# Photoemission and Optical Studies of Cu-Ni Alloys. II. Ni-Rich and Nearly Equiatomic Alloys*

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We report and discuss photoemission and optical reflectivity data for Cu-Ni alloys containing $\geq 38\%$ Ni. Our results indicate that the filled densities of states for Ni-rich alloys (those containing $\leq 20\%$ Cu) are little changed from that of pure Ni. Data for alloys containing as little as 39% Cu give evidence that the Cu $d$ states remain about 2 eV below the Fermi energy, and it is suggested that the Cu $d$ states are well below the Fermi energy for lower Cu concentrations as well, in agreement with the assumptions of the minimum-polarity model, proposed by Lang and Ehrenreich, for Ni-Cu alloys. The Ni $d$-state density is modified significantly, in both width and shape, as the Ni content in Cu-Ni alloys increases. On the basis of the optical and photoemission data for pure Cu, pure Ni, and all alloys studied, it is suggested that structure in the optical transition strength $\omega\sigma$ near $h\nu = 5.0$ eV is due to transitions from deep hybridized $d$ states to states just above the Fermi level, these transitions occurring with enhanced matrix elements.

## I. INTRODUCTION

In the preceding paper[1] (hereafter referred to as I), a discussion of new photoemission and optical experiments on Cu-rich Cu-Ni alloys has been given. In this paper, we present photoemission and optical reflectivity data for several other Cu-Ni samples, ranging from 62% Cu-38% Ni to pure Ni, which complete our study of this important and interesting alloy system over the entire composition range. These data provide information concerning the filled densities of states in the alloys and, when coupled with the results of I, make possible a description of the density-of-states variations over the entire Cu-Ni composition range. Recently, the magnetic and other properties of Ni-rich Ni-Cu alloys have been discussed in terms of models, quite different from the rigid-band model, which emphasize a lack of sharing of the Cu and Ni electrons in an alloy[2-5]; our photoemission and optical data are consistent with and are discussed in terms of these concepts.

## II. EXPERIMENTAL TECHNIQUES

Photoemission and reflectivity experiments have been performed on pure Ni and alloys of composition 89% Ni-11% Cu, 81% Ni-19% Cu, 61% Ni-39% Cu, 51% Ni-49% Cu, and 38% Ni-62% Cu. The pure Ni, 81% Ni, and 51% Ni samples were obtained from Research Crystals, Inc., Richmond, Va. and the 89% Ni and 38% Ni samples were obtained from Aremco, Inc., Briarcliff Manor, N.Y. A sample of 61% Ni-39% Cu was cut from an alloy crystal kindly made available to the authors by W. Scouler of Lincoln Laboratories, Lexington, Mass.

The alloy rods of composition 81% Ni, 89% Ni, and 51% Ni were annealed in vacuum at 1000 °C for approximately 15 days. The other alloy samples (61% Ni and 38% Ni) were not annealed; because of the lack of homogenization treatment and the fact that clustering effects appear to be most important near a composition of 50% Cu-50% Ni (see I), data for these two compositions might be influenced somewhat by clustering effects.

After annealing and air quenching, specimens suitable for measurement were prepared as described in I. Final polishing of Ni, 89% Ni, and 81% Ni samples was done using a chemical polishing solution for Ni described by Tegart[6] and the 62% Cu-38% Ni sample was electropolished using the same procedures as used for Cu (I). Alloy samples of composition 61% Cu and 51% Ni were mechanically polished only because a suitable chemical or electrochemical polishing technique for these compositions was not found.

A sample of composition 81% Ni-19% Cu was checked for dendritic inhomogeneity using an electron microprobe. Some inhomogeneity was found, but the deviations from the average compositions were not as great as found for 77% Cu (I). The actual Cu concentration in the 81% Ni-19% Cu sample ranged from 16.5% to 21.5%.

Unlike the situation for Cu and Cu-rich Cu-Ni alloys, heating of Ni and Ni-rich alloy samples did not always lead to adequate cleaning of the photoemitting surfaces. Pronounced EDC structure at low kinetic energies, similar to the anomalous peak in Ni (see Sec. III), appeared in most instances when cleaning by heating alone was attempted. In such cases, argon bombardment with annealing heat treatment was used to prepare the sample surfaces for the photoemission studies.

In order to accomplish the surface cleaning by

argon bombardment, approximately 25 $\mu$ of high-purity tank argon was admitted to the experimental chamber. A large voltage, typically 1.2 kV, was applied between the sample and the photodiode collector can in order to initiate and maintain the sputtering glow discharge. The current due to the discharge was monitored by a series resistor and was typically 300 $\mu$A. Argon bombardment was usually continued under these conditions for approximately 15 min and then the argon was pumped out. The sample was then heated to drive off embedded argon and anneal any surface damage. After heating, photoemission from the sample could be measured and the effectiveness of the cleaning process could be assessed. The bombardment and annealing treatments were continued until no further changes occurred in the photoelectron energy-distribution curves (EDCs) and the number of photoemitted electrons with low kinetic energies was minimized. The annealing temperature was approximately 350 °C, well above the temperature at which phase separation could occur.

For reflectivity measurements, the Ni and Ni-rich samples were prepared by heating in high vacuum only. While heating alone did not always lead to adequate photoemission results for these samples, it is expected that reflectivity results will be much less sensitive to surface contamination than photoemission results. Vehse and Arakawa[7] have found that Ni photoemission data can degrade drastically with time but, under the same sample conditions, Ni reflectivity data change very little. Ni reflectivity data obtained using different sample-preparation techniques are quite similar,[7] further indication that reflectivity data should be affected less than photoemission data by surface-preparation problems.

Other aspects of the experimental procedures have been given in I. The photoemission and optical data for the Ni-rich and intermediate composition alloys have been analyzed using the approaches described in I.

## III. EXPERIMENTAL RESULTS

### A. Photoemission from Pure Nickel

Photoemission from pure Ni has been extensively studied and discussed.[7-11] From our studies of bulk argon-bombarded Ni samples an optical density of states (ODS) has been obtained using the procedures outlined in I. This ODS is shown in Fig. 1; for comparison the ODS for Ni obtained by Eastman and Krolikowski [9] is also shown. At the present time this latter ODS appears to be the most representative of the true density of states of Ni.

Both ODS exhibit a fairly sharp peak just below the Fermi energy ($E_F$). In the present work this peak is smaller compared to other structure and less sharp than in the ODS of Eastman and Krolikowski. A second peak is evident in both ODS near $-2.0$ eV, although there is a discrepancy of about 0.4 eV in the actual peak position in the two cases. These differences may be due to the different means of sample preparation used in the two studies – the data of Eastman and Krolikowski[9] were obtained from evaporated films prepared in ultrahigh vacuum.

