\Theta^3 = \frac{9\pi}{4\pi V} \left(\frac{h}{k}\right)^3 \left(\frac{c_{44}}{\rho}\right)^{\frac{3}{2}} \frac{9}{18+\sqrt{3}} f(s,t), \quad (17)$$

where $f(s,t)$ is a tabulated function of the variables $s = (c_{11} - c_{44}) / (c_{12} + c_{44})$ and $t = (c_{12} - c_{44}) / c_{44}$. For a metal satisfying the Cauchy relation $c_{12} = c_{44}$, we have $s = (c_{11} - c_{12}) / 2c_{44}$, $t = 0$.

From (17) it is easily seen that

$$\Theta^3 \left[(M^3 / M_0^3) (V_0 / V) \right]^{\frac{1}{2}} = \alpha c_{44}^{\frac{3}{2}} f(s,t), \quad (18)$$

where M_0 and V_0 are the molar mass and volume of pure copper, respectively, and α is a constant. The right-hand side of this equation is a function only of the elastic constants of the system, and one might suppose that in the present case these would depend on the relevant lattice spacing of the alloy and the electron concentration. If, however, the reduced Debye temperature $\Theta_r = \Theta \left[(M / M_0) (a_0 / a) \right]^{\frac{1}{2}}$ is plotted against electron concentration for *both* the Cu-Zn and Cu-Ge systems, the same functional dependence is obtained, as may be seen from Fig. 5. This strongly suggests that the variation of elastic constants for these alloys is determined principally by the electron concentration, since the lattice expansion is not the same in both cases. Further evidence that this situation holds quite generally for the primary solid solutions of copper alloys is given in Fig. 6, in which the room-temperature shear constants $C = c_{44}$ and $C' = (c_{11} - c_{12}) / 2$ are plotted

as functions of electron/atom ratio for a number of systems. Most of these data are due to Neighbours and Smith,¹⁸ with the exception of the data for copper and the Cu-28% Zn alloy, which are due to Lazarus¹⁹ and Masima and Sachs,²⁰ respectively. As can be seen, C and C' vary linearly with electron concentration to within the experimental error.

The success of fitting the data in this way is somewhat surprising since one would expect that the crystal energy is markedly dependent on lattice spacing. Thus the total crystal energy U may be written

$$U = U_{\text{electrostatic}} + U_{\text{exchange}} + U_{\text{electronic}},$$

where $U_{\text{electrostatic}}$ is the energy of interaction between the valence electrons and the ions of the lattice, U_{exchange} is the repulsive exchange interaction between the ions themselves, and $U_{\text{electronic}}$ is the energy of the valence electrons. Both the first and second terms depend strongly on the lattice parameter, and hence one

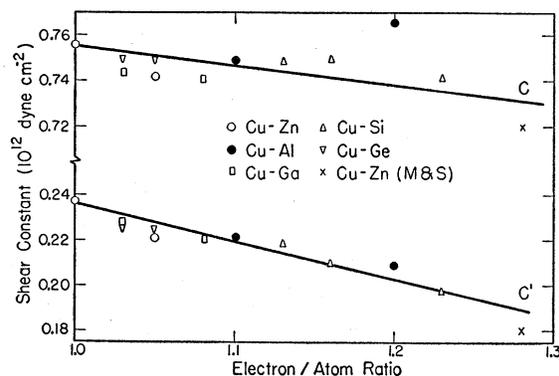


FIG. 6. Variation with electron concentration of room temperature elastic constants for various copper alloys.

would expect a similar situation for the shear constants

$$C = \frac{1}{2V} \frac{\partial^2 U}{\partial \alpha^2}, \quad C' = \frac{1}{2V} \frac{\partial^2 U}{\partial \beta^2}, \quad (19)$$

the differentiations being with respect to the appropriate shears. A possible explanation for the observed behavior is to suppose that the variations in these terms on alloying cancel one another, although no plausible reason can be advanced for this being the case. Since shearing affects the way in which the Fermi surface distorts in the vicinity of the $\{111\}$ faces of the Brillouin zone, $U_{\text{electronic}}$ contributes to C and C' in the case where zone contact is imminent. It is then supposed that this term, which presumably depends only on the electron/atom ratio, is responsible for the observed variation of the shear constants.

