# Modifications of the electronic structure of Ni/Cu(001) as a function of the film thickness

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We report angle-dependent near-edge x-ray-absorption fine-structure measurements of tetragonal Ni films [0.6–14.4 monolayers (ML)] grown on a Cu(001) surface. The analysis of the Ni $L_{3,2}$ white-line intensities show that the density of $3d$ holes ($n_h$) increases almost by 20% from a submonolayer to a 5 ML thick film, clearly showing that a constant value of $n_h$ cannot be used in sum rules to estimate spin and orbital momentum contributions to the local magnetic moment by magnetic circular dichroism. Therefore, caution must be exercised before claiming an enhancement of spin and orbital magnetic moment at lower film coverages. Also, a difference in the number of $d$ holes having in- and out-of-plane symmetries and modifications in the near-edge features was observed. [S0163-1829(97)50532-7]

The magnetic circular dichroism (MCD) in both soft and hard x-ray regions at core-level edges has been used to study magnetism.[1,2] Furthermore, MCD at different edges, e.g., $L_2$ and $L_3$, made it possible to separate and estimate the spin and orbital momentum contributions to the local magnetic moment using the sum rules.[3–7] However, the values of magnetic moments determined by MCD, especially for the overlayer systems, are not always in agreement with the theoretical values.[8] It has been pointed out in several studies[8–10] that one of the main sources of this disagreement is lack of knowledge about the number of $3d$ holes ($n_h$) used in the sum rules. Until now, the values of $n_h$ estimated from different theoretical calculations for bulk metals (i.e., fcc, bcc, or hcp) have been used to determine the local magnetic moment even for overlayer systems. The question arises whether it is justified to use $n_h$ of bulk for thin films or not. We have addressed this question for different thicknesses of Ni films on the Cu(001) substrate.

Various theoretical approaches, e.g., tight binding and the linear muffin-tin orbital (LMTO) method,[11–14] have shown that the band structure of bulk Ni is not similar to that of Ni thin films on Cu(001). Also, recent experimental studies using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED)[15,16] have shown that Ni films grow pseudomorphically in a layer-by-layer mode on Cu(001) having tetragonal structure instead of cubic. The difference in structure produces different electronic and magnetic properties.[17,18] The above facts suggest that changes in the lattice and band structure may also reflect in the values of $n_h$ of thin films and bulk Ni. Moreover, the values of $n_h$ for bulk Ni used in the sum rules have varied from $n_h = 1.0$ (Ref. 19) through 1.66 (Ref. 20) to 1.8.[21] The scattering in the value of $n_h$ even for bulk Ni indicates the need of reliable systematic experimental study on the present system. Although a number of studies have been reported to understand the magnetic properties of the Ni/Cu(001) system,[17] very few[22] have studied changes in electronic structure as a function of Ni thickness on Cu(001).

In the past, theoretical calculations have suggested that $3d$ partial density of states (DOS) of the Ni overlayers is different from that of bulk Ni.[11–14] Also, in our earlier publication,[18] using the white-line intensities of Ni $L_{3,2}$ edges (which is a direct measure of unoccupied $d$ states), it has been pointed out that $n_h$ for a Ni thin film (4 ML) on Cu(001) is lower than that for a thick one (23 ML). In the present paper, we report thickness and angle-dependent near-edge x-ray-absorption fine-structure (NEXAFS) measurements at Ni $L_{3,2}$ edges of Ni films (0.6–14.4 ML) grown on Cu(001). Changes in the white-line intensity and near-edge features are discussed in detail.

Ni films were grown on Cu(001) substrate at a pressure $\leq 4.5 \times 10^{-10}$ mbar. Afterwards evaporated films were characterized by means of *in situ* LEED. The thickness calibration was done by using a quartz microbalance and cross checked with Ni and Cu $L$-edges jump ratios, as described elsewhere.[6] The Ni $L_{3,2}$ spectra were recorded at room temperature in total electron yield mode using linearly polarized light at Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. using SX 700 monochromators.

