Photoemission: A Probe of the Surface and Bulk Electronic Structure in Metallic Alloys

Alloy Research Center and Department of Physics
Florida Atlantic University, Boca Raton, FL 33431-0991

Many of the properties of metallic alloys are determined by the underlying electronic structure, that is, the distribution of electrons in energy, space, and momentum, within the material. In order to understand the properties of alloys, therefore, one seeks a realistic description of the electron states. Sophisticated calculation schemes exist for determining electronic structures, but it is important that results are compared with suitably discriminating experimental probes, such as ultraviolet and x-ray photoelectron spectroscopy. This paper describes recent work on Cu-Au and Fe-Ni alloys to demonstrate some applications of photoemission as a probe of the surface and bulk electronic structures in metallic alloys.

Introduction

It is now accepted that photoemission is the most useful probe of the surface and bulk electronic structures in metallic solids. When measurements are combined with a proper first-principles analysis, theory can be confronted in a most detailed manner. This is because quantities of particular interest—for example, the densities of states or the electronic spectral density—can be probed more or less directly using photoemission. For instance, it can be shown that at photon energies in excess of 50 to 100 eV, the angle-integrated photocurrent can be written as (Ref 1, 2):

\[ I(\omega, \varepsilon) = \sum_{j,l} |M_{lj}(\omega, \varepsilon)|^2 n_l(\varepsilon) \]  

(Eq 1)

where \( \omega \) is the photon energy, \( n_l(\varepsilon) \) is the resolved density of states at site \( j \) and energy \( \varepsilon \), and \( M_{lj}(\omega, \varepsilon) \) is the electron-photon matrix element at site \( j \) connecting the initial and final states (with \( l = l' \pm 1 \)). Thus, the photocurrent is directly related to a sum of the local densities of states modulated by the site-dependent photoemission cross section. The cross section is atomic in nature, and its variation with energy depends on the type of atom and the angular momentum of the initial state; calculated values of the atomic photoionization cross sections for the elements \( 1 < Z < 103 \) have been tabulated by Yeh and Lindau (Ref 3). In the cases of pure metals or alloys in which the local densities of states do not overlap, it is relatively straightforward to obtain quantitative information about densities of states from angle-integrated photoemission measurements. The only effect of the energy dependence of the cross section is to "skew" the density-of-states function, an effect that can be accounted for using a suitable calculational scheme (Ref 2). However, in the case of metallic alloys where the local densities of states overlap—such as in transition metal alloys—the extraction of "experimentally determined" densities of states becomes more difficult. Nevertheless, as shown below, one can make use of the different energy dependencies of the cross sections from the constituents in the alloy to obtain local densities of states.

In the case of angle-resolved photoemission, the photocurrent can be expressed as (Ref 4):

\[ I(\vec{k}^\parallel, \omega, \varepsilon) = \sum_n \int d\varepsilon' \left| \langle f | \delta(\varepsilon' - \varepsilon) | i \rangle \right|^2 A_n(\vec{k}^\parallel, \varepsilon) \]  

(Eq 2)

where \( \langle f | \delta(\varepsilon' - \varepsilon) | i \rangle \) is the final state that propagates into the detector with wave vector \( \vec{k}^\parallel \) parallel to the sample surface, \( \Delta = -iA^* \cdot \vec{p} = iA^* \cdot \nabla / \omega \) in which \( A^* \) is the fine structure constant, \( A^* \) is the photon vector potential, \( \vec{p}^* \) is the electron momentum, \( \nu \) is the potential in which the electron moves, \( \omega \) is the photon energy, and \( A_n(\vec{k}^\parallel, \varepsilon) \) is the Bloch electronic spectral density. In an ordered system, for example, and ignoring the effects of the surface, the electronic spectral density can be expressed in terms of the Bloch eigenvalues of the infinite crystal, \( \varepsilon_n(\vec{k}^\parallel) \), namely:

\[ A(\vec{k}^\parallel, \varepsilon) = \sum_n A_n(\vec{k}^\parallel, \varepsilon) = \sum_n \delta(\varepsilon - \varepsilon_n(\vec{k}^\parallel)) \]

where \( n \) is the band index. In crossing the surface the parallel component of the photoelectron wave vector is conserved modulo a surface reciprocal lattice vector, that is:

\[ \vec{k}^\parallel = \vec{k}^\parallel + G^\parallel \]

