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Band Structure of Noble Metal Alloys: Optical Absorption in α-Brasses at 4.2°K

M. A. BIONDI AND J. A. RAYNE
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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Calorimetric optical absorption measurements at 4.2°K have been made on a representative series of α brasses over the wavelength range 0.23 to 4.0 microns using electropolished bulk specimens. Changes in the absorption spectrum below 6000 A are interpreted in the light of current theories concerning the band structure of noble metal alloys. The variation of the infrared absorptivity with residual resistivity shows that the impurity relaxation time for copper is anisotropic. This anisotropy increases on alloying and suggests that the Fermi surface becomes more distorted with increasing solute concentration.

I. INTRODUCTION

RELATIVELY little attention has been given to optical absorption measurements as a means of studying the electronic structure of alloys, particularly those involving the noble metals as solvents. Until quite recently, the only data relating to the latter were those given by early experiments on the copper-nickel,[1,2] copper-zinc,[3] and copper-aluminum[4] primary solid solutions. These measurements were all made on mechanically polished surfaces, using the conventional polarimetric method of Drude[5] to obtain values of n and k over a relatively restricted range (approximately 0.4-1 μ). Owing to the disturbed nature of the reflecting surfaces caused by mechanical polishing, the sensitivity of the Drude method to fine scratches on the samples and also owing to the fact that, at room temperature, the effects of lattice vibrations and the diffuseness of the Fermi distribution function smear out the transitions, the data gave very little detailed information on the changes in the absorption structure on alloying.

According to Mott,[6] the main absorption edge in copper is due to electron transitions from the d-band of the crystal to unoccupied states at the top of the Fermi distribution, the minimum frequency of the edge corresponding to the energy separation between the two. Hence on alloying, the shift in the absorption edge should equal the associated displacement of the Fermi level, it being supposed there is very little change in the relatively low-lying d-band. The addition of zinc or aluminum, which contribute additional electrons to the conduction band, should therefore give a shift in the absorption edge to higher energy, i.e., shorter wavelengths. More recently, however, Friedel[7] has proposed a modification of the Mott theory taking into account the screening by the conduction electrons of the hole in the d-band. According to this view, the main absorption edge in copper should not differ sensibly from the excitation energy $3d^{10} \rightarrow 3d^9 4s$ for the isolated Cu^+ ion, the secondary structure in the region below 3000 A[8] being associated with the excitation energy $3d^{10} \rightarrow 3d^9 4p$. Alloying should therefore not cause any appreciable shift in the absorption edge, apart from relatively small effects due to changes in Coulomb interaction between the screening charge and the lattice, exchange interactions, etc.

As a result of the broadness of the absorption edges, the restricted frequency range covered, and the small number of alloy systems studied, the older work is not capable of discriminating between these theories in a satisfactory way or of providing useful information about the band structure of noble metal alloys in general. There is thus a great need for reliable optical absorption measurements, using the improved techniques of sample preparation and measurement now available, on an extensive series of alloy systems. The present work was undertaken to provide such data, and in this paper the results of experiments on the copper-zinc primary solid solutions, covering the wavelength range 0.23-4 μ, are presented.

II. EXPERIMENTAL

Measurements were made at liquid helium temperatures using the calorimetric technique developed for experiments[9] on the infrared absorptivity of copper and silver at 4.2°K. A schematic diagram of the apparatus is shown in Fig. 1. Light from a grating monochromator or suitable infrared filter enters the system through an electropolished stainless steel light pipe, which also serves to evacuate the inner assembly, thereby preventing significant gas conduction. A quartz lens focuses the incident energy at an angle of incidence of 15° onto the target, which is screwed into a copper stage containing a carbon resistance thermometer and a 100-ohm manganin wire heater. The radiation is then reflected onto an absorber, which has a similar heater and thermometer and which is coated with palladium black so as to have substantially zero reflectance over the wavelength range of the present experiments.

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[1] Lowery, Bor, and Wilkinson, Phil. Mag. **20**, 390 (1935).

[2] Bor, Hobson, and Wood, Proc. Phys. Soc. (London) **51**, 942 (1939).

[3] Lowery, Wilkinson, and Smare, Proc. Phys. Soc. (London) **49**, 345 (1937).

[4] L. McPherson, Proc. Phys. Soc. (London) **52**, 210 (1940).

[5] See, for example, M. P. Givens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 336.

[6] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 119.

[7] J. Friedel, Proc. Phys. Soc. (London) **B65**, 769 (1952).

[8] W. Meier, Ann. Physik **31**, 1017 (1910).

[9] M. A. Biondi, Phys. Rev. **102**, 964 (1956).

Both the target and absorber stages are supported by thin walled stainless steel tubing connected to a heavy copper base in contact with the helium bath. This base also contains a heater and a thermometer, which are used in an electronic control circuit to maintain the base temperature constant to within about 0.0001°K. Fine copper wires provide the desired heat leaks from the stages to the base so that, with radiant energy incident on the system, temperature differences are set up across the heat leaks proportional to the power absorbed by the target and absorber. These temperature differences are measured by the carbon resistance thermometers. By reproducing the resistance changes by means of dc power applied through the respective heaters, the absolute absorptivity can be simply calculated from the formula, $A=P_T/(P_T+P_A)$, where P_T and P_A are the power required to reproduce the temperature rises of the target and the absorber, respectively.

In applying this formula to calculate the absorptivity of the samples in the infrared, small corrections have to be applied to allow for the effects of scattered light leaking onto the target stage. Although this stray radiation is minimized by placing behind the target a blackened stop in good thermal contact with the base, the residual leakage still accounts for a few percent of the total absorption owing to the high reflectivity of the targets in the infrared. The appropriate corrections were determined by noting the apparent heat flux to the target stage with a dummy sample, thermally isolated from the stage, reflecting the incident radiation.