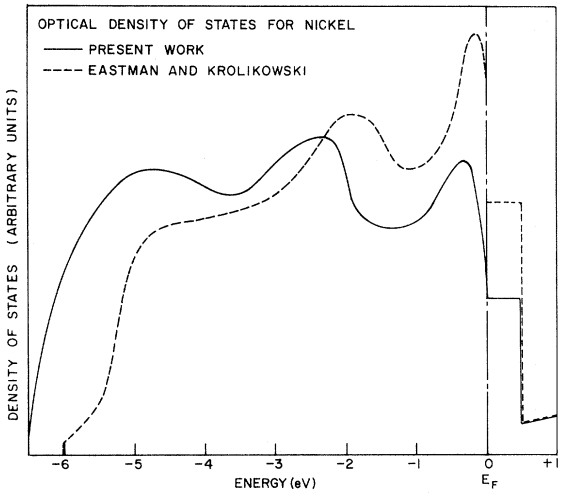


FIG. 1. ODS for Ni from the present work and from the work of Eastman and Krolikowski (Ref. 9). The two ODS differ in relative peak heights and also in the energy position of the peak near $-2$ eV.

Early studies of photoemission from Ni [8] showed a relatively large dominant structure, the "anomalous peak," which appeared to originate from initial-state energies less than $-3$ eV. The careful work of Eastman and Krolikowski,[9] Vehse and Arakawa,[7] and Callcott and MacRae[11] showed, however, that the large strength of this structure was apparently due to sample surface conditions. The argon-bombardment cleaning procedure used in the present experiments eliminates most of the anomalously large strength of this low-energy structure, although the reduction is not as complete as in the work of Eastman and Krolikowski.

In both ODS of Fig. 1, a high density of states has been included between 0 and $+0.5$ eV to approximately represent the unfilled, $d$-derived states of Ni. For energies higher than $+0.5$ eV, the empty density of states is taken to be free-electron-like.

For the present purposes, the discrepancies between the two Ni ODS are not of primary importance: the major interest here is in the changes which occur in EDC structure when Cu is alloyed with Ni. Therefore, the alloy data reported here from bulk argon-bombarded single crystals will be compared to the results we have obtained for bulk Ni samples of the same type and prepared in the

same way.

### B. Photoemission from Ni-Rich Ni-Cu Alloys

Photoemission results for 89% Ni-11% Cu were obtained from a sample with the surface cleaned by argon bombardment following the procedures described above. In the case of 81% Ni-19% Cu the results reported below were obtained from a sample cleaned by heating only. The sample was heated for 5 h at 450 °C; after this heating the photoemission data satisfied the criteria of surface cleanliness – sharp structure at high kinetic energies appeared and large anomalous low-energy structure was absent.

In Fig. 2 the absolute quantum yields for 89% Ni and 81% Ni alloy samples are shown. For comparison the yield of pure Ni is also shown in Fig. 2. The surface of the 89% Ni sample was about 4° from a {100} plane and a work-function value of 4.6 eV was obtained from a Fowler plot of the yield data. The 81% Ni sample had a work function of 4.9 eV; the sample surface was 15° from a {311} plane. The work function of the pure Ni sample was found to be 4.6 eV ({100} plane). Comparison of the yields of pure Ni, 89% Ni, and 81% Ni indicates that the yield at high photon energies increases with increasing Cu content. This same trend – increasing yield with increasing solute content – was noted for the Cu-rich Cu-Ni alloys in I.

We show in Fig. 3 some typical EDCs at high exciting photon energy for the sample of composition 89% Ni-11% Cu. These EDCs are plotted versus the initial-state energy $E_i$ on the horizontal

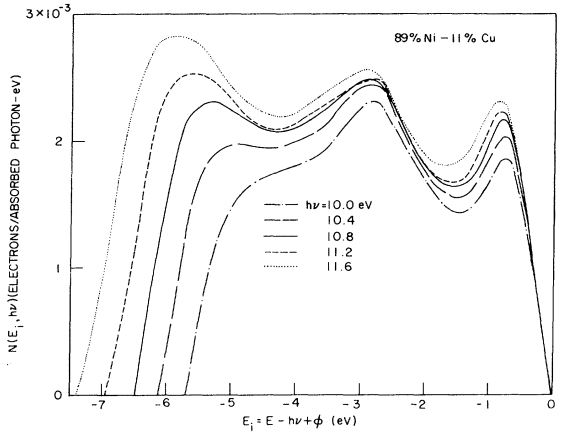


FIG. 3. EDCs for 89% Ni-11% Cu for $10.0 \leq h\nu \leq 11.6$ eV.

axis and are normalized to the quantum yield. In these EDCs two peaks, at – 0.7 and – 2.8 eV, superimpose in initial-state energy, implying that these peaks are due to structure in the filled alloy density of states. The relatively large structure appearing at initial-state energies between – 5 and – 6 eV is assumed to correspond to anomalous structure found in pure Ni [8,9] rather than to true structure in the alloy ODS. The two peaks observed at initial-state energies of – 0.7 and – 2.8 eV are quite similar in energy position, shape, and relative height to structure which is observed in EDCs from samples of pure Ni. (The EDCs for Ni are quite similar in shape to the ODS shown in Fig. 1.)

EDCs for the sample of composition 81% Ni-19% Cu are given in Fig. 4. Structure at initial-state

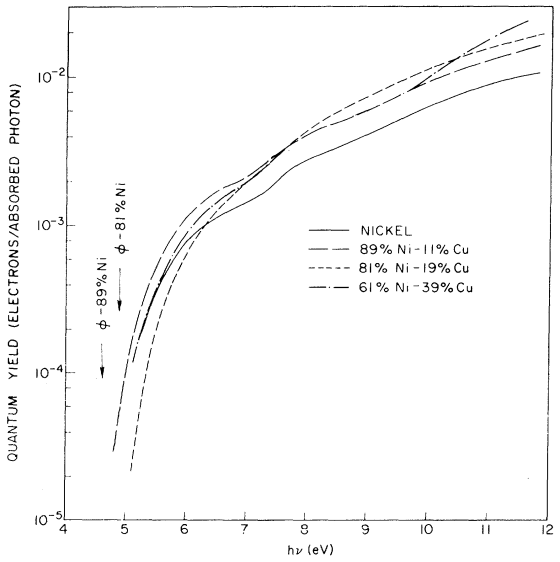


FIG. 2. Quantum yields for 89% Ni-11% Cu, 81% Ni-19% Cu, and 61% Ni-39% Cu alloys and pure Ni.