The electron state at the detector is a plane wave, \( |K_p> \), with:

\[ |\vec{k}^\parallel> = [2(\varepsilon - V_0)]^{1/2} \sin \theta \]

where \( V_0 \) is the inner potential. Thus, from Eq 2 it can be seen that angle-resolved photoemission measurements provide more or less direct information concerning the \( \vec{k}^\parallel \) dependence of the electronic structure. Of course, in general, the electronic
Section I: Basic and Applied Research

The Cu-Local Density of States in Equiatomic CuAu

Figure 1(a) shows a selection of valence band spectra for CuAu (Ref 6, 7). The spectra are dominated by emission from the Cu 3d states in the energy range 1 to 3 eV and Au 5d states in the energy range 1 to 7 eV. Clearly, the Cu and Au contributions overlap in these spectra. It turns out that the individual Cu and Au photoemission cross sections are comparable in magnitude at a photon energy of about 50 eV, but at about 160 eV the ratio of the Cu 3d to Au 5d photoemission cross section is about 20 to 30 (Ref 3, 6). Thus, the large difference in cross sections at this photon energy allows one to probe the Cu local density of states in the alloy.

Figure 1(b) shows a series of photocurrent calculations using the code developed by Durham and Guo (Ref 2) that includes a relativistic form of the electron-photon interaction. The authors used the potential functions and densities of states obtained from a fully relativistic KKR calculation of the electronic structure in CuAu. They included a hole inverse lifetime of 0.2 eV and folded in a Gaussian function with a full spectral density being probed is that in the surface region, and so the photocurrent includes contributions from “surface states” as well as “bulk states” (although it is not really appropriate to separate the two). The electron-photon matrix elements are strongly polarization dependent, and so by a judicious choice of photon-incidence angles and polarization one can probe initial states of particular symmetry.

The description so far contains approximations that may limit the applicability of the approach. Not contained in these expressions are many-body effects. When the electron is excited, it produces a “hole,” and following the creation of the electron-hole pair, many-body interactions occur (Ref 5). The key quantity for describing this behavior is the self-energy, which represents a “correction” to the 1-electron (ground state) eigenvalues. Providing self-energy effects are not too large and vary slowly with respect to energy, then the main features of the (ground state) spectral function remain distinct, although broadened and shifted from their ground state values (Ref 5). Thus, comparisons between photoelectron spectra and band calculations are still possible.

This paper describes some of the authors’ recent photoemission investigations involving angle-integrated and angle-resolved measurements. In particular, the authors show how it is possible (1) to determine experimentally the Cu-local density of states in equiatomic CuAu, (2) to investigate the magnetic state of Fe atoms in Fe-Ni alloys in the bcc and fcc structures, (3) to utilize Shockley-type surface states to examine the variation of the neck radius on the Fermi surface with composition of Cu-Au alloys, and (4) to utilize Tamm-type surface surfaces to investigate the different environments at the (100) and (001) surfaces of CuAu.
width at half maximum of 0.4 eV to simulate the experimental resolution. They included the effect of segregation of Au to the surface by taking the photocurrent to be a sum over layers of the form:

$$I_{\text{total}} = \sum_n (c_n I_{\text{Au}} + (1 - c_n) I_{\text{Cu}}) e^{-\frac{n\lambda}{\lambda}}$$  \hspace{1cm} (Eq 3)

