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Thickness dependence of the electronic structure of ultrathin, epitaxial Ni(111)/W(110) layers

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Ultrathin, epitaxial Ni(111) layers on a W(110) substrate have been investigated by means of angle-resolved photoemission spectroscopy using synchrotron radiation ($9 \text{ eV} \leq h\nu \leq 25 \text{ eV}$). Layers in the submonolayer regime exhibit strictly two-dimensional behavior, while the $\mathbf{k}_\perp$ dispersion starts to develop for layers with thicknesses $d \geq 2$ atomic layers. The formation of the bulk band structure of Ni is almost completed for only five atomic layers of Ni.

I. INTRODUCTION

Many interesting and exciting properties of solids, such as ferromagnetism, are caused by cooperative phenomena and thus cannot be explained by the properties of the individual atoms. Investigation of the evolution of such physical properties in going from the atom to the solid has long been a challenge. Technologically the question of how small a piece of matter can still have bulk electronic and magnetic properties is of great importance.

Reducing the size of the sample under investigation in just one dimension is one way of tackling this difficult problem. Experimentally this can be done by studying epitaxial layers with thicknesses from less than a single atomic layer (AL) to several hundreds of atomic layers. We have investigated epitaxial Ni(111) layers on a W(110) single-crystal substrate by means of angle-resolved photoemission spectroscopy (ARPES) using synchrotron radiation from BESSY, Berlin. Taking advantage of the success of ARPES in determining bulk electronic properties in terms of the dispersion $E(k)$, we have studied the thickness dependence of the electronic structure and the formation of the bulk band structure with increasing layer thickness.

II. PREPARATION AND CHARACTERIZATION OF EPITAXIAL Ni(111) LAYERS ON W(110)

Previous results[1,2] suggest that W(110) is an ideal substrate for the growth of epitaxial layers. The high surface energy and the closed bcc (110) surface allow for a high mobility of the condensing atoms on the substrate surface but inhibit any layer-substrate interdiffusion. The epitaxial growth takes place in the Nishiyama-Wassermann mode, as in the case for fcc (111) films on bcc (110) substrates, i.e., the $[1\bar{1}0]$ axis of Ni aligns parallel to the [001] axis of W.[2,3] Most important for high quality epitaxial growth is the matching of the substrate and layer lattices. In the case of Ni(111) on W(110) the matching works well along the W$[1\bar{1}0]$ axis, i.e., the Ni$[\bar{1}\bar{1}2]$ direction, with a relatively small misfit of 3.6%. However, along the W[001] axis, i.e., the Ni$[1\bar{1}0]$ direction, the misfit amounts to 21.5%, which is far more than the maximum 8% critical misfit for pseudomorphic growth.[3] The resulting structure of the layer will be discussed below. The substrate used was a 2.5-mm-thick W single-crystal platelet with a diameter of about 7 mm and oriented within ±1° along the [110] surface normal. Cleaning was achieved by heating at 1800 °C in an O_2 atmosphere of 10^{-6} mbar and flashing up to 2300 °C. The temperature was monitored by a (W–3 at. % Re)–(W–25 at. % Re) thermocouple spotwelded onto the sample.

The epitaxial Ni(111) layers were grown at a pressure of 1×10^{-9} mbar by evaporation from a watercooled Knudsen-type cell, while the thickness was simultaneously monitored by a quartz microbalance. The best epitaxial layers were obtained by evaporation onto a heated substrate at a rate of about one atomic layer per minute. The optimum substrate temperature was found to be 300 °C for the first atomic layer and 170 °C for all consecutive layers.

The growth mechanism was investigated by Auger-electron spectroscopy and low-energy electron-diffraction (LEED). In Fig. 1 we show the intensity of the very surface-sensitive 60-eV *MMM* Auger line of Ni as a func-

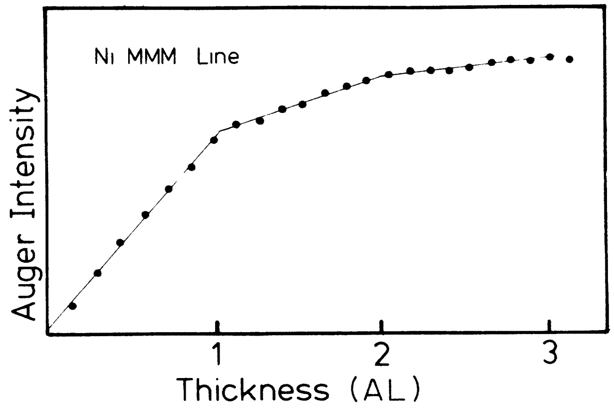

FIG. 1. Intensity of the 60-eV Ni *MMM* Auger line as a function of the atomic layer thickness of Ni(111) on W(110).

