Rev. Letters 19, 644 (1967)], of a simple treatment of band structures (ibid.), and even of finite d-band conduction would further decrease L_i. Such calculations would indicate an L_i for Pd of the order of a few tenths of 1×10^{-8} V^2 deg^{-2} [a Lorenz number of this order has been suggested for Pt by the recent experimental work of Anderson, Peterson, and Robichaux, Ref. 3; however, recent revision of the laboratory temperature scale at liquid He^3 temperatures (see, for example, Ref. 5) will increase the observed value of L_i for Pt (A. C. Anderson, private communication)] in contrast to Schriempf's (Ref. 5) observed value of 1.1×10^{-8} V^2 deg^{-2}.

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EXPERIMENTAL EVIDENCE FOR THE VALIDITY OF THE VIRTUAL BOUND-STATE MODEL FOR Cu-Ni ALLOYS*

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Photoemission and reflectivity data from copper-rich copper-nickel alloys are presented. A rigid-band model is found not to hold for these alloys; rather the virtual-bound-state model gives a more adequate description of the electronic structure.

In this Letter we present experimental results for the copper-nickel alloy system which appear to distinguish between two models that have been used previously to describe the electronic structure of these alloys, namely the rigid-band model[1] and the virtual–bound-state model.[2,3] In the rigid-band model the copper and nickel atoms are assumed to form common d bands, as well as common s-p conduction bands. Then when nickel, which has one less electron than copper, is alloyed with copper, this model predicts that the s-p bands should empty progressively, decreasing the d-band to Fermi-level energy separation. At 40 to 50% nickel the Fermi level should coincide with the top of the d band. Quite different behavior is predicted by the virtual–bound-state model. In this case the nickel d states (in a copper-rich alloy) would not form a common band with the copper d states; rather they would form virtual bound levels, probably with energy between that of the copper d states (located about 2.1 eV below the Fermi level) and the Fermi level. With this model the energy difference between the top of the copper d levels

and the Fermi surface might remain constant as nickel is alloyed with copper.

Previous optical data for copper-nickel alloys, obtained calorimetrically by Schröder and Önengüt,[4] appeared to disagree with the rigid-band model. In particular, in measurements of absorptivity for nickel concentrations less than about 15%, the threshold for copper d-state excitation seemed unchanged while additional transitions from states between the copper d states and the Fermi level appeared, presumably because of the excitation of nickel d states. Recent reflectivity measurements by Scouler, Feinleib, and Hanus[5] and by the present authors give similar results. In addition to the measurement of optical reflectivity, we have made photoemission measurements of some copper-rich alloys. By measuring the energy distribution of photoemitted electrons, one can obtain much more detailed information about the density of electronic states (and hence the electronic structure) than through optical measurements alone. This is because the optical measurements depend upon an integral of the transition probabilities from all possible ini-

tial states, while it is possible through the photo-emission measurement to obtain the transition probability from initial states at a given energy and thus to obtain a direct measure of the density of states at that energy. In particular, we will show that it has been possible to locate the position of the copper d states relative to the Fermi energy in copper-rich copper-nickel alloys by using the photoemission technique. It has also been possible to detect the build-up of additional states between the top of the copper d states and the Fermi level as the nickel content increases.

Photoelectron energy distributions and quantum yield have been measured in the spectral energy region $5.0 \leq h\nu \leq 11.8$ eV for single crystals of copper and for alloys of composition 90% Cu: 10% Ni and 77% Cu:23% Ni. The samples were prepared from alloy crystals obtained from Research Crystals Inc. and Aremco, Inc. The alloy crystals were made by the Bridgman technique from 99.999%-pure materials. After annealing, the samples were spark cut to size and mechanically polished. The pure copper and 90% Cu:10% Ni samples were electropolished and 77% Cu:23% Ni sample was chemically polished to remove layers damaged by the mechanical treatment. The final cleaning of the surfaces prior to photoemission measurements was accomplished by heating the samples in a high-vacuum chamber. Chamber pressure during heating was approximately 10^{-8} Torr; pressure during measurement was approximately 10^{-9} Torr. Heating to temperatures of about 600°C for about 12 h was found sufficient to clean the sample surfaces. By using this heat-cleaning technique, we have been able to completely reproduce photoemission results from pure copper and pure nickel that were obtained previously using evaporated films of these materials[6,7] and nickel surfaces prepared by argon bombardment.[8] The 77%-Cu alloy showed visible evidence of some inhomogeneity due to dendritic growth. Microprobe analysis made after the photoemission and optical measurements (with resolution of about 2 μ) revealed that the nickel content in various regions of the sample varied from 19 to 27%.

