

v_s is the sound velocity, and assumes for a simple deformation potential, $|M(\mathbf{q})|^2 = g^2 \Omega_q$, where g^2 is a coupling constant¹⁵ with dimensions (energy \times volume), one obtains

$$\sigma_{dc}^{-1} = \frac{g^2}{3\pi^3} \left(\frac{m}{\hbar e n} \right)^2 \frac{v_s}{(\beta \hbar v_s)^5} J_5(\beta \Omega_m), \quad (85)$$

$$J_5(\beta \Omega_m) = \int_0^{\beta \Omega_m} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}. \quad (86)$$

Expression (85) is, of course, the standard Bloch-Grüneisen result.

¹⁵ For a screened Coulomb interaction between the electrons and ion cores, one may reasonably expect that $g^2 = \alpha^2 (4\pi e^2 / k_s^2)$, where k_s is the inverse Thomas-Fermi screening length, and where α^2 is a dimensionless coupling constant of order unity.

In conclusion, it would appear to be of some interest to develop methods of applying these variational principles in a more systematic fashion. Another aspect of the general problem, which merits further consideration, is the question of how to generalize these variational methods to take account of the "phonon-drag" effect.

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Optical Absorption of Copper and Copper-Rich Copper Nickel Alloys at Room Temperature

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The optical absorption of Cu and Cu-Ni alloys was measured on solid samples at room temperature. Light in the visible and ultraviolet region was used. It was found that the wavelength position of the main absorption edge did not change with alloying. It disappeared, however, for alloys with 20 and 25 at.% Ni. The position of the secondary absorption peak moved slightly to lower wavelengths with increasing nickel concentration. The measurements indicate that the optical properties of Cu-Ni alloys cannot be described with a rigid-band model. It is more likely that the addition of nickel to copper creates "virtual energy states," instead of shifting the Fermi energy.

INTRODUCTION

THE optical absorption of copper in the visible and ultraviolet region shows two absorption structures. The secondary absorption edge (its maximum is approximately at 300 nm) and the main absorption edge (its maximum is approximately at 550 nm) have been attributed to interband transitions by several authors with different models. Mott and Jones¹ have attributed the secondary absorption edge to the transitions of electrons near the Fermi surface to the next higher zone, and the main absorption edge to the transitions from the d band to the empty states above the Fermi surface. The longer-wavelength side of the main absorption edge (approximately at 575 nm) has been interpreted as the minimum energy distance between the d band and the Fermi surface of copper.

Ehrenreich and Philipp^{2,3} compared the absorption

edge energies of copper determined from experiments with the energy distances between the symmetry points of the d band and the conduction band which have been obtained from Segall's⁴ calculations. They have found good agreement between calculated band structure and experiment. According to their interpretation, the secondary absorption edge corresponds to the transitions between X_5 and X_4' , and the main absorption edge corresponds to the transitions between L_{32} and the neck region near L_2' .

Mott and Jones have assumed that the addition of small amounts of impurities into copper will not affect the inner d band. Therefore, the changes will occur only at the Fermi surface. For example, alloying Cu with Zn increases the electron concentration. This will shift the Fermi level to higher energies but will not affect the d band. This rigid-band model predicts that the addition of Zn to Cu shifts the position of the main absorption edge to shorter wavelengths and the position of the secondary absorption edge to longer ones. The results of the systematic studies of Cu-Zn alloys by Biondi

¹ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc. New York, 1958), p. 118.

² H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).

³ H. Ehrenreich, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Company, Amsterdam, 1966), pp. 109-133.

⁴ B. Segall, *Phys. Rev.* **125**, 109 (1962).

and Rayne⁵ are in qualitative agreement with the rigid-band model of Mott and Jones, although the shifts predicted by the rigid-band theory were much larger than the observed values.

Although for the copper-zinc system the rigid-band model is a good first approximation, it seems doubtful that this model will describe the optical properties of copper-nickel alloys, since nickel has an unfilled *d* shell.

