Exchange-split electronic states of ultrathin Co layers on Cu(111)

U. Alkemper, C. Carbone, E. Vescovo, and W. Eberhardt
Institut für Festkörperforschung des Forschungzentrums Jülich, D-52425 Jülich, Germany

O. Rader and W. Gudat
Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY), Lentzeallee 100, D-14195 Berlin 33, Germany

(Received 8 July 1994)

By spin- and angle-resolved photoemission we have studied the electronic structure of ultrathin Co overlayers on Cu(111). For coverages below 2 ML, we observe electronic states that are different from those of bulk Co but we find no in-plane ferromagnetic order. Above 2 ML the spectra show exchange-split and spin-polarized states, whose binding energy depends very little on the overlayer thickness. A previously unresolved separation of 0.3 eV between two occupied bands of opposite spin character could be observed. The experimentally determined exchange splitting for the two sets of d bands near Γ is thus found to be 1.4 ± 0.15 and 1.15 ± 0.15 eV, respectively. These values are larger than those derived from previous spin-integrated measurements and in closer agreement with band-structure calculations.

I. INTRODUCTION

Most of the recent experimental work on ultrathin magnetic layers has been dedicated to relatively simple systems, of which transition-metal overlayers on noble-metal substrates occupy a prominent place.[1] In these systems, the interaction between the overlayer and the substrate is relatively weak because of the limited energy overlap between the d states of the two elements. For this reason, they are considered good cases for testing purely dimensional effects on the electronic structure of the overlayer. In the monolayer regime the reduced atomic coordination and the weak hybridization with the substrate should cause an appreciable narrowing of the bands. In some cases, this can considerably increase the magnetic moment and in a few instances even induce ferromagnetism in otherwise nonmagnetic materials.[2] Experimentally, these predictions have been only partially verified. The evidence for a modification of the electronic states in the monolayer regime is limited to a few cases[3,4] and no new magnetic metal has been yet discovered. It has been realized, however, that the growth of a transition-metal overlayer on noble metals[5,6] is often far from the simple model assumed in the theoretical studies and it is possible that this explains some of the discrepancies.

In this paper, we present the results of a spin- and angle-resolved photoemission experiment for Co on Cu(111). The choice of this system was motivated by previous photoemission and inverse photoemission investigations performed without spin analysis. There are apparent discrepancies between experiment and theory concerning primarily the exchange splitting of Co films on Cu(111) and of hcp Co(0001). The experimental values[7–10] of the exchange splitting reported for these systems are systematically smaller than those theoretically predicted for Co monolayers[11] and for bulk Co.[12]

de la Figuera *et al.*[6] have studied the electronic structure of one and two monolayers of Co on Cu(111) by angle-resolved photoemission. The exchange splitting at the $\bar{\Gamma}$ point of the Brillouin zone has been determined to be 0.7 eV for both coverages. The unoccupied states of Co films on Cu(111), as seen in inverse photoemission spectra, display little dependence on the coverage between 1 and 7.5 ML.[9] Combining inverse photoemission and photoemission data, Mankey, Willis, and Himpsel[9] obtain an exchange splitting of 1.05 ± 0.1 eV in a 7.5-ML film and of 1.1 ± 0.1 eV in bulk Co, for states approximately midway along the Γ-A direction. These values can be compared to the measured exchange splitting near Γ in bulk hcp Co(0001),[10] which is 0.85 ± 0.2 eV for the upper d bands and 1.2 ± 0.3 for the lower d bands.

There have been theoretical investigations of the ground-state electronic structure of Co monolayers on Cu(111) and of fcc and hcp bulk Co. A theoretical study by Victora and Falicov[11] predicts the exchange splitting for one and two monolayers to be about 1.4 eV, that is considerably larger than the corresponding experimental values. Furthermore, the calculations by Victora and Falicov show a binding-energy shift of the electronic states between one and two monolayers which has not been until now experimentally observed. For thicker films and bulk Co, there is some disagreement between theory and experiment as well. The calculated exchange splitting for bulk Co (between 1.4 and 1.6 eV), either in the fcc or hcp phase, is significantly larger than the one measured for hcp Co(0001) or for Co on Cu(111). Such discrepancies seem to be beyond the uncertainty of the theory, also because the calculations derive correctly the well-known magnetic moment of bulk Co phases. They could be attributed to correlation effects in photoemission as for Ni, the following element in the periodic table. Chen[13] has recently shown that correlation might be important in Co monolayers as well. However, in spin-resolved photoemission studies of fcc Co on Cu (100), where many-electron effects are expected to be of similar

magnitude or even larger, the experimental exchange splitting of thick films (1.4–1.5 eV) (Ref. 4) is close to the theoretical expectations based on a single-particle picture. This seems to indicate that correlation alone may not explain the small values of the exchange splitting reported for Co on Cu(111) and for hcp Co(0001).