The spectra shown (Fig. 1) are normalized to yield information on a per atom basis. Corrections for saturation effects for electron yield have been taken into account.[8,23] To extract the number of $d$ holes ($n_h$), the area under the absorption edge was integrated after fitting the step functions below the spectra. The $L_3$- to $L_2$ intensity ratio was taken as 2:1. As the area over the $L_3$-edge maximum is bound to be influenced by near-edge features, the spectra were integrated up to their $L_3$ maximum.

Figures 1(a) and 1(b) show Ni $L_{3,2}$ spectra at normal (90°) and grazing (15°) incidence angles for different coverages of Ni. Several modifications in the edge and near-edge region are visible for both normal and grazing spectra. First the white line, marked as $A$, second the 6 eV satellite, marked as $B$, and third the continuum region, marked as $C$, show changes in the intensity as a function of thickness.

We start with feature $A$. The white-line intensity of $L$ edges is a direct measure of unoccupancy of $d$ states, i.e., $n_h$. The continuous increase in the intensity of white lines belonging to $2p^5 3d^{10}$ configuration, for both normal and grazing spectra, unambiguously shows that $n_h$ increases as the thickness of Ni is increased on the Cu(001) surface. This is more evident from Figs. 2(a) and 2(b) where we have
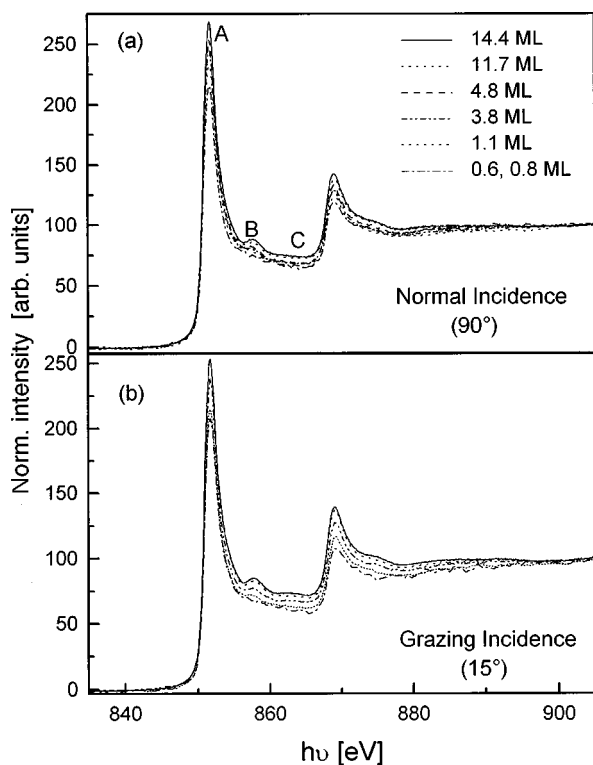
FIG. 1. Ni $L_{3,2}$-edge spectra at (a) normal and (b) grazing x-ray incidence for different Ni coverages on Cu(001). In the submonolayer region, 0.6 and 0.8 ML films belong to grazing and normal incidence, respectively. All spectra were measured from 825 to 905 eV. Features marked as $A$, $B$, and $C$ are discussed in the text.