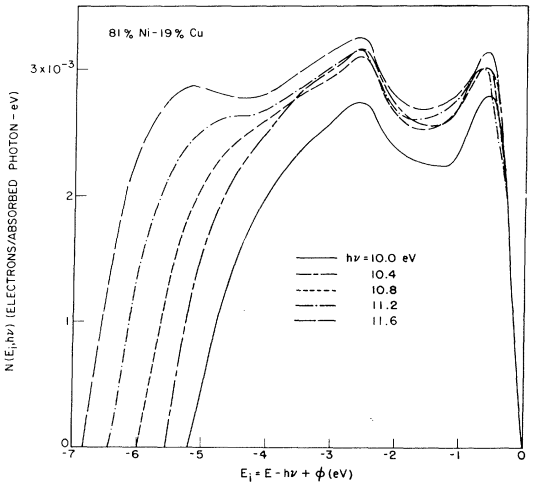


FIG. 4. EDCs for 81% Ni-19% Cu for $10.0 \leq h\nu \leq 11.6$ eV.

energies of about − 0.6 and − 2.6 eV superimposes in energy and is quite similar in energy position and form to the structure observed in EDCs for pure Ni and the 89% Ni alloy.

We have also obtained photoemission data for a sample of composition 61% Ni-39% Cu. The absolute quantum yield for this sample has been shown in Fig. 2. Although the 61% Ni sample was cleaned using the argon-bombardment procedure described above, a large number of low-energy electrons, similar to the anomalous peak in pure Ni, was never completely reduced in this sample. This fact is illustrated in Fig. 5, where EDCs for photon energies between 9.2 and 10.4 eV are shown for the 61% Ni sample. As the photon energy is increased in this range, structure at initial-state energies of − 4.5 to − 5.5 eV increases very rapidly and dominates the EDCs. This structure could not be reduced by further argon-bombardment treatment. However, two other peaks, at initial-state energies of about − 0.75 and − 2.65 eV, are clearly resolved and superimpose in initial-state energy quite well. The energy positions of these two peaks are quite similar to the positions of structure in pure Ni and the 89% Ni and 81% Ni alloys. However, in the EDCs for the 61% Ni alloy the height of the peak at − 0.75 eV is significantly less than the height of the − 2.65-eV peak, whereas in pure Ni and the other Ni-rich alloy samples the heights of these two peaks are nearly equal. While relative peak heights in photoemission data must be interpreted with caution, because of the sensitivity of peak height to surface treatment, it appears that

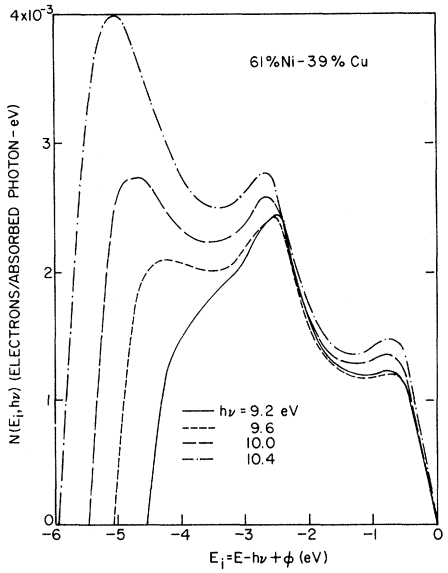


FIG. 5. EDCs for 61% Ni-39% Cu for $9.2 \leq h\nu \leq 10.4$ eV. The major portion of the structure near − 5.0 eV appears to be due to anomalous surface effects.

the increase in strength of structure at about − 2.6 eV in 61% Ni EDCs may be due to the Cu $d$ states existing as relatively localized levels 2 to 3 eV below $E_F$. Optical data (Sec. IIIC) also suggest that the Cu $d$ states in 61% Ni-39% Cu may lie at these energies and make a significant contribution to the alloy optical absorption for photon energies in the range 2–3 eV.

Thus, the most notable feature of photoemission data for the Ni-rich alloys containing up to 39% Cu is the essentially identical structure in the EDCs for initial-state energies of about − 0.7 and − 2.7 eV. This similarity is graphically illustrated in Fig. 6 where normalized EDCs for all four materials at $h\nu = 10.0$ eV are shown. Figure 6 indicates that there is no apparent trend for the first two peaks to shift either closer to or further away from the Fermi energy as the Cu content in the alloys increases. Peak shapes and relative heights do not change markedly, except in the case of 61% Ni-39% Cu.

Because of the close resemblance of EDCs for 89% Ni and 81% Ni to those for pure Ni, the ODS for these two alloys has not been derived but is taken to be nearly identical to that for pure Ni. No ODS has been obtained for 61% Ni-39% Cu because of the presence of strong structure in the photoemission data at an initial-state energy of about − 5.0 eV, which is apparently due to surface effects.

EDCs for $h\nu = 7.8$ eV and $h\nu = 10.2$ eV are shown for an alloy sample of composition 38% Ni-62% Cu in Fig. 7. These EDCs are *not* normalized to quantum yield. They were obtained after an electropolished 38% Ni alloy sample was heated for $2\frac{1}{2}$ h at 500 °C. Unfortunately, before data for all $h\nu$ were taken the sample was reheated and a drastic deterioration in the EDCs obtained resulted. Hence the EDCs of Fig. 7 represent the best photoemission data obtained for this sample.

The EDC for $h\nu = 10.2$ eV in Fig. 7 is quite similar in many respects to EDCs for 77% Cu-23% Ni discussed in I. The number of photoemitted electrons between 0 and − 2 eV is relatively large but featureless. A fairly sharp edge occurs between − 2 and − 2.5 eV; this edge and structure below − 2.0 eV are reminiscent of the Cu $d$-state contribution to the 77% Cu EDCs (I). The photoemitted electrons between 0 and − 2.0 eV are believed to be due to excitation of the filled Ni $d$ states and the EDC at $h\nu = 7.8$ eV suggests that there is some structure within the Ni $d$-state density in this energy range. A peak is seen at about − 1.3 eV and a fairly pronounced shoulder, indicated by the arrow, is present at about − 0.5 eV. The structure near − 2.3 eV is due to the Cu $d$ states just becoming exposed.

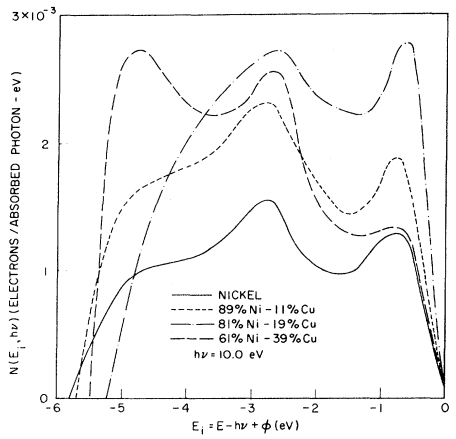


FIG. 6. Comparison of EDCs for Ni, 89% Ni, 81% Ni, and 61% Ni. The curves are normalized to their respective yields. Structure near $-0.7$ and $-2.7$ eV remains essentially constant in energy position in the four materials.