We show, in this paper, that the disagreement between theory and experiment for Co on Cu(111) is to a good extent resolved by the direct measurement of the photoelectron spin polarization. The spin analysis allows one to separate closely located spectral features of opposite spin character, leading to a reinterpretation of the previous spin-integrated measurements and to a better agreement with the theory.

II. EXPERIMENT

The experiments have been performed at the TGM1 and TGM5 beamlines at BESSY in Berlin with the spin- and angle-resolved photoemission apparatus already described elsewhere.[14] The Cu(111) sample was prepared by repeated sputtering and annealing cycles. Co has been evaporated by electron bombardment from a high-purity Co wire. During evaporation, the pressure in the chamber remained below $4\ 10^{-10}$ mbar. The evaporation rate was checked with an oscillating quartz crystal thickness monitor.

We used low-energy-electron-diffraction (LEED) and Auger spectroscopy to follow the growth mode of Co on Cu(111). The Auger results show, in agreement with the data of Gonzales *et al.*,[15] that the substrate emission is rapidly reduced indicating that no major interdiffusion is taking place. As has recently been shown by de la Figuera *et al.*,[6] however, the morphology of the overlayer growth is complicated by formation of islands with different crystallographic orientations. Our LEED study confirms the previous observations made for this system.[5,6] The Cu(111) substrate displays a threefold symmetry, characteristic of the fcc Cu structure. Upon deposition of Co at room temperature the symmetry gradually changes and becomes hexagonal at a thickness of about 3 ML. At variance with the most simple explanation of these results, which would lead to the conclusion that Co grows hcp on Cu(111), a recent scanning-tunneling-microscopy study[6] has proven that the sixfold symmetry is the result of the superposition of diffracted beams from different fcc-Co islands rotated by 60° with respect to each other.

The sample was magnetized by letting an electric pulse pass through a coil, mounted near the sample. The magnetic field was applied along the $[\bar{2}11]$ direction. All the measurements have been performed in magnetic remanence. Spin- and angle-resolved photoemission spectra have been measured with synchrotron radiation (10–70-eV photon energy). The electron analyzer is a 90° spherical capacitor coupled to a 100-kV Mott detector for spin analysis. The spectra presented here are measured for normal incident light and normal electron emission.

III. RESULTS

A. Electronic structure of the thicker films (10–30 ML)

The electronic structure of the thicker Co films presents exchange-split valence-band states. We compare our results to previous spin-integrated photoemission data on bulk Co and to its calculated electronic structure. As will be shown here and in agreement with the recent results on the unoccupied states, the electronic structure of these films is very similar to that of their bulk counterpart (hcp or fcc Co). Angle-resolved photoemission without spin analysis has been used by Himpsel and Eastman[10] to investigate the band structure of hcp Co. They studied the (0001) surface of a single crystal and compared the data to a self-consistent band-structure calculation. Due to the fact that the hcp and fcc electronic structure is very similar, the same band-structure calculation can be used for the Γ-A-Γ (hcp) and for the Γ-L (fcc) directions. They are probed in normal electron emission from the (0001) hcp surface and the (111) fcc surface, respectively. Since we are taking the spectra with s-polarized light in normal incidence, we expect to observe two bands of Λ_3 symmetry, each of them split by the exchange interaction into two spin-polarized subbands.