It is important to consider the possibility of clustering in the alloys studied. Clustering would be of critical importance only if clusters of almost pure nickel too small to be detected by the microprobe analysis occurred in the alloy. Recent studies of short-range order in the copper-nickel system[9] have shown that clustering

does not occur to anything approaching that extent. For example, in an alloy of composition 52.5% Cu:47.5% Ni, the probability of a nickel atom having a nickel nearest neighbor has been found to be 0.54 instead of 0.475. In other compositions the magnitude of the effect is expected to be similar. Thus, the effects of inhomogeneity and short-range order cause only slight deviations from the average composition; they do not lead to clusters of almost pure nickel.

In Fig. 1 we show typical energy distribution curves (EDC) from pure copper and alloys containing 10 and 23% nickel in copper. The exciting photon energy is 10.2 eV. The curves were obtained using an ac modulated-retarding-potential technique which has been previously described.[10,11] The horizontal axis is calibrated so that the zero of energy is the Fermi energy and the emitted electrons are referred to their initial-state energy with respect to the Fermi energy. This is accomplished by subtracting the exciting photon energy from the kinetic energy of the emitted electrons and adding the work function. All curves are referred to the same zero in this way. The number of photoelectrons near the Fermi energy is reduced in the EDC by electron scattering and resolution effects. Examination of alloy EDC for different exciting photon energies indicated that the structure in the curves moved with $h\nu$ (except for the shoulder in the 90% Cu:10% Ni curve at low energies, which appears to be due to structure in the effective final density of states).
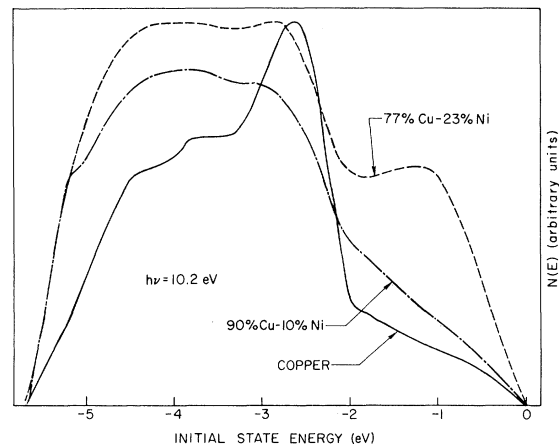

FIG. 1. Photoelectron energy distributions from copper and two copper-rich copper-nickel alloys. The number of photoemitted electrons, in arbitrary units, is plotted versus initial-state energy. Constant Fermi level to copper d-state energy separation is indicated by the change in slope and rapid rise at about 2.1 eV in all three compositions.

For example, this behavior is clearly seen in Fig. 2, where alloy EDC are shown for three different exciting photon energies. The emitted electrons are referred to their initial energies as before. It can be seen that structure in the curves for differing photon energies superimposes in energy very well, viz., the peak at about −1.2 eV in the 77% Cu alloy. In this type of plot, superposition in energy of structure is equivalent to movement of the structure with photon energy in the unshifted EDC (since the photon energy has been subtracted from the kinetic energy of the electrons). Movement of structure with photon energy implies that the structure originates in the filled density of states and that direct conservation of $\vec{k}$ is not an important selection rule.[12]

Several interesting points are evident from the curves of Fig. 1. EDC for the alloys, as well as for pure copper, exhibit a region of relatively low state density from 0 to −2.0 eV followed by a distinct change in slope and rapid rise in the density of filled states. In pure copper this rapid rise is due to the d states, indicating that the d-state to Fermi-level energy separation is 2.1 eV. That the slope change occurs at precisely the same energy in the alloys studied indicates that the copper d-state to Fermi-level separation is unchanged upon alloying. This is in contrast to predictions based on the rigid-band model, which would imply that the energy separation between the d state and Fermi level should decrease as nickel is alloyed with copper. It is in agreement with the virtual−bound-state model for the alloys. Furthermore, the constant energy separation between the d states and the Fermi level suggests that a resonant description of the copper d states may be appropriate.[13]

The relative number of states in the region between 0 and −2.0 eV is seen to increase with increasing nickel content; in fact a broad peak occurs at about −1.2 eV in the curve for 77% Cu: 23% Ni. This increase is due to the nickel d states, which appear to exist as virtual bound levels in this energy region. Another effect of the alloying process is to smear out structure in the valence-band optical density of states. In particular, the first d-state peak, which is very large in pure copper, is greatly reduced in the alloys.