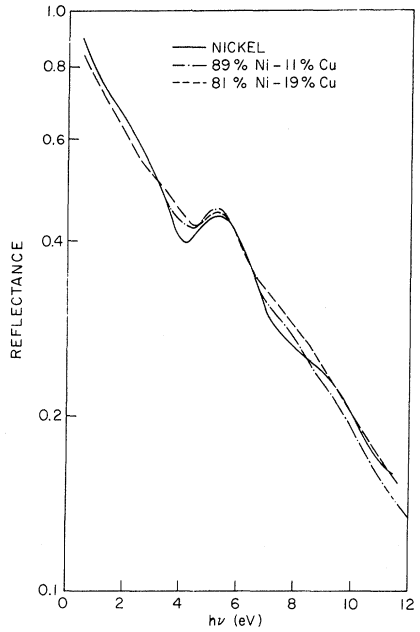


FIG. 8. Reflectivity of Ni and 89% Ni and 81% Ni alloys.

### C. Reflectivity and Absorption Spectra

Reflectivity spectra for pure Ni and Ni-Cu alloys containing 89% Ni, 81% Ni, 61% Ni, and 38% Ni are shown in Figs. 8 and 9. In addition, a reflectivity spectrum for 51% Ni-49% Cu is shown in Fig. 9. For this composition no good photoemission data were obtained because the sample could be mechanically polished only, and anomalous low-energy EDC structure resulted for all argon-bombardment and heat-cleaning treatments that were attempted.

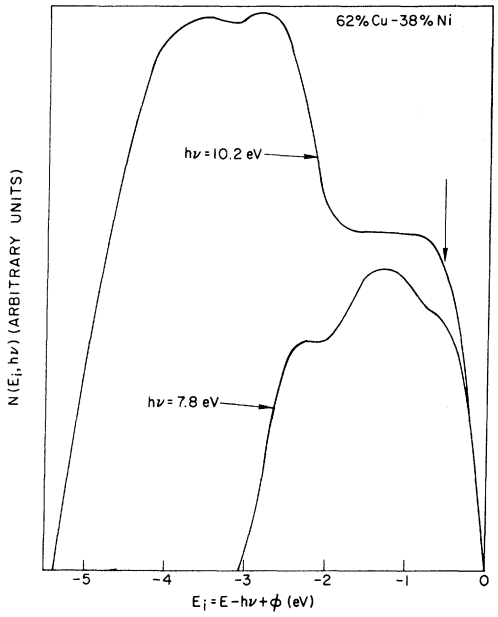


FIG. 7. EDCs for 62% Cu-38% Ni. The shoulder at $-0.5$ eV in the $h\nu = 7.8$-eV EDC suggests that interaction among Ni atoms are reshaping the Ni $d$-state density.

Our reflectivity results for pure Ni are in reasonably good agreement with other measurements (summarized by Vehse and Arakawa[7]) made after various kinds of sample preparation. In particular, our Ni spectrum agrees well at lower energies with that measured by Ehreneich, Philipp, and Olechna,[12] who used bulk samples with initial preparation similar to that used in the present experiments. However, the present results are somewhat higher than those of Ehrenreich *et al.*[12] at high photon energies, probably because our sample was heat cleaned while that of Ehrenreich *et al.*[12] was not.

Just as in the case of the photoemission results (Sec. III B), the reflectivity spectra of 89% Ni and 81% Ni are little changed from that of pure Ni. Ni and 89% Ni reflectivities are identical for $h\nu < 3.0$ eV. For the 89% Ni and 81% Ni alloys the peak in the vicinity of 5 eV is less pronounced than in pure Ni but there is no appreciable shift in its position.

The reflectivity spectrum for 61% Ni-39% Cu (Fig. 9) is practically identical to that reported by Scouler, Feinleib, and Hanus[13] for this same composition (the samples used in the two different measurements were in fact cut from the same crystal boule). For the 61% Ni alloy (and the 51% Ni and

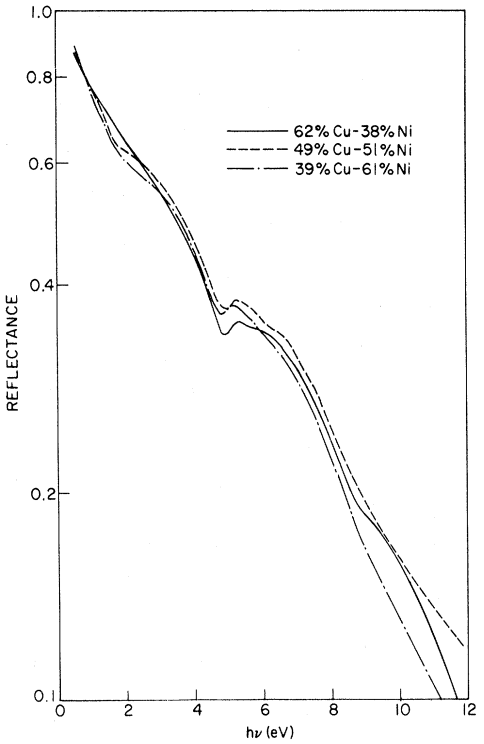


FIG. 9. Reflectivity of 61% Ni, 51% Ni, and 38% Ni alloys.

38% Ni alloys as well) the peak near 5.2 eV has almost disappeared. However, in 51% Ni there is a slight shoulder near 6.4 eV, and in 38% Ni a shoulder near 6.4 eV is even more pronounced than in 51% Ni. It appears that with increasing Cu concentration a relative increase in reflectivity structure near $h\nu \cong 6$ eV occurs and this structure eventually develops into the broad peak in reflectivity seen in Cu-rich alloys (I).

In the 61% Ni and 51% Ni spectra, a shoulder is also discernible in the range $h\nu = 2$ to 3 eV. No such shoulder is seen in either the 81% Ni or 62% Cu spectra.

The reflectivities for the alloys of intermediate composition (Fig. 9) are generally lower than the spectra for Ni-rich alloys (Fig. 8) for $h\nu > 4$ eV. The problems of sample preparation, both initial preparation and cleaning in vacuum, were most severe for the alloys of intermediate composition, so the low values of sample reflectivity may be due to some remaining surface contamination.

In Figs. 10 and 11 we show the optical transition strength $\omega\sigma$ for the six materials, obtained by Kramers-Krönig analysis as described in I.[14] For 89% Ni and 81% Ni alloys (Fig. 10) $\omega\sigma$ is little changed from that of pure Ni although the structure near 5.0 eV becomes less pronounced as the Cu

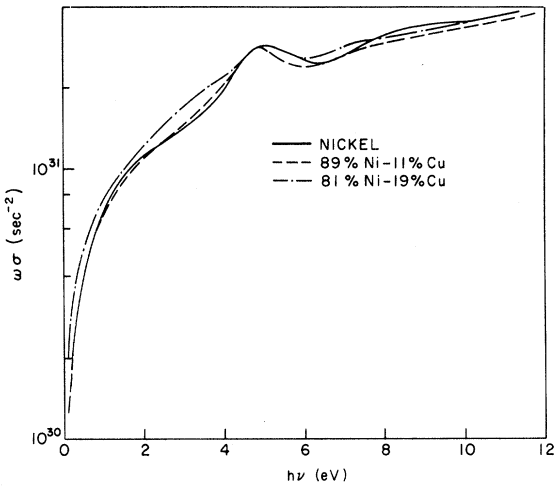


FIG. 10. $\omega\sigma$ for Ni and 89% Ni and 81% Ni alloys.

content in these alloys increases.