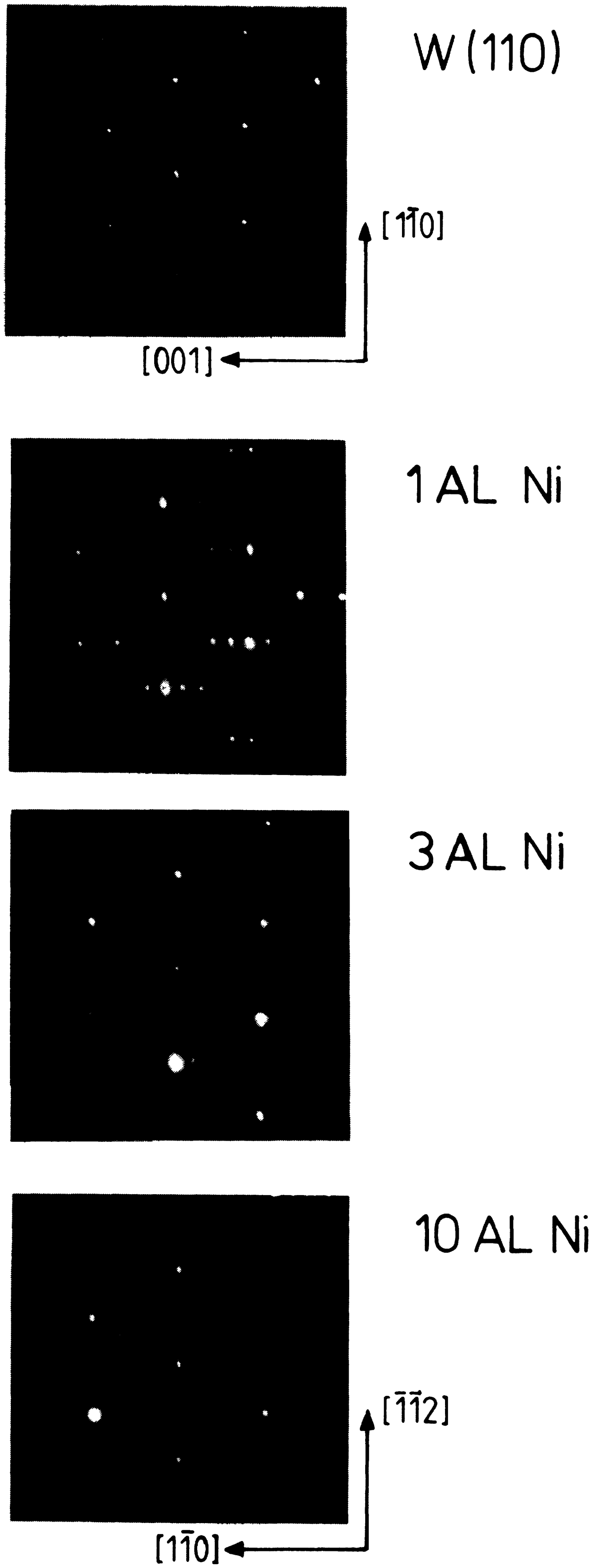

FIG. 2. LEED patterns of the clean W(110) substrate surface, one AL Ni, three AL Ni, and ten AL Ni on W(110) (from top to bottom).

tion of the layer thickness *d*. The characteristic kinks after the completion of one and two atomic layers indicate layer-by-layer growth up to at least three atomic layers The LEED patterns of the clean substrate and layers with one three, and ten AL of Ni are shown in Fig. 2. It can be seen from the one AL pattern that in covering the substrate with Ni the LEED pattern changes from that of the clean W(110) surface to that of a 7×1 superstructure. This happens at a coverage of $d \geq 0.5$ AL. In the LEED pattern of the three-AL-thick film the superstructure is already strongly weakened. One can only see two satellite reflections. The ten AL film exhibits the usual hexagonal LEED pattern of an fcc (111) surface.