where \( n (= 0, 1, 2, \ldots) \) is the layer number, \( c_n \) is the Au concentration in layer \( n \), \( I_{\text{Au}} \) and \( I_{\text{Cu}} \) are the individual Au and Cu contributions to the photocurrent from Eq 1, and \( \lambda \) is the electron mean free path (in numbers of layers). In these calculations the authors took \( c_0 = 0.8 \), \( c_{\text{seg}} = 0.5 \) (Ref 6, 7), and \( \lambda = 3 \). The overall agreement is very striking, although there are some small discrepancies, for example, in the weight of the Au-related emission at \(-4 \) eV and the overall positions of the peaks in the calculations are shifted toward the Fermi energy by about 0.7 eV. Thus, one can conclude that the calculated Au contribution to the density of states in the 4 to 5 eV range is rather too large. It should be noted that differences in peak positions of the magnitude observed here are not unusual with such comparisons and are due to the authors' neglect of the real part of the self-energy.

Figure 2 shows an overlay of the theoretical and experimental spectra at a photon energy of 160 eV after aligning the peaks positions; this is essentially a direct comparison of the calculated Cu local density of states with that observed experimentally. The very good agreement suggests that the calculated local density of states is certainly realistic. The small discrepancies may be due to the assumption of a simple energy-independent Lorentzian function for the lifetime broadening and/or the choice of the magnitude of the hole inverse lifetime (Ref 7).

Now that a method of extracting experimentally the Cu local density of states in CuAu has been obtained, a number of other comparisons can be made, for example, with pure Cu (see Fig. 3) and between the Cu local densities of states in ordered and disordered equiatomic CuAu, as shown in Fig. 4. In the comparison shown in Fig. 3, the spectra have been normalized to peak height; note that there is a small shift of the peak positions to increased binding energy in the alloy and the density of states in pure Cu is about 0.6 eV broader. The latter is likely due
to the fact that Cu has 12 like-nearest neighbors (2.56 Å apart), whereas in CuAu the Cu atoms have only 12 like-neighbors (2.80 Å apart). Thus, pure Cu has a larger d-band width. The comparison shown in Fig. 4 suggests that there is little difference in d-band width of the Cu-related states in ordered and disordered equiatomic CuAu, although the peak in the ordered case is shifted by 0.27 eV to increased binding energy.

**Magnetic State of Fe Atoms in Some bcc and fcc Fe-Ni Alloys**

Figure 5 shows a plot of the experimentally determined average magnetic moment in Fe-Ni alloys (Ref 8). As Fe is added to Ni, the moment of the disordered fcc, γ phase alloys increases approximately linearly, following the Slater-Pauling curve, until about 50% Fe, where the moment falls below the line. At about 70% Fe, the moment drops rapidly, but on transforming to the bcc, α phase, the moment is recovered. The question is: what causes the drop in the observed moment?

Table 1 Spin-Splittings Obtained by Fitting Doniach-Šunjic Lineshapes to the Spectra in Fig. 6(a) and (b) and to a Pure Fe 3s Spectrum

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spin-splitting (±0.2 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Fe</td>
<td>4.5</td>
</tr>
<tr>
<td>αFe-27.5%Ni</td>
<td>4.1</td>
</tr>
<tr>
<td>γFe-27.5%Ni</td>
<td>4.1</td>
</tr>
<tr>
<td>αFe-30%Ni</td>
<td>4.2</td>
</tr>
<tr>
<td>γFe-30%Ni</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Note: The measurements were made at room temperature.

One suggestion that can be investigated using photoemission is whether the local moment on the Fe atoms, which provides the major contribution to the total moment, collapses in the γ phase, but can be recovered in the α phase.

It has been shown previously that one can use the spin-splitting observed in the photoemission spectrum of the Fe 3s core as a "measure" of the local moment on the Fe site (Ref 9, 10). Thus, a comparison of the Fe 3s core level spectra in the α and γ phases indicates any environmental dependence of the Fe local moment. Accordingly, Fig. 6 shows two such comparisons for alloys containing 70% and 72.5% Fe. It is immediately apparent that there is little change in the spin-splitting in the two phases (Ref 11) (see also Table 1).