Spin-integrated photoemission spectra for normal electron emission measured with various photon energies are shown in Fig. 1. They closely correspond to the hcp Co(0001) spectra of Ref. 10. The main feature in all the spectra is a peak near the Fermi level. A weaker shoulder is observed in some cases at about 2-eV binding energy. In the proximity of the Γ point, corresponding to a photon energy of 25–28 eV, Himpsel and Eastman[10] determined a splitting of 1.2 ± 0.2 eV for the lower d band

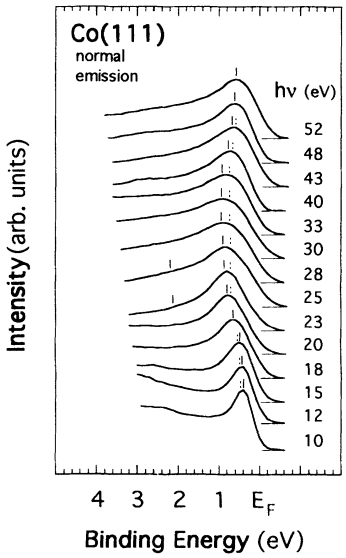

FIG. 1. Angle-resolved photoemission spectra for a 20-ML Co film deposited on a Cu(111) substrate. The spectra have been measured in normal emission at various photon energies. The incident light is normal to the sample surface.

and of 0.82±0.15 eV for the upper *d* band. They assumed the spin-up lower band to correspond to the weak shoulder at about 2 eV, the spin-up upper band and the spin-down lower band to be degenerate under the main peak at 0.8-eV binding energy, the spin-down upper band to cause a shoulder near E_F (which is better resolved in their data than in ours). The spin-resolved data show that this interpretation, although substantially correct, leads to an underestimate of the value of the exchange splitting.

Spin-resolved photoemission spectra corresponding to the spin-integrated ones discussed above are presented in Fig. 2. The spin-resolved spectra show peaks near the Fermi level in both the spin-up and the spin-down curves. With increasing photon energy between 15 and 25 eV, the spin-up peak moves to higher binding energy, whereas the spin-down peak remains almost stationary. At the Γ point (25–28-eV photon energy) the two peaks are separated by about 0.3 eV. Their binding energy is 0.7 eV (spin down) and 1 eV (spin up), corresponding to the emission from the spin-down lower band and from the spin-up higher band, respectively. A rather broad feature at higher binding energy is due to emission from the spin-up lower band. This structure is located at a binding energy of about 2.1 eV, in substantial agreement with the previous findings. The resulting exchange splitting between the two exchange-split lower bands at Γ is, therefore, 1.4±0.15 eV, the uncertainty being essentially due to the difficulty of locating precisely the position of the spin-up emission. This value has to be compared with the 1.2±0.2 eV obtained by spin-integrated photoemission on hcp bulk Co. The difference between the two estimates can be attributed to the previously unresolved, but theoretically predicated,[12] 0.3-eV splitting between the upper spin-up band and the lower spin-down band. The exchange splitting we have determined is, within the error limits, also consistent with the value obtained for the same bands in Co films on Cu(100), 1.55±0.15 eV.[4]

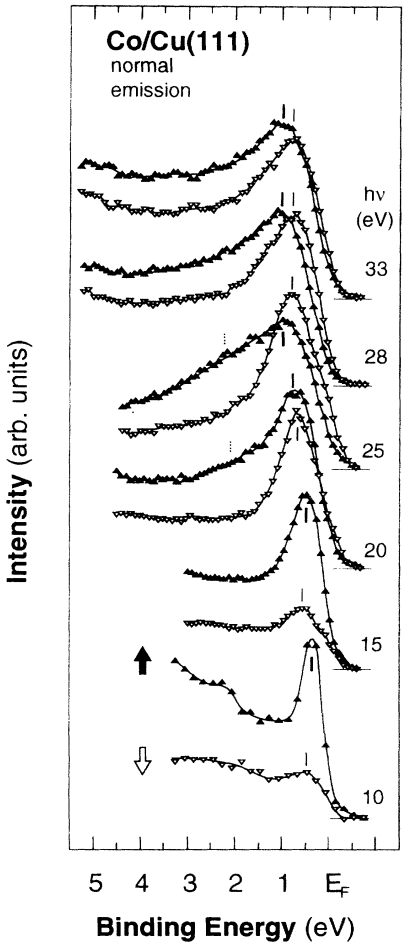

FIG. 2. Angle- and spin-resolved photoemission spectra for a 20-ML Co film deposited on a Cu(111) substrate. The spectra have been measured in normal (light) incidence and normal (electron) emission at various photon energies. Full (empty) pointing up (down) triangles label spin-up (down) EDC's.

