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## Spin-resolved electronic bands of FCT cobalt

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**Abstract.** The understanding of itinerant ferromagnetism—usually involving a band structure approach—may be put on a broader basis by considering the magnetic properties of the normally inaccessible metastable crystalline phases of Fe, Co and Ni. We prepared one of these systems, namely ferromagnetic FCT cobalt, by epitaxial growth of typically five atomic layers onto carefully characterized Cu(001) surfaces, and mapped the majority and minority spin bands along the surface normal for the first time with spin- and momentum-resolved photoemission with circularly polarized UV synchrotron radiation. The results are compared with two fully relativistic state-of-the-art bulk band structure calculations for FCC Co.

'Monolayer engineering', i.e. the controlled fabrication of monocrystalline, epitaxially grown layered structures, has had a strong impact on the search for novel magnetic materials [1, 2] in the past few years. It is possible now to fabricate elemental materials in modifications that either do not exist in nature (such as BCC Cu [3] and BCC Co [4]) or that exist only under extreme conditions of temperature and/or pressure. The interest in these 'exotic' phases goes far beyond pure scientific curiosity, since future technological applications of novel materials inevitably require a basic understanding of their electronic and magnetic properties. On the other hand, these advances in materials science now enable experimentalists to test theoretical predictions of the electronic structure of crystal phases, which are inaccessible under ambient thermodynamic conditions. As an example, Co assumes the HCP structure at low temperatures and transforms into the FCC phase above 750 K, accompanied by a drastic change of the magneto-crystalline anisotropy. A (non-relativistic) band structure of FCC Co has been proposed already, in the late seventies, by Moruzzi *et al* [5]. Studying the electronic structure of this material by angle-resolved photoemission, however, is extremely difficult, because at the high sample temperature required ( $\geq 800$  K), the rapid surface contamination by segregating impurities and the strong presence of non-direct transitions [6] preclude a reliable band mapping. Consequently, no such attempt, spin-resolved or not, has been made for pure cobalt.

Although the existence of the FCC phase (mixed with the HCP phase) in polycrystalline evaporated films has been known for a long time, only 'monolayer engineering' with

Carefully prepared and characterized Cu(001) substrates produces monocrystalline films that are sufficiently perfect over large areas [7, 8]. By growing relatively thick layers, the electronic structure of FCC Co may thus be studied by spin- and momentum-resolved photoemission at room temperature. These experiments yield a reliable band mapping, which may serve to test spin-polarized band structure calculations. On the other hand, very thin Co layers on Cu(001) are known from LEED studies [9] to assume a tetragonally distorted face-centred cubic structure ('FCT') in registry with the Cu substrate. This situation offers the interesting possibility of studying the effects of tetragonal distortion on the spin-resolved band structure for sufficiently thin films.

Our measurements have been made on films five monolayers (ML) thick. On the one hand, this is thick enough to develop a fully three-dimensional dispersion behaviour, as was verified experimentally by varying the film thickness. This allows us to make contact with recent state-of-the-art, spin-resolved, relativistic band structure calculations for bulk FCC Cobalt. On the other hand, they are thin enough to lead us to expect a sizeable average tetragonal distortion (about 4–5%) throughout the film. In fact, the experimental data from these FCT Co(001) films are in good agreement with the corresponding calculations as far as the spin character and the single-group symmetries of the bands are concerned. For the energy eigenvalues, however, we do find some deviations, which we attribute to the tetragonal compression in the cobalt lattice.