The absorption spectra for 61% Ni-39% Cu, 51% Ni-49% Cu, and 38% Ni-65% Cu are somewhat different from the spectra for alloys containing more Ni. (In Fig. 11, $\omega\sigma$ spectra for these three alloys

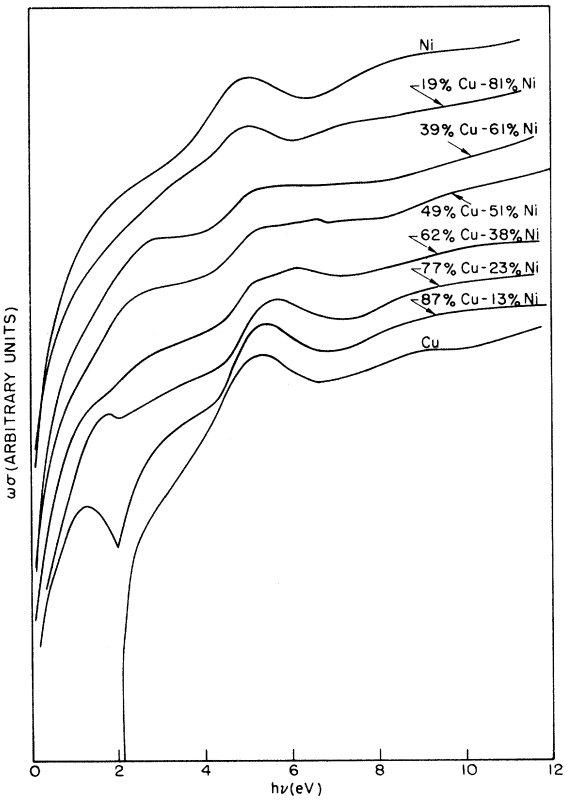


FIG. 11. $\omega\sigma$ for pure Cu and Ni and the Cu-Ni alloys studied. The curves are shifted in magnitude for clarity.

are shown together with $\omega\sigma$ spectra for all other alloys studied for purposes of comparison and summary. The curves are shifted in magnitude for clarity.) $\omega\sigma$ for all alloys of Fig. 11 has an increase starting at $h\nu \cong 4.4$ eV. In 61% Ni, $\omega\sigma$ is rather flat for $h\nu > 5.2$ eV, with no dip occurring in the absorption. At 51% Ni the absorption structure between 5.2 and 6.8 eV becomes somewhat more pronounced and a dip in $\omega\sigma$ occurs at 6.9 eV. Also in 38% Ni the absorption structure between 5.2 and 6.8 eV is further increased relative to other structure – a weak peak appears at about 6.1 eV in addition to the shoulder at 5.3 eV – and the dip in absorption in the vicinity of 7.1 eV becomes even more pronounced. It appears that the structure developing at $h\nu = 6.0$ eV as the Cu content increases eventually becomes the peak observed in $\omega\sigma$ for Cu and Cu-Ni alloys (I).

In the $\omega\sigma$ spectra for 61% Ni-39% Cu and 51% Ni-49% Cu, a quite distinct and pronounced shoulder is observed between $h\nu = 2.0$ and 3.0 eV. This shoulder suggests that there is an increased density of states 2 to 3 eV below $E_F$, which gives rise to strong optical absorption for $h\nu \cong 2$ to 3 eV. This increased density of states could perhaps arise from the Cu $d$ states, which might exist as virtual-bound-type levels several eV below $E_F$, as suggested by the 61% Ni-39% Cu photoemission data in Sec. III B.

## IV. DISCUSSION

### A. Densities of States in Ni-Cu Alloys

The photoemission data for Ni-Cu alloys containing between 38% and 100% Ni which were presented above, in conjunction with the results of I, allow a description of the alloy density of states over the entire composition range to be given. First of all, it is evident from the present data, and a great deal of other evidence as well,[2-5] that the rigid-band model does not describe the electronic structure of the Ni-Cu alloys. This model predicts that the densities of states for Ni and Ni-Cu alloys are identical in shape (except for an exchange splitting which is a function of composition), the density of states being filled to a higher and higher level as the Cu content and hence the electron-to-atom ratio increases. The changes in EDCs for alloys containing Cu-rich Cu-Ni alloys (I) indicate that the rigid-band description of alloying behavior cannot be correct.

It appears that the Cu $d$ states in Cu-Ni alloys remain well below the Fermi energy for all compositions. In I we showed that the Cu $d$ states in Cu-Ni alloys containing up to 23% Ni are at the same energies as the $d$ states of pure Cu. The limited data for 62% Cu-38% Ni (Fig. 7) also indicate that the Cu $d$ states are well defined at energies greater than 2 eV below $E_F$ for this alloy composition. We have also seen evidence in both the photoemission data (Fig. 5) and optical-absorption data (Fig. 11) for 61% Ni-39% Cu that the Cu $d$ states in this alloy exist at energies 2 to 3 eV below $E_F$. In data for the two alloys containing 81% Ni and 89% Ni, no evidence of the Cu $d$ states is found because of the high density of states of the Ni host. However, the direct observation that the Cu $d$ states remain well below $E_F$ for Cu concentrations down to 40% suggests that these states also remain well below $E_F$ in alloys with less Cu content as well. This latter conclusion is further supported by the success of the minimum-polarity model for Ni-Cu alloys, which has been formulated by Lang and Ehrenreich[2] and by Kirkpatrick, Velický, Lang, and Ehrenreich.[3] This model assumed that the Cu $d$ states in Ni-Cu alloys were always filled and hence were well below $E_F$. Our present data, as well as the success of the minimum-polarity model in treating many properties of Ni-Cu alloys, appear to justify this assumption. The approximately constant-energy position of the Cu $d$ states relative to $E_F$ in all Cu-Ni alloys may be a consequence of the fact that the $s$- and $p$-derived, nearly free-electron-like band is modified only slightly in passing from pure Cu to pure Ni. Hence, the properties of the Cu $d$-state scattering resonance, particularly its energy position, might also be expected to be relatively unchanged upon alloying.