To cover the wavelength range of these experiments, band pass interference filters were used in conjunction with a Nichrome glower for the region 3.0–4.0 microns. From 1–2.5 microns, a Bausch & Lomb 250-mm monochromator with a grating blazed at 1 micron and a tungsten light source were employed. Below 1 micron a grating blazed at 0.3 micron was used, the tungsten source replaced by a high-pressure mercury arc lamp to cover the region from 0.23–0.6 micron. The intensity of the arc lamp was sufficient to enable the monochromator to be operated with good resolution (a window half-width of 60 A) over most of the visible and ultraviolet regions of the spectrum, while still maintaining adequate accuracy. Below about 0.28 micron some difficulty was encountered with scattered light in the monochromator. Although corrections were made for this effect, the absorptivity values in this region are of somewhat doubtful accuracy and should only be taken as indicating the trend of the actual behavior.

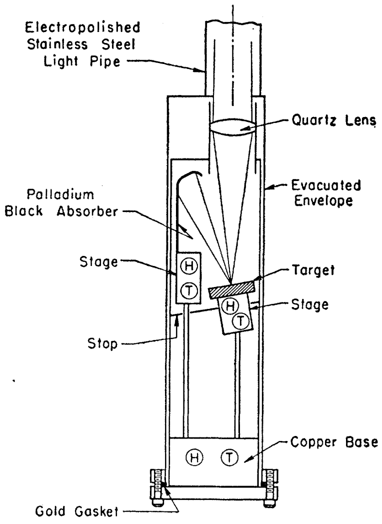

FIG. 1. Schematic diagram of the optical absorption apparatus, which is immersed in the liquid helium bath. The symbols H and T refer to heaters and thermometers, respectively.

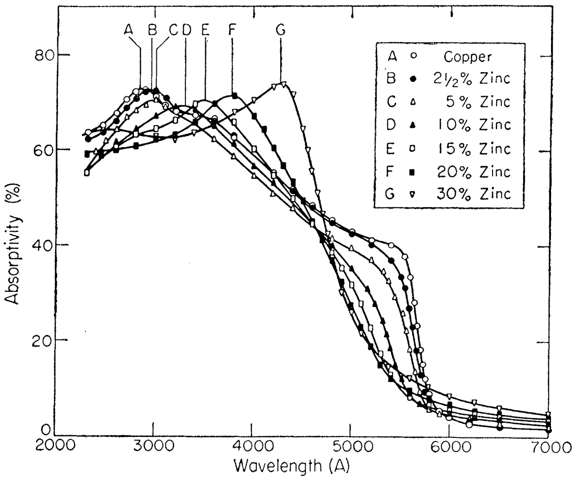

FIG. 2. Optical absorptivity of α-brasses in the ultraviolet and visible wavelength regions. The ultraviolet absorption peaks move toward longer wavelengths (A-G) with increasing solute concentration.

The specimens used in these experiments were machined from ingots, which were formed by induction melting appropriate quantities of high-purity copper and zinc in a helium atmosphere. These ingots were cast in graphite molds, cold worked and subsequently maintained at 800°C for 24 hours to remove coring and to assist in their homogenization. They were next subjected to further cold work in three mutually perpendicular directions (to prevent preferential grain growth) after which optical and residual resistance specimens were machined from them. The resulting samples were then sealed with brass shavings of the same composition in a Pyrex tube under a helium atmosphere and annealed. To prevent exaggerated grain growth, the duration and the temperature of this heat treatment were varied with solute concentration. By careful control of the annealing conditions, a grain size of about 1/100 mm was obtained in all specimens, so that the measured properties can be taken with confidence to be characteristic of polycrystalline material of random orientation.

The targets for the optical absorption measurements were all electropolished using an 80% orthophosphoric acid solution. By varying the voltage across the cell with changing solute concentration, satisfactory surfaces could be obtained for all the specimens used

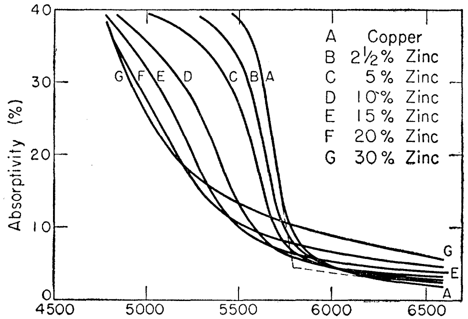

FIG. 3. Details of main absorption edge for α-brasses. The dashed lines indicate the extrapolation procedure used to determine the onset of the main absorption.

in this work. After polishing, the specimens were washed in running hot and cold water to remove the phosphate film on the surface, rinsed and then immersed in distilled water, and finally transferred to a helium dry box where they were dried in a current of helium gas and mounted in the apparatus. The latter was evacuated and cooled to nitrogen temperature as soon as possible after the mounting operation was completed to minimize the danger of surface deterioration in the specimens. In this way quite reproducible absorptivity results were obtained, giving a reasonable assurance that properties measured were in fact those associated with the bulk material.

III. RESULTS

Absorptivity data for the various alloys in the visible and ultraviolet regions of the spectrum are shown in Fig. 2. The main absorption edges are shown in more detail in Fig. 3. Owing to the improved surface quality, the residual absorption beyond the edge is quite small even in the alloys with large zinc concentrations. This circumstance, together with the fact that the measurements were made at low temperatures, thereby eliminating the effects of lattice vibrations and the diffuseness of the Fermi distribution function,[10] results in much sharper edges than had been previously reported.

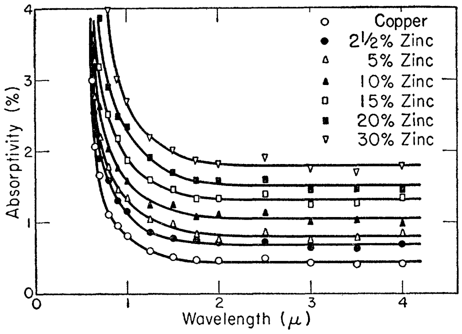

FIG. 4. Infrared absorptivity of α-brasses. It should be noted that the absorption scale is one-tenth that used in the previous figure.

