Thin Fe films grown on Ag(100) studied by angle- and spin-resolved inverse-photoemission spectroscopy

G. Chiaia, S. De Rossi, L. Mazzolari, and F. Ciccacci
Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
(Received 12 February 1993; revised manuscript received 4 May 1993)

We present an investigation of the empty electronic states of thin Fe films epitaxially grown on Ag(100), by means of angle- and spin-resolved isochromat inverse-photoemission spectroscopy. Results for film thicknesses in the range from 1 to 50 bcc-Fe monolayers are reported. The evolution of the bands when going from very thin to bulklike films is considered. It is found that the bulk electron *d*-band structure develops after the deposition of many layers (about 15), while for thinner films the exchange splitting is reduced with respect to the bulk value.

I. INTRODUCTION

Recently, there has been an increasing amount of interest in magnetism of thin films.[1] In fact, thin films exhibit magnetic properties which can be different with respect to bulk magnets. Actually, much of the experimental work has been oriented towards the understanding of two-dimensional magnetic phenomena.

Two-dimensional magnetic systems are predicted to have enhanced magnetic momenta, due to reduced dimensionality and coordination.[2,3] On the other hand, the interaction of the film with the substrate is generally non-negligible:[4,5] significant changes in the electronic structure occur at the interface. Such properties, characteristic of the interface, may be important when many units of substrate/film are grown, as is the case of superlattices.[6,7]

Electron spectroscopies are very powerful tools to directly investigate the electronic structure of solids. In particular, inverse-photemission spectroscopy (IPE) gives important information about unoccupied bands in the vicinity of the Fermi level;[8] such empty bands contain, in the case of ferromagnets, the unbalanced minority-spin holes that make up the magnetic moment. In the angle-resolved mode of operation, both electron energies and electron momenta are simultaneously probed. In this spectroscopy, as well as in photoemission spectroscopy, direct transitions dominate the transitions between bulk bands; this makes band mapping in the Brillouin zone (BZ) possible.[9,10] Moreover, if spin resolution is also achieved, a direct experimental study of the spin character of the empty states can be performed.[11]

The aim of this work is to present an accurate investigation of the empty electron states of thin iron films grown onto the silver (100) surface, by means of angle- and spin-resolved isochromat IPE, for different film thicknesses. In particular, we consider the evolution of the empty states when going from very thin to bulklike films. We present results for film thicknesses in the range from 1 to 50 monolayers (ML, 1 bcc Fe ML = 1.43 Å). This systematic study has to be considered as an extension of the reported IPE data on bulk Fe (Refs. 10 and 12) and on Fe/Ag(100) films that are 10-ML thick.[13]

II. EXPERIMENTAL

The experiments have been performed in an ultrahigh-vacuum (UHV) system composed of three stainless-steel chambers, coupled by gates valves (see Fig. 1) and pumped by turbomolecular, ion, and liquid-nitrogen-cooled titanium sublimation pumps. The base pressure in all chambers is in the range of low 10^{-10} Torr.

The first chamber contains a differentially pumped Ar-ion gun and several evaporation cells for sample preparation and film deposition. The second chamber holds a standard electron-energy analyzer (cylindrical mirror analyzer), x-ray and ultraviolet (He resonance lamp) photon sources, and low-energy electron diffraction (LEED), as well as inverse-photoemission apparatus.

The Ag single crystal is clamped by Ta wires mounted on an insulating ceramic plate. It can be heated by elec-

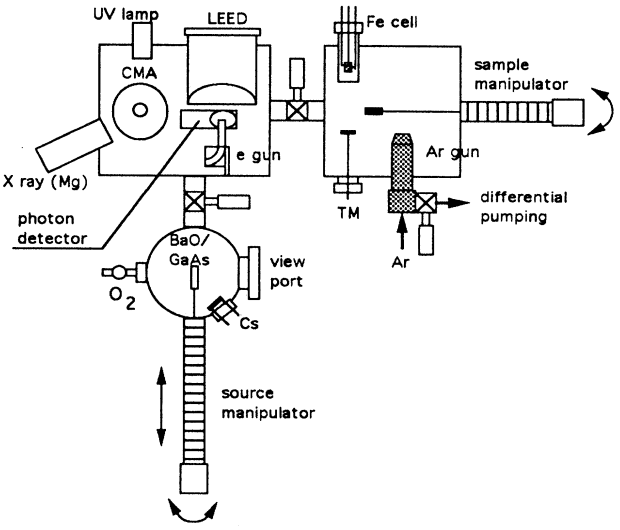

FIG. 1. Schematic view of the experimental apparatus. The sample is prepared in the right-hand chamber and then transferred to the left-hand (top) one, where the IPE measurements are performed. The third chamber is devoted to the electron source preparation (either NEA GaAs photocathode or BaO dispenser).

