Bulk and Surface Effects in Photoemission from Disordered *Cu*-Ni Alloys

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We report a synchrotron-radiation study of angle-resolved photoemission from single crystals of the random alloy Cu–40%-Ni, combined with first-principles Korringa-Kohn-Rostoker coherent-potential-approximation photocurrent calculations. We find that the intensity of emission from the Ni *d* states, relative to that from the Cu *d* states, reveals the $\vec{k}$ and energy dependence of the disorder broadening of the electron states. Our results indicate that the surface composition profile is monotonic and not, as previously reported, oscillatory.

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Because of its interesting properties in many areas of solid-state physics (e.g., magnetism), the random-alloy system Cu-Ni has long been the subject of intense theoretical and experimental scrutiny.[1] Its electronic structure is the classic example of split-band behavior, with two sets of *d* bands clearly visible in uv photoemission[2,3]; indeed, this observation stimulated the development of the modern electronic theory of alloys.[1] In a recent (angle-integrated) photoemission study of a single-crystal alloy containing 40% Ni, Ling *et al.*[4] measured the relative intensity of the photoemission from the Ni and Cu *d* bands, $I(\mathrm{Ni})$ and $I(\mathrm{Cu})$, respectively. They found that the ratio $R(\nu) = I(\mathrm{Ni})/I(\mathrm{Cu})$ varied with photon energy ν in an oscillatory fashion. To explain this phenomenon they made the suggestion, frequently quoted in the literature of surface segregation, that the composition of the alloy exhibits very strong oscillations in the vicinity of the surface, with the first (surface) layer being Cu rich, the second Ni rich, and so on. They argued that the energy dependence of the photoelectron escape depth would cause measurements at different photon energies to probe regions of different average composition producing, roughly, the observed Ni to Cu emission ratio $R(\nu)$. Crucial to their argument is the assumption that the relative cross section for excitation from the Ni and Cu *d* bands is constant as a function of ν. In this Letter we use first-principles calculations, based on the Korringa-Kohn-Rostoker coherent-potential approximation (KKRCPA), together with more detailed angle-resolved photoemission measurements, to demonstrate (a) that the relative cross section for excitation from the two sets of *d* bands is a strong, and in fact oscillatory, function of ν, (b) that this variation arises directly from a key effect in alloy theory, namely, the energy and $\vec{k}$ dependence of the disorder self-energy, and (c) that although Cu certainly segregates strongly to the surface, there is no evidence from photoemission for compositional oscillations normal to the surface in Cu-Ni alloys.

Angle-resolved uv photoemission measurements were made on three single-crystal specimens of Cu–40%-Ni, with (100), (110), and (111) faces, at the 2-GeV synchrotron radiation source at the Daresbury Laboratory, using a VG ADES400 spectrometer on beam line 6. The specimens were cleaned *in situ* by a series of Ar^+ bombardment (800 V, 6 μA cm^{-2} for 30 min) and annealing (430 °C for 30 min) cycles; we have established in earlier work that this procedure results in stable and reproducible equilibrium surfaces.[3] We collected spectra in the energy range 40 eV $< h\nu <$ 180 eV, and the total energy resolution was 0.3 eV. In Fig. 1 we show a selection of normal-emission spectra from the (100) face. The prominent peaks at binding energies of ~ 0.8 and ~ 2.5 eV arise from the Ni and Cu *d* bands,[3] respectively, and the strong variation of their relative intensity with ν is clear. Also shown are calculated spectra, evaluated according to the one-electron theory of Durham.[5]

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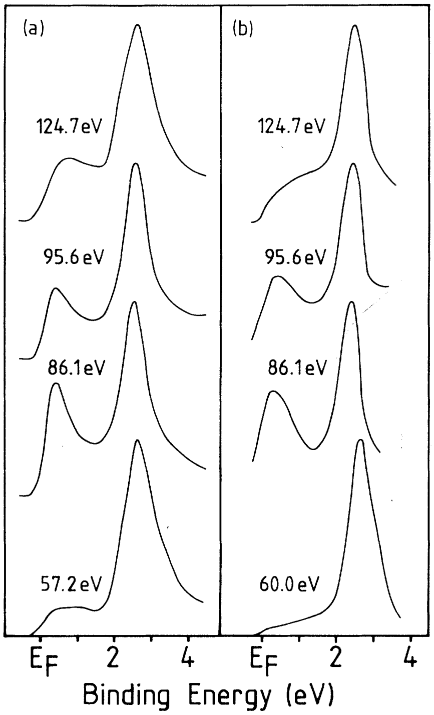

FIG. 1. (a) Experimental and (b) calculated normal-emission spectra from Cu–40%-Ni (100) with p-polarized photons incident at 20°.