From the observed sequence of LEED patterns we deduce the following stages of the epitaxial growth of Ni on W(110). For coverages below 0.5 AL we do not see any changes in the LEED pattern, i.e., the Ni grows pseudomorphically on the W(110) substrate (that is, it is commensurate or in registry with the substrate). For higher coverages ($d \geq 0.5$ AL) the pseudomorphic type of growth continues along the W[$1\bar{1}0$] direction, but along the W[001] direction such growth is not possible due to the large misfit. However, by a slight compression of the Ni lattice in the W[001] direction by about 1%, the layer and substrate lattice match along this direction in so far as each ninth Ni atom coincides with each seventh W atom. This coincidence structure is responsible for the 7×1 superstructure observed in the LEED pattern (Fig. 2). A similar behavior is also reported in Ref. 4, although there the superstructure appears at somewhat larger thicknesses than 0.5 AL and is described to be initially a 8×1 superstructure. The distortion of the Ni lattice continues for the first few atomic layers, as can be seen from the LEED pattern of the three AL film in Fig. 2. For the thicker layers the lattice constant in the [$1\bar{1}0$] direction of Ni adjusts to the stretched one in the Ni [$\bar{1}\,\bar{1}\,2$] direction. For example, for ten AL (Fig. 2) we find an undistorted fcc lattice, except for a slight stretching by about 3.7% in both the [$1\bar{1}0$] and [$\bar{1}\,\bar{1}\,2$] directions of Ni. Layers thicker than five AL display a regular fcc (111) crystal face showing a threefold, instead of a sixfold, LEED pattern. The latter would be expected if both possible orientations of Ni(111) would share equal areas on the bcc (110) crystal substrate. Evidently there is a preferred orientation. The same behavior was observed previously for Cu(111) on W(110).[5] The authors explained the preference by a slight topographical asymmetry in the tungsten substrate, which probably occurs also in our case of Ni(111) on W(110). In conclusion, Ni(111) on W(110) is an almost ideal system for epitaxy, except for the 3.6% expansion and 1% compression of the Ni lattice in the [$\bar{1}\,\bar{1}\,2$] and [$1\bar{1}0$] directions, respectively, in the regime of the 7×1 superstructure, and the 3.6% expansion in both directions for the thicker layers.

III. PHOTOEMISSION SPECTRA

The Ni(111) layers prepared and characterized in the above described manner were investigated *in situ* by means of angle-resolved photoemission spectroscopy.

The spectra were acquired with a commercial ADES 400 spectrometer using polarized light from the TGM 2 beamline at the synchrotron radiation source BESSY, Berlin. The energy and angle resolution were 100 meV and ±1°, respectively. The light was incident in the plane spanned by the surface normal and the W [001] direction under an angle of 22.5° to the W [110] surface normal, i.e., the light was almost completely polarized parallel to the W [001] direction (see inset of Fig. 5). Additionally we took spectra with unpolarized light using a He I resonance lamp. The apparatus used for the latter measurements has an energy and angle resolution of ±100 meV and ±3°, respectively, and is described in detail in Ref. 6.

Figure 3 shows normal emission spectra of the clean W substrate and a series of Ni layers with different thicknesses measured with unpolarized light and a photon energy of 21.2 eV. Covering the substrate with only 0.3 AL already changes drastically the energy-distribution curve (EDC) of the photoelectrons of the W substrate. As the most prominent feature a relatively sharp peak appears at a binding energy (E_b) of 0.75 eV which is attributed to a localized Ni d state. Besides this we observe for 0.3 AL of Ni a shift in energy of the emission from W near $E_b = 1.8$ eV by about 0.2 eV towards lower binding energy, showing the strength of the interaction at the layer-substrate interface. This peak may originate from an interfacial state, since it exists in the coverage range up to 2 AL, but does not show on the pure W or Ni surface. Interface states of Cu layers on Ru(0001) have been observed in the coverage range from 0.4 to 2.2 AL of Cu.[7] Upon increasing the coverage to more than 0.5 AL, which coincides with the appearance of the 7×1 superstructure in the LEED pattern, the EDC changes drastically once more. In addition to the sharp peak at $E_b = 0.75$ eV a second peak appears at $E_b = 0.53$ eV as shown for, e.g., 0.6 AL in Fig. 3. The d-like states corresponding to these two peaks have different symmetry as can be seen from their polarization dependence, and they exhibit completely two-dimensional behavior (see below). Upon increasing the thickness from 0.6 to 1 AL the two sharp d peaks broaden considerably and can only barely be resolved. The monolayer of Ni on W(110) still displays mainly two-dimensional behavior, since we do not observe any changes in binding energy with photon energy. This behavior includes also a new feature in the vicinity of the Fermi level. We speculatively attribute this peak to a Ni surface state, which can only exist at the surface of the monolayer and is strongly suppressed by covering it with another atomic layer of Ni. Hence the surface state is quenched by the bulk Ni d states, which begin to develop for layers with $d \geq 2$ AL. The peak corresponding to the surface state varies in intensity with the photon energy and is most pronounced at a photon energy of $h\nu = 25$ eV. The possibility that this peak is due to an interface state is ruled out because of its pronounced appearance for just 1 AL.