Thus, it would appear that the splittings in the alloys are about 10% less than that in pure Fe, so that, according to the authors' approach, the Fe local moment in the alloys appears smaller than that in pure Fe. In fact, this is consistent with the polarized neutron diffraction results of an alloy containing 34% Ni, which showed that at room temperature the Fe local moment was some 20% lower in the alloy than that in pure Fe (although at lower temperatures it was larger).

The authors' observation that the Fe local moment does not collapse implies the existence of antiferromagnetically coupled or randomly oriented local moments in the γ phase alloys in this composition range. There is some previous work that would suggest that the apparent reduction is due to antiferromagnetism (see references in Ref 11).

**Surface States in Cu-Au Alloys**

The spectral density probed in photoemission measurements is that of the surface region. Thus, it contains both "surface" and "bulk" contributions. Whereas in most applications, pho-
toemission is used to provide details about bulk states—for comparison with band structure calculations, for example—surface states can also furnish highly detailed information. Surface states result from the change in periodicity of the lattice (Ref 12); true surface states—in contrast to surface resonances—are located in energy gaps of the bulk band structure. There are two types of surface states, and they are identified by their angular momentum character, namely “Shockley” (s,p-like) and “Tamm” (d-like) states. The former arise from the boundary conditions that are introduced by the surface, and they occur in the energy gaps at the Brillouin zone boundary caused by the hybridization of s-p bands in which the lower band has odd parity (p-like) and the upper band has even parity (s-like). Shockley-type states decay exponentially into the crystal, but often extend over several atomic spacings. They are derived from bulk states and, as shown below, can provide information about those bulk states. Tamm-type states, on the other hand, are split off from bulk states by the surface potential. They are confined to the outermost layer of the crystal and are very sensitive to the charge distribution in the surface plane. They can be used therefore as a probe of the structure at the surface. In the following two sections, some of the authors' very recent studies of surface states in Cu-Au alloys are described.

Shockley-Type Surface States in Cu-Au Alloys

Probably the most well-known Shockley-type surface state is that which is located in the gap between the L₂ and L₁ states at the L-point in Cu (Ref 13). It is observed near the Fermi energy in the normal emission spectrum from the (111) surface; the intensity is strongly polarization and photon energy dependent, being excited by p-polarization (i.e., with \( \vec{A} \) perpendicular to the surface) and enhanced at low photon energies (e.g., ArF radiation) (Ref 14, 15). The energy of the surface state does not change with photon energy (Ref 14), that is, it does not disperse with \( k \rightarrow \frac{\pi}{a} \), but it does follow the dispersion of the uppermost occupied band in the \( k \rightarrow \frac{\pi}{a} \) direction, for example, along \( LW \) and \( LK \). Because this band is responsible for forming the “neck” on the Fermi surface at the L-point, the occupied extent of the surface state in \( (E, k^2) \) space is related directly to the radius of the neck (Ref 16).

The occurrence of a Shockley-type state is a direct consequence of the presence of the surface, but it turns out that segregation probably does not play a significant role. In Cu-Pd disordered alloys (Ref 17), for example, it has been shown that the bulk “L₂ state” in the electronic spectral density at the L-point is very sharp with a considerable coherence length. Consequently, it is only slightly perturbed by the surface and the energy of the surface state derived from it will remain largely unaffected by the surface potential. In addition, at the L-point in the surface Brillouin zone the surface-state wave function has p-character, and because the scattering in the p-channel is small, the surface state is rather free-electron-like and not particularly sensitive, therefore, to the surface potential. (This is in direct contrast to Tamm-type states.) As a result, there is now a method to probe the variation of the neck radius at the L-point in noble metal based alloys such as Cu-Au.

**Fig. 7** Photoemission spectra from the (111) surface of Cu showing the dispersion of the Shockley-type surface state; (unpolarized) ArF radiation at an incidence angle of 66° with the emission angles shown to the right of the spectra. The dashed curve shows the locus of the peak positions.