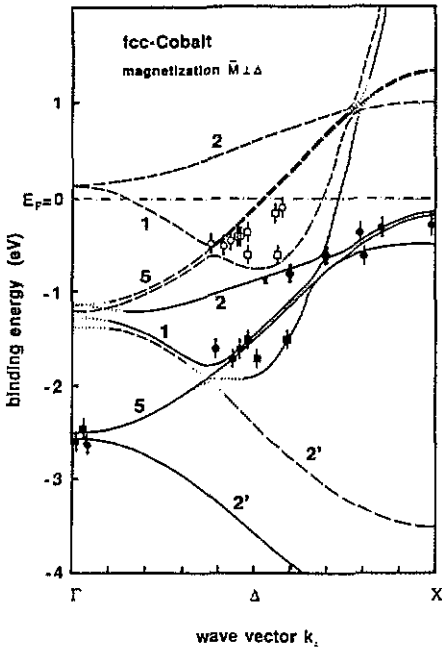
Since the sample preparation is crucial, a few words are in order. The Co layers are deposited *in situ* at a rate of about  $0.5 \text{ ML min}^{-1}$  from a Co wire, heated by electron bombardment, onto the Cu(001) substrate held at 450 K in UHV in the medium  $10^{-10}$  Torr range. The sample temperature represents an optimum compromise between nearly defect-free layer-by-layer growth and interdiffusion of Co into the Cu substrate [10]. The growth is monitored by intensity oscillations in medium-energy electron diffraction (MEED) at  $\approx 2 \text{ keV}$ . By simultaneously measuring the Auger electrons excited by the same primary beam, we were able to verify that the 'breaks' in the Auger intensity versus evaporation time curves correspond to maxima in the diffracted (00) beam intensity [11]. Thus, our term 'monolayer' refers to the number of MEED intensity oscillations, the procedure yielding a thickness calibration with  $\pm 0.1 \text{ ML}$  accuracy. The LEED patterns of the clean Cu(001) and of the system 5 ML Co/Cu(001) are virtually identical. The LEED  $I$ - $V$  curves for the  $\{10\}$  and  $\{11\}$  beam families taken with a TV system are also very similar over the range from 70 eV to 200 eV, except for an energetic shift of the order of 10 eV (at 150 eV). Of particular importance, though mostly neglected, is the substrate topography. Optimum growth was obtained only after an extensive period ( $\approx 100 \text{ h}$ ) of heating at  $\approx 1000 \text{ K}$  and simultaneous sputtering ( $\text{Ne}^+$  or  $\text{Ar}^+$ ,  $3 \text{ keV}$ ,  $3 \mu\text{A cm}^{-2}$ ), followed by annealing to  $\approx 1100 \text{ K}$  until the implanted sputter gas was desorbed. The topography of this surface was studied by scanning tunnelling microscopy (STM). It consists of large, atomically flat terraces of typically  $0.2$  to  $1 \mu\text{m}^2$  size, separated from each other by bands of agglomerated atomic steps, up to 10 nm high. The fraction of these disturbed areas is less than 10% of the total area. By contrast, the same surface, deliberately roughened by sputtering without subsequent annealing, exhibits a very rough topography, very poor MEED and LEED patterns, and no oscillations of the MEED specular intensity during growth. In order to avoid contamination affecting the photoemission measurements, the Co layers were removed by sputtering after 4–6 h, and a fresh layer was deposited, each time with monitoring of the MEED oscillations to ensure optimum reproducibility.

The photoemission experiments were carried out at the 6.5 m normal-incidence monochromator at the BESSY storage ring, Berlin, using the spin- and momentum-resolving spectrometer described earlier [12]. UV light in the range 11 eV to 27 eV was

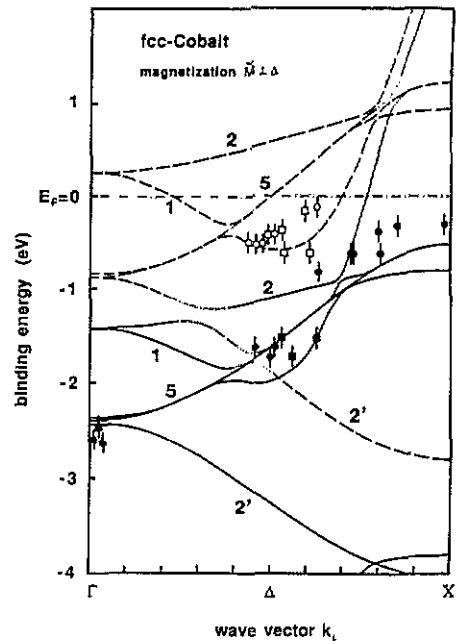
used, at an overall energy resolution of typically 250 meV. In order to exploit the (non-relativistic) dipole selection rules, two sets of data were taken, both at normal electron emission: at normal incidence of the light (purely s-polarized light), and at  $64^\circ$  with respect to the surface normal (mixture of s- and p-polarized light). The sample was magnetized in-plane along the [100] direction to make contact with the relativistic band structure calculations assuming this geometry. Although this is not the easy axis of magnetization (this is [110], [13]), the in-plane magnetic anisotropy is sufficiently small to keep the sample remanently in saturation. This was checked *in situ* by magneto-optic Kerr effect measurements [10, 11]. The analysis of the polarization vector of the emitted electrons proved that the magnetization vector was indeed along the [100] direction, as far as the emission from the Co-related part of the spectra is concerned. The electrons from the Cu d bands showed a different behaviour, similar to that from Ag(001) [14], because of a circular component in the UV light. Nevertheless, the findings in Cu demonstrate the significance of spin-orbit coupling even in 3d transition metals, which motivates our use of fully relativistic band structure calculations in the mapping procedure.