limited ourselves to the $L_3$ edge after subtracting the step function from Fig. 1 and enlarged both the white line and the satellite. The increase in $n_h$ from thin to relatively thick films can be understood in the following way. As pointed out earlier,[11] the reduction of $n_h$ for thin films is due to the hybridization of the Cu and Ni $d$ bands resulting in a charge transfer from Cu to Ni $d$ orbitals. If one extends this explanation, the degree of hybridization should reduce as the thickness of Ni films increases on the Cu(001) surface, increasing $n_h$. This can be seen from Figs. 1 and 2. Apart from this, as proposed in the configuration-interaction (CI) viewpoint,[24] $n_h$ of a Ni atom of interest can fluctuate through the hybridization between the $3d$ atomic orbital of the Ni atom and the orbitals of surrounding atoms, i.e., Ni $3d$ orbitals in the present case. Again, the degree of this hybridization should reduce as the cluster becomes larger, i.e., as the thickness of the film increases. Our results suggest that either both these effects go hand in hand or one dominates the other as we observe a very systematic trend in the rise of $n_h$ as a function of thickness. One can argue that the changes induced in the band structure due to these hybridization effects should start saturating after a certain thickness (2–3 ML) of Ni film, at which the band structure starts to stabilize. This tendency can be seen from Fig. 3, where we have normalized the largest integrated area (14.4 ML, normal incidence) of the white line to a value of $n_h$ equal to 1.45 by taking the $d$ electron count ($n_e$) as 8.55 ($n_h + n_e = 10$). This value of $n_e$ is proposed by LMTO calculations.[25] The choice of this value was not arbitrary. In our earlier publication,[18] the values of $n_h$ obtained for 4 and 23 ML films from the
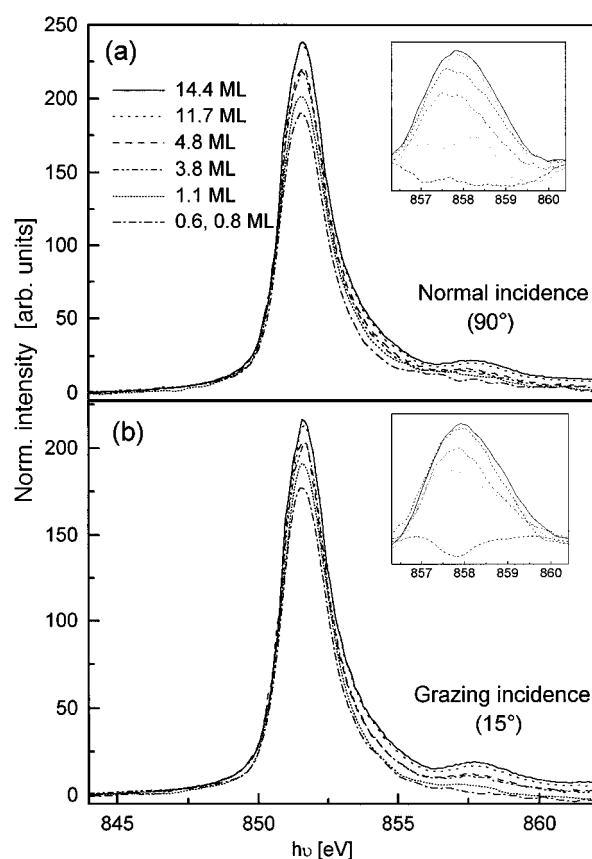


FIG. 2. Ni $L_3$ edge (feature $A$ in Fig. 1) and the satellite (feature $B$ in Fig. 1) after subtracting the step function at different film thicknesses for (a) normal and (b) grazing x-ray incidence. An enlarged picture of the satellite is shown in each inset.

spectra at grazing incidence were 1.2 and 1.5, respectively, by normalizing with $n_h = 2$ for NiO. One can consider the 23 ML film as thick and therefore the choice of $n_h = 1.45$ for a 14 ML film. Also, this results in $n_h \approx 1.2$ for 3.8 ML (at grazing incidence) which is quite close to the value obtained for the 4 ML film by a different normalization and independent analysis. The trend in the increase of $n_h$ is more linear
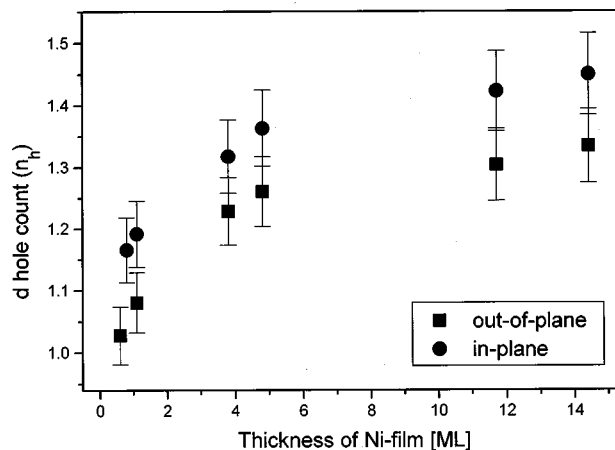