The density of Ni $d$-derived states appears to undergo quite pronounced changes in alloys ranging in composition from pure Cu to pure Ni. In I we have shown that for very dilute Ni concentrations the Ni $d$ electrons exist in virtual-bound states with total width at half-maximum of about 0.8 eV. The effects of interactions among Ni atoms become quite important as the Ni content increases – at 23% Ni in Cu the Ni $d$ states are broadened by interactions so that the total width at half-maximum is about 1.3 eV. The data for 62% Cu-38% Ni (Fig. 7) suggest that the interactions among Ni $d$ states reshape as well as broaden the Ni $d$-state density. The EDC for this alloy at $h\nu = 7.8$ eV (Fig. 7) suggests that in the Ni $d$-state density there is a peak 1.3 eV below $E_F$ and a shoulder 0.5 below $E_F$, rather than the single peak 1.0 eV below $E_F$ that is found in the Ni $d$-state density of 77% Cu and 87% Cu alloys (I). This shoulder may eventually develop into the sharp structure just below $E_F$ that is observed in alloys containing > 60% Ni; however, this suggestion is somewhat tentative because of the lack of sufficiently detailed photoemission data for nearly equiatomic Cu-Ni alloys. The peak just below $E_F$ in the Ni-rich alloys is found to decrease in total weight as the Ni content decreases, although its shape appears to be fairly well defined in alloys containing only

about 60% Ni. Thus, the Ni $d$-state structure is very different in Cu-rich and Ni-rich alloys, with important changes – the development of structure just below $E_F$ – appearing to occur for compositions near the critical composition for ferromagnetism. The development of this structure may have an influence upon the onset of ferromagnetism in the Cu-Ni alloys.

### B. Optical Absorption of Ni, Cu, and Cu-Ni Alloys

Certain features of the optical-absorption spectra of Cu and Ni, particularly structure in $\omega\sigma$ (or $\epsilon_2$) in the vicinity of 4.5–5.0 eV (Figs. 10, 11, and 13 of I), are still not completely understood. On one hand, this structure in Cu [15–17] and Ni [15] has been attributed in large part to transitions from the low-lying hybridized $d$-derived states to states just above $E_F$, with a portion (30% or more) of the transition strength for $h\nu = 4.5$–$5.0$ eV assigned in some treatments[15,16,18] to direct transitions near the $L$ point of the Brillouin zone. Also, for Cu an explanation of $\epsilon_2$ has been given in terms of the photoemission optical density of states and nondirect transitions with constant matrix elements.[19] Having obtained data for pure Cu and Ni as well as several Cu-Ni alloys spanning the entire composition range (see Fig. 11), it appears worthwhile to attempt another explanation of the structure in $\omega\sigma$ near $h\nu = 5.0$ which accounts for the similarities observed in the spectra of all of these materials. As seen in Fig. 11, all Cu-Ni alloys studied exhibit structure in $\omega\sigma$ for $4.0 \leq h\nu \leq 6.0$ eV; in particular a distinct rise occurs in $\omega\sigma$ at about 4.4 eV. Direct transitions at $L$ are not expected to contribute to optical absorption in the alloys.[20] Note, for example, the close similiarity between $\omega\sigma$ for pure Ni and that for Ni with 11% Cu (Fig. 10). $L$ transitions should be negligible in an 11% alloy, yet $\omega\sigma$ for $4.0 \leq h\nu \leq 6.0$ eV is changed very little. On the other hand, as will be seen below, constant-matrix-element calculations of $\omega\sigma$ from photoemission ODS do not give good agreement with the experimental $\omega\sigma$ spectra of Cu and Ni. Therefore, another approach appears to be required to explain the observed data.

Considering first the case of pure Ni, Fig. 12 shows the experimental $\omega\sigma$ for Ni and the curve calculated from the ODS of Eastman and Krolikowski (Fig. 1) using Eq. (2) of I and constant matrix elements. In the calculation the empty states of Ni were approximated by an empty $d$-state portion, as shown in Fig. 1, and by a free-electron-like band, with the band bottom at $-7.0$ eV, for energies greater than 0.5 eV above $E_F$. The large discrepancy at low photon energies between the experimental curve and the curve calculated with constant matrix elements arises because the constant-matrix-element assumption apparently overestimates the strength of transitions from the filled Ni $d$ states to the empty $d$ states just above $E_F$. In an atom, $d$-state–to–$d$-state transitions are forbidden, suggesting that the matrix element for transitions from the filled $d$ states to the empty $d$ states in Ni may be smaller than the matrix element for transitions between $d$ states and $s$- and $p$-derived states. However, optical matrix elements may also vary over the width of the filled $d$ states. Phillips[21] and Cuthill, McAlister, Williams, and Watson[22] have suggested that enhanced matrix elements can result for states at the bottom of transition-metal $d$ bands, since these states are more spatially extended than the other $d$ states[23] because of hybridization with nearly free-electron-like states. Therefore, the matrix element for transitions coupling the lower hybridized $d$ states to the empty $d$ states in Ni may be greater than the matrix elements coupling the higher-energy $d$ states to these same final states.

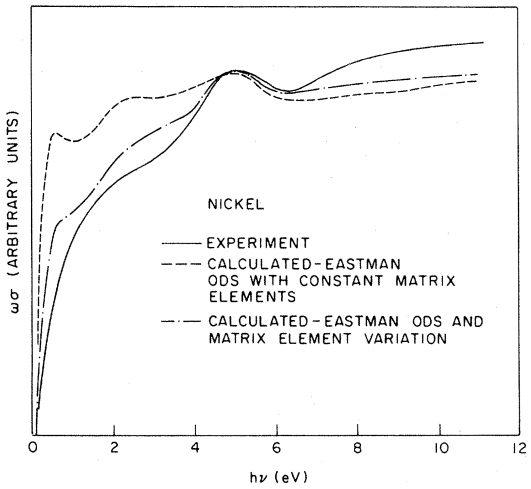


FIG. 12. $\omega\sigma$ for Ni compared to that calculated from the Ni ODS (Ref. 9) assuming constant matrix elements and assuming matrix-element variations for filled $d$-state to empty $d$-state transitions.

The matrix-element variation suggested by the discussion above has been incorporated in an approximate manner in a recalculation of $\omega\sigma$. In this calculation, the coupling of the filled Ni states to free-electron-like states above $E_F$ was given a strength of one. The relative strength of the matrix element for transitions coupling filled Ni $d$ states between 0 and $-4.0$ eV to the empty $d$ states just above $E_F$ was taken to be 0.4 and the relative strength assigned to the coupling of initial states between $-4.0$ and $-5.5$ eV to the empty $d$ states was 0.8. The results of this calculation are also shown in Fig. 12; the agreement between calculated and experimental $\omega\sigma$ is much better than when con-

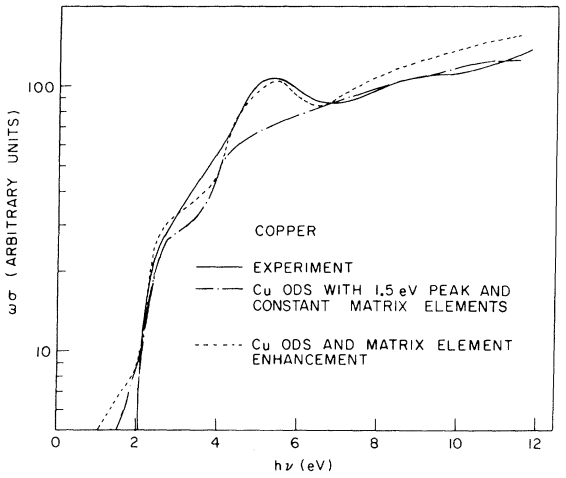


FIG. 13. Experimental $\omega\sigma$ for Cu compared to $\omega\sigma$ calculated from the Cu ODS (Ref. 19) assuming constant matrix elements and assuming matrix-element enhancements for low-lying hybridized $d$ states.

stant matrix elements were assumed. We suggest, then, that in Ni the structure in $\omega\sigma$ near $h\nu$ 4.5 eV arises from lower $d$ band to $E_F$ transitions, which have an enhanced matrix element relative to other $d$ band to $E_F$ transitions.