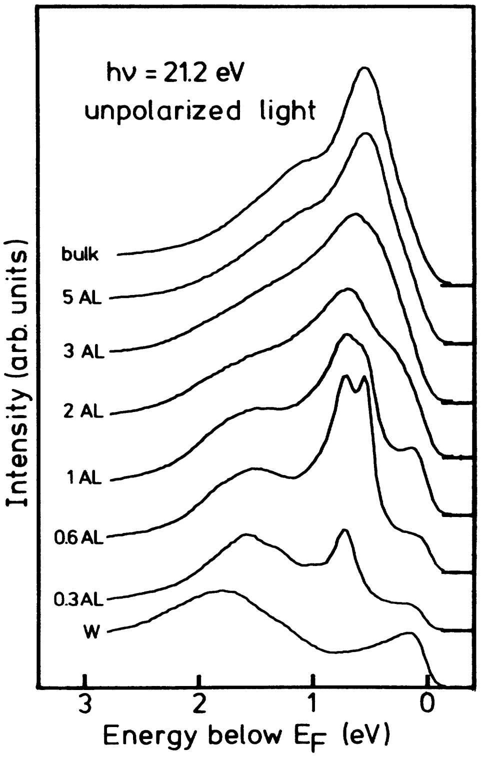

FIG. 3. Normal emission spectra of Ni layers with varying thickness, recorded with unpolarized light of energy $h\nu = 21.2$ eV. The top curve shows the spectrum of bulk Ni(111).

For two AL the d-like peak at about 0.7-eV binding energy broadens further (most pronounced on the low-binding-energy side) and varies in binding energy with the photon energy (see below). Measurements with spin-resolved photoemission for two AL of Ni (Ref. 8) show that the broad peak at $E_b \simeq 0.7$ eV consists of two spin-split peaks with a reduced exchange splitting $\Delta_{ex} \approx 95$ meV (compared to the bulk exchange splitting of 160 meV at this **k** point). For three and more atomic layers of Ni on W(110) the spectra in Fig. 3 can be compared with the bulk single-crystal spectra and reflect already the most prominent features of the bulk band structure.

Figure 4 shows the spectra taken at a similar photon energy ($h\nu = 21$ eV), but with light polarized parallel to the W [001] direction. The spectra of layers thinner than one AL show the largest difference to the spectra recorded with unpolarized light (Fig. 3). The spectra of the layers with a thickness of 0.5 and 0.7 AL in Fig. 4 exhibit only one strong peak at $E_b = 0.53$ eV. The electrons of the Ni state at 0.75-eV binding energy contribute only very weakly. Thus the two states are of different symmetry, the electrons of the state at $E_b = 0.75$ eV can be emitted only with light polarized parallel to the W $[1\bar{1}0]$ direction, while transitions out of the state at $E_b = 0.53$ eV are allowed for light polarized parallel to the [001] direction of W.

The symmetry selection rules found for the d peaks in the submonolayer regime are weakened for the monolayer, since we observe only slight differences in intensity between the spectra recorded with polarized and unpolarized light. This is reasonable because of the symmetry change with increasing thickness from bcc (110) to fcc (111). The selection rules for the fcc (111) face do not differentiate between different orientations of the light polarization in the (111) plane.[9]