tron bombardment from electrons thermoemitted by a nearby W filament; the temperature is measured by a Pt/Pt-Rh thermocouple attached to the specimen. Surface cleaning is achieved by the well-known procedure based on 0.5–1-keV Ar sputtering and 500–550 °C annealing cycles. The clean surface does not present any trace of contaminants as seen by x-ray photoemission spectroscopy (XPS) and exhibits a sharp 1×1 LEED pattern.

Fe is evaporated from a water-cooled evaporation cell based on electron bombardment heating of a high-purity iron rod supported by a W wire.[14] The cell is accurately outgassed for many hours before use; after that, in order to avoid contamination, it is continuously kept on at a reduced heating power when not evaporating. Fe films are deposited at room temperature at a rate of ≈0.5 ML/min, as measured by a calibrated quartz microbalance. During evaporation the pressure in the chamber remains in the 10^{-10} torr range. High-purity films are grown as confirmed by XPS analysis. Epitaxial growth of the film is checked by LEED. All the data reported here have been taken on freshly grown films, each time deposited on a clean Ag(100) surface.

IPE is performed in the isochromat mode, collecting the emitted photons at a fixed energy while changing the electron-beam energy. The electron source is prepared in another UHV chamber and then moved to the operating position (see Fig. 1); it consists either of a BaO thermocathode, for spin-integrated measurements, or a GaAs photocathode in negative electron affinity (NEA), for spin-resolved experiments.[15] The electrons are transported onto the sample by an electron-optical system, which consists of three parts: (i) the cathode region, (ii) the spin rotator, and (iii) the decelerating and focusing lenses. The electron gun, described in detail elsewhere,[16] delivers currents up to 15 μA in the energy range 7–50 eV, with energy and angular spreads less than 0.3 eV (full width at half maximum) and 5° (full divergence angle) respectively; in the spin-resolved mode of operation, the electron beam is transversely polarized (spin perpendicular to electron momentum), with a polarization $P_0=27\%\pm3\%$.

Photons are detected by a band-pass ultraviolet photon detector operating at $h\nu=9.8\pm0.5$ eV. The photons arriving onto the detector are filtered by a CaF_2 window (low-pass energy filter) before exciting electrons of a KBr-coated photocathode (high-pass energy filter); photoelectrons are collected by a channeltron and detected by standard pulse-counting electronics. The acceptance angle of the detector, in our geometry, is 0.5 sr and the counting rate is about 3×10^2 counts $\mu A^{-1}\,s^{-1}\,sr^{-1}$).[17]

The experimental setup for the spin-resolved IPE measurements is sketched in Fig. 2. The film is magnetized in-plane along a [110] direction of the Fe lattice by means of a current pulse sent through a small coil surrounding the sample: measurements are performed in magnetic remanence. In our geometry, the incident beam polarization is parallel to the surface: in this way we maximize the spin-dependent interaction of the electron beam with an in-plane magnetized film.[18] On the other hand, in such a configuration no spin-dependent effects are measurable for perpendicularly magnetized films.

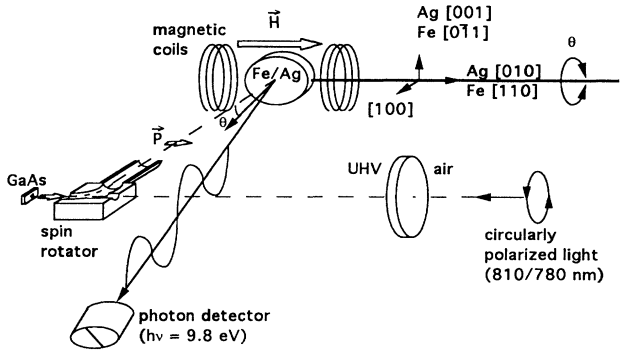

FIG. 2. Sketch of the experimental setup for spin-resolved IPE. The spin-polarized electron source consists of a NEA GaAs photocathode excited by the circularly polarized light from an infrared laser. The beam polarization is transformed from longitudinal to transversal by means of a 90° spin rotator; it can be reversed by changing the elicity of the exciting light.