The assumption of a similar matrix-element enhancement in Cu also results in better agreement between experimental and calculated $\omega\sigma$ spectra. Figure 13 compares the experimental $\omega\sigma$ curve with the curve calculated using the Cu ODS of Krolikowski and Spicer,[19] and the nondirect constant-matrix-element model. This calculation does not give the experimentally observed structure near $h\nu = 5.0$ eV. If it is assumed that the 5.0-eV structure in $\omega\sigma$ is due to transitions from deep hybridized Cu $d$ states just above $E_F$ with an enhanced matrix element, then the second calculated curve results and is in much better agreement with experiment. In this calculation, the matrix element which couples initial states at $-4.0$ to $-5.5$ eV to final states between 0 and $+1.0$ eV above $E_F$ was taken to be three times as large as the matrix element for all other transitions. (In this second calculation, the peak at $+1.5$ eV above $E_F$ in the ODS of Cu given by Krolikowski and Spicer[19] was omitted. This peak had been scaled in magnitude by Krolikowski and Spicer to obtain best agreement between the calculated and experimental $\epsilon_2$ of Cu, but the curve labeled constant matrix elements in Fig. 13 indicates that the presence of this peak in the ODS does not give good agreement between the calculated and experimental $\omega\sigma$ spectra.) The reason why transitions with enhanced matrix elements should occur for only a limited range of empty states is less apparent in Cu than in Ni, where empty $d$ states just above $E_F$ were involved.

The above calculations for Cu and Ni involving matrix-element enhancements are intended to illustrate that the assumed variations can lead to reasonable agreement with experiment. Because of the many ways the matrix elements could be varied (magnitude, shape of energy dependence, etc.) it is not meaningful to attempt to obtain exact agreement with experiment. However, the matrix-element variations used above seem plausible in light of the previous assignments of structure in $\omega\sigma$ near 5.0 eV in Cu [15-17] and Ni [15] to lower $d$ band to $E_F$ transitions, and the known variations in the nature of transition-metal $d$ states with energy.[23]

With the above assignment of the $\omega\sigma$ structure near 5.0 eV in Ni and Cu to transitions originating from the hybridized $d$ states, the similarity of this structure in the two materials follows directly from the similarities of the deep $d$ states. Most importantly, the structure in the alloy $\omega\sigma$ curves (see Figs. 10 and 11) in the vicinity of 5.0 eV can be attributed to transitions from low-lying $d$ states in the alloys. The detailed changes in the structure which do occur in the various alloy compositions may be due to changes in both the empty states near the Fermi level and the states near the bottom of the $d$ bands. Understanding of the detailed changes in these spectra could contribute strongly to a detailed understanding of the electronic structure of

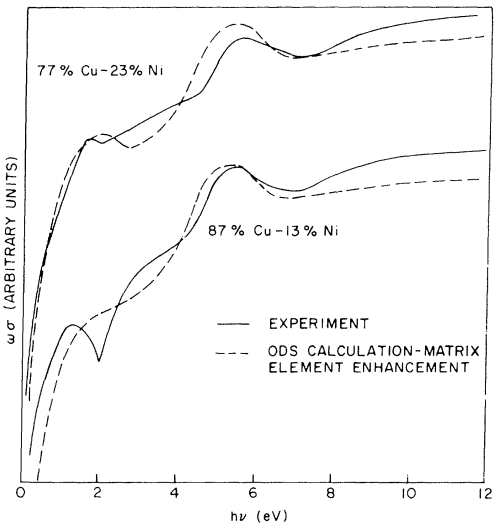


FIG. 14. Experimental $\omega\sigma$ spectra for 87% Cu-13% Ni and 77% Cu-23% Ni compared to $\omega\sigma$ calculated from the photoemission ODS (Fig. 11 of I). The calculations assumed matrix-element variations for transitions involving the low-lying hybridized Cu $d$ states and the Ni virtual-bound states.

the alloys.

One final aspect of the alloy optical-absorption data that is worthy of further comment is the absorption due to Ni virtual-bound states for $0 \leq h\nu \leq 2.0$ eV in 87% Cu-13% Ni and 77% Cu-23% Ni (Fig. 13 of I). Figure 14 compares the experimental $\omega\sigma$ curves for these two alloys with curves calculated from the alloy densities of states (Fig. 11 of I). To obtain the over-all agreement in magnitude between the experimental and calculated curves of Fig. 14 the same matrix-element enhancement was assumed for the low-lying hybridized Cu $d$ states as was assumed for pure Cu. In addition, transitions from filled states between 0 and $-2.0$ eV (the Ni virtual-bound states) to final states between 0 and 1 eV above $E_F$ were assumed to have a matrix element three times larger than the matrix element for other transitions. Theoretical expressions given by Caroli[24] and Kjöllerström[25] for the optical absorption of virtual-bound states suggest qualitatively the same behavior as is given by this assumed matrix-element enhancement.

## V. SUMMARY AND CONCLUSIONS

The photoemission and optical data for Ni-rich Ni-Cu alloys and for alloys of intermediate composition lead to the conclusion that the density of states in alloys containing $\leq 20\%$ Cu is little changed from the density of states of pure Ni. Also, for alloys containing up to 61% Ni, the Cu $d$ states can be identified at energies greater than 2 eV below $E_F$. This and other evidence[2,3] suggests that the Cu $d$ states lie at these energies for higher Ni contents as well. Broadening and reshaping of the Ni $d$ states through interactions is quite important as the Ni content in Cu-Ni alloys increases, and the changes in density-of-states structure in nearly equiatomic alloys may have important bearing on the ferromagnetic properties of these alloys.