The two theoretical band structures have been obtained by two different approaches. The first one, called HE in the following, uses the spin-polarized relativistic version of the KKR band structure method [15]. This approach allows us to treat spin polarization and all relativistic effects on the same footing, and therefore describes the hybridization of the ('non-relativistic') minority and majority bands due to spin-orbit coupling in a most rigorous way. In calculating the bands shown in figure 1, we have used the potential as tabulated by Moruzzi *et al* [4, 16]. This should, however, cause no serious problems, because the orbital and spin magnetic moments obtained this way are in very good agreement with recent self-consistent calculations [17–19]. The band structure HE in figure 1 presumes the equilibrium lattice constant of FCC Cobalt ( $a_0 = 3.51 \text{ \AA}$ ). The theoretical results referred to as calculation FN have been obtained by means of the linear rigorous cellular (LRC) method [20]. The inclusion of spin-orbit coupling for spin-polarized systems within the LRC method is described in detail in [17]. Here, we use the exchange/correlation potential given by von Barth and Hedin [21], which is also used by Moruzzi *et al* [4]. Self-consistent spin-polarized LRC calculations for lattice constants of  $3.5 \text{ \AA}$  (FCC Co) and  $3.61 \text{ \AA}$  (FCC Cu) yield magnetic moments per atom of  $1.59 \mu_B$  and  $1.65 \mu_B$ , respectively. This seems to be in accordance with the value of  $1.56 \mu_B$  obtained by Moruzzi *et al* for a lattice constant of  $3.46 \text{ \AA}$ . The somewhat larger exchange splitting in the LRC calculations, however, may be due to our use of the scalar-relativistic one-particle equations that include all relativistic effects apart from spin-orbit coupling. In doing so, one goes definitely beyond the non-relativistic approximation that the results of Moruzzi *et al* refer to. The results of the calculation FN for the lattice constant  $a_0 = 3.61 \text{ \AA}$  (bulk FCC copper) are displayed in figure 2. Because of the different lattice parameters involved, these two calculations represent two different approximations to the real experimental situation of a face-centred-tetragonal lattice structure.

For the analysis of the band structure, the spin-polarization curves as a function of electron binding energy, as well as the partial intensity curves, obtained from the total intensity together with the polarization along the magnetization vector were used. The data have been published previously [22] and will not be repeated here. Our experimental data allow an unequivocal determination of the spin character of the Co bands, independently of the theoretical results. For the final states, individual free-electron parabolas were assumed for calculations HE and FN, with effective mass  $0.29m_e$  (FN:  $0.23m_e$ ) and inner potential  $V_0 = 10.9 \text{ eV}$  (FN:  $10.7 \text{ eV}$ ) (with respect to  $E_F$ ) as obtained by fitting



**Figure 1.** Comparison of a band structure calculation, type HE, for bulk FCC Co (lattice parameter  $a_0 = 3.51 \text{ \AA}$ ) with experimental band mapping results for FCT Co. Note the change of the spin character within particular bands from majority (full) to minority (broken) via intermediate-character (dotted) hybridization points due to spin-orbit coupling. The circular symbols refer to normal light incidence, the square ones to oblique incidence.