FIG. 3. Number of $3d$ holes ($n_h$) as a function of Ni coverage on Cu(001) for in-plane (solid circle) and out-of-plane (solid square) symmetries. The largest value of $n_h$ is taken as 1.45 (see text).

up to 4–5 ML and after that it starts saturating, and within error limits can be considered as constant. The tendency of the curves for both normal and grazing shows that for thick films, $n_h$ may attain a stable value. This in turn indicates that the band structure, though different from bulk Ni, starts to stabilize after 4–5 ML thickness. This is in agreement with a recent study on Cu/Ni(001) interfaces in which near-edge features of Cu *L*-edge spectra were observed to resemble that of bulk Cu when the film thickness was 4 ML.[26] However, $n_h$ changes almost by 20% from a submonolayer thickness to approximately 5 ML. This means one simply cannot use the same value of $n_h$ while calculating local magnetic moment for a thin and a relatively thick film. Also, it implies that one should be very careful while drawing a conclusion about spin and orbital magnetic moments. In the previous publication,[27] we have determined an enhancement of the ratio of orbital and spin moment ($M_L/M_S$) for Co films on Cu(001). This conclusion is safe as in determining the ratio $n_h$ cancels out. However, reports claiming an enhanced orbital and/or spin moments stand on solid ground only when the variation in $n_h$ as a function of thickness is taken into account. For example, in the present case an apparent enhancement of 20% in orbital or spin moment will be completely nullified by a 20% reduction of $n_h$ as shown in Fig. 3. Here, it should be pointed out that an alternative way to circumvent the lack of knowledge of $n_h$ is to use a standard sample with a known magnetic moment.[28] One then determines a constant $C = I_{wl}/n_h$, where $I_{wl}$ is the white-line intensity for the standard sample, and transfers it to the sample under study.

Another very interesting result which is evident from Fig. 3 is that more *d* holes have in-plane character irrespective of the film thickness. This means that DOS above the Fermi level ($E_F$) have more $d_{x^2-y^2}$, $d_{xy}$ character as compared to $d_{z^2}$, $d_{xz}$, and $d_{yz}$ in the present system. This seems to be the first direct observation of an anisotropic charge distribution in ultrathin Ni films on Cu(001) and the most obvious explanation can be derived from the fact that Ni films on the Cu(001) surface are known to have face centered tetragonal (fct) structure (even above 10 ML) instead of cubic as for bulk Ni.[16] This means that Ni atoms on the Cu(001) surface would not have a perfect octahedral environment around them, which may result in a different degree of hybridization between in- and out-of-plane orbitals, giving rise to observed angular dependence. However, in the future, this explanation should be examined by studying other overlayer systems which show structural transition as a function of thickness or temperature, e.g., Fe/Cu(001). Also, theoretical calculations can help in this regard provided actual structural parameters [e.g., for Ni/Cu(001) fct instead of fcc] are taken as an input.