According to Mott,^{6,7} the *d* band in copper nickel alloys containing less than 40% nickel is completely filled. Alloying Cu with up to 40% Ni should shift the Fermi energy toward smaller energy levels. The energy gap between the top of the *d* band and the Fermi level should therefore decrease. The position of the main absorption edge is given by (7) as $[(1-x)^{2/3} - (0.6)^{2/3}]E_F$, where Ω_0 = atomic volume, x = atomic concentration of Ni, and $E_F = (h^2/8m)(3/\pi\Omega_0)^{2/3} = 7.1$ eV. For 10 at. % of Ni this formula gives the long-wavelength limit as 800 nm.

The present experiment was undertaken to see if the rigid-band model of Mott and Jones adequately describes the optical interband transition properties of copper-rich Cu-Ni alloys, or if the concept of "virtual energy states" is more appropriate to describe the position of the absorption edges. According to the models by Friedel *et al.*^{8,9} and Anderson,¹⁰ "virtual energy states" are created above and below the Fermi surface, if certain impurity atoms are added to the matrix.

Previously, the optical properties of Cu-Ni alloys have been studied by Lowery, Bor, and Wilkinson¹¹ and by Bor, Hobson, and Wood.¹² The polarimetric method of Drude was used to obtain values of n and k . Lowery *et al.* have made measurements only in the visible and infrared region, using mechanically polished samples. They have reported that if there is any shift at all in the position of the main absorption edge, it is not more than 50 nm. However, it was not possible to deduce from their results whether the addition of a small amount of Ni to Cu changes the position of this absorption edge, because the wavelength intervals they have used are too large, and the Drude method is too sensitive to surface defects of the samples.

We used solid samples and measured the absorptivity A in wavelength intervals usually of 10 nm and sometimes even of 5 nm. The correlation between the absorptivity, which is in our case equal to 1 minus the reflectance R , and the dielectric constants may be rather

complex. For copper, the reflectance R and the dielectric constants are available over an extended wavelength range. From these data, it has been reasonably well established that the rapid increase of the absorptivity near 600 nm with decreasing wavelength is associated with the onset of interband transitions.^{2,3} Such an onset of interband transition should lead to an absorption edge.

EXPERIMENTAL PROCEDURE

Experimental Principle

The experimental assembly consists essentially of a thin copper plate which is blackened on one end (absorber section), and supports the sample at the other end. A monochromatic light beam can be directed either on the black absorber or on the sample. The temperature of this assembly is measured by a thermocouple.

The change of the heating rate with the light turned on, compared to the temperature drift rate of the sample and sample holder with the monochromator turned off, is proportional to the light absorption. The ratio of the change in heating rates of sample and black absorber is equal to the absorptivity of the sample, because both have similar geometries, are in the same system, and are exposed to the same light beam. The temperature change is measured with a differential Fe-constantan-Fe thermocouple. One junction is attached to the sample stage; the other is a short distance away inside the vacuum system. Without the light, the temperature drift rates of the two junctions are very similar.

Experimental Arrangement

A high-pressure mercury lamp and a Bausch and Lomb monochromator are used as light source. Higher harmonics are removed by Kodak filters (Nos. 2E and 24). The monochromatic light is reflected by a front-plated plane mirror onto the surface of the sample or the black absorber. The distance between mirror and sample is much larger than the distance between sample and black absorber. Only a very small rotation of the mirror is necessary to put the light beam on the black absorber or on the sample. By using appropriate entrance and exit slits in the monochromator, a light beam with a high intensity of approximately 5×8 mm is obtained with diffuse low-intensity light around it. A thin blackened brass plate with two openings of equal size (7×10 mm) is placed about 1 cm above the sample stage. One opening is on top of the sample, the other on top of the black absorber. Only a small fraction of the diffuse light is admitted to the sample stage. As these two plates are black on both sides, they also serve as absorbers for stray radiation. These plates have no thermal contact with the sample stage. The system was calibrated with a blackened copper sample. Two

⁵ M. A. Biondi and J. A. Rayne, *Phys. Rev.* **115**, 1522 (1959).

⁶ N. F. Mott, *Proc. Phys. Soc. (London)* **47**, 571 (1935).

⁷ N. F. Mott, *Phil. Mag.* **22**, 287 (1936).

⁸ P. de Faget de Casteljau and J. Friedel, *J. Phys. Radium* **17**, 27 (1956).