**Figure 2.** Comparison of a band structure calculation, type FN, for bulk FCC Co (based on a lattice parameter of  $a_0 = 3.61 \text{ \AA}$ ) for bulk FCC Co with experimental band mapping results. Notation: as in figure 1.

to the average of two calculated spin-split bands of  $\Delta_1$  symmetry. In view of the parabolic shape of these bands and their small exchange splitting this is a good approximation over most of the  $\Gamma$ -X line. By using the non-relativistic dipole selection rules for transitions along the surface normal [001] [15] the single-group symmetries of the initial bands were determined from the two sets of measurements at normal and oblique angle of incidence of the light. The experimental results, together with the two calculated band structures are displayed in figures 1 and 2. The minority bands are shown as broken curves, and the experimental minority-type eigenvalues are shown as open symbols. Majority bands are drawn as full curves, the experimental data as full symbols. Dotted parts of the curves indicate mixed spin character, caused by hybridization of electronic states of opposite spin character due to spin-orbit coupling. We recall that the detailed behaviour of the bands at hybridization points depends on the direction of the magnetization ( $M$  along [100] in theory and experiment). The s-p-type bottom of the conduction band is not shown, because the emission from the Cu d bands, which contribute most of this region of the experimental spectra, precludes a reliable analysis of the Co bands in this energy region. The experimental data represented by circles have been obtained at normal light incidence (pure s polarization), where only initial states of  $\Delta_5$  symmetry are allowed to

contribute, except near hybridization points. The square symbols refer to oblique incidence, where transitions from  $\Delta_5$  and  $\Delta_1$  bands are allowed due to the mixed light polarization character. Bands of  $\Delta_2$  symmetry have not been observed (except in hybridization regions) in agreement with the selection rules. It should be noted in this context that a single-group classification (being non-relativistic) of these bands is only partly justified, since the electronic states are energetically split and strongly hybridized because of the relativistic interactions. Strictly speaking, the above single-group notation applies only to those regions in the band structure that are not affected by hybridizations. A rigorous group theoretical treatment shows that the bands in a fully relativistic system with  $M$  along  $[100]$  all belong to the same co-representation of the relevant magnetic group [23]. Nevertheless, for the readers' convenience and to make it easier to follow the discussion of the experimental data, the bands in figures 1 and 2 are labelled by single-group symbols. These have to be understood, however, as appropriate symmetries only.

Comparing theory and experiment, one has to keep in mind that the calculations describe ground state properties only, whereas the photoemission measurement samples excited states of the system. Nevertheless, for the results displayed in figures 1, 2 we note good agreement as far as the spin character and the single-group symmetries of the bands are concerned. The difference between the free-electron final states from the calculations FN and HE leads to slightly different  $k_{\perp}$ -values of the experimental data points in figures 1 and 2. We note also that calculation HE yields somewhat less exchange splitting, which is in better agreement with experiment, although still slightly too large. Apparently, a somewhat larger discrepancy (although still small in absolute numbers) between experiment and theory is found near  $\Gamma$  and X in figure 2 (FN), where the calculated majority-type  $\Delta_5$  bands are predicted at relatively lower and higher binding energies, respectively. At this point we wish to recall that calculation FN refers to a bulk FCC structure with a lattice spacing of  $a_0 = 3.61 \text{ \AA}$  (Cu), which is larger than the equilibrium lattice constant of FCC cobalt ( $a_0 = 3.51 \text{ \AA}$ ). In the absence of any tetragonal distortion, the larger lattice parameter causes a 'narrowing' of the d bands in calculation FN, together with a higher magnetic moment ( $1.65 \mu_B$ ). The energetic displacements of the electronic states due to the band narrowing turn out to be largest at the edges of the Brillouin zone. This suggests that the above discrepancy between theory and experiment at  $\Gamma$  and X arises very probably because of the relatively large lattice constant assumed in calculation FN. In this context we should mention that the above effect of band narrowing is partly counteracted by a reduction of the distance between the lattice planes normal to the surface, i.e. the introduction of a tetragonal compression. This situation, however, comes closer to the actual experiment, which refers to FCT cobalt, with the in-plane lattice constant  $a$  expanded by 2% with respect to the equilibrium value of FCC cobalt ( $a_0 = 3.51 \text{ \AA}$ ) and the  $c$ -axis compressed. While it is difficult to predict without detailed calculations how this might affect the magnetic moment, we recall from total energy calculations for FCC Co [24, 25] that a decrease of the atomic volume by 12 to 16% leads to a complete collapse of the magnetic moment, bringing FCC Co into the paramagnetic state. We speculate that the tetragonal distortion might cause a similar effect, leading initially to a reduction of the exchange splitting. The precise amount of compression along the  $c$ -axis is not known, since a detailed LEED study for 5 ML FCT Co has not yet been made. However, to zeroth order, we may estimate the  $c$ -axis compression from continuum mechanics by assuming the atomic volume to be constant. The biaxial in-plane expansion by 2% then leads to a  $c$ -axis compression by 4% and a ratio  $c/a \approx 1/1.06$ . This is a crude estimate. However, a recent LEED study [8] for a 'thick' Co film (8 ML or more) determined a top-layer contraction of 6% and a second-layer