Data acquisition is achieved by means of a personal computer, through appropriate input-output cards. For each incidence angle two IPE spectra are taken by step sweeping the electron-beam energy and collecting data at each step for both directions of the beam polarization with respect to the sample magnetization **M**. The impinging current is also continuously monitored for normalization purposes, taking into account the electron optics transmission and the GaAs photocathode finite lifetime. Spectra can be measured for two opposite directions of **M** to get rid of spurious asymmetries that could be introduced by stray magnetic fields. However, working with thin films these problems are considerably reduced and no evidence of such effects has been detected.

III. RESULTS AND DISCUSSION

A. Film growth

It is well known that, owing to the small lattice mismatch (0.8%), bcc Fe films can be epitaxially grown on an Ag(100) substrate.[19–21] In this case, the Fe lattice is rotated by 45° in the (100) plane with respect to the Ag lattice.

During film growth, we find the following evolution of the LEED pattern. At first for very thin films the pattern remains quite good, even if the spots get broader than those of clean Ag. Then, after some three Fe ML's have been deposited, the pattern becomes more and more diffuse while the background increases considerably. Eventually, however, after deposition of about ten monolayers, the LEED pattern improves again, with less broad spots and a much reduced background. These qualitative observations agree with previously reported results[19,20] including a very accurate LEED study, indicating that the very thin films are neither very flat nor very well ordered.[20] The LEED pattern from the deposited film can be considerably improved by annealing the sample at ≈250 °C: in this case a very sharp 1×1 pattern as good as for clean Ag is observed, independent of the Fe film thickness. However, even at this moderate temperature,

interdiffusion takes place as demonstrated by XPS analysis, showing a much larger Ag signal than for the unannealed case. The study of these annealed films is beyond the purpose of the present work and will be presented elsewhere; from now on we shall always refer to unannealed films deposited at room temperature.

B. Angle-resolved IPE

The **k**-resolved measurements have been carried out by rotating the sample around the [001] direction of the Ag lattice corresponding to the [110] direction of the 45° rotated Fe lattice. In this way the ΓXWK plane of the fcc BZ of Ag and the ΓNPH plane of the bcc BZ of Fe are experimentally accessible.

Isochromat spectra for Ag (100) in the ΓXWK direction have already been measured[22,23] and our results essentially agree with those previous works. At normal incidence the spectrum shows a large peak A slightly above E_F due to bulk transitions and a steplike feature S at about 4 eV, which is due to radiative transitions into image potential states (see Fig. 5). For off-normal incidence both features disperse towards higher energies. The image potential states are very sensitive to the surface conditions and the presence of the structure S in the spectra is a clear indication of a clean and well-ordered substrate surface.

A selection of the spectra for different incident angles relative to 50-ML-thick Fe films, which can be considered to have the same electron properties as bulk iron, are shown in Fig. 3. Two structures, labeled B_1 and B_2, are clearly visible in the spectra at small angles and are still detectable, though not very well resolved, at large angles, too. These features can be attributed to bulk transitions to majority and minority spin states, respectively, in agreement with previous works on iron single crystals.[10–12] For off-normal incidence, B_1 disperses towards higher energies, while B_2 is always located at the same energy. However, while the peak position energy compares very well with the findings on bulk Fe, the spectral shape for the films is somehow different from the spectrum relative to the Fe(100) single crystal taken in similar experimental conditions,[12] shown as the top curve in Fig. 3. In fact, the peak due to the majority empty d band at the Fermi level has a lower intensity in the film than in the bulk. This behavior has already been reported in an IPE study on a 10-ML-thick Fe film, and is attributed to some disorder present in the epitaxial film.[13] This is also supported by the fact that the transition to the image state, analogous to the S structure well visible in the case of Ag(100) (see Fig. 5 below), is completely absent in the spectra taken from the epitaxial films. Similar findings have been found in spin-resolved direct photoemission from the same system:[24] also in that case the large background in the spectra and the variation of the relative intensities of the observed peaks with respect to bulk Fe samples has been interpreted in terms of poor crystalline quality of the films.