The infrared data for the alloys are shown in Fig. 4, which is drawn on a much enlarged scale compared to Figs. 2 and 3. It will be seen that the absorptivity drops quite sharply in the vicinity of 1 micron and then becomes substantially constant from 1.75 to 4 microns. If the latter values are plotted against the corresponding residual resistivities of the samples, the graph of Fig. 5 results. It is of interest that our residual resistivity data are in good agreement with those of previous workers[11] as may be seen from Fig. 6. This agreement suggests that the metallurgical procedures used in the present work were such as to give reliable, well-annealed samples.

IV. DISCUSSION

(a) Absorptivity in the Visible and Ultraviolet

Reference to Fig. 3 shows quite clearly that alloying moves the main absorption edge to shorter wavelengths. To determine the magnitude of the shift as a function of solute concentration, it is necessary to adopt a somewhat arbitrary procedure as a result of tailing in the data on the long-wavelength side of the edge. Accordingly, we have approximated the curves by straight lines after the manner shown by the dashed lines in Fig. 3 and have taken their point of intersection as the wavelength λ_0 where interband transitions begin. The relative sharpness of the curves on the short-wavelength side of the edge, even for the more concentrated alloys, minimizes the errors involved in this procedure.

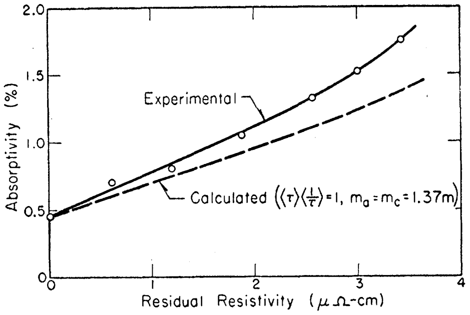

FIG. 5. Variation of infrared absorptivity with residual resistivity of α-brasses. The dashed curve was calculated on the assumption of isotropic impurity scattering from the solute atoms

Values of λ_0 as a function of solute concentration are given in Table I, from which the full curve of Fig. 7 is derived. The displacement of the edge, which is initially quite small, becomes linear with concentration for zinc contents in excess of three percent. Such behavior is not at all consistent with the original theory of Mott, according to which the shift of the edge δE on alloying is equal to the change of the Fermi level, as computed from the rigid band model. In this case we have

$$\delta E = Z\int_0^c \left(\frac{dN}{dE}\right)^{-1} dc, \tag{1}$$

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[10] G. Joos and A. Klopfer, Z. Physik **138**, 251 (1954).

[11] Kemp, Klemens, Tainsh, and White, Acta Met. **5**, 303 (1957).

for a concentration c of solute having a valence Z relative to the solvent. Using the density of states data obtained from low-temperature heat capacity measurements on the α-brasses,[12] Eq. (1) gives for δE the dashed line of Fig. 7. Clearly, it does not represent an adequate fit to the data.

According to Friedel,[13] the Fermi level in an alloy does not behave in the manner predicted by the rigid band model. Thus when zinc is added to copper, the additional valence electrons contributed by the solute are localized in the immediate vicinity of the zinc atoms in order to screen out their additional ionic charge. Because the screening distance is small, the copper atoms in dilute alloys see virtually the same potential as that in the pure metal. This is equivalent to saying that the Fermi level in dilute alloys does not alter appreciably. For more concentrated alloys there is a displacement of the Fermi level, but it is much smaller than that predicted by the older theory. Using the Thomas-Fermi model to treat the effects of screening, Friedel has obtained an expression for the shift in the Fermi level

$$\Delta E = \frac{Zq}{qR\cosh qR - \sinh qR}, \tag{2}$$

where the screening parameter q is related to the density of states in the alloy by the relation

$$q^2 = 4\pi(dN/dE)_0, \tag{3}$$

and where

$$1/R^3 = c/r_s^3, \tag{4}$$

r_s being the radius of the atomic sphere for the solvent atoms. For copper, Eq. (3) gives $q=1.12$ (atomic units)$^{-1}$.

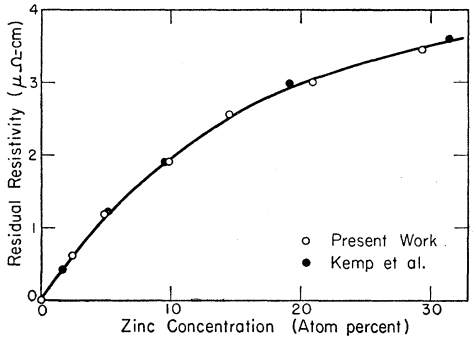

FIG. 6. Variation with solute concentration of residual resistivity for α-brasses.

TABLE I. Values of λ_0, the wavelength corresponding to the main absorption edge, in α-brasses.

Solute concentration (at. %)	λ_0 (A)	E_0 (ev)	δE (ev)
0	5790	2.150	0
2.44	5760	2.161	0.011
4.96	5720	2.177	0.027
10.00	5600	2.223	0.073
14.40	5480	2.272	0.122
21.00	5350	2.327	0.177

If we retain the idea that the energy separation between the top of the d-band and the Fermi level corresponds directly to the quantum energy of the absorption edge, then the displacement of the latter should be given by Eq. (2). As may be seen from Fig. 7, which shows this relation plotted for $q=1.12$, there is a slightly better fit to the data in that the theoretical curve has zero slope as $c \rightarrow 0$ and at least gives the right order of magnitude for the energy shift. No reasonable choice of q, however, gives complete agreement with the experimental results. Hence if the present picture is correct, the screening must differ considerably from that given by the simple Thomas-Fermi model. This, of course, is not unlikely, since the applicability of the Thomas-Fermi model to a stituation where the calculated screening length is considerably smaller than the ionic radius is somewhat doubtful.