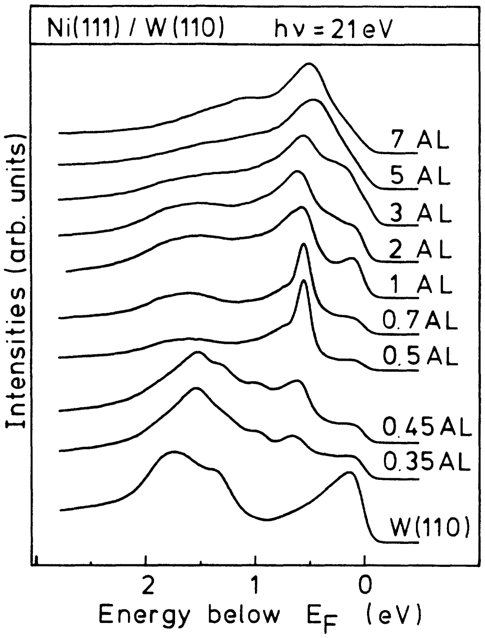

FIG. 4. Normal emission spectra of Ni(111) layers with varying thickness, recorded with light polarized parallel to the [001] direction of W and with $h\nu=21$ eV.

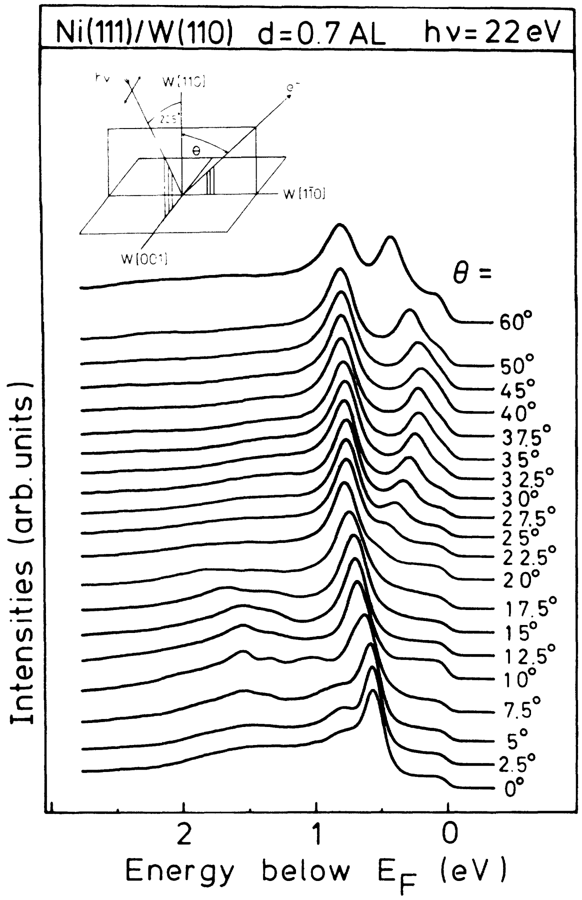

FIG. 5. Photoemission spectra ($h\nu=22$ eV) of a Ni layer with a thickness of 0.7 AL, taken under various emission angles θ in the plane given by the $[1\bar{1}0]$ direction of W and the surface normal (see inset).

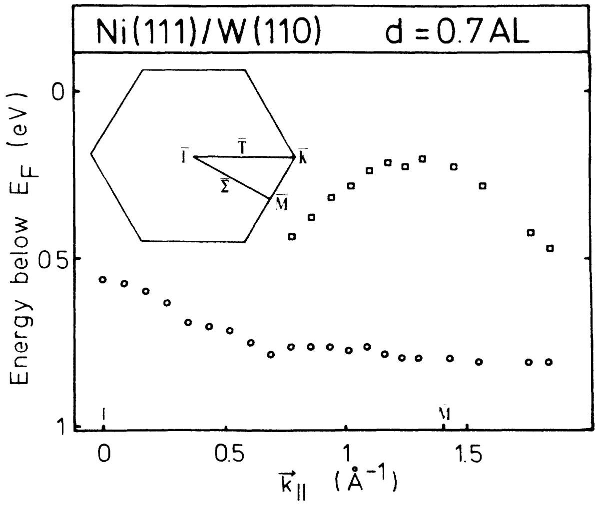

FIG. 6. $\mathbf{k}_{\parallel}$ dispersion of the 0.7-AL Ni layer along the $\bar{\Gamma}$-$\bar{M}$ direction of the surface Brillouin zone, "$\bar{\Gamma}$" and "$\bar{M}$" indicate the $\mathbf{k}_{\parallel}$ values which correspond, respectively, to the $\bar{\Gamma}$ and $\bar{M}$ points of the surface Brillouin zone of intrinsic Ni(111), which is shown in the inset.