⁹ J. Friedel, *Can. J. Phys.* **34**, 1190 (1956); *J. Phys. Radium* **19**, 573 (1958).

¹⁰ P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

¹¹ H. Lowery, J. Bor, and H. Wilkinson, *Phil. Mag.* **20**, 390 (1935).

¹² J. Bor, A. Hobson, and C. Wood, *Proc. Phys. Soc. (London)* **51**, 942 (1939).

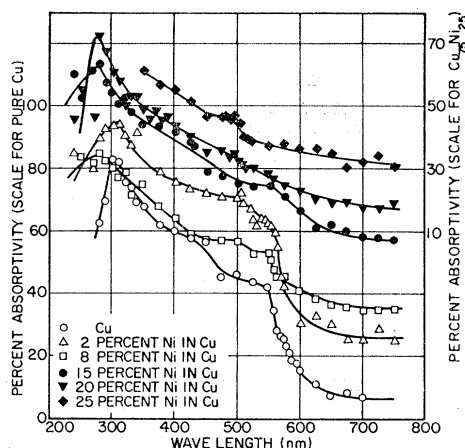


FIG. 1. Optical absorptivity of Cu and Cu-Ni Alloys. Each curve is shifted 10% up with respect to the next lower alloy concentration.

different absorber geometries were used, one is a plate, the other an inverted pyramid in which most of the light beam is reflected several times before back reflection is possible. The absorptivity of the two absorbers was identical within experimental error, indicating that more than 95% of light is absorbed by carbon black. No wavelength dependence of the carbon black absorptivity was found.

Both junctions of the thermocouple system and the entire sample stage are placed in a high-vacuum system evacuated by mechanical, diffusion, and Vac-Ion pumps. When the pressure has dropped to the operating range of the vacuum ion pump, the high-vacuum section is closed and the system is left with the Vac-Ion pump operating alone. The pressure during the testing was of the order of 10^{-7} Torr.

The iron thermocouple wires are led out of the vacuum system by means of an electrical feed-through and connected to an amplifier. The output of the amplifier is then recorded.

Preparation of Samples

Specimens are prepared in a tungsten arc furnace from 99.999% pure copper and 99.98% pure nickel in an argon atmosphere. Heats are melted four times before machining the resulting alloys to a size of $3 \times 8 \times 12$ mm. They are mechanically polished with a final polish powder size of 0.05μ . Then they are wrapped in vanadium foil and annealed for 10 h at about 750°C in a vacuum of about 10^{-5} Torr in a Brew furnace. Pure copper, and 2- and 8-at. % Ni in Cu alloys, are next electropolished using a copper electropolishing solution (250-cc phosphoric acid, 250-cc ethanol, 50-cc propanol, 500-cc water, 3-g urea). By changing the voltage across the cell and changing the concentration of the solution, shiny surfaces free of pits and scratches are obtained. After electropolishing,

samples are washed in running distilled water, kept 10 min in boiling distilled water, multiply rinsed with absolute alcohol and distilled cold water, and then dried with a cold air blast. These specimens are next studied under the microscope for surface defects and found appropriate for experiment. Specimens of 15, 20, and 25 at. % Ni in Cu cannot be electropolished by the previous method, since electropolishing always leaves some surface pits. Therefore, they are first electropolished and then mechanically polished with 0.1- and $0.05\text{-}\mu$ polish powders. Then they are treated as the other specimens and studied under the microscope to show that the surfaces are free of scratches and pits.

RESULTS AND DISCUSSION

The results of the optical absorption measurements from 240 to 750 nm are shown in Fig. 1. The reproducibility of the data is $\pm 5\%$.

The pure copper sample was tested in both the annealed, electropolished state and the unannealed, mechanically polished state. The optical absorptivities obtained for the former case were about 10% smaller than for the latter. Nevertheless, the same basic absorption behavior was observed; the position of the absorption edges did not change. Agreement with previous measurements⁵ is good. It seems, therefore, likely that the absorptivity values obtained for samples with 15, 20, and 25 at. % Ni are higher than if they were electropolished, but that the position of the main absorption edge of copper is not changed by mechanical polishing.