The exchange splitting between the upper bands is more difficult to establish. We observe a weak shoulder very close to the Fermi level in the spin-down spectra at 25-eV photon energy (i.e., near Γ). This structure probably corresponds to the feature identified by Himpsel and Eastman as the spin-down upper band. However, the difficulty in precisely determining the binding energy of a structure near the Fermi level is well known. In our opinion, it is not clear whether the peak position corresponds to the critical-point energy, or rather it represents the tail of a structure lying above the Fermi level. Also, the inverse-photoemission measurements are not conclusive in locating the upper spin-down band at Γ, because spectra at the proper photon energy are not available. In all cases, however, taking into account the 0.3-eV splitting we observe experimentally, the exchange splitting of the upper band in the Co films on Cu(111) turns out to be larger than the one previously determined (0.85 eV) for hcp Co. Combining the recent inverse photoemission data by Mankey, Willis, and Himpsel[9] (see their Figs. 3 and 6) and our spin-resolved photoemission data for 20-eV photon energy, corresponding to about midway along the hcp Γ-*A* direction, we obtain an exchange splitting for the upper bands of 1.15±0.15 eV. This value is also slightly larger than the one quoted in Ref. 9 (1.05 eV) for a 7.5-ML Co film on Cu, again because of the incorrect identification of the maximum of the spin-integrated spectra as the position of the upper spin-up band. The values of the exchange splitting we determine for the thicker layers are close to the expected theoretical values. Remaining small deviations of the order of 0.1–0.2 eV, which are anyhow within the experimental errors, are possibly a result of electron correlation.

B. Electronic structure of the thinner films (0.5–10 ML)

In this section, we examine the evolution of the electronic structure with increasing film thickness. The results can be compared with previous photoemission and inverse-photoemission data, obtained without spin analysis, and with the corresponding theoretical results

for Co monolayers on Cu(111). Also, we compare the results with those on thicker films and bulk Co discussed in the preceding section.

In Fig. 3, we show spin-integrated photoemission spectra measured with 15- and 25-eV photon energy for increasing Co thickness. The spectra are normalized to the incoming photon flux. With increasing Co coverage the intensity of the Cu signal, between 2- and 4-eV binding energy, decreases but its lineshape does not change. This indicates that the corresponding Cu states are only slightly influenced by the interaction with Co. The spectra give no evidence of Cu surface segregation through the Co film which would probably affect the lineshape and binding energy of the Cu emission. The presence of a significant amount of segregated Cu and uncovered substrate regions at coverages above 10 ML is ruled out by the absence of the Cu $3d$ emission peak in the corresponding spectra. The Co $3d$ emission develops with increasing coverage within 3 eV from the Fermi level. Small changes of its lineshape can be detected as a function of film thickness. A careful examination of the spectra on an expanded energy scale (Fig. 4) shows that the Co peak position shifts to higher binding energy for coverages between 0.55 and 1.8 ML. Above 3-ML coverage the binding energy of the Co features essentially coincides with that of the thicker films.

In the monolayer regime, one expects the electronic structure to be two dimensional in character for an ideally flat and weakly interacting overlayer. In an angle-resolved photoemission experiment, states localized in two dimensions display a lack of dispersion with varying photon energy. This is indeed observed, as in Fig. 5, for 0.55-ML coverage. The position of the Co $3d$-derived peak remains essentially stationary. In contrast, a dispersion similar to the one observed for thicker films and bulk Co is obtained at 5.5 ML (Fig. 5). The results are summarized and compared with the dispersion of the Cu substrate in Fig. 6. A transition occurs at a very low coverage from a two-dimensional to a three-dimensional character of the electronic structure. Already at one-monolayer coverage the data show some weakly dispersive features, which are perhaps a manifestation of the tendency of Co to grow as a bilayer or even in three-dimensional clusters as discussed elsewhere.[6]

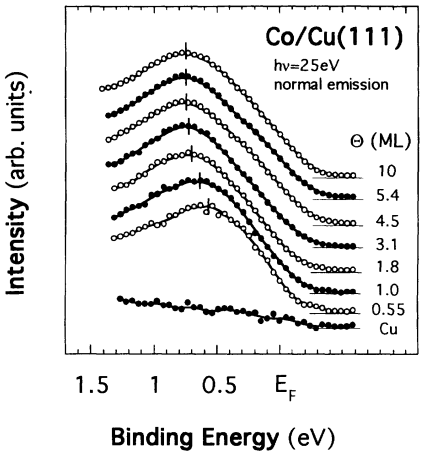

FIG. 4. Expanded view of the region close to the Fermi level of the spectra shown in Fig. 3 with 25-eV photon energy.