For the 0.7-AL-thick Ni layer we studied the $\mathbf{k}_{\parallel}$ dispersion by collecting the photoelectrons at different polar angles θ in the plane given by the [110] direction of W and the surface normal (see inset of Fig. 5). Neglecting the 3.6% expansion of the Ni layer in the [110] direction of W and the 1% contraction in the [001] direction, $\mathbf{k}_{\parallel}$ would vary along the nominal $\bar{\Gamma}$-$\bar{M}$ symmetry line of the two-dimensional surface Brillouin zone (see inset of Fig. 6), where $\bar{\Gamma}$ and $\bar{M}$ originate from surface-projected Γ and L points, respectively. The peak of the d-like state, which is observed in normal emission at $E_b=0.53$ eV, shifts with increasing polar angle θ towards higher binding energy. For polar angles $\theta \geq 20°$ a second peak emerges at lower binding energy. In Fig. 6 the binding energies of the peaks in the energy distribution curves is plotted as a function of the wave vector parallel to the surface,

$$\mathbf{k}_{\parallel}=(2mE_{\text{kin}}/\hbar^2)^{1/2}\sin\theta \ ,$$

where E_{kin} is the kinetic energy of the emitted electrons. The measured $\mathbf{k}_{\parallel}$ dispersion is approximately symmetric about $\mathbf{k}_{\parallel}=1.4$ Å^{-1}, which would correspond to the $\bar{M}$ point of a fcc (111) surface with the stretched lattice constant of Ni. From the rather flat dispersion of the d-like state with $0.6<E_b<0.8$ eV in Fig. 6 we conclude that the overlap between states on adjacent sites is quite small.

Figure 7 shows the EDC's of a layer with $d=2$ AL for different photon energies. For layers of this thickness we already observe considerable dispersion with $\mathbf{k}_{\perp}$ and the bulk Ni d states begin to develop. Unfortunately the spectra are too complex to allow for a simple interpretation. This is especially true for the spectra recorded with photon energies in the range from 22 to 25 eV, where one observes essentially one broad maximum extending from

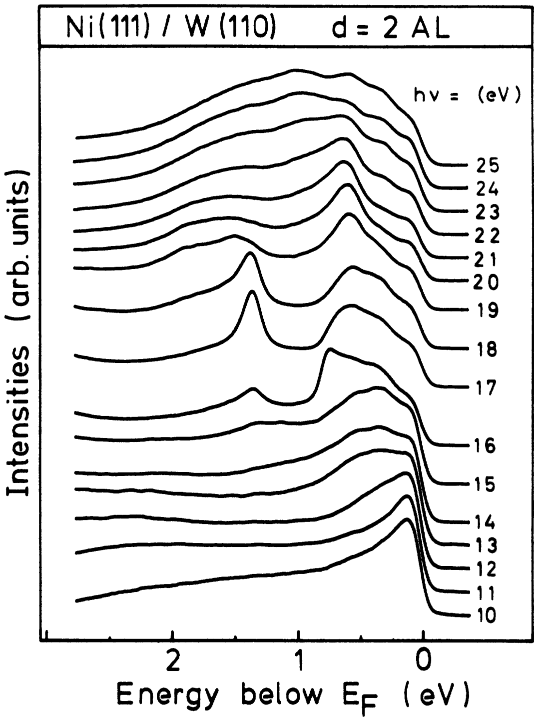

FIG. 7. Normal emission spectra of a two-AL Ni layer recorded for various photon energies using a light polarization parallel to the [001] direction of W.

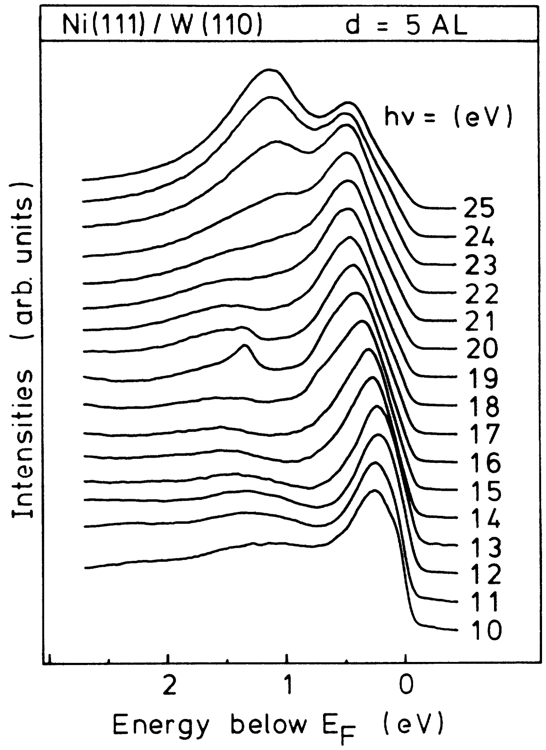

FIG. 8. Normal emission spectra of a five-AL Ni layer recorded with various photon energies (light polarization parallel to the [001] direction of W).