contraction of 3.3%. If we assume similar contractions of our 5 ML film at the Cu interface, we end up with an average contraction of 4.7%. Finally, if we simply translate the energetic shift of the  $I$ - $V$  curves between clean Cu(001) and 5 ML FCT Co/Cu(001), reported above, into an average contraction along the  $c$ -axis, we find about 5%. While none of these arguments alone should be depended on too fully, they all point towards an average  $c$ -axis contraction between 4% and 5% relative to the equilibrium lattice constant of FCC Co.

One is led to wonder whether this tetragonal distortion might show up in the measured band dispersion. A clue to what might be expected can be found in a recent fully relativistic model calculation for simple tetragonal iron [26]. Upon expanding the  $c$ -axis along  $\Delta$  a  $d$ -like band moves upwards across the Fermi energy, eventually leading to a flip of the easy axis of magnetization. Conversely, if we assume a similar behaviour for a FCT lattice, we would expect the  $d$  band to move downwards upon compression. In fact, looking at the experimental minority data points in figures 1, 2 near the  $\Delta_5$ -band crossing the Fermi energy, about midway in  $\Gamma$ - $X$ , we find them all lower than the calculated FCC band values. To study this point further, we performed thickness-dependent measurements at fixed photon energy, selective to  $\Delta_5$  initial-state band symmetry, near the  $k$ -point where the band crosses the Fermi energy. We varied the film thickness between 3 ML and 8 ML, thus presumably varying the average tetragonal distortion. We observed clearly that the minority band moved upwards across the Fermi energy with increasing film thickness, i.e. decreasing average  $c$ -axis compression.

In this context, it is of interest to speculate about the origin of the easy magnetization axis lying along [110]. For thick, relaxed films this is probably caused by the shape anisotropy, forcing the easy axis from the [111] direction, typical for FCC lattices, into the next easy axis, which is [110]. In thin films, however, the surface anisotropy often tends to turn the easy axis out-of-plane, against the shape anisotropy, but supported by the [111] easy axis. Experimentally, though, we always observed in-plane magnetization, even down to 1.5 ML. Expanding on the results reported by Strange *et al* [16] we speculate that for very thin films the cause for the in-plane magnetization is the tetragonal distortion, rather than the shape anisotropy. It would be very interesting to see whether realistic band structures for FCT cobalt confirm our results and conclusions.

In conclusion, the above results show how carefully prepared epitaxially grown films may be employed to study the electronic states of structural modifications, in this case FCC Co. The agreement of the data with fully relativistic calculations is encouraging, although the comparison also reveals two important issues, which have to be pursued in the future. First, the theoretical methods involved in predicting electronic structures of ferromagnets are highly sophisticated nowadays, but may still exhibit significant differences if it comes to details of the band structure. Second, small changes in the films' structural parameters may show up clearly in the electronic structure. Since these changes do subtly alter the magnetic properties (e.g. anisotropies), their characterization (both in experiment and theory) will be of great importance to the understanding of itinerant ferromagnetism.

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