In addition to EDC we have measured optical reflectivities [of the alloy samples] at near-normal incidence from $h\nu = 0.5$ to 11.8 eV. From 1.2 to 11.8 eV the measurements were made in vac-
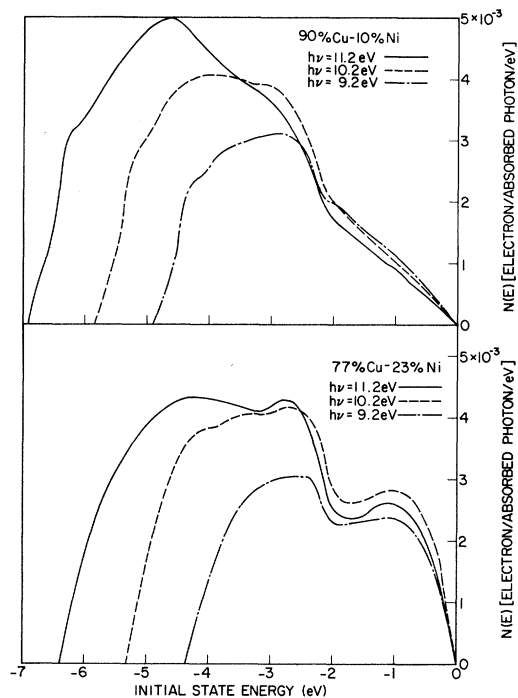

FIG. 2. Photoelectron energy distribution curves for copper alloys. The horizontal axis gives the initial-state energy and the vertical axis the number of emitted electrons per absorbed photon per eV in absolute units. The fact that the position of structure coincides on such a plot independent of $h\nu$ indicates that direct conservation of $\vec{k}$ is not an important selection rule.

uum on heat-cleaned samples; measurements from 0.5 to 1.2 eV were made in air. The results of these measurements are shown in Fig. 3 along with data of Ehrenreich and Philipp[14] for pure copper. As previously noted, these reflectivity spectra are consistent with those obtained by other workers.[4,5] Copper exhibits a sharp drop in reflectivity at $h\nu = 2.1$ eV because of strong absorption by electrons excited from the d states to the Fermi level. The reflectivity of the 90%-copper sample also exhibits a sharp drop at exactly the same photon energy, and the 77%-copper sample shows a rapid, though not so steep, decline beyond 2.0 eV. The constant energy position of the reflectivity drop in the alloys is further indication that the Fermi level to copper d-state energy separation is unchanged upon alloying. It is also evident that the reflectivity between 0 to 2.0 eV decreases monotonically with increase in the nickel content. This is additional evidence for the build-up of states between the Fermi level and the top of the copper d states. Similar results have been obtained by Abeles[15] for Au:Pd alloys and by Karlsson, Myers, and
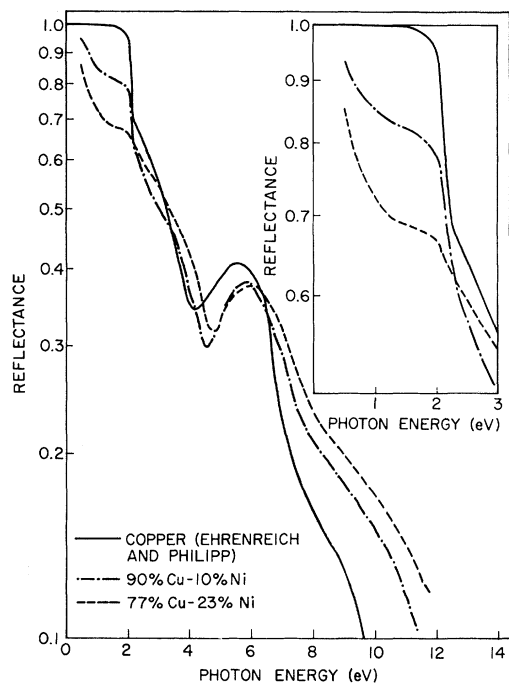
FIG. 3. Reflectivity at near-normal incidence for copper and two copper-rich alloys. The insert shows in more detail the energy region where transitions from the copper d states begin.

Wallden[16] for Au:Pd, Ag:Pd, Ag:Mn, and Cu:Pd alloys.

Two striking conclusions can be drawn from the data presented here. First, the energy separation between the top of the copper d states and the Fermi level does not change appreciably with the alloying of up to 23% nickel. Second, the addition of nickel produces a strong increase in the number of states between the top of the copper d states and the Fermi level. These results are strongly in disagreement with the predictions of the rigid-band model[17] but are in basic agreement with the virtual–bound-state model.[18] The lack of sensitivity of the energy spacing between the top of the copper d states and the Fermi energy to alloying with nickel supports the suggestion of a resonant-state description for the copper d states. If the lifetime of a d-state hole in a resonant state is comparable with or longer than the optical excitation time (about 10^{15} sec), this would provide sufficient localization so that conservation of $\vec{k}$ would not constitute an important selection rule.

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[18]It has been pointed out to the authors by Dr. Edward Stern that the present experimental results can be understood in terms of his charging model, which reduces to the virtual–bound-state model when the solute has d states in the "s-p" conduction continuum of the solvent [E. A. Stern, Physics 1, 255 (1965)].