the Fermi level to below 2 eV binding energy on which some broad structures are superimposed. To analyze this interesting stage of the development of the bulk band structure it would be necessary to compare the measured spectra with a detailed electronic structure calculation for the system Ni(111) on W(110).

Interpretation of this spectra becomes much easier for layers with $d \geq 5$ AL. For those thicker layers it is possible to compare the measured spectra with the bulk band structure. Figure 8 shows the EDC's for a five-AL-thick Ni layer. Except for the photon energies around $h\nu = 17$ eV, where the strong W resonance near 1.3-eV binding energy can still be seen, the spectra are completely dominated by emission from Ni states and look similar to the spectra of bulk Ni(111).[10] One can identify the peaks next to the Fermi level as originating from emission out of the Λ_3 band, for which the exchange splitting is barely resolved for the lowest photon energies used. Emission out of bands with Λ_1 symmetry is strongly suppressed for the chosen light polarization due to dipole selection rules.[9] In the spectra recorded with the lower photon energies we observe a very weak, broad peak above 1 eV binding energy which can be attributed to Λ_1 emission. For the highest photon energies used we observe a strong peak at about 1 eV binding energy, which is mainly due to emission out of the lower-lying Λ_3 band. The $E(\mathbf{k}_\perp)$ dispersion of the five-AL-thick Ni layer along the Γ-L symmetry line of the Brillouin zone was calculated from the measured binding energies using the calculated final-state band of Ref. 8. Figure 9 shows the $E(\mathbf{k}_\perp)$ dispersion of the five-AL-thick Ni layer (open circles) together with the $E(\mathbf{k}_\perp)$ data of bulk Ni(111) (solid circles) obtained by Himpsel *et al.*[10] The $E(\mathbf{k}_\perp)$ dispersion of the five-AL Ni and the bulk Ni single crystal compare quite well with each other, especially for the Λ_3 band near the Fermi energy. Larger deviations are observed mainly for the Λ_1 band which are probably due to inaccuracies in determin-

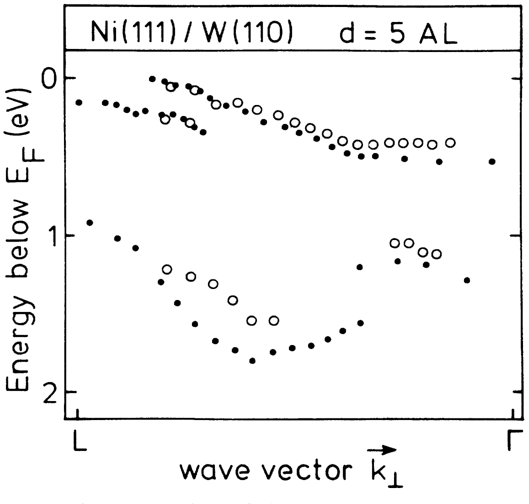

FIG. 9. $E(\mathbf{k}_\perp)$ dispersion of the five-AL Ni layer (open circles) along the Γ-L line in the Brillouin zone together with the $E(\mathbf{k}_\perp)$ dispersion of a single crystal of Ni(111) (solid circles), taken from Ref. 8.

ing the binding energies of the very weak and broad emission peaks. Despite these deviations we can conclude that already five atomic layers of Ni on W(110) resemble the $E(\mathbf{k}_\perp)$ dispersion of bulk Ni(111) quite well. Upon increasing the thickness beyond seven AL the spectra do not change any more and are very similar to the bulk spectra of Ref. 9. Similar investigations have been carried out for, e.g., Ag or Au on Cu(001) and for Ag on Pd(100).[11–14] Bulklike electronic structure was found for about 5 AL of Ag on Cu(001) (Refs. 11 and 12), 12 AL of Al on Cu(001) (Ref. 13), and 16 AL of Ag on Pd(100) (Ref. 14).

