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This is the published version of a paper published in *Physical Review B Condensed Matter*.

Citation for the original published paper (version of record):

Karis, O., Magnuson, M., Wiell, T., Weinelt, M., Wassdahl, N. et al. (2001)
Probing surface states of Cu/Ni thin films using x-ray absorption spectroscopy
Physical Review B Condensed Matter, 63(11): 113401
<https://doi.org/10.1103/PhysRevB.63.113401>

Access to the published version may require subscription.

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Probing surface states of Cu/Ni thin films using x-ray absorption spectroscopy

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 (Received 2 October 2000; published 26 February 2001)

Surface and interface properties of Cu thin films (1–4 monolayers) deposited on Ni(100) have been extracted by means of x-ray absorption spectroscopy and analyzed in combination with *ab initio* density-functional calculations. An unoccupied Cu surface state is identified in an x-ray absorption spectra and studied as a function of film thickness. Experimental data is supported by calculations of the layer-resolved density of states and the results from this combined theoretical-experimental effort show that the surface state is almost entirely located on the atomic layer closest to the vacuum. Our results also indicate strong hybridization between unoccupied states at the Cu/Ni interface boundary.

DOI: 10.1103/PhysRevB.63.113401

PACS number(s): 73.20.At, 73.21.–b, 78.70.Dm

Recent techniques for growing high-quality layered nano devices have created a number of fascinating possibilities in materials science. By reducing the dimension of a system, effects may occur due to the finite size of the samples. Surface and interface properties, which can be very different from the bulk values, may especially dominate the behavior of thin-film materials, as well as the interface interference effects. This applies to magnetic, electronic, and mechanical properties. It is thus of large interest to be able to study different features specific to low-dimensional systems.¹ It is particularly interesting to understand the transition of the electronic structure when continuously going from a low-dimensional thin-film system to the corresponding bulk material.

Inverse photoemission spectroscopy (IPES) is a well-established technique for probing unoccupied band states, including surface states. With angle-resolved IPES, it is possible to map the dispersion of the unoccupied bands (see, e.g., Refs. 2–4). X-ray absorption spectroscopy (XAS) is also a technique that maps the empty electronic states, but through a core excitation process.⁵ However, it has often been assumed that unoccupied surface states are not manifested in XAS. This conclusion is predominantly based on the observation that in the total-yield mode, normally used for investigating bulk systems, XAS is not particularly surface sensitive. The atom-specific nature of this experimental technique would, however, make it extremely useful for studying processes on surfaces. In this report we show that it is indeed possible to detect surface features using XAS. The surface sensitivity is greatly enhanced by employing XAS in the partial-yield mode. The prospective presence of surface states in XAS has implications of both technological and fundamental importance. IPES, bremsstrahlung isochromat spectroscopy, and valence-band ultra-violet photoemission spectroscopy provide information on the joint density of states.⁶ Core-level probes, on the other hand, 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. XAS yields information on small changes in the electronic struc-

ture, even for small changes in, e.g., elemental or structural composition. For a correct interpretation of experimental XAS data, it is important to identify the presence of surface states. Since XAS is one of the basic tools in the investigation of magnetic properties, in, for instance, spin valves, this fundamental issue also has technological implications.

Here we apply XAS to a set of thin Cu films (1–4 monolayers) deposited on Ni(100). The Cu/Ni system is experimentally well characterized.⁷ In order to analyze the spectra, detailed comparisons with data from first principles density functional calculations have been performed.

The experiments were performed at the *Advanced Light Source* at Lawrence Berkeley National Laboratory, using undulator beamline 8.0. The end station is comprised of an electron energy analyzer (Scienta SES-200) (Ref. 8) and a multichannel plate detector used for x-ray absorption spectroscopy.⁵ 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. The Cu films were prepared at room temperature. Film preparation was carefully investigated in terms of structure and alloying, using low-energy electron diffraction and carbon monoxide titration. Plots of the Cu and Ni *2p* x-ray photoelectron (XPS) intensities versus evaporation time, showed distinct changes in the slope at the completion of each of the first two monolayers. This indicates a good layer-by-layer growth. For more details, see Ref. 7. Spectra for bulk Cu were obtained with the sample covered by a thick film of Cu, which completely suppressed the Ni signals in XPS spectra. The sample was oriented so that the photons were incident at an 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 screened Korringa, Kohn, and Rostocker (Ref. 10) method within the tight-binding,¹¹ frozen core, and atomic-sphere approximations together with the local spin-density approximation as parametrized in Ref. 12. An advantage of the Green's function technique is that it ensures a correct description of the