Though not as well resolved as in the bulk, however, the presence of both B_1 and B_2 features in our spectra is well established and an experimental determination of the

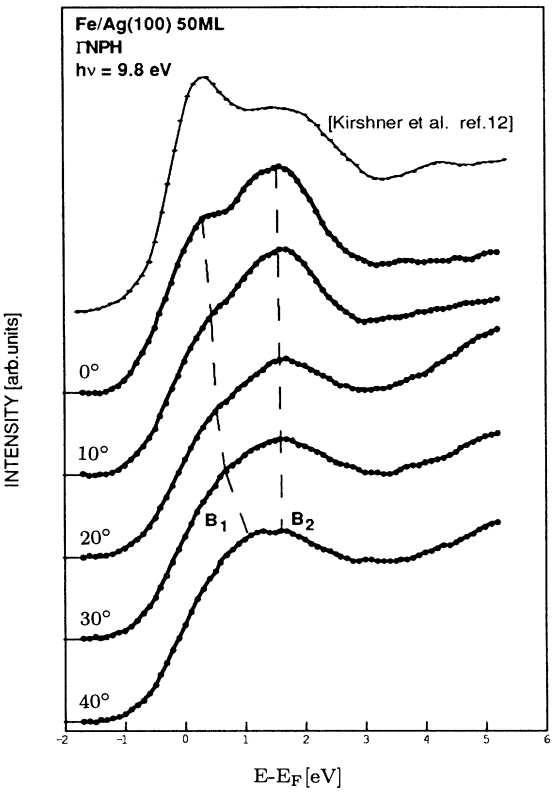

FIG. 3. **k**-resolved inverse-photoemission spectra at $h\nu = 9.8$ eV from a 50-ML-thick Fe film grown on Ag(100) for various electron incidence angles in the ΓNPH azimuth of the bcc Brillouin zone. The spectrum taken from bulk iron is also reported (after Ref. 12).

empty band dispersion for the Fe(100) surface is possible, as it is usual in angle-resolved IPE. Because the B_1 peak is located near the Fermi level, an accurate analysis is necessary in order to determine its actual position. We fitted the spectra with two Lorentzians of equal area, cutoff by the Fermi function and convoluted with the known resolution function of the experimental apparatus. The results are summarized in Fig. 4, where we show an $E(k_\parallel)$ diagram. The parallel component $k_\parallel$ of the wave vector, which is conserved when the electron crosses the surface, apart from a generally vanishing[25] surface reciprocal-lattice vector, is along the ΓN direction. As seen in Fig. 4, we find a majority empty band with large dispersion and an almost flat minority empty band. Full triangles in the figure indicate the expected $E(k_\parallel)$ values for bulk direct transitions at 9.8 eV photon energy, as deduced from the bulk band structure of iron.[26] The agreement between experimental and theoretical values is quite good. The resulting splitting of the two bands, 1.6 eV, agrees very well with the known exchange splitting δE_{ex} at the H point of the bcc Fe BZ, namely 1.8 eV.[10] In isochromat IPE, in fact, the electron wave vector is not constant in the spectrum, so that the two transitions to majority and minority states take place in different points of the band structure at different **k** values. Therefore, the real δE_{ex} value at the same **k** point has to be extrapolated

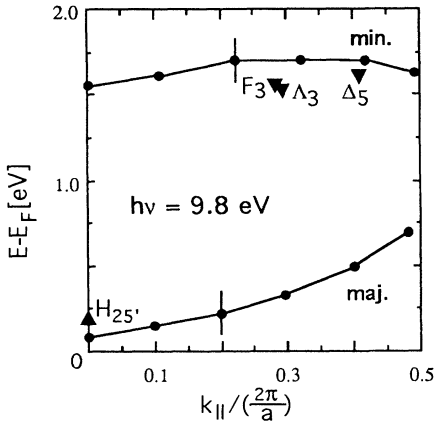

FIG. 4. Majority and minority empty band dispersion versus the parallel component of the electron wave vector along the ΓN direction for a bulklike 50-ML-thick Fe film grown on Ag(100). Full dots are the experimental results, as obtained by the data in Fig. 3; for the sake of clarity the error bar is shown only for one point. Triangles are values deduced from the calculated Fe bulk band structure.

from our measurements: a difference of 0.2 eV between the splitting of the bands at the H point and the energy difference between the two features in the measured spectra is consistent with the Fe bulk band structure.[26]

In Fig. 5 we show spectra for different Fe coverages varying the incidence angle. As can easily be seen, for coverages of one or two monolayers the main feature in the spectrum is the one due to the Ag contribution (feature A). This substrate peak does not shift in energy with increasing Fe coverage, at variance with what was recently reported for Fe on Cu(100),[27] suggesting that in our case the Ag electron band structure is not affected by Fe deposition. Concerning the Fe films, it is seen that at low coverages the two peaks B_1 and B_2 collapse towards the same energy position. This reduction of the energy splitting of the two features is well visible in our spectra at all the different incidence angles investigated.

