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Observation of short- and long-range hybridization of a buried Cu monolayer in Ni

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The electronic structure of a Cu monolayer buried in Ni fcc(100) is studied by means of x-ray emission and absorption spectroscopies in combination with first principles calculations. The local character of the x-ray probes allows us to investigate changes in the chemical interaction for these ultrathin film systems. In comparison to bulk Cu, the occupied *d* states of a buried Cu monolayer, as mapped in the x-ray emission spectrum, remain mostly unaltered. The absorption spectrum on the other hand shows that the empty states of the buried Cu monolayer are modified, and instead resemble the unoccupied electronic density of bulk Ni. These findings agree well with our first principle electronic structure calculations and the results are interpreted in terms of short- and long-range hybridization.

New techniques for growing high quality layered nanodevices have created a number of fascinating possibilities in materials science. By reducing the dimensionality, new effects may occur due to finite size effects, especially the surface and interface features, which can be very different from the bulk properties, and may dominate the behavior of thin film materials. This applies to magnetic, electronic, and mechanical properties. This area also attracts much attention from a technological point of view, such as, for instance, in connection with the development of new magnetic materials and the exploitation of new magnetic phenomena. The magneto-electronics industry focuses on low-dimensional electronic systems that display spin-dependent phenomena to create magnetic storage and reading media such as computer memories and magnetic sensors. It is thus of great interest to be able to study different features specific for this kind of low-dimensional systems.¹

In the present work we address the question of how different states, characterized by different degrees of localization, behave in connection with the interaction between layers of different atomic species. Core level probes provide information on the electronic structure with elemental specificity. This has many advantages in the investigation of interface systems, in particular, and heterostructures in general. X-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) provide site-projected electronic structure information on the occupied and unoccupied electronic states, respectively. XAS yields information on changes in the electronic structure, even for small changes in, e.g., elemental or structural composition. Due to the appreciable penetration depth of soft x rays, it is possible to detect a buried layer.^{2,3} XAS has also found important applications in magnetic x-ray circular dichroism (MXCD) of thin film magnetic structures.⁴⁻⁶

We have chosen to study the experimentally well-characterized Cu/Ni system.⁷ We demonstrate how different types of metallic states in this system, with varying degrees of localization, give rise to very different behavior in the XA

and XE spectra. We show how this behavior can be understood in terms of hybridization. Similar findings for Cu-Ni systems have previously been discussed for CuNi alloys.⁸ The results of that work are consistent with the picture presented here. We compare the spectral properties as viewed by the XA and XE spectra to calculated, ground state, partial density-of-states (pDOS), using a linear muffin-tin orbital (LMTO) Green's function method.⁹ Although the calculations do not account for the core hole, the agreement between theory and experiment is very good.

The experiments were performed at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL), using the undulator beamline 8.0. The end-station is comprised of a x-ray fluorescence spectrometer,¹⁰ an electron energy analyzer¹¹ (Scienta SES-200), and a MCP detector used for XAS.¹² To record the XAS spectra, a photon resolution of 0.4 eV was used. Spectra were recorded in the partial-yield mode by applying a retardation voltage of 900 V. During the XE measurements, the photon bandwidth was 1.0 eV, while the resolution of the x-ray fluorescence spectrometer was 1.1 eV. The Ni(100) single crystal was cleaned and checked using standard procedures. During Cu evaporation the pressure was 5×10^{-10} Torr, which was performed at room temperature. In order to avoid diffusion and alloying of the Cu-Ni interface, the sample was cooled to liquid nitrogen temperature during the Ni evaporation and measurements. Spectra from "bulk" Cu were recorded when the sample was covered with enough evaporated Cu to completely suppress the Ni signals in XPS spectra. The sample was oriented so that the photons were incident at a glancing angle of about 7° and with the polarization vector parallel to the surface plane.

The *ab initio* calculations were performed by using the interface Green's function technique developed by Skriver and Rosengaard.⁹ The method is based on the LMTO method^{13,14} within the tight-binding,¹⁵ frozen core, and atomic-sphere approximations (ASA), together with the local spin density approximation as parametrized by Vosko, Wilk,

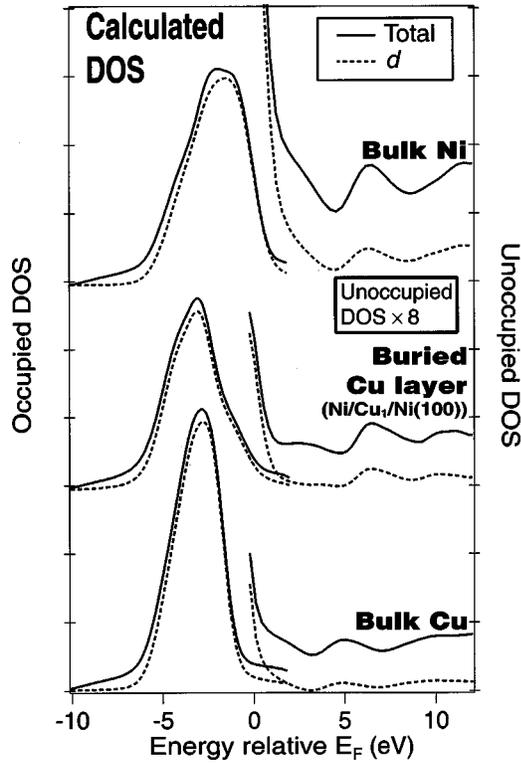


FIG. 1. Calculated DOS and d partial DOS (p -DOS). In order to compare theory with our experimental findings, the calculated occupied and unoccupied p -DOS were convoluted with 1.0 eV and 0.4 eV Gaussians, respectively, to account for the instrumental resolution.