**Fig. 8** Photoemission spectra from (a) the (100) and (b) the (001) surfaces of CuAu; (unpolarized) He\( \alpha \) radiation at an incidence angle of 55° with the emission angles as shown. The incidence/emission planes are (001) and (100) for (a) and (b), respectively. The shaded feature labeled S is a Tamm-type surface state.
The authors have begun an investigation of the Shockley-type surface states on the (111) surfaces of Cu-Au alloys. Figure 7 shows some results for pure Cu. (The two peaks that are visible are due to two components in ArI radiation at 11.68 eV and 11.82 eV and demonstrate the high resolution of the authors' instrument.) The surface state disperses across the Fermi level, and the extent in \( k^* \) space is 0.220 Å⁻¹. Initial results for Cu₃Au(111), CuAu(111), and Au(111) indicate that the neck radius does not vary linearly between pure Cu and Au; it appears that the neck radius in Cu₃Au is smaller than that in pure Au. However, these results are preliminary. Nevertheless, the potential of the method has been demonstrated. Indeed, by investigating the dispersion of the surface states along different directions in \( k^* \) space it will be possible to determine if the neck is circular in section.

**Tamm-Type Surface States in Cu₃Au**

Figure 8 shows a series of angle-resolved spectra from the (100) and (001) surfaces of Cu₃Au. The spectra are relatively complicated, but this discussion is restricted to the features labeled S. These features are Tamm-type surface states that are split off from the Cu-related d bands. They occur in energy gaps and so are confined to particular regions in the Brillouin zone; in this case they appear near the \( M \) point of the surface Brillouin zone.

Figure 9 shows the energy variation with \( k^* \) along the \( \Gamma M \) direction. The different dispersions are due to the different environments—hence surface potentials—that exist at the (100) and (001) surfaces. One interesting feature to note is that the extremes occur not at \( |k^*| = 1.58 \) Å⁻¹ but at \( |k^*| = 1.62 \) Å⁻¹. The former value corresponds to the position of the \( M \) point if the measured bulk lattice constants and the free-electron mass are used. Therefore, one can conclude that either the atomic spacings at the surface are reduced or the electron mass is a few percent smaller than the free-electron mass.
Figure 10 shows the variation of the extreme binding energy of the Tamm-type states with Cu/Au composition. To vary the composition, the authors used low energy Ar⁺ bombardment that preferentially removes Au from the surface region, as shown by Auger electron spectroscopy. Note that the variation is approximately linear and the two lines intersect at a binding energy of 1.8 eV. This is exactly the value one obtains for the Tamm-type surface state on pure Cu(100). However, according to the AES measurements there is a signal from Au atoms in the surface region. Because the Tamm-type state is localized in the surface layer, one must conclude that at the extrapolated “position” there are no Au atoms in the first and second layers; the first two layers “look” like pure Cu.

Conclusions

A number of different applications of photoelectron spectroscopy to probe the surface and bulk electronic structures in metallic alloys have been described. In particular, the authors have given examples of both angle-integrated and angle-resolved measurements. An important extra feature of the photoemission technique is that measurements can be made over a range of temperatures, and so it is possible to probe the electronic structure in different phases and across phase transitions, and so forth. As a result, photoelectron spectroscopy is the most useful spectroscopic technique for investigating the surface and bulk electronic structures in metallic alloys.

Acknowledgment

The work described here is supported by the NSF (Award numbers: DMR-9120120 and DMR-9500654). The authors acknowledge the important contributions of their collaborators, Dr. G.M. Stocks (ORNL), Dr. B. Ginatempo (University of Messina), and Dr. G.Y. Guo and P.J. Durham (DRAL Daresbury). Some of the experimental measurements were carried out at the NSLS, and the authors are grateful for the help provided by Dr. Myron Strongin, Mark Ruckman, and Mei-Ling Shek. They also thank the Pittsburgh Supercomputing Center (C-90) and Florida State University (CRAY-YMP) for the provision of supercomputing facilities.

Cited References