At a coverage just below 2 ML, we also observe a transition in the magnetic properties of the overlayer. Figure 7 shows the spin polarization for increasing Co coverage, measured at two different binding energies with 15-eV photon energy. The spin polarization is defined as usual as $[N^{\uparrow}(E)-N^{\downarrow}(E)]/[N^{\uparrow}(E)+N^{\downarrow}(E)]$, where $N^{\uparrow}(E)$ and $N^{\downarrow}(E)$ are, respectively, the number of spin-up and spin-

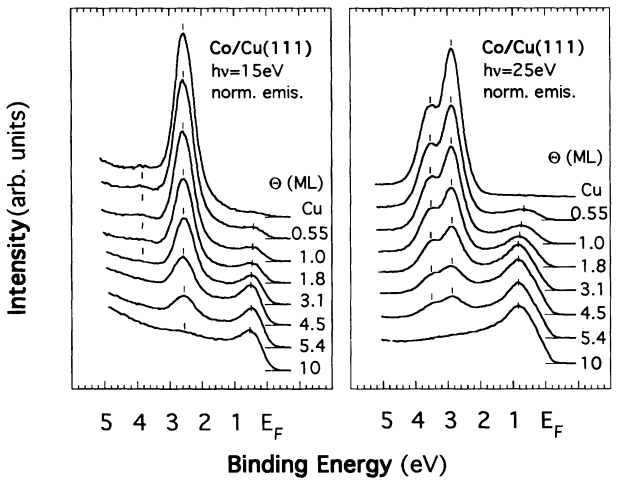

FIG. 3. Thickness dependence for Co thin films deposited on a Cu(111) substrate. The photoemission spectra have been taken in normal incidence and normal emission at photon energies of 15 and 25 eV.

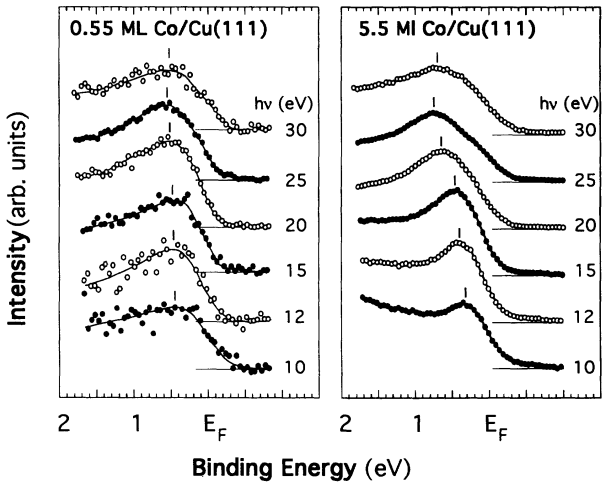

FIG. 5. Energy distribution curves for a 0.55-ML (left panel) and 5.5-ML (right panel) Co films deposited on Cu(111) as a function of the photon energy. In the spectra for 0.55 ML, the Cu contributions have been subtracted. The transition between two-dimensional and three-dimensional character of the Co electronic structure as a function of film thickness is immediately apparent.

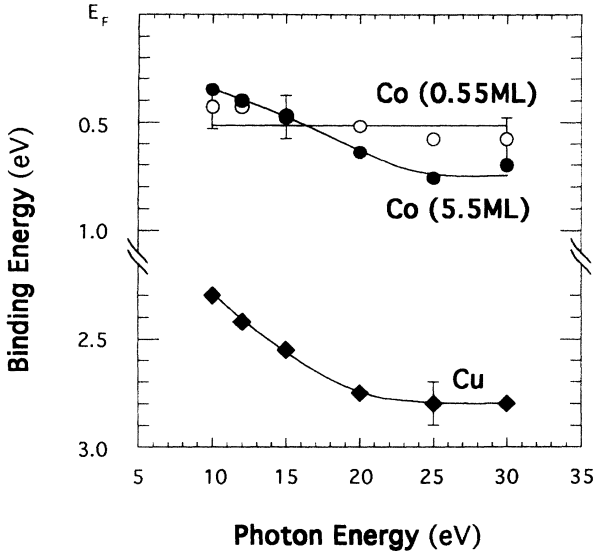

FIG. 6. Comparison of the binding-energy positions of the main Co structure in the valence-band spectra of a 0.55-ML (empty circles) and a 5.5-ML (full circles) Co film as a function of the photon energy. For comparison the corresponding energy dispersion of the bulk Cu peak is also shown (full diamonds).