C. Spin-resolved IPE

The above findings are confirmed by the analysis with spin resolution using a polarized electron beam. In the spin-resolved spectra, however, the structures can be directly identified and are much better resolved. Moreover, new relevant information on film magnetization is gained. The results for very thin films are collected in Fig. 6, whereas measured IPE spectra for electron-beam polarization parallel and antiparallel to the applied magnetic field are shown. It is clearly seen that polarization effects are visible only in films more than 5-ML thick, whereas the spin-up and spin-down spectra for smaller thicknesses are identical to within experimental accuracy. Since our measurements are sensitive only to the in-plane component of the sample magnetization, this result indicates that at room temperature the few-monolayer films cannot be permanently magnetized in the film plane. Such a behavior has already been observed in Fe/Ag(100) films by spin-resolved direct photoemission:[24] it was sug-

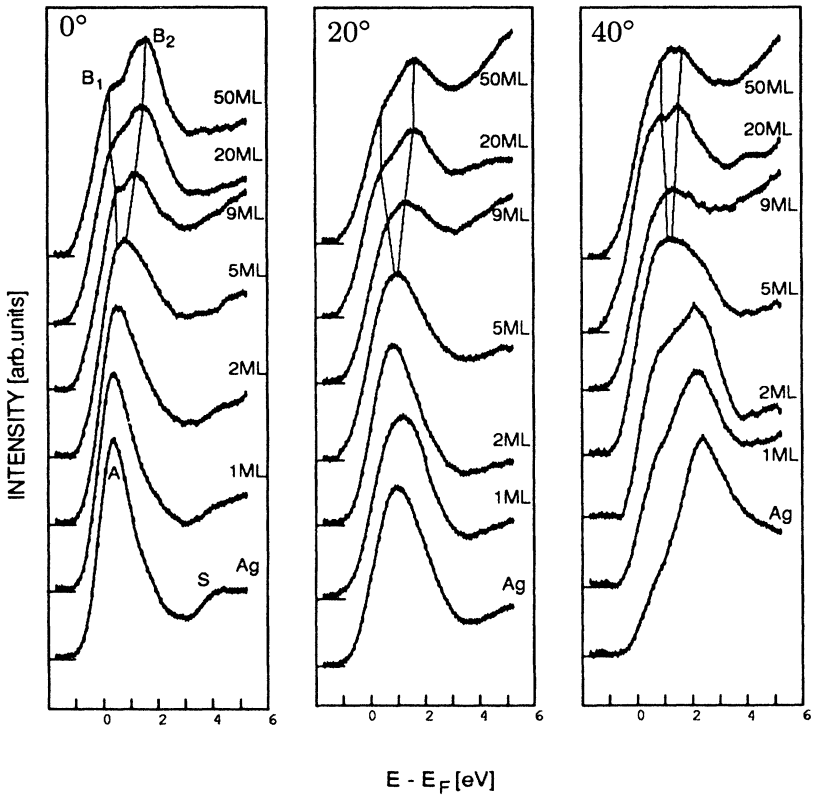

FIG. 5. Inverse-photoemission spectra as function of Fe coverage on Ag(100). Spectra are shown for three different incidence angles relative to the normal direction.

gested that in ultrathin films surface anisotropy forces the magnetic moment to lie perpendicular to the surface. This idea has been successively confirmed by conversion-electron Mössbauer measurements on Fe/Ag(100) multilayers[28] which indicate that, at room temperature, a transition from perpendicular to in-plane magnetized films actually occurs at about 5 ML. At variance with these findings, in magneto-optical experiments on clean uncapped films the same transition has been found at 2–3 ML.[29] It was also suggested that different results can be expected for not perfectly clean layers, since small amounts of adsorbed oxygen can dramatically affect the magnetic anisotropy.[30] However, as mentioned above, in our experiment we do not find any evidence of film contamination, so that the discrepancy with the data of Ref. 29 cannot be ascribed to such an effect. Moreover, a very recent accurate investigation on magnetic anisotropies in wedge-shaped Fe overlayers grown on Ag(100)[31] supports our results. In fact, in such work, which points out the presence of a very rich magnetic phase diagram for Fe/Ag(100) films, the perpendicular-to-parallel easy axis transition is found to occur above 6 ML,[31] in good agreement with our data.