The above treatment does not take any account of the screening of the hole in d-band caused by the ejection of an electron to the Fermi level. Friedel[7,13,14] has considered this effect in some detail and has concluded that the main edge in pure copper essentially corresponds to the excitation energy $3d^{10} \rightarrow 3d^9 4s$ for the isolated Cu$^+$ ion, corrected for the Coulomb attraction between the hole and the lattice, exchange effects, etc. Of these the most important appears to be the former, so that on alloying the displacement of the edge should be given by the change in the Coulomb interaction. Hence, using Eqs. (2) and (4), we have[15]

$$\begin{aligned}\delta E &= (p+Zc)\partial\Delta E/\partial c \\ &\simeq \frac{2(p+Zc)Zq^3R^2}{3c(qR-1)^2\exp(qR)},\end{aligned} \tag{5}$$

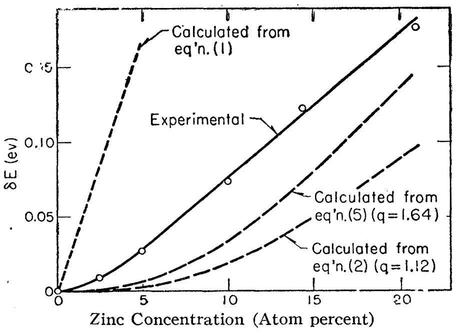

FIG. 7. Variation with solute concentration of displacement of main absorption edge for α-brasses. The dashed curves indicate the displacement expected from the models of Mott and of Friedel.

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[12] J. A. Rayne, Phys. Rev. **108**, 22 (1957).

[13] J. Friedel, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 461.

[14] J. Friedel, Ann. phys. **9**, 158 (1954).

[15] Atomic units are used in these equations.

TABLE II. Values of δE_{Zn} and ΔE_{Zn} for α-brasses.[a]

Solute concentration (at. %)	δE_{Zn} (ev)	ΔE_{Zn} (ev)
5	0	0
10	0.048	0.058
15	0.095	0.107
20	0.143	0.147

[a] Referred to 5% alloy.

where p is the number of conduction electrons/atom of solvent.

The magnitude of the screening constant q may differ from the Mott value given by Eq. (3), because of exchange effects and also because of the more diffuse nature of the screening of the hole in the d-band relative to that of the zinc ions. Taking $q=1.64$, given by Friedel as the screening parameter for copper if exchange effects are considered, we obtain the dashed curve shown in Fig. 7 for the variation of δE with solute concentration. Although the fit to the experimental data is better than that given by the Mott formula, Eq. (1), the concentration dependence does not appear to be correct. If we reduce q to take screening differences into account, no improvement is effected. It must therefore be concluded that the Friedel theory, although correct in a qualitative way, does *not* correctly describe the screening in an alloy for finite solute concentrations.

It is of interest to compare the displacement of the optical absorption edge with the changes in the energy of solution for the copper-zinc system. We define E_A, the energy of solution per atom A at a concentration c in the alloy $A_{cN}B_{(1-c)N}$, by the relation

$$A_{cN-1}B_{(1-c)N}+A \rightarrow A_{cN}B_{(1-c)N-1}+B+E_A, \qquad (6)$$

N being a large number. Experimental data are usually interpreted in terms of a quantity E_A' given by

$$A_{cN-1}B_{(1-c)N}+A \rightarrow A_{cN}B_{(1-c)N}+E_A', \qquad (7)$$

which is related to E_A by the Duhem-Margules equation[13]

$$E_A=\frac{E_A'}{1-c}-\int_0^c E_A' d\left(\frac{c}{1-c}\right). \qquad (8)$$

Friedel has shown that the changes in energy of solution on alloying ΔE_{Zn}, should be the same as the displacements δE_{Zn} of the optical edge, apart from differences in screening between a hole in the d-band and a zinc ion. Using the data of Herbenar *et al.*[16] giving E_{Zn}', ΔE_{Zn} can easily be computed from Eq. (8). The values of ΔE_{Zn} relative to the alloy for $c=0.05$ are given in Table II, together with the associated values of δE_{Zn} taken from the smooth curve of Fig. 7. The agreement is very good, being within experimental error, and suggests that the above-mentioned differences in screening are small.

Reference to Fig. 2, Curve A, shows that the absorption in pure copper exhibits secondary structure at about 3200 A. It has been suggested by Friedel[7] that this structure is associated with a screening of the hole in the d-band corresponding to the excitation energy $3d^{10} \rightarrow 3d^9 4p$ for the free Cu$^+$ ion. One would thus expect relatively little change in the form of this part of the absorption curve on alloying, or at least a shift in the same direction as the main edge. Such is clearly not the case; the peaks of the absorption curves, which are designated by the letters A to G in Fig. 2, move from 2900 A in pure copper to 4300 A for a thirty percent zinc alloy. It thus seems unlikely that Friedel's theory is correct.

The interpretation of the absorptivity data below the main edge is complicated by the fact that transitions can take place both from the d-band to the Fermi level and from the Fermi level to the next zone, presumably in the $\langle 111\rangle$ directions. There is consequently considerable uncertainty about the wavelength at which the latter process is initiated. In particular no quantitative information can be obtained regarding its change with alloying, except that it definitely shifts to longer wavelengths.