and Nusair.¹⁶ An advantage of the Green's function technique is that it ensures a correct description of the loss of translational symmetry perpendicular to the interface without the use of an artificial slab or supercell geometry. For the investigation of the electronic structure, the spectral density function

$$D^\sigma(k_{\parallel}, E) = \frac{1}{\pi} \text{Im Tr } G^\sigma(k_{\parallel}, E), \quad (1)$$

calculated from the Green's function $G^\sigma(k_{\parallel}, E)$ of spin σ , energy E , and wave vector k_{\parallel} in the 2D Brillouin zone (BZ) was used. Layer and symmetry resolved spectral densities may be obtained by restricting the trace to specific single atomic layers or orbitals of different symmetries. When integrated over the entire system, the state density function yields the total density of states. All calculations were performed using an fcc lattice.¹⁷ The studied situations were bulk Cu, bulk Ni, and a buried Cu layer in Ni. The model system for the buried monolayer Cu consisted of 15 layers ($\text{Ni}_{\text{bulk}}/\text{Ni}_7/\text{Cu}_1/\text{Ni}_7/\text{Ni}_{\text{bulk}}$) where all parts were treated self-consistently. The boundary conditions on both sides of the system were the self-consistently calculated bulk Ni potentials.

In Fig. 1, we show the calculated spin-integrated total DOS and $3d$ p DOS curves (solid and dotted lines, respectively). In general, the valence electronic structure of Cu is characterized by a broad free-electron-like sp band and a narrow, almost fully occupied $3d$ band. In the case of Ni, the sp bands are similar to Cu, but the $3d$ band is located closer

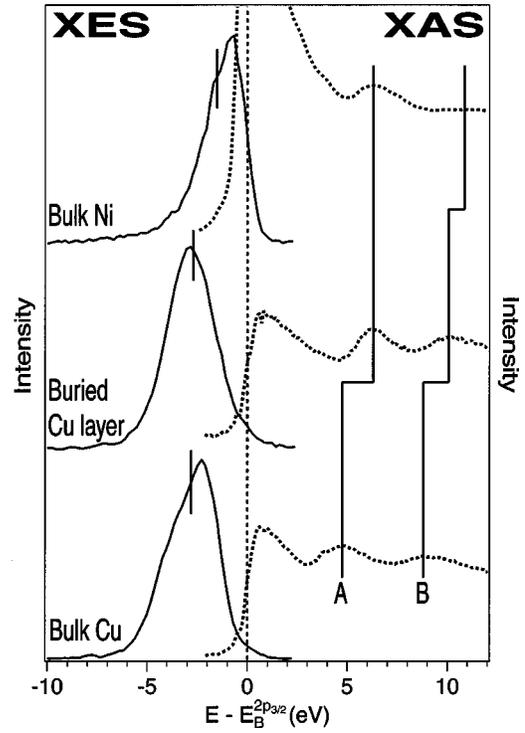


FIG. 2. Occupied (solid lines) and unoccupied (dotted lines) valence region of bulk Ni, a buried Cu layer in Ni, and Bulk Cu as mapped by XES and XAS. The short vertical lines in the XE spectra indicate the centroids derived from the spectral data. The vertical lines in the XA spectra serve as guides for the eye, and indicate the peak positions of the features discussed in the text (see text).

to the Fermi level, and is only partially occupied. The p DOS of the buried Cu layer reveals only small changes from bulk Cu in the energy region (0–2 eV) above E_F . However, beyond this region, the calculated DOS of the buried Cu layer is quite different from that of bulk Cu but remarkably similar to that of bulk Ni. This effect cannot be attributed to a change in the lattice parameter for the buried layer, since calculations (not shown) of the band structure of Cu using the lattice parameter of Ni results in a DOS function that shows very small or no difference to the DOS of bulk Cu at its experimental lattice constant.