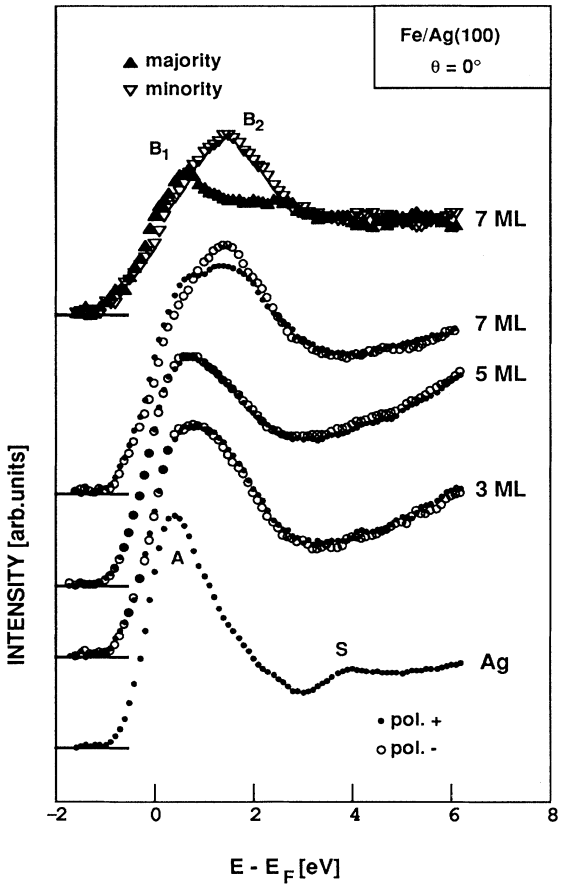

FIG. 6. Spin-polarized IPE spectra from very thin Fe films grown on Ag(100), taken at normal incidence. Polarization effects are seen only in the 7-ML-thick film: in this case also the spin-resolved spectra normalized to a 100% polarized incident beam are shown at the top (see text).

In films thicker than 5 ML a polarization effect is indeed clearly observed in our IPE measurements, as seen for the 7-ML spectrum in Fig 6. In this case, the known value of P_0 can be used to reconstruct the spin-resolved spectra for a hypothetical 100% polarized beam (see Ref. 11 for details). The results are shown as top curves in Fig. 6 for the 7-ML film: the two structures B_1 and B_2 are now clearly resolved and directly identified with transitions to the majority and minority spin empty states, respectively.

A selection of the spin-resolved spectra for thicker films at normal incidence is presented in Fig. 7. The reduction of the energy splitting between peaks B_1 and B_2 with decreasing film thickness is here very evident even without any kind of fitting procedure. However, an accurate analysis as depicted above has been performed, in order to extract quantitative information for the exchange splitting at various Fe coverages. The results are summarized in Fig. 8. The energy splitting δE for a 5-ML film is 0.8 ± 0.25 eV. With increasing film thickness, δE increases up to 1.2 ± 0.15 eV for a 9-ML film, and eventually reaches the bulk value 1.6 eV above 15 ML. As noted above, 0.2 eV has to be added to δE to obtain the real exchange splitting δE_{ex}. Note that the error bars are quite smaller in the region where the sample magnetization lays in plane so that the spin-resolved spectra can be effectively used. The most relevant result pointed out from such analysis is that the Fe empty band structure is not completely developed for coverages below 15 ML. This finding is at variance with what is observed in the