down photoelectrons at a binding energy E. At 0.6-eV binding energy a Co spin-up peak gives rise to a large positive polarization. The spin polarization is weaker at 1.4 eV, where neither Cu nor Co shows strong emission at this photon energy. As shown in Fig. 7, the onset of the Co $3d$ polarization occurs at about 2 ML. This corresponds to the threshold coverage for in-plane magnetic ordering at room temperature. These results are consistent with the earlier work of Gradmann.[16] In these studies, the Co films deposited on Cu(111) were covered with a Cu layer to prevent contamination. It was discovered that one Co monolayer is spontaneously magnetized in a direction perpendicular to the surface plane. The easy axis was found to rotate in plane at about two monolayers.

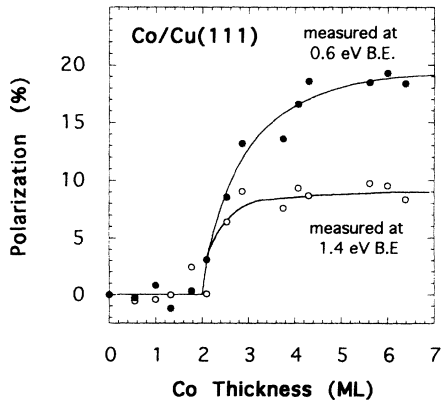

FIG. 7. Spin polarization of the photoemitted electrons (photon energy: 15 eV) at the binding energy of 0.6 eV (full circles) and of 1.4 eV (empty circles) as a function of the Co film thickness. The continuous lines are only guides for the eyes.

We were able to measure spin-resolved photoemission spectra of the in-plane magnetized films, above two-monolayer coverage. Some results obtained with 15- and 25-eV photon energy for normal electron emission are shown in Fig. 8. The most strongly polarized structures appear in correspondence to the Co $3d$ emission near E_F. At all coverages, the spectra show mostly spin-up emission near E_F and 15-eV photon energy but mainly spin-down emission in the 25-eV spectra. This is due to the selective excitation of states of different $k_\perp$ by varying photon energy, a further manifestation of a three-dimensional character of the electronic structure. The most important information provided by these spin-resolved spectra is that shape and binding energy of the polarized Co $3d$ emission do not vary with thickness. In good agreement with our findings, recent inverse-photoemission data[9] display some modification of the spectral features only for coverages below 2 ML. On this basis we conclude that the relevant parameters of the electronic structure, namely, the exchange splitting and the magnetic moment, remain basically unvaried in the thinner films down to about 2 ML.

Our results can further be compared with earlier spin-integrated photoemission data, measured in similar experimental conditions.[8] In contrast to our results, no change was found in the binding energy of the Co states between one and two monolayers. An extremely small value of the exchange splitting (0.7 eV) was derived by a deconvolution of the spin-integrated spectra. The deconvolution was based on the former interpretation of the Co bulk data, which we have shown above leads to an underestimation of the exchange splitting. In fact, our spin-resolved data do not support the assumptions of Ref. 8 nor do they indicate a significant reduction of the exchange splitting from the bulk value, at least for the 2-ML case. For 1 ML, we cannot reliably determine the

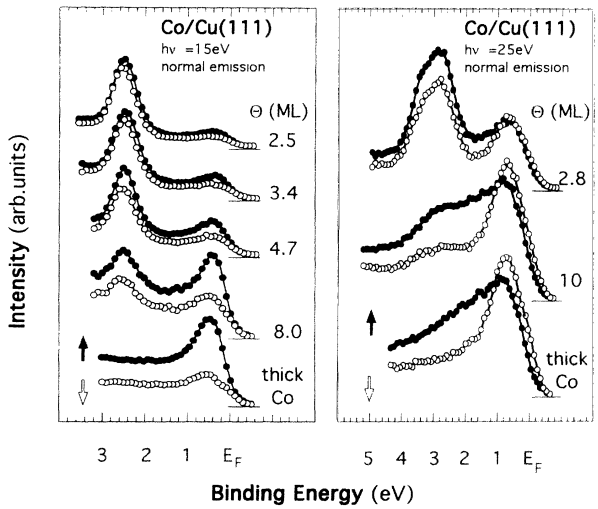

FIG. 8. Spin- and angle-resolved spectra for Co films of various thickness deposited on a Cu(111) substrate. The spectra have been taken in normal incidence and normal emission at photon energies of 15 and 25 eV.