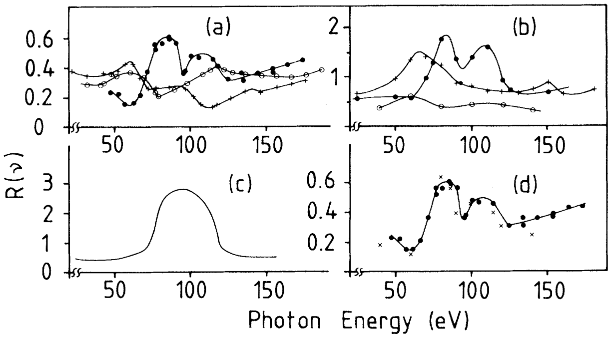

FIG. 2. (a) Experimental and (b) calculated $R(\nu)$ for the, closed circles, (100); open circles, (110); and pluses, (111) faces. (c) Calculated ratios for the (100) face assuming a free-electron final state. (d) Full calculation (crosses) for the (100) face of an alloy of uniform composition with a surface layer of pure Cu compared with experiment (closed circles).

The model underlying these calculations is a semi-infinite random substitutional lattice of Cu and Ni muffin-tin potentials plus, as an approximation to the surface dipole, a step-function potential tangential to the uppermost layer of muffin tins. The KKRCPA is used to determine the configurationally averaged photocurrent. We have applied this formalism in an intensive study of the bulk[3] and surface[6] spectral density of Cu-Ni alloys and there, as in Fig. 1, the agreement with experiment is satisfactory. Since the present work is concerned with the intensities of photoemission features, we stress that our calculations contain electron-photon matrix elements which are exact in the nonrelativistic one-electron limit. The only (undetermined) parameters in our theory represent the lifetime broadening of the excited state; as realistic values we used a width of 0.14 eV for the d-band, and an energy-dependent broadening for the photoelectron taken from Müller, Jepsen, and Wilkins.[7]

After background subtraction, we obtain the Ni to Cu intensity ratio, $R(\nu)$, shown in Fig. 2(a), from our experimental spectra. "Oscillations" similar to those reported by Ling *et al.* are evident, but $R(\nu)$ has a markedly different form for each face. The calculated intensity ratios, in Fig. 2(b), show just the same features, with the difference between the faces being particularly well reproduced.[8] (Note, however, the discrepancy in amplitude—we return to this shortly.) Since in the calculations in Fig. 2(b) we assumed uniform concentration throughout the alloy (i.e., no surface segregation), the oscillations in $R(\nu)$ have nothing to do with the surface composition profile. In fact, the characteristic form of $R(\nu)$ is a consequence of variations in initial-state density across the Brillouin zone, as we now demonstrate.

A convenient $\vec{k}$-space representation of the electronic structure of a substitutionally disordered system is the Bloch spectral function,[1,9] $A_B(\vec{k},E)$, which gives the average number of states in the in-

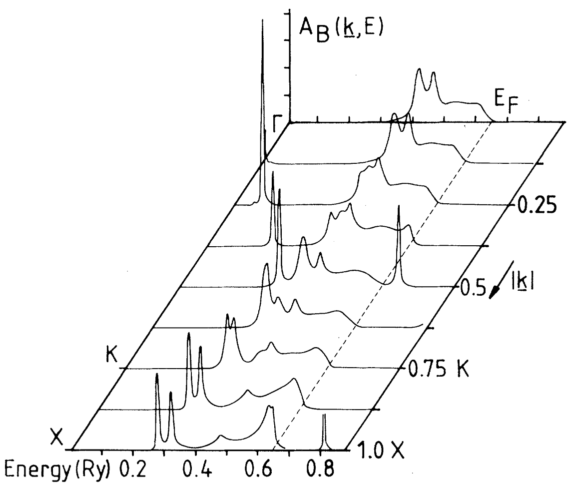

FIG. 3. KKRCPA calculation of the Bloch spectral function for Cu–40%-Ni along ΓKX. Energy scale is in rydbergs.