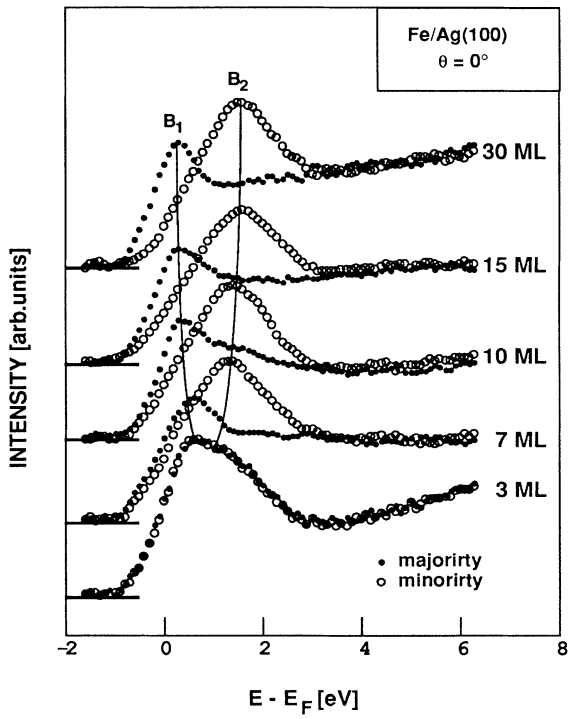

FIG. 7. Spin-resolved spectra normalized to a 100% polarized incident beam from Fe films grown on Ag(100), taken at normal incidence. The majority and minority B_1 and B_2 structures appear in two different spin channels.

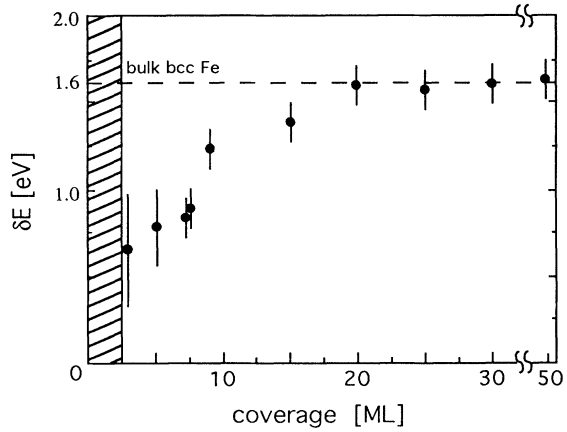

FIG 8. Energy separation between the structures in the IPE spectra as a function of the Fe coverage on Ag(100). The ferromagnetic exchange splitting at the H point of the Fe BZ is obtained by this energy splitting by adding 0.2 eV: $\delta E_{ex} = \delta E + 0.2$ eV (see text).

occupied states spectroscopy. In spin-resolved photoemission from Fe/Ag(100) films, in fact, only minor variations in the intensity of the peaks and no variation in their position have been reported when going from very thin up to 30-ML films.[24] Such discrepancy seems to indicate that the empty states are more sensitive to the film geometry than the occupied ones. Actually, a reduction of the exchange splitting in the empty states in thin bcc Fe grown on Cu(100), very similar to our results, has been recently reported.[27]

On the other hand, theoretical calculations assuming completely flat layers have predicted an enlargement of exchange splitting due to the high anisotropy in ultrathin films.[2,32] This case corresponds to the shaded region in Fig. 8, which unfortunately is not experimentally accessible for a δE analysis. In fact, at these low Fe coverages, the main structure in the spectra is the Ag peak, covering other weak features arising from Fe. Moreover, no additional information is gained here working with polarized electrons, since the spectra do not show any spin up-down asymmetry. Anyway, the trend of the experimental data is definitively in contrast with the theoretical expectations. As pointed out above, however, the present and previously reported[24] spectroscopic results as well as accurate LEED studies[19,20] indicate that Fe films grown on Ag(100) are not completely ordered. This fact may have a non-negligible effect on the film electronic structure.

IV. CONCLUSIONS

In conclusion, we have extensively investigated with spin- and angle-resolved inverse photoemission the empty states of Fe thin films grown on a Ag(100) surface, for coverages varying from 1 up to 50 layers, representative of bulk iron. Our results point out that the true bulk electron d-band structure for the empty states develops after the deposition of many layers (about 15), while for thinner films the exchange splitting is reduced with respect to the bulk value. Experiments with polarized electrons directly show the spin dependence of the bands and confirm this picture. Moreover, they give spectroscopic evidence that films thinner than 5 ML cannot be permanently magnetized in the film plane.