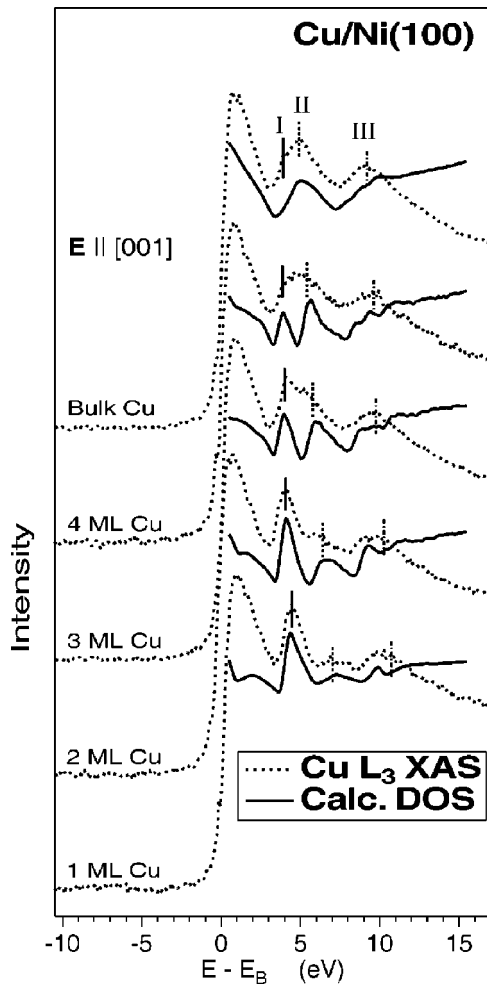


FIG. 1. X-ray absorption spectra of thin films of Cu on Ni(100) (dotted lines) are compared to calculated ($s+p+d$) DOS. The experimental data averages over the state density in the different layers of the films. The calculated DOS is normalized and summed over all Cu layers for each system.

loss of translational symmetry perpendicular to the interface without the use of an artificial slab or supercell geometry. All calculations were performed in an fcc lattice and to investigate global volume effects, calculations were performed in the bulk volumes of Cu and Ni, respectively. The studied situations were nonreconstructed (100) surfaces of Cu, Ni, and surfaces of the form vacuum/Cu $_n$ /Ni, where $n=1-4$.

Figure 1 displays the Cu L_3 XA spectra for 1–4 ML Cu on Ni(100), and for a Cu crystal, denoted bulk, together with the calculated total (spd) density of states (DOS) of the Cu layers for the corresponding systems. The spectra have been normalized to a common onset-to-continuum step, which corresponds to a per-atom normalization of the absorption.⁵ To have the energy scale relative to E_F , the measured $2p_{3/2}$ XPS binding energy (peak position) has been subtracted for each situation. The binding energy ranges from 932.3 eV for the monolayer to 932.5 eV for bulk Cu. Except for the monolayer, the recorded binding energies correspond to weighted averages of two or more chemically shifted XPS energies originating from the different layers. It is therefore not strictly correct to discuss the spectral contributions in the

absorption measurements for the different layers in terms of one common E_F . However, due to the small overall shifts, this is of no practical importance to the discussion here. A general interpretation of the data, in particular related to the features denoted (II) and (III) and the “white lines,” is given elsewhere.¹³ Only a summary will be given here, in order to facilitate the discussion. The low-energy (L_3 absorption edge) region, 0–3 eV above E_F , is remarkably similar for the different overlayers. The intensity and shape of the “white line” appears to be essentially unchanged even when comparing the 1 ML spectrum to the spectrum of bulk Cu. The main differences occur in the energy range 3–10 eV above threshold. For bulk Cu, two features are clearly seen at 4.5 and 9 eV above E_F , denoted (II) and (III), respectively. These features are also revealed in the calculated DOS (cf. Fig. 1) and are due to Van Hove singularities at the L and X points in the three-dimensional Brillouin zone.¹⁴ The calculations show that the peaks have s , p , and d characters, 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%.¹⁴ Therefore, the absorption spectra are expected to essentially map the d DOS.¹⁴ However, all features in the total (spd) DOS are represented in the d DOS since the dominating p DOS is flat and the s and d DOS have the same structure. It is therefore valid to compare the XAS spectra to the total DOS.