It is interesting to note, in light of the inadequacy of the rigid-band model for explaining the densities of states in Cu-Ni alloys, that Eastman and Krolikowski[9] have found that the rigid-band model can relate the density of states of pure Ni to that of pure Cu (and vice versa) with fairly good agreement. In particular, the $d$-band ODS for Ni can be constructed from that of pure Cu using an exchange splitting of $0.4 \pm 0.2$ eV. This result does not necessarily conflict with the finding for the Cu-Ni alloys. In the pure materials, the most important factor determining the electronic structure and the density of states of the $d$ band is the interaction of the $d$ states on different lattice sites. Pure Cu and pure Ni are adjacent to one another on the Periodic Table, have the same fcc crystal structure, and the lattice constants differ by only about 2.5%. Therefore, it is not too surprising that much the same $d$-state structure should result in the two pure materials. However, the fact that the Cu and Ni $d$-state scattering resonances are separated in energy in Cu-Ni alloys and the exclusion of $d$ holes from Cu sites in Ni-rich alloys prevent the common-band behavior and sharing of electrons between the two different atomic species which would be predicted by the rigid-band model.

In principle, the measurement of soft x-ray emission spectra can also give direct information about the density of states of a metal. Such measurements have been made for Cu-Ni alloys by Clift, Curry, and Thompsen.[26] From their measurements, Clift *et al.*[26] drew the correct conclusion that in Cu-Ni alloys there is little sharing of electrons between the two kinds of atoms and that there is no common $d$ band. However, quantitatively the results of Clift *et al.*[26] are quite different from the results found here. Clift *et al.*[26] found that the x-ray emission spectra for any Cu-Ni alloy composition was exactly a compositionally weighted superposition of the spectra from pure Cu and pure Ni. That is, the width and shape of the density of states appropriate for Ni did not appear to change from 10% Ni in Cu to pure Ni. This is in contrast to the finding in the present work that the Ni density of states is narrow ($\sim 1$ eV) at low concentrations and broadens to about 5 eV for pure Ni. This difference in experimental results suggests that the effect of final-state interactions between conduction electrons and the deep hole state[27] or other broadening effects may have been more important in determining the x-ray spectra than the properties of the $d$-band density of states.

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[1] D. H. Seib and W. E. Spicer, preceding paper, Phys.

Rev. B 2, 1676 (1970).
[2]N. D. Lang and H. Ehrenreich, Phys. Rev. 168, 605 (1968).
[3]S. Kirkpatrick, B. Velický, N. D. Lang, and H. Ehrenreich, J. Appl. Phys. 40, 1283 (1969).
[4]C. G. Robbins, H. Claus, and P. A. Beck, Phys. Rev. Letters 22, 1307 (1969).
[5]J. N. Cable, E. O. Wollan, and H. R. Child, Phys. Rev. Letters 23, 1256 (1969).
[6]W. J. Tegart, *The Electrolytic and Chemical Polishing of Metals* (Pergamon, London, 1956), p. 102.
[7]R. E. Vehse and E. T. Arakawa, Oak Ridge National Laboratory, Report No. ORNL-TM-2240, 1968 (unpublished); Phys. Rev. 180, 695 (1969).
[8]A. J. Blodgett and W. E. Spicer, Phys. Rev. 146, 390 (1966).
[9]D. E. Eastman and W. F. Krolikowski, Phys. Rev. Letters 21, 623 (1968).
[10]W. M. Breen, F. Wooten, and T. Huen, Phys. Rev. 152, 505 (1967).
[11]T. A. Callcott and A. U. MacRae, Phys. Rev. 178, 966 (1969).
[12]H. Ehrenreich, H. R. Philipp, and D. J. Olechna, Phys. Rev. 131, 2469 (1963).
[13]W. Scouler, J. Feinleib, and J. Hanus, J. Appl. Phys. 40, 1400 (1969).
[14]A complete compilation of the deduced optical parameters can be found in D. H. Seib, Ph.D. thesis, Stanford University, 1969 (unpublished), which may be obtained by writing Xerox Corp., University Microfilms, 300 N. Zeeb Road, Ann Arbor, Mich. 48106.
[15]F. M. Meuller and J. C. Phillips, Phys. Rev. 157, 600 (1967).
[16]U. Gerhardt, Phys. Rev. 172, 651 (1968).
[17]G. Dresselhaus, Solid State Commun. 1, 419 (1969).
[18]M. Shiga and G. P. Pells, J. Phys. C 2, 1847 (1969).
[19]W. Krolikowski and W. E. Spicer, Phys. Rev. 185, 882 (1969).
[20]D. H. Seib and W. E. Spicer, Phys. Rev. Letters 22, 711 (1969); Phys. Rev. 187, 1176 (1969).
[21]J. C. Phillips, J. Appl. Phys. 39, 760 (1967).
[22]J. R. Cuthill, A. J. McAlister, M. L. Williams, and R. F. Watson, Phys. Rev. 164, 1006 (1967).
[23]J. H. Wood, Phys. Rev. 117, 714 (1960).
[24]B. Caroli, Physik Kondensierten Materie 1, 346 (1963).
[25]J. Kjöllerström, Phil. Mag. 19, 1207 (1969).
[26]J. Clift, C. Curry, and B. J. Thompsen, Phil. Mag. 8, 593 (1963).
[27]B. Roulet, J. Gavoret, and P. Nozières, Phys. Rev. 178, 1072 (1969).

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# Electronic Structure of Alpha-Brass - Coherent-Potential Approach

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The coherent-potential approximation is used to describe the electronic spectrum of disordered alloys. Model potentials of the form used by Soven are employed to calculate the $t$ matrices. The spectral density of states are calculated for various representations at the symmetry points $\Gamma$, $X$, and $L$, and along the $\Delta$ axis for $\alpha$-$Cu_{0.70}Zn_{0.30}$. The results are compared with data derived from the optical studies of the alloy.

## I. INTRODUCTION

The most attractive of the existing theories of the electronic structure of disordered alloys is the coherent-potential (CP) approach discussed by Soven[1] and Velický *et al.*[2] It has been successfully applied to a model one-dimensional alloy of $\delta$-function potentials. In three dimensions, the procedure has been applied to a model alloy described by tight-binding wave functions. This hypothetical alloy is presumed to have constituents whose atomic wave functions are essentially identical but whose atomic eigenvalues are different. Soven[3] and Velický *et al.*[2] have applied the CP model to this hypothetical system (they assumed a special form for the host density of states), and concluded on the basis of the results that the CP model is the best among all single-site approximations.

The object of this work is to apply the CP theory to real disordered alloys. This necessarily calls for some further approximations, but the errors thus introduced should not be more serious than those involved in conjecturing about real alloys from accurate calculations for hypothetical alloys. We chose $\alpha$-brass for this calculation because a number of theoretical calculations with simpler models[4-7] have been done for this alloy. The CP theory as presented by Soven[1] and used in this calculation neglects the presence of the short-range order. Thus, $\alpha$-brass is a suitable system for application of this theory because neutron-diffraction experiments indicate that there is no short-range ordering in $\alpha$-brass.[8]

The essence of the CP model is to place at each site of the alloy lattice a potential $V_c$, which will simulate the electronic properties of the actual al-