IV. CONCLUSIONS

As generally expected, we observe truly two-dimensional behavior for Ni layers with $d \leq 1$ AL, whereas the electronic states of layers consisting of two or more atomic layers of Ni show a $\mathbf{k}_\perp$ dependence of their binding energies. Surprisingly enough, upon reaching a thickness of five AL the formation of the Ni bulk band structure is almost completed. In this context it is interesting to note that spin-resolved photoemission measurements of the same system[8] show at room temperature ferromagnetic order for layers with $d \geq 2$ AL. While the exchange splitting is reduced by 40% for two AL of Ni, it exhibits the bulk value for $d \geq 3$ AL. Thus the electronic structure of Ni(111) layers on W(110) converges rather rapidly with increasing number of atomic layers to the bulk band structure of Ni(111). It is surprising that for already five atomic layers the wave vector $\mathbf{k}_\perp$ is a "good" quantum number. For such few layers one would expect a quantization of $\mathbf{k}_\perp$ but we have not found any evidence for such a $\mathbf{k}_\perp$ quantization, such as photon energy-dependent intensity variations in our spectra. Such quantization of electronic states with $\mathbf{k}_\perp$ was observed for ultrathin Au or Ag films on a Si(111) substrate which exhibited quantum-well states derived from *sp* bands of the bulk.[15] However, to our knowledge no $\mathbf{k}_\perp$ quantization effects have been reported for the more localized *d*-like electronic states.

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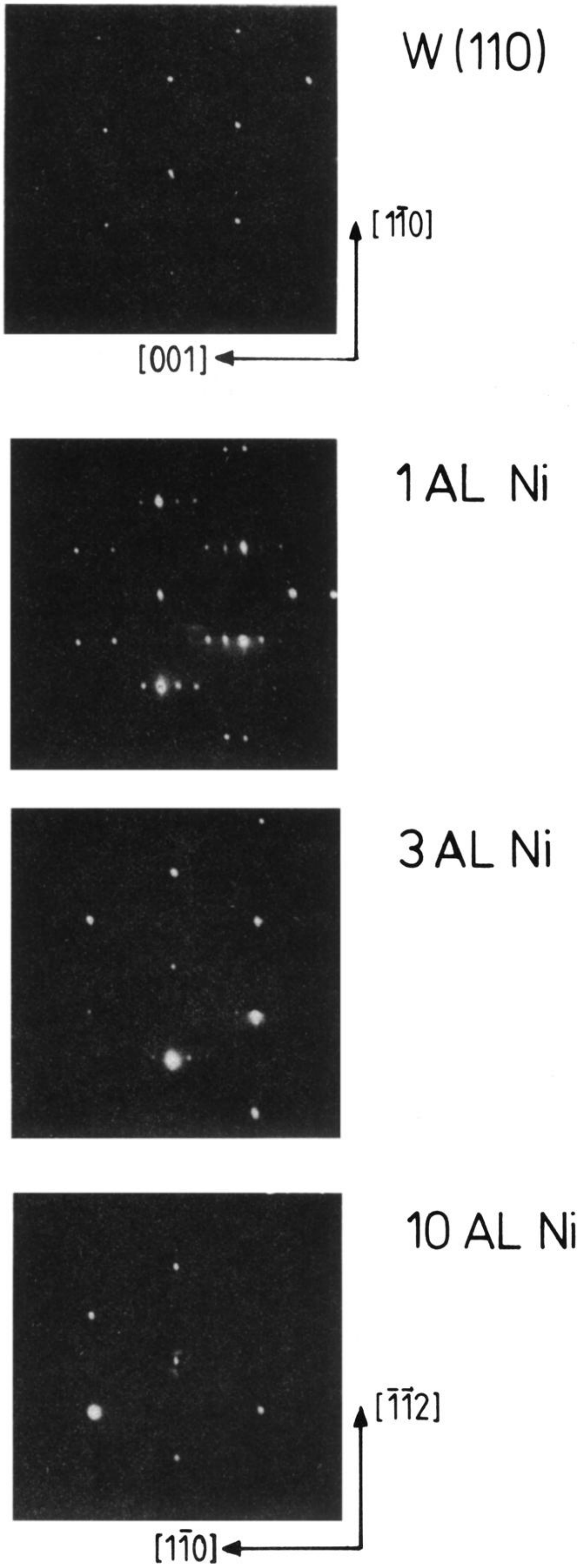

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