In the case of 1 ML Cu on Ni, there is a low-energy feature denoted (I) at ~ 4.2 eV above E_F , observed both in the XA spectra and in the calculated DOS. Two broader features at higher energies, (6.5 and 10 eV) denoted (II) and (III), respectively, can also be seen. When the Cu film thickness is increased from 1 to 4 ML, the three peaks are asymptotically shifted towards lower energies, approaching the Cu bulk limit. The XAS technique, thus, makes it possible to study a continuous transition of the electronic structure of a low-dimensional thin-film system towards the bulk limit when the film thickness is increased. Of special interest here, is the behavior of feature (I). The intensity of this peak decreases as a function of increased Cu film thickness. Only a small fraction remains in the XAS spectra of bulk Cu. The same behavior is found in the calculated DOS, however in this case, no intensity corresponding to peak (I) remains in the bulk DOS. This is natural, since the theoretical bulk calculation, in contrast to the bulk experiment, is characterized by the absence of any surface, assuming an infinite crystal. The intensity variations found both experimentally and theoretically indicate a surface or Cu/Ni interface origin of feature (I). Another possible explanation would be to attribute the peak to a quantum-well state.

Figure 2 shows a comparison between the layer resolved DOS of a Cu $_4$ /Ni(100) system and the spectral density along $\bar{\Gamma}-\bar{X}-\bar{M}$ of the outermost Cu surface layer. The first peak, denoted (I) in Fig. 1, at 3.25 eV, is here identified as a van Hove singularity corresponding to the band minima at the \bar{X} point, as indicated by the left arrow. The states in this band are localized to the surface layer and decays quickly deeper inside the Cu film and out into the vacuum. Furthermore, the calculations show that this band has very small, or negli-

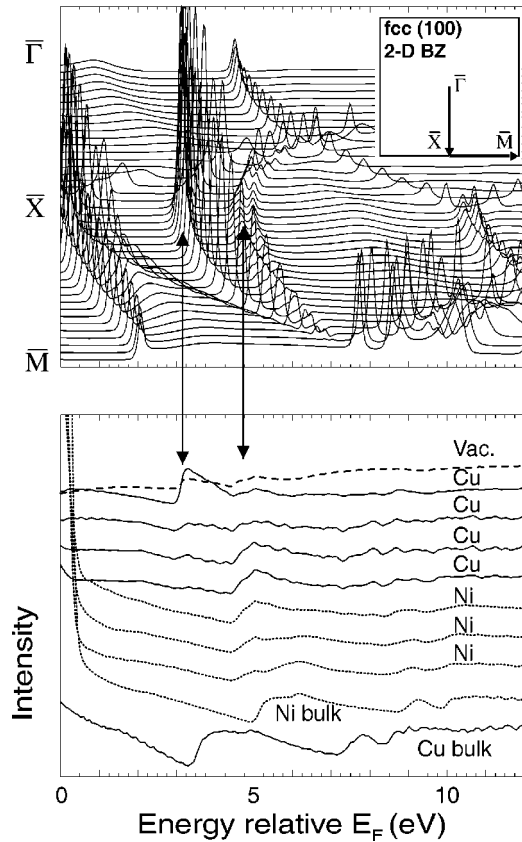


FIG. 2. Top panel: The $k_{||}$ -resolved DOS of the outermost Cu layer of the 4 ML Cu/Ni(100) system in two symmetry directions. The relevant two-dimensional Brillouin zone is shown in the inset. Lower panel: Layer-resolved DOS of the 4 ML Cu/Ni(100) system. Solid and dashed lines correspond to Cu and Ni monolayers, respectively. The DOS for bulk Ni and Cu are also shown for comparison. By summing the 4 Cu layers and normalizing, the 4 ML Cu DOS curve of Fig. 1 is obtained. All calculations presented in the figure were performed assuming an unrelaxed bulk Cu lattice.