In proceeding further with the analysis of the lattice

¹⁷ J. DeLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 285.

¹⁸ J. R. Neighbours and C. S. Smith, *Acta Met.* **2**, 591 (1954).

¹⁹ D. Lazarus, *Phys. Rev.* **76**, 545 (1949).

²⁰ N. Masima and G. Sachs, *Z. Physik* **50**, 161 (1928).

heat capacities of the Cu-Zn and Cu-Ge systems, it is necessary to assume a central-force model for the alloys. This model correctly describes the shear constants of the alloys, and enables their variation as a function of electron concentration to be determined. Thus, referring to Eq. (18), we have in the case $t=0$

$$\Theta_r^3 = \alpha C^{\frac{3}{2}} f(C'/C). \quad (20)$$

Differentiation of this relation then gives us the equation

$$3\Theta_r^2 \Delta\Theta_r = \frac{3}{2}\alpha C^{\frac{3}{2}} f\left(\frac{C'}{C}\right) \Delta C + \alpha C^{\frac{3}{2}} f'\left(\frac{C'}{C}\right) \left\{ \frac{\Delta C'}{C} - \frac{C' \Delta C}{C^2} \right\},$$

whence, dividing by (20), we find

$$\frac{\Delta\Theta_r}{\Theta_r} = \frac{\Delta C}{C} \left(\frac{1}{2} - \frac{C' f'}{3C f} \right) + \frac{\Delta C' C' f'}{C' 3C f}. \quad (21)$$

In the present case the coefficients in the right-hand side of (21) can be obtained from the work of Overton and Gaffney²¹ on the elastic constants of copper at 4°K and from a graphical differentiation of $f(s,0)$ at the corresponding value of $s=0.314$. Equation (21) then gives

$$\Delta\Theta_r/\Theta_r = (0.324\Delta C + 0.914\Delta C') \times 10^{-12}. \quad (22)$$

Figure 7 shows the observed variation of $\Delta\Theta_r/\Theta_r$ and that calculated from (22), using the room-temperature variation of C and C' with solute concentration. It is clear that, although there is a general agreement about the magnitude of the change, the two curves differ significantly in their markedly different curvatures. This difference is not due to any effects arising from the approximations used in calculating the coefficients in (21), since the second derivative of $f(s,0)$ is relatively small. Presumably, then, the functional dependence of the shear constants on electron concentration must alter appreciably as the temperature is lowered. It is believed that this alteration results from the effects of electron excitation on the shear constants. When the Fermi

²¹ W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1955).

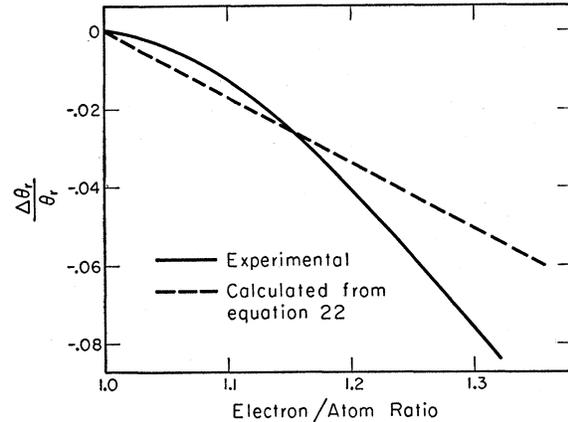


FIG. 7. Comparison of experimental and calculated $\Delta\Theta_r/\Theta_r$.

surface is at or near a zone boundary, these effects can be quite marked. Low-temperature ultrasonic pulse measurements of the elastic constants for these alloy systems are planned in order to check these conclusions.

V. CONCLUSION

From experiments on the low-temperature heat capacity of the primary phases of the copper-zinc and copper-germanium systems, it is concluded that the Fermi surface in copper departs appreciably from sphericity and in fact almost touches the hexagonal faces of the first Brillouin zone. The dependence of the reduced Debye temperature on electron/atom ratio is the same for both systems, which suggests that it is the principal factor influencing the variation of shear constants with solute concentration. It is also concluded that the functional dependence of the shear constants on electron concentration varies with temperature as a result of electron excitation effects.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of Mr. C. P. Mueller of the Technology Department of the Westinghouse Research Laboratories in preparing the specimens used for these experiments.