terval $(E,\vec{k})$ to $(E+dE,\vec{k}+d\vec{k})$. A KKRCPA calculation for Cu–40%-Ni along the ΓKX direction is shown in Fig. 3. In the limit of weak disorder, where the virtual crystal approximation holds, $A_B(\vec{k},E)$ has the form of a set of delta-function peaks at $E=E_k^{vc}$, i.e., the virtual crystal bands. Strong disorder broadens and shifts these peaks, and sometimes even splits bands into contributions associated with each component. One could attribute such modifications to a disorder self-energy. Figure 3 shows that the KKRCPA produces a very complex self-energy which varies strongly with E and $\vec{k}$. For the present purposes, the most important feature is the behavior of the Ni d states ~1 eV below the Fermi level. At the Γ point these states are considerably broadened by disorder, but they rapidly sharpen as the X point is approached,[3] where one can even resolve X_2- and X_5-type Ni states. A similar narrowing occurs also around the K and L points, but the effect is greatest at the X point. (The plot of the spectral density along the Σ direction shown in Fig. 3 conveniently illustrates the behavior at the high-symmetry points Γ, K, and X.)

In the direct transition picture, varying the photon energy in normal emission amounts to scanning $\vec{k}$, in a given direction, at a rate determined by the dispersion of the final state.[10] Therefore, we would infer from Fig. 3 that for the (100) face, $R(\nu)$ should be large for transitions near the X point, and smaller elsewhere. This is the basic mechanism at work in Fig. 2. To support this suggestion we have approximated the dispersion of the final Δ_1 state by a free-electron fit, determined the $\vec{k}$ point of the direct transition for each value of ν, and then used the amplitude of peaks in $A_B(\vec{k},E)$ to estimate $R(\nu)$ for the (100) face. The result, shown in Fig. 2(c), clearly follows that in Fig. 2(b) in overall shape. [The minimum in the latter at ~95 eV is due to a final-state band gap at the X point. This effect is included implicitly in our full photocurrent calculations but not, of course, in the free-electron final-state model used in Fig. 2(c). The agreement between the calculated and experimentally observed positions implies that the final states (calculated with use of the KKRCPA) are accurate.] The face dependence of $R(\nu)$ is qualitatively explained by the same model—the positions of the maxima and minima are simply a consequence of the geometry of the Brillouin zone. The direct transition picture also implies a small but characteristic variation of peak binding energies with ν (and hence $\vec{k}$), and we find this effect. We conclude, therefore, that the form of $R(\nu)$ is a direct reflection of the disorder self-energy in different regions of $\vec{k}$ space.

Most experimental studies suggest that the surfaces of *Cu*-Ni alloys are ~100% Cu. In Fig. 2(d) we show a full calculation of $R(\nu)$ for an alloy of uniform composition with a surface layer of pure Cu. The calculation agrees remarkably well with experiment, not only as regards the shape of the oscillation, but also in amplitude. Clearly, d states in the top (pure Cu) layer contribute significantly to the photocurrent, and they are approximately degenerate with those in the bulk. However, the form of $R(\nu)$ still reflects the bulk spectral density. Thus, the experimentally observed $R(\nu)$ provides strong (quantitative) evidence for Cu segregation, but no evidence for an oscillatory concentration profile at equilibrium surfaces, at least for the (100) surface. [Such composition profiles have been predicted[11] for the surfaces of alloys with a tendency to order (e.g., Cu-Pd), but not for clustering alloys like Cu-Ni.]

In summary, we have shown that the *form* of $R(\nu)$ reveals the energy and $\vec{k}$ dependence of the disorder self-energy rather than the surface composition profile. This self-energy is an important aspect of any realistic alloy theory; its detailed behavior near the Fermi level has been shown to determine transport properties of Ag-Pd alloys,[12] for example. Here, we see directly that it is described well by first-principles KKRCPA calculations. On the other hand, the *magnitude* of $R(\nu)$ is sensitive to the surface composition; we suggest that for split-band alloys measurements of $R(\nu)$ may provide a general method for separating surface and bulk effects in photoemission.

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