Figure 2 shows L_3 XE and XA spectra of bulk Ni, bulk Cu, and of a Cu monolayer buried in Ni, on a common energy scale, obtained by subtracting the corresponding $2p$ XPS binding energies, recorded in connection to the measurements. In order to enhance the relevant spectral features, an arbitrary normalization between the XA data sets of the different systems was adopted. The XE spectra were obtained using the excitation energies 852.7, 932.5, and 932.2 eV, respectively. This corresponds to threshold excitation, in order to avoid contributions from initial-state satellites. The XE spectra are dominated by $3d_{3/2,5/2} \rightarrow 2p_{3/2}$ transitions and map the occupied $3d$ bands.¹⁸ We find the centroid of the bulk Cu L_3 XE spectrum at -2.8 eV (marked by a vertical line in Fig. 2). The corresponding position for bulk Ni is -1.5 eV.¹⁹ We find the widths (FWHM denotes full width at half maximum) of these bands to be 2.9 and 2.2 eV, respectively. The $3d$ centroid for the buried Cu layer is located at -2.7 eV and the width of this band is also 2.7 eV, which is slightly narrower than for bulk Cu. The main effect of

replacing the Cu neighbors by Ni atoms is therefore that the Cu d bands are somewhat narrower, as a consequence of the reduced number of scatterers at the energy of the Cu states. Furthermore, the calculations indicate very small charge transfer (~ 0.005 electrons) from Cu to Ni. Consequently, the general appearance is that the occupied part of the Cu d band is little affected by the replacement of Cu with Ni atoms.

The XA spectrum of bulk Cu has previously been described in the literature (see, e.g., Ref. 20). The two features in Fig. 2, denoted as A (4.7 eV) and B (9.0 eV), are due to van Hove singularities at the L and X points of the Brillouin zone, respectively. The calculations show that the peaks have s , p , and d character, but due to the small $p \rightarrow s$ radial matrix elements, the overall contribution from this $p \rightarrow s$ absorption channel to the experimental spectrum is only 5%.²⁰ Therefore the absorption spectra are expected to essentially map the d -DOS.²⁰ However, all features in the total (spd) DOS are represented in the d -DOS and it is therefore valid to compare the XAS spectra to the total DOS.

When comparing to the occupied states, dominated by the d band, we find a different overall behavior for the unoccupied states above E_F . First we note that the near threshold region (0–2 eV above E_F), is similar for bulk Cu and the buried Cu layer spectra. In this region, the calculations show that the unoccupied states are mainly of d character, and in the same fashion as described above for the occupied d band, we do not observe any large change in the electronic density between bulk Cu and the buried Cu layer.

In the energy region 3–10 eV above E_F there are considerable differences between the spectra for bulk Cu and for the buried monolayer spectra. Structures A and B in the bulk spectrum, coincides with minima in the spectrum of the buried interface layer. Instead, we find that the spectrum of the buried Cu layer in this energy regime is similar to the spectrum of bulk Ni. The features found at 4.7 and at 9.0 eV for bulk Cu, are shifted for the buried Cu layer and coincide with the features, at approximately 6.0 and 10.9 eV in the bulk Ni spectrum. The same shift can also be seen in the calculated pDOS, in Fig. 1. From this observation, we conclude that the projected Cu DOS in this energy region for the buried Cu interface layer is dominated by the features characteristic of the surrounding Ni. This implies that the unoccupied Cu states are strongly influenced by the chemical environment, and therefore characterized by their hybridization with Ni atoms. We note in passing that the above-mentioned result shows that the 6 eV feature in the Ni XA spectrum, which has been discussed both in terms of localized multi-electron states and delocalized one-electron band states,^{21–23} is best described within a band structure picture.

In the spectral region (≥ 3 eV above E_F), where the corresponding DOS is dominated by highly delocalized states,

the XA spectrum of the buried Cu layer will reflect the properties of the chemical surrounding. Consequently, the delocalized states will not be particularly sensitive to the site at which they are probed, i.e., whether the states are projected onto a Cu or Ni site. Hence, our theory demonstrates that an element specific probe can also be used to detect delocalized states, distributed over several atomic layers of different atom types. States that are less influenced by hybridization effects, e.g., the occupied part of the d bands, show a different behavior in the studied systems. As seen primarily from the XE spectra, the position of the electronic d states is predominantly set by local (atomiclike) properties. The Ni neighbors have d states at lower binding energy, and the Cu d states do not shift significantly in energy when the Cu-Ni coordination is altered. Instead, a slight decrease of the Cu d bandwidth is observed in the XE spectra when the Ni coordination is increased. The main effect of replacing the Cu neighbors by Ni atoms is therefore that the Cu d bands become somewhat more narrow, as a consequence of the reduced number of states to overlap with at the energy of the Cu states. The small changes in the XE spectrum of the buried Cu layer compared to bulk Cu, indicate only a weak effect of hybridization due to the more localized character of these d states.

In summary, we carried out XAS and XES measurements on a single buried monolayer Cu in bulk Ni that were in excellent agreement with our KKR-ASA DOS calculations. In this way we demonstrated the unique power of the combination soft x-ray emission and absorption spectroscopies for resolving changes of the local electronic structure with elemental specificity. The results of our combined experiment-theory approach are that the occupied states of the Cu monolayer buried in fcc Ni exhibits a small narrowing of the $3d$ band due to coordination effects, but shows a very weak hybridization with the Ni d states. On the other hand, the unoccupied states in the energy regime ≥ 3 eV above E_F of the buried Cu layer largely resemble the unoccupied states in bulk Ni. Consequently they do not depend strongly on the local atom they are probed at, but rather depend on the chemical environment. This latter finding gives strong support for a band-structure interpretation of the feature at 6 eV in the Ni x-ray absorption spectrum. It also shows that via an atomic specific probe it is possible to detect delocalized states that are located on many different atom types in a crystal.

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