The shape of the absorption curve for the 30% alloy suggests that both transitions begin simultaneously at about 4800 A, i.e., 2.6 ev. On the basis of this hypothesis, we can make an estimate of the energy gap for copper along the [111] direction. Let us first adopt the rigid band model and suppose that the Fermi surface in copper, although nonspherical, does not touch the zone boundary and that on alloying contact takes place at a zinc concentration of about 10%.[17] Once contact has occurred, transitions from the center of the zone face can no longer take place. However, one may reasonably suppose that, providing the contact area does not become too large, the minimum energy for excitation from the Fermi surface into the next zone will still approximate the gap in the [111] direction for pure copper. Thus, the value of the gap is roughly 2.6 ev. Various theoretical estimates of the energy gap are available but none of these can be taken very seriously as a result of the extreme sensitivity of the value to the starting ionic potential used in the calculations. Thus, for example, Howarth,[18] using the cellular method, found a value of 0.24 ev with a Hartree Cu$^+$ potential and 1.7 ev with a Hartree-Fock potential. The present figure is much lower than the value of 7.65 ev deduced by Pippard[19] from his work on the anomalous skin effect in copper.

If instead of the above model we adopt that of Cohen and Heine,[20] which assumes that contact between

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[16] Herbenar, Siebert, and Duffenback, J. Metals **188**, 323 (1950).

[17] At this value the variation of γ with zinc concentration exhibits a marked change in slope. See reference 12.

[18] D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).

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

[20] M. H. Cohen and V. Heine, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 7, p. 395.

the Fermi surface and the Brillouin zone already occurs in copper across the {111} faces, then the gap across these faces decreases on alloying. This model would thus predict that the resulting absorption edge moves to longer wavelengths with increasing zinc concentration, in apparent agreement with the present work. Provided that contact between the zone face and the Fermi surface is maintained on alloying, the energy gap for the alloy with $c=0.3$ would be 2.6 ev according to this view. To obtain the gap for pure copper, it is necessary to use the formula[20]

$$\bar{\Delta}_{sp}-(\Delta_{sp})_{\text{solvent}}$$
$$=\frac{e/a-1}{e/a}\left(1+\frac{1}{Z}\right)[(\Delta_{sp})_{\text{solute}}-(\Delta_{sp})_{\text{solvent}}]. \quad (9)$$

For $(\Delta_{sp})_{\text{solute}}=5.8$ ev, $(\Delta_{sp})_{\text{solvent}}=3.8$ ev, $c=0.3$, Eq. (9) gives

$$\bar{\Delta}_{sp}-(\Delta_{sp})_{\text{Cu}}=0.9 \text{ ev}. \quad (10)$$

Since the p level is presumed to lie below the s level, the gap for copper is thus estimated to be 3.5 ev.

As will presently be demonstrated, however, the infrared absorptivity data suggest that the Fermi surface must become *more* distorted on alloying. This would necessitate that the gap *increase* and hence that the corresponding absorption edge move to shorter wavelengths. The present data are inconsistent with such a conclusion and hence we must depend on the rigid band model for an estimate of the gap.

(b) Absorptivity in the Infrared

From Fig. 4 it can be seen that the absorption data beyond the main absorption edge exhibit considerable tailing out to approximately 1.75 μ. In this region the curves all behave in a strikingly similar way, being roughly parallel to each other. It has been suggested by Biondi[9] that, in the case of copper, the tailing may result from the effect of indirect transitions. Such a suggestion cannot be correct, since phonons having an energy of approximately 1 ev would be required in such processes and these cannot exist in a metal. Again, it has been suggested that the effects of electron-electron interactions could account for the observed behavior. This explanation also cannot be correct, since the frequency dependence of such an absorption process would in a simple theory be given by[21]

$$A_{\text{electron-electron}} \propto \omega^2, \quad (11)$$

which exponent is far too small to account for the above data. It is equally impossible to ascribe the effects to collision damping, since for copper the plasma frequency $\omega_p=(4\pi Ne^2/m)^{\frac{1}{2}}$ corresponds to a wavelength of 1400 A. At the moment, no plausible explanation can be advanced for the observed behavior.

Beyond 1.75 microns the absorption is constant, within experimental error, up to the wavelength limit of the present data; *viz.*, 4 μ. In this range, the absorptivity can be written as the sum of three contributions,

$$A=A_{\text{surface}}+A_{\text{volume}}+A_{\text{impurity}}, \quad (12)$$

where the effects of these can be considered *independently* provided that the scattering probabilities for each process are small. This condition is presumably satisfied for the systems studied here.

The first term of Eq. (12) results from scattering of the electrons by the surface of the metal. It has been shown[22] that for the case of diffuse scattering, which assumption best fits the experimental data at microwave frequencies,[23] the surface absorption of a cubic metal is given by an expression

$$A_{\text{surface}}=\tfrac{3}{4}v/c, \quad (13)$$

where v is an effective electron velocity defined in terms of an integral over the Fermi surface of the metal. For a nonspherical energy surface v is a function of the crystallographic direction, but if we consider polycrystalline specimens, an equation of the form given by (13) will still apply if for the velocity we take a simple geometrical average, $\tilde{v}$, given by

$$\tilde{v}=(1/4\pi)\int v(\Omega)d\Omega. \quad (14)$$

In order for Eq. (13) to hold, the condition

$$\omega_0 \gg \omega \gg v/\delta_f; \quad \delta_f=(mc^2/4\pi Ne^2)^{\frac{1}{2}}, \quad (15)$$

must be fulfilled, ω_0 being the frequency corresponding to the onset of the internal photoelectric absorption. It is easily shown that this equation is satisfied for the wavelength region being considered.