[1]See, for instance, *Magnetism in Ultrathin Films* edited by D. Pescia [Appl. Phys. (to be published)].
[2]C. L. Fu, A.J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985).
[3]J. G. Gay and R. Richter, Phys. Rev. Lett. **56**, 2728 (1986).
[4]N. B. Brookes, Y. Chang, and P. D. Johnson, Phys. Rev. Lett. **67**, 354 (1991).
[5]J. E. Ortega and F. J. Himpsel, Phys. Rev. Lett. **69**, 844 (1992).
[6]D. Pescia, D. Kerkmann, F. Schumann, and W. Gudat, Phys. B **78**, 4 75 (1990).
[7]B. Heinrich, Z. Celinski, J. F. Cochran, W. B. Muir, J. Rudd, Q. M. Zhong, A. S. Arrott, K. Myrtle, and J. Kirschner, Phys. Rev. Lett. **64**, (1990).
[8]For a review on IPE see N. V. Smith, Rep. Prog. Phys. **51**, 1227 (1988).
[9]H. Scheidt, M. Globl, V. Dose, and J. Kirschner, Phys. Rev. Lett. **51**, 1688 (1983).
[10]A. Santoni and F. J. Himpsel, Phys. Rev. B **43**, 1305 (1991).
[11]For a review on spin-resolved IPE see V. Dose and M. Glöbl, in *Polarized Electrons in Surface Physics,* edited by R. Feder (World Scientific, Singapore, 1985), p. 547.
[12]J. Kirshner, M. Globl, V. Dose, and H. Scheidt, Phys. Rev. Lett. **53**, 612 (1984).
[13]F. J. Himpsel, Phys. Rev. Lett. **67**, 2363 (1991).
[14]S. De Rossi, M. Tosca, E. Vescovo, and F. Ciccacci, Vuoto **XXI**, 51 (1991).
[15]F. Ciccacci and G. Chiaia, J. Vac. Sci. Technol. A **9**, 2991 (1991).
[16]F. Ciccacci, E. Vescovo, G. Chiaia, S. De Rossi, and M. Tosca, Rev. Sci. Instrum. **63**, 3333 (1992).
[17]M. Finazzi, A. Bastianon, G. Chiaia, and F. Ciccacci, Meas. Sci. Technol. **4**, 234 (1993).
[18]The easy magnetization axis in Fe is along the [100] direction, thus a remanent magnetization reduced by a cos(45°) factor along the [110] direction is expected, because of domain formation along the $[\bar{1}00]$ and $[0\bar{1}0]$ directions. This has been taken into account by using a reduced value for $P_0 = 0.27\cos(45°) \simeq 19\%$.
[19]G. C. Smith, H. A. Padmore, and C. Norris, Surf. Sci. Lett. **119**, L287 (1982); B. T. Jonker and G. A. Prinz, *ibid.* **172**, L568 (1986).
[20]H. Li, Y.S. Li, J. Quinn, D. Tian, J. Sokolov, F. Jona, and P. M. Marcus, Phys. Rev. B **42**, 9195 (1990).
[21]H. Li and B. P. Tonner, Phys. Rev. B **40**, 10 241 (1989).
[22]B. Reihl, K. H. Frank, and R. R. Schlittler, Phys. Rev. B 7328 (1984).
[23]W. Altmann, V. Dose, and A. Goldmann, Z. Phys. B **65**, 171 (1986).
[24]B. T. Jonker, K. H. Walter, E. Kisker, G. A. Prinz, and C. Carbone, Phys. Rev. Lett. **57**, 142 (1986).

[25]R. Schneider and V. Dose, in *Unoccupied Electronic States,* edited by J. C. Fuggle and J. E. Inglesfield, Topics in Applied Physics Vol. 69 (Springer-Verlag, Berlin, 1992), p. 277.
[26]J. Callaway and C. S. Wang, Phys. Rev. B **16**, 2095 (1977); see also Refs. 9 and 10.
[27]H. Glatzel, R. Schneider, T. Fauster, and V. Dose, Z. Phys. B **88**, 53 (1992).
[28]N. C. Koon, B. T. Jonker, F. A. Volkening, J. J. Krebs, and G. A. Prinz, Phys. Rev. Lett. **59**, 2463 (1987).
[29]J. Araya-Pochet, C. A. Ballentine, and R. J. Erskine, Phys. Rev. B **38**, 7846 (1988).
[30]J. Chen, M. Drakaki, and J. Erskine, Phys. Rev. B **45**, 3636 (1992).
[31]Z. Q. Qiu, J. Pearson, and S. D. Bader, Phys. Rev. Lett. **70**, 1006 (1993).
[32]R. Richter, J. G. Gay, and J. R. Smith, Phys. Rev. Lett. **54**, 2704 (1985).