Now, we turn to the second feature (*B*), namely the satellite. The origin of this feature has been explained in one-electron band-structure terms[29] and attributed to states of *d* character hybridized with the unoccupied *sp* band. As discussed earlier, with increasing film thickness the partial density of *d* states near $E_F$ is changing. This will influence the band structure and in turn the satellite intensity. However, as can be seen from Fig. 2 (see inset), the satellite intensity tends to saturate after a 4–5 ML thickness, suggesting that there are less changes in the band structure above this thickness. In the CI approach,[24] the satellite intensity arises both by mixing between $2p^5 3d^9$ and $2p^5 3d^{10}$ configurations in
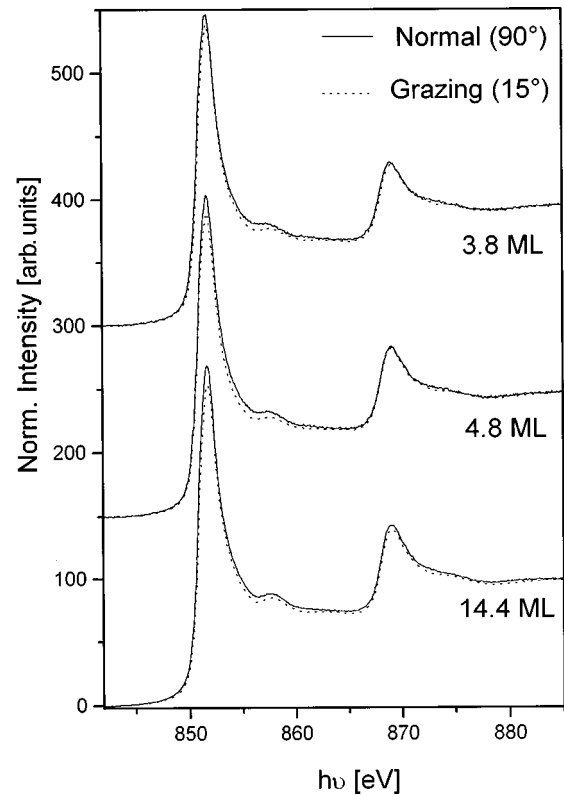


FIG. 4. Normal and grazing spectra of three film thicknesses superimposed over each other. Note that the continuum region (marked as *C* in Fig. 1) corresponding to 4*s*-like states shows almost no angular dependence. There is an offset of 150 a.u. for every pair of spectra.

the final states and the presence of a $3d^8$ character in the ground state. Here, the growth of the satellite as a function of film thickness can be explained due to an increase in the $3d^8$ character in the ground state as $n_h$ is increasing up to $\approx 5$ ML and due to a change in hybridization between $2p^5 3d^9$ and $2p^5 3d^{10}$ configurations with increasing Ni cluster size. However, from the present measurements, it is difficult to attribute changes in the satellite intensity to one mechanism.

Finally, we focus on the intensity of the continuum region (marked as *C* in Fig. 1). This indicates that as a function of thickness, unoccupancy of *d* and *s*-*d* hybridized states is also increasing. First, one should remember that the contribution from the $L_3$ edges is shown to extend even beyond the $L_2$ edges. This has been shown by tight-binding calculations[1] for Cu $L_{3,2}$ edges where the spin-orbit splitting is more than Ni. In the present case, the white-line intensity is shown to increase with increasing Ni thickness. This effect is bound to reflect in the continuum region. Second, as suggested previously and also by the present work, the band structure of a thin film is different from a thick film. The present results suggest that the density of *d* states above $E_F$ changes with the increasing thickness. However, no information can be drawn on *s* density of states, as the overall contribution from the *p* to *s* absorption channel to the *L*-edge absorption spectra is only 5%.[30] To rule out possibilities of any data treatment artifact, in Fig. 4 normal and grazing spectra for three different thicknesses are superimposed over each other. As evident from this, in the energy range of unoccupied 4*s* states, both normal and grazing spectra almost overlap with

each other. Indeed, this should be the case as $s$-like states should not show any angular dependence. However, a recent study[31] has found that the photoelectron angular distributions from the Fermi surface of a monolayer Ni film on Cu are identical to those from thick Ni films and single-crystal Ni(001). It is very surprising that the changes in the partial density of states near $E_F$, observed from a thin to a thick film in the present study, and changes observed both theoretically[14] and experimentally[27] in orbital/spin momentum contributions from surfaces to bulk in various $3d$ metal overlayers on Cu, would have no influence on the Fermi surface.

In summary, the present study provides experimental evidence: (1) The density of $3d$ holes ($n_h$) changes almost by 20% from a submonolayer thickness to approximately 5 ML for the present system and therefore care should be taken in the estimation of spin and orbital momentum using techniques like MCD. (2) The changes in the lattice structure of Ni films on Cu(001) as compared to the Ni bulk reflect in the electronic structure of the present system giving rise to anisotropy in density of holes in and out of plane. (3) Band structure of the Ni/Cu(001) system changes as a function of thickness and the band structure of a thin film cannot be treated on an equal footing with Ni bulk.

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