The volume absorption arises from the interaction of the electrons with the zero-point vibration of the lattice. This interaction has been considered by Holstein[24] and also by Gurzhi.[25] Using the usual approximations of conductivity theory, *viz.*, spherical energy surfaces, acoustical isotropy, etc., Holstein was able to obtain an explicit expression for the volume absorption of the form

$$A_{\text{volume}}=(m^*/\pi Ne^2)^{\frac{1}{2}}(1/\tau_{\text{eff}}), \quad (16)$$

where τ_{eff} is an effective relaxation time related to the usual conductivity relaxation time τ at a temperature $T \gg \theta$ by the equation

$$\tau_{\text{eff}}=\tfrac{5}{2}T\tau/\theta, \quad (17)$$

θ being the Debye temperature. Although no closed ex-

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[21] V. P. Silin, J. Exptl. Theoret. Phys. U. S. S. R. **34**, 707 (1958) [translation: Soviet Phys. JETP **7**, 486 (1958)].

[22] T. Holstein, Phys. Rev. **88**, 1427 (1952); M. I. Kaganov and V. Slezov, J. Exptl. Theoret. Phys. U. S. S. R. **32**, 1496 (1957) [translation: Soviet Phys. JETP **6**, 1216 (1957)].

[23] R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).

[24] T. Holstein, Phys. Rev. **96**, 535 (1954).

[25] R. N. Gurzhi, J. Exptl. Theoret. Phys. U. S. S. R. **33**, 451 (1957) [translation: Soviet Phys. JETP **6**, 352 (1958)].

pression for the volume absorption of a material with a nonspherical Fermi surface and arbitrary acoustical properties is available, one may anticipate that it is possible to define a suitably averaged relaxation time which will result in an equation similar to (16) for this case.

An expression for the impurity absorptivity may be obtained by solving the Boltzmann equation for a periodic electromagnetic field assuming the existence of a relaxation time for impurity scattering. In the near infrared, where $\omega\tau\gg1$, the absorptivity may be expressed in the form (see Appendix)

$$A_{\text{impurity}}=\langle\tau\rangle\langle1/\tau\rangle(Ne^2/\pi m_a)^{\frac{1}{2}}\rho_{\text{impurity}}, \tag{18}$$

where ρ_{impurity} is the residual resistivity due to impurities and $\langle\tau\rangle$, $\langle1/\tau\rangle$ are averages of the impurity relaxation time defined by the following integrals over the Fermi surface:

$$\langle\tau\rangle=\int\tau vdS\Big/\int vdS;\quad \langle1/\tau\rangle=\int\frac{vdS}{\tau}\Big/\int vdS. \tag{19}$$

From the Schwarz inequality it may readily be shown that

$$\langle\tau\rangle\langle1/\tau\rangle\geqslant1, \tag{20}$$

the equality sign holding for isotropic impurity scattering. The quantity $1/m_a$ appearing in (18) is the usual inverse effective mass, which for cubic metals is given by the equation

$$\frac{1}{m_a}=\frac{1}{12\pi^3N\hbar^2}\int\nabla_k{}^2Ed\mathbf{k}, \tag{21}$$

N being the density of conduction electrons.

In the region of interest, the absorptivity of the alloys may thus be expressed in the form

$$A=A_{\text{surface}}+A_{\text{volume}}+\beta\rho_{\text{impurity}}, \tag{22}$$

where

$$\beta=\langle\tau\rangle\langle1/\tau\rangle(Ne^2/\pi m_a)^{\frac{1}{2}}. \tag{23}$$

It may readily be shown that the first two terms change only slowly with solute concentration, so that the impurity term dominates the variation of the absorptivity with residual resistivity. In particular, the initial slope of the curve of absorptivity *versus* residual resistivity should be essentially equal to β_0, the value of β for pure copper. Using the value of $m_a=1.45m$ for copper derived from the room temperature measurements of Schulz[26] and setting $\langle\tau\rangle\langle1/\tau\rangle=1$, we obtain a slope from (22) which deviates markedly from the experimental one. No reasonable choice of m_a effects a material improvement in the fit to the data, a value of $m_a/m=0.61$ being required to obtain complete agreement with experiment. Such a figure is clearly untenable and we must conclude that $\langle\tau\rangle\langle1/\tau\rangle$ is greater than unity, i.e., the impurity scattering relaxation time in copper is *anisotropic.*

This result is of considerable importance, since it constitutes experimental proof that much theoretical work done in the past is based on an unjustified assumption. In particular, the analysis by Olsen and Rodriguez[27] of their magnetoresistance data on copper at low temperatures cannot be correct since they assumed τ to be isotropic. Their conclusions relating the magnetoresistance coefficients to the geometry of the Fermi surface in copper are consequently open to question. Furthermore, if the *impurity* relaxation time in copper is anisotropic, there is very little doubt that the *phonon* relaxation time at high temperatures is also anisotropic. Thus treatments of transport processes, which make the assumption of isotropy for phonon scattering, are probably not accurate and conclusions about the Fermi surfaces in metals derived from them must be viewed with some suspicion.

As shown in the Appendix, τ will be isotropic and the product $\langle\tau\rangle\langle1/\tau\rangle$ will be unity, if the Fermi surface is spherical and the scattering probability $P(\mathbf{k},\mathbf{k}')$ depends only on the angle between $\mathbf{k}$ and $\mathbf{k}'$. No general proof exists for the conditions under which the second requirement will hold, but it seems reasonable to suppose that it will be true for spherical energy surfaces and that the product $\langle\tau\rangle\langle1/\tau\rangle$ is only unity in such cases. Further one may assume that this product is a monotonic function of the deviation of the Fermi surface from sphericity and that the larger the distortion of the surface, the greater will be the value of $\langle\tau\rangle\langle1/\tau\rangle$. For pure copper our data indicate that $\langle\tau\rangle\langle1/\tau\rangle=1.30\pm0.05$, which suggests a highly distorted Fermi surface, in agreement with the results of other experiments.[20]

Now according to Cohen and Heine the Fermi surface in copper alloys becomes *less* distorted with increasing solute concentration. In particular, they claim that, at the limit of the α phase of systems such as the one studied here, the Fermi surface is essentially spherical and just touches the zone boundary. If this were true and our assumptions regarding the isotropy of τ are correct, then the experimental data of Fig. 5 would tend towards the dashed curve[28] defined by Eq. (22) with $\langle\tau\rangle\langle1/\tau\rangle=1$ and $m_a=m_c=1.37m$. The latter value corresponds to the effective mass parameter of the *spherical* parts of the Fermi surface in copper[29] as derived from cyclotron resonance measurements.[30] This behavior clearly does not take place, and we must conclude that the energy surface does *not* become more spherical on alloying. In fact the experimental data are consistent with a $\langle\tau\rangle\langle1/\tau\rangle$ which increases on alloying, leading

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[26] L. G. Schulz, J. Opt. Soc. Am. **44**, 540 (1954); J. Phil. Mag. **6**, 102 (1957).