value of the exchange splitting. The electronic states of a monolayer cannot be directly compared to those of thicker films because some modification takes place related to the reduced dimensionality of the system. Without spin-polarized measurements, the identification and precise location of the spectral structure (the most intense have peaks at 0.5 eV below E_F in photoemission and at about 0.5 above E_F in inverse photoemission) seem ambiguous. The calculation predicts a narrowing of the $3d$ bands, accompanied, however, by only a marginal increase of the magnetic moment.[17] Co on Cu(111) is a rather special case in this respect because the almost saturated Co bulk moment and the close-packed structure of this surface reduce considerably the enhancement of the moment in comparison to similar systems [i.e., Fe(111) monolayers or Co on Cu(100)].

IV. CONCLUSION

We have studied the electronic states of Co epitaxial films grown on Cu(111). By spin- and angle-resolved photoemission with synchrotron radiation, we have followed the development of the exchange-split electronic structure with increasing film thickness. Above 2-ML coverage the films become in-plane magnetized. Their electronic states are already very similar to those of thick films (> 15 ML) and (hcp and fcc) bulk Co. Through spin analysis, we have determined the value of the exchange splitting near the center of the Brillouin zone. Our experimentally determined values for the exchange splitting are larger than the ones previously derived from non-spin-resolved measurements. These results lead to a close agreement with the theoretical predictions.

[1]A. J. Freeman and Ru-qian Wu, J. Magn. Magn. Mater. **100**, 497 (1991).

[2]M. Weinert and S. Blügel, in *Magnetic Multilayers,* edited by L. H. Bennett and R. E. Watson (World Scientific, Singapore, 1993).

[3]B. T. Jonker, K. H. Walker, E. Kisker, G. A. Prinz, and C. Carbone, Phys. Rev. Lett. **57**, 142 (1986); W. Heinen, C. Carbone, T. Kachel, and W. Gudat, J. Electron Spectrosc. **51**, 701 (1990).

[4]W. Clemens, T. Kachel, O. Rader, E. Vescovo, S. Blügel, C. Carbone, and W. Eberhardt, Solid State Commun. **81**, 739 (1992).

[5]M. T. Kief and W. F. Egelhoff, Jr., Phys. Rev. B **17**, 10758 (1993); G. L. Nyberg, M. T. Kief, and W. F. Egelhoff, Jr., *ibid.* **48**, 14509 (1993).

[6]J. de la Figuera, J. E. Prieto, C. Ocal, and R. Miranda, Phys. Rev. B **47**, 13043 (1993).

[7]F. J. Himpsel and Th. Fauster, Phys. Rev. B **26**, 1679 (1982).

[8]R. Miranda, F. Yndurain, D. Chandesris, J. Lecante, and Y. Petroff, Phys. Rev. B **25**, 527 (1982); Surf. Sci. **117**, 319 (1982).

[9]G. J. Mankey, R. F. Willis, and F. J. Himpsel, Phys. Rev. B **47**, 190 (1993).

[10]F. J. Himpsel and D. E. Eastman, Phys. Rev. B **21**, 3207 (1980).

[11]R. H. Victora and L. M. Falicov, Phys. Rev. B **28**, 5232 (1983).

[12]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[12]C. Chen, Phys. Rev. Lett. **64**, 2176 (1990); Phys. Rev. B **48**, 1318 (1993).

[14]E. Kisker and C. Carbone, in *Angle-Resolved Photoemission,* edited by S. Kevan (Elsevier, Amsterdam, 1992).

[15]L. Gonzales, R. Miranda, M. Salmerón, J. A. Vergés, and F. Ynduráin, Phys. Rev. B **24**, 3245 (1981).

[16]U. Gradmann, Appl. Phys. **3**, 161 (1974).

[17]Chun Li, A. J. Freeman, and C. L. Fu, J. Magn. Magn. Mater. **75**, 53 (1988); **94**, 134 (1991).