gible, amplitude at all layers except for the surface layer. This excludes the possibility that the experimentally observed peak (I) is an interface-related state or a quantum-well state. We can consequently conclude that the above-mentioned feature is due to a surface state, which is manifested in the XA spectra. The above-mentioned existence of the surface-state-derived feature in the bulk spectrum is attributed to the use of XAS in the partial yield-mode, which greatly enhances the surface sensitivity of the technique.⁵ This surface state corresponds to what has previously been observed for the (100) surfaces of Cu and Ni.¹⁵

The second feature in Fig. 2, pointed out by the right arrow, is due to the van Hove singularity of a bulklike band in Cu that is shifted towards higher energies by the influence of the Ni substrate. This feature is also seen in Fig. 1 and is there denoted (II). A weak intensity of this band still remains at the surface and can be seen in the upper panel of Fig. 2. Deeper inside the Cu film these states increase in amplitude, which is understood from the increased amplitude of feature (II) in the lower panel of Fig. 2. In addition, there is a free-electron like band with minima at 4.5 eV at the $\bar{\Gamma}$ point that

is interpreted as a tail of an image potential state localized above the Cu surface.^{16,18,19} It is also seen from Fig. 2 that the DOS of the Cu and Ni layers closest to the Cu/Ni interface are very similar. This resemblance is typical for electronic states that hybridize strongly. In this case, it is the extended states of Cu and Ni that dominate the unoccupied part of the electronic structure, which lead to an intermediate situation for the interface layers, between bulk Cu and bulk Ni (cf. Fig. 2). The apparent dispersion of peaks (II) and (III) in Fig. 1 thus reflects a transition from a bulk feature into an interface feature that is driven by this strong hybridization.¹³ However, one should keep in mind that the spectroscopy probes the DOS through mostly d -projected states. The common interface features observed in the experiments are due to electronic states that are combined of extended, essentially sp , states of Ni and Cu, which hybridize strongly. These extended states also hybridizes with the d states of Ni and Cu, giving rise to common d -derived features in the spectra [peaks (II) and (III)]. Strong hybridization has previously been reported for Cu and Ni in a Ni/Cu₁/Ni system.¹³ In this context it is interesting to compare the Cu₁/Ni system with clean Ni and Cu surfaces to see the relative position of their surface states and the effect of hybridization. The energies of the Ni and Cu surface states were calculated to be 4.31 and 3.19 eV, respectively (using the lattice constant of Cu, data not shown). The surface state of the Cu₁/Ni system was calculated to be 3.71 eV and is, thus, intermediate to the energies for the two ideal surface states. The apparent dispersion of the surface related peak (I) may therefore be understood as a transformation from a surface state that splits from the hybridized band at the interface (right arrow in Fig. 2) in the Cu₁/Ni system to a surface state of an ideal Cu surface.

In summary, we have performed a systematic investigation of 1–4 monolayers of Cu on Ni(100). A surface state has been identified in x-ray absorption spectra demonstrating the potential of this method for determining surface related properties. The electronic states in the energy region above 3 eV show a large dependence on the number of deposited Cu layers. We argue that it is due to strong hybridization between the Cu and Ni bands at the interface that leads to this apparent dispersion as a function of Cu film thickness. The experiment averages over states involving a surface state, an interface state, and a bulk derived state. The x-ray absorption spectra in combination with our *ab initio* theoretical calculations demonstrate that the surface state of Cu(100) or monolayers of Cu on Ni is located primarily on the atomic layer closest to the vacuum. Hence, this demonstrates the possibility to probe electronic properties of a single atomic layer using XAS.

This work was supported by Swedish Natural Science Research Council (NFR and TFR), the Swedish Foundation for Strategic Research (SSF), and by the Göran Gustafsson Foundation for Research in Natural Science and Medicine. The use of the LMTO Green's-function code developed by H. L. Skriver for the electronic structure calculations is gratefully acknowledged.

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