[27] R. L. Olsen and R. Rodriguez, Phys. Rev. **108**, 1212 (1957).

[28] The theoretical dashed curve has been corrected for changes in A_{surface} and A_{volume} on alloying.

[29] It is assumed that the curvature of these sections of the surface does not change appreciably on alloying.

[30] Langenberg, Kip, and Rosenblum, Bull. Am. Phys. Soc. Ser. II, **3**, 416 (1958).

to the conclusion that the Fermi surface becomes more distorted with increasing zinc concentration.

This result again raises the fundamental difficulty, pointed out by Cohen and Heine, of reconciling the Hume-Rothery rules and results of specific heat measurements on the α-brasses with the shape of the Fermi surface for copper derived by Pippard.[19] If we rule out the possibility of an increase in the sphericity of the Fermi surface on alloying, then the energy gap in the [111] direction cannot *decrease* with increasing zinc concentration. The present data for the visible and ultraviolet show, however, that it cannot *increase*. Thus, we can only conclude that the gap remains essentially constant, i.e., the rigid band model still applies. In this situation the only possible way of obtaining consistency between the experiments is to suppose that the Fermi surface in copper is only *close* to the {111} faces of the first Brillouin zone, but does not actually touch them.

This hypothesis also presents difficulties, since the measurements of Schulz have shown that for copper $m_a/m_t>1$, where the effective thermal mass m_t is given by the relation

$$m_t/m=\gamma/\gamma_{\text{free}}. \tag{24}$$

γ is the coefficient of the linear term in the heat capacity of a metal at low temperatures, and γ_{free} is the corresponding coefficient for an electron gas of the same density. Cohen[31] has demonstrated that a ratio greater than unity indicates a Fermi surface having *considerable* area of contact with the zone boundaries, which is contrary to our previous conclusion. It is possible of course that the value of m_a for copper, deduced from Schulz' measurements, is inaccurate because of the difficulty of making experiments on thin films. If such is not the case, one must entertain doubts either about our assumptions regarding the relation between the shape of the Fermi surface and the anisotropy of τ or about the applicability of the one-electron theory to alloys at all. Before making such inferences, however, more experiments on other alloys (including those based on silver and gold) should be made.

V. CONCLUSIONS

From the results of optical absorption measurements on the α-brasses at 4.2°K, it is concluded that the main absorption edge in copper is due to electron transitions between the d-band and the Fermi level. The observed shift of the edge on alloying is found to be inconsistent with the original theory due to Mott. Although the Friedel theory gives a better fit to experiment, there is still quantitative disagreement regarding the dependence of the shift on solute concentration. From the secondary structure of the absorption in the ultraviolet, it is concluded that the gap across the {111} faces in copper is approximately 2.6 ev. The variation of infrared absorptivity with residual resistivity indicates that anisotropy of the impurity relaxation time increases on alloying and that the Fermi surface becomes more distorted with increasing solute concentration.

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APPENDIX

Assuming the existence of a relaxation time τ, the general form of the Boltzmann equation is

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{r}}+\frac{e}{\hbar}(\boldsymbol{\mathcal{E}}+\mathbf{v}\times\boldsymbol{\mathcal{H}})\cdot\frac{\partial f}{\partial \mathbf{k}}=-\frac{f-f_0}{\tau}. \tag{A1}$$

For a plane electromagnetic wave polarized along the x direction this reduces to

$$\frac{\partial f}{\partial t}+\frac{e}{\hbar}\mathcal{E}_x\frac{\partial f}{\partial k_x}=-\frac{f-f_0}{\tau}, \tag{A2}$$

which has a periodic solution of the form

$$f=f_0-\frac{\tau e}{\hbar}\frac{\partial f_0}{\partial k_x}\operatorname{Re}\left(\frac{\mathcal{E}_x}{1+i\omega\tau}\right). \tag{A3}$$

Using Eq. (A3), we find for the current

$$\begin{aligned} J_x&=\frac{2e}{(2\pi)^3}\int f v_x d\mathbf{k}\\ &=-\frac{e^2}{4\pi^3\hbar^2}\int \tau\frac{\partial f_0}{\partial E}\left(\frac{\partial E}{\partial k_x}\right)^2\operatorname{Re}\left(\frac{\mathcal{E}_x}{1+i\omega\tau}\right)d\mathbf{k}. \end{aligned} \tag{A4}$$

For a cubic metal this reduces to

$$J_x=-\frac{e^2}{12\pi^3\hbar^2}\int \tau\frac{\partial f_0}{\partial E}|\nabla_k E|^2\operatorname{Re}\left(\frac{\mathcal{E}_x}{1+i\omega\tau}\right)d\mathbf{k}. \tag{A5}$$