Figure 1 shows that the shorter-wavelength limit (approximately at 550 nm) and the longer-wavelength limit (approximately at 575 nm) of the main absorption edge of copper are unaffected by the addition of up to 15 at. % nickel to copper. These curves also show that the absorptivity in the near infrared increases with nickel concentration. The absorptivity of the 20 at. % Ni alloy in the infrared is so high that the main absorption edge seems to disappear. This edge is completely suppressed in the 25 at. % Ni alloy. These observations are in reasonable agreement with the results of the early experiments by Bor *et al.*,¹² except that their absorption edges are not sharply defined.

The peaks of the secondary absorption edges of Cu and of the 2 at. % Ni in Cu alloy are observed at approximately 300 nm. There is probably a small shift of about 20 nm to lower wavelength in the position of this peak for alloys with higher Ni concentration.

There seems to be some microstructure in the absorption curves between the main and the secondary absorption edges. Within the experimental accuracy, however, it is difficult to say if they are real.

The main absorption edge does not seem to move upon alloying copper with nickel, and the shift in the secondary absorption edge is very small. This is in conflict with the rigid-band model. It is therefore likely

that the rigid-band model can be used only for alloys of copper with nontransition elements such as zinc. The addition of zinc to copper increases the electron concentration and therefore shifts the Fermi level to higher energies. Even for this case, the rigid-band model has to be modified, since Biondi and Rayne's data⁵ show that the shift in the absorption edges with solute concentration is less than the amount suggested by the rigid-band model. Furthermore, while the rigid-band model predicts a linear shift in the position of the main absorption edge with zinc concentration, the data show that the displacement of the edge is initially very small and becomes linear with concentration for zinc contents above 3%. Friedel¹³ has proposed an atomic model in which the screening of the additional charges of zinc ions in a copper matrix and the screening the d holes created by the ejection of electrons are taken into account. Although Friedel's model gives a better fit to the data in that the theoretical curve has zero slope as the concentration of zinc goes to zero, and gives the right order of magnitude for the displacement of the main absorption edge, his method cannot explain the shifts in the position of the secondary absorption edge. The data of Biondi and Rayne also indicate that Ehrenreich and Phillip's^{2,3} inferences about the absorption edges of copper from the Segall's⁴ band calculations may have to be modified. The secondary absorption peak may be due to the transitions between the Fermi level near L_2' and a higher band near L , because the Fermi energy moves upwards upon alloying Cu with Zn, and therefore the energy gap corresponding to the secondary absorption edge decreases. The deductions from the band calculations on copper are in qualitative agreement with the rigid-band model, and therefore do not explain the behavior of the absorption edges of Cu-Ni alloys.

The rigid-band model would predict a change in the position of the absorption edges of copper with increasing nickel concentration. This is contrary to the experimental results. The present data can be analyzed with the concept of virtual impurity states. The model of "virtual energy states," as proposed by Friedel,^{8,9}

indicates that small amounts of impurities would not change the Fermi level, but would create new states below and above the Fermi energy. Anderson,¹⁰ modifying Friedel's theory of the localized states, worked out a model whose validity depends on the differences in size and symmetry of d orbitals of the impurity ion and the band functions of the matrix. He suggested that transition-element ions can produce a "virtual impurity band" distinct from the band functions of the host metal. These virtual impurity bands are just above and below the Fermi surface, depending upon the spin state, and they are filled up to the Fermi surface. According to this model, no shifts in the positions of absorption edges are expected if transition-element impurities are added to copper. This model seems to be confirmed also by low-temperature specific-heat measurements¹⁴ which indicate that the density of states at the Fermi level is larger than expected from the rigid-band model.

CONCLUSION AND SUMMARY

The calorimetric optical absorption measurements of Cu and Cu-Ni alloys at room temperature have indicated that the position of the main absorption edge of Cu is not changed by the addition of small amounts of nickel. As nickel concentration of the solution is increased, the second absorption edge seems either to stay stationary or to shift towards shorter wavelengths, but not by more than 20 nm. This observation is not in agreement with the rigid-band model, which predicts a shift in the position of the main absorption edge towards longer wavelengths as the Ni concentration in the matrix is increased. It seems that nickel behaves as a neutral atom in copper-rich alloys. This is possibly due to the existence of "virtual impurity states."

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