Since $d\mathbf{k}=dSdE/|\nabla_k E|$, (A5) may be written as

$$J_x=\frac{e^2}{12\pi^3\hbar^2}\int \tau|\nabla_k E|\operatorname{Re}\left(\frac{\mathcal{E}_x}{1+i\omega\tau}\right)dS, \tag{A6}$$

where the integration over E has been carried out. Thus we have

$$J_x=\left(\frac{e^2}{12\pi^3\hbar^2}\int\frac{|\nabla_k E|\tau dS}{1+\omega^2\tau^2}\right)\mathcal{E}_x-\left(\frac{e^2}{12\pi^3\hbar^2}\int\frac{|\nabla_k E|\tau^2 dS}{1+\omega^2\tau^2}\right)\frac{\partial\mathcal{E}_x}{\partial t}. \tag{A7}$$

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

Identifying the real and imaginary parts of the dielectric constant $\epsilon=(n+ik)^2$ with the coefficients of these terms we have, since $k\gg n$ in this region,

$$nk\omega=\frac{e^2}{6\pi^2\hbar^2}\int|\nabla_kE|\frac{\tau dS}{1+\omega^2\tau^2},$$
$$n^2-k^2=1-\frac{e^2}{3\pi^2\hbar^2}\int|\nabla_kE|\frac{\tau^2dS}{1+\omega^2\tau^2}. \qquad \text{(A8)}$$

For $\omega\tau\gg1$, which condition holds for all alloys studied here, Eqs. (A8) reduce to

$$nk=\frac{e^2}{6\pi^2\hbar\omega^3}\int\frac{vdS}{\tau},$$
$$k^2=\frac{e^2}{3\pi^2\hbar\omega^2}\int vdS. \qquad \text{(A9)}$$

At normal incidence we have

$$A=1-\frac{(n-1)^2+k^2}{(n+1)^2+k^2}\simeq\frac{4nk}{k^3}, \qquad \text{(A10)}$$

so that from Eqs. (A9)

$$A=\frac{1}{(e^2/12\pi^2\hbar)^{\frac{1}{2}}}\int\frac{vdS}{\tau}\bigg/\left(\int vdS\right)^{\frac{3}{2}}. \qquad \text{(A11)}$$

Since

$$\rho_{\text{impurity}}=\frac{1}{(e^2/12\pi^3\hbar)}\frac{1}{\int\tau vdS},$$

Eq. (A10) may be written in the form

$$A_{\text{impurity}}=\left(\frac{e^2}{12\pi^4\hbar}\right)^{\frac{1}{2}}\left(\int vdS\right)^{\frac{1}{2}}\langle\tau\rangle\langle1/\tau\rangle\rho_{\text{impurity}}, \qquad \text{(A12)}$$

where

$$\langle\tau\rangle=\int\tau vdS\bigg/\int vdS;\quad \langle1/\tau\rangle=\int\frac{vdS}{\tau}\bigg/\int vdS.$$

Equation (A12) may further be reduced if we introduce the inverse effective mass defined for a cubic metal by the equation

$$\frac{1}{m_a}=\frac{1}{12\pi^3N\hbar^2}\int\nabla_k{}^2E d\mathbf{k}=\frac{1}{12\pi^3N\hbar}\int vdS, \qquad \text{(A13)}$$

N being the density of conduction electrons. Substituting Eq. (A13) into Eq. (A12) we find

$$A_{\text{impurity}}=\langle\tau\rangle\langle1/\tau\rangle(Ne^2/\pi m_a)^{\frac{1}{2}}\rho_{\text{impurity}}. \qquad \text{(A14)}$$

The Schwarz inequality gives the result

$$\int\tau vdS\int\frac{v}{\tau}dS\geqslant\left(\int vdS\right)^2, \qquad \text{(A15)}$$

whence from Eq. (A12)

$$\langle\tau\rangle\langle1/\tau\rangle\geqslant1, \qquad \text{(A16)}$$

the equality holding for isotropic scattering.

If we write $f=f_0+\phi$, the equation giving the rate of change of f due to collisions is

$$\left(\frac{\partial f}{\partial t}\right)_{\text{collisions}}=\int[\phi(\mathbf{k}')-\phi(\mathbf{k})]P(\mathbf{k},\mathbf{k}')dS', \qquad \text{(A17)}$$

where

$$P(\mathbf{k},\mathbf{k}')dS=|\langle\mathbf{k}'|V|\mathbf{k}\rangle|^2\frac{dS}{4\pi^2\hbar|\nabla_kE|}.$$

For spherical energy surfaces and for $P(\mathbf{k},\mathbf{k}')$ depending only on the angle θ between $\mathbf{k}$ and $\mathbf{k}'$, we may write $\phi=k_xc(E)$, assuming the field to be along the x axis. Equation (A17) then reduces to

$$\frac{1}{\tau(\mathbf{k})}=\int P(\mathbf{k},\mathbf{k}')\left(1-\frac{k_x'}{k_x}\right)dS', \qquad \text{(A18)}$$

i.e.,

$$\frac{1}{\tau(\mathbf{k})}=2\pi k^2\int_0^\pi P(\theta)(1-\cos\theta)\sin\theta d\theta,$$

which depends only on the magnitude of k, i.e., τ is isotropic.

Since $\psi_k(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_k(\mathbf{r})$, the general form of the matrix element determining the scattering probability $P(\mathbf{k},\mathbf{k}')$ is

$$\langle\mathbf{k}'|V|\mathbf{k}\rangle=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{\mathbf{k}'}{}^*(\mathbf{r})V(\mathbf{r})u_{\mathbf{k}}(\mathbf{r})d\mathbf{r}. \qquad \text{(A19)}$$

Clearly, the explicit dependence of this integral on $\mathbf{k}$ and $\mathbf{k}'$ is determined by the nature of $u_k(\mathbf{r})$ and $u_{k'}(\mathbf{r})$. As far as is known, there is no general proof that $P(k,k')$ will depend only on θ and that τ will be isotropic if and only if the Fermi surface is spherical. Such an assumption, however, does not seem unreasonable and we suppose that the product $\langle\tau\rangle\langle1/\tau\rangle$ is a measure of the sphericity of the Fermi surface.