

Magnetic properties of Cr overlayers on Fe (invited)

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The magnetic properties of Cr overlayers deposited on Fe(100) were investigated by spin-resolved photoemission. Valence band spectra show a reduction of the overall polarization after deposition of Cr. Data of the Cr 3*p* core level show for Cr coverages up to about 2 monolayers a polarization opposite to that of the Fe 3*p* core level. Both findings are evidence for an orientation of the Cr moments antiparallel to the Fe moments. The core level as well as the valence band results are consistent with an average moment of about 1 μ_B per Cr atom, which is significantly smaller than calculated for a monolayer of Cr on Fe.

Metallic multilayers containing one or more magnetic components (transition or rare-earth metals) have attracted considerable attention both because of their potential for applications and their physical properties which quite often cannot be understood just by interpolating between the bulk properties of the constituent metals.¹⁻⁴ The experimental progress in preparation and characterization of such systems was accompanied by a remarkable theoretical development, so that it is now possible to predict in detail properties like the magnetic moment for individual layers in the vicinity of a surface or an interface.⁵⁻⁷

Systems which have been extensively studied e.g., by Brillouin light scattering are multilayers of Fe and Cr.¹⁻⁴ It has been demonstrated that the magnetizations of two Fe layers separated by a layer of Cr are coupled to each other. The coupling constant decreases with increasing interlayer thickness. The magnetizations of the Fe layers are parallel to each other for interlayer thicknesses smaller than ≈ 5 Å and larger than ≈ 15 Å, whereas for interlayer thicknesses between 5 and 15 Å an antiparallel coupling has been established. An intriguing aspect of this coupling between magnetic layers via a nonferromagnetic interlayer is its surprisingly long range of the order of a few atomic layers. Following the coupling to larger thicknesses, there appears to be an oscillatory dependence of the sign with a periodicity of ≈ 15 Å: The coupling across the interlayer oscillates between ferro- and antiferromagnetic. Similar effects have been observed for a multitude of other combinations of magnetic and nonmagnetic metals.^{1,2}

The appeal of multilayer systems comes from the possibility to artificially make materials with properties which are not just an interpolation between the bulk properties of the constituents. Such a behavior can have two sources: either the limited thickness of the individual layers, or influence of the interfaces between the layers. An example is the magnetoresistance of Fe/Cr systems, which has been ascribed to spin-dependent scattering of the electrons at the interface. To understand the physics of multilayer systems, it is necessary to characterize the properties of the interfaces. This was our motivation to investigate experimentally the electronic and magnetic properties of thin Cr layers on Fe by spin-polarized photoemission spectroscopy. The spin polarization is defined as $P = (I_{\uparrow} - I_{\downarrow}) / (I_{\uparrow} + I_{\downarrow})$, where $I_{\uparrow, \downarrow}$ refer to intensities of electrons with spin parallel or antiparallel to the majority electrons in the sam-

ple. In principle, the average orientation and size of the magnetic moment can be determined from the spin polarization of the emission from those states which carry the magnetic moment, in our example the 3*d* states of Cr. However, the Cr 3*d* states of the overlayer have similar binding energies (BEs) as the 3*d* states of the Fe substrate, and their cross section is only half that of the substrate states. As a consequence, it is difficult to separate the overlayer states from substrate states and/or possible changes induced in these.

To circumvent this difficulty we use core level spectra as fingerprints for the magnetic properties of the overlayer. This is based on the empirical finding that the 3*p* levels of the ferromagnets Fe, Co, and Ni all show a negative polarization.⁸⁻¹⁰ We anticipate that for Cr with long range magnetic order and a net moment one would also observe a negative 3*p* core level polarization with respect to the Cr valence electrons, i.e., a *higher* intensity in that channel which has its spin *opposite* to the spin of the majority valence electrons of Cr.

The experiments were performed on the undulator beamline TGM 5 at the BESSY storage ring in Berlin.¹¹ Light incidence and electron emission were normal to the surface. The spectrometer was a commercial hemispherical analyzer of 50 mm mean radius, complemented on the exit side by a simple electron lens to image the energy-analyzed electrons onto the spin analyzer. Spin-resolved core level spectroscopy of thin overlayers on solid samples requires not only a high photon flux at suitable energy as provided by undulator radiation, but also an efficient spin analyzer. We used very low-energy electron diffraction (VLEED) from a Fe(100) surface magnetized parallel to the surface.^{12,13} At 12 eV incident energy and normal or nearly normal incidence, the specular reflection of electrons from this surface is spin-dependent. Spin-polarized energy distribution curves (EDCs) were obtained by subsequently taking data for four combinations of sample and analyzer magnetization. The analyzer was a freshly prepared Fe(100) film grown epitaxially on Ag(100). The figure of merit of this spin analyzer is about ten times higher than that of the more widely used Mott or LEED techniques. The sample was a ≈ 100 Å film of α -Fe deposited onto Cu₃Au(100). Fe and Cr were evaporated from high-purity rods heated by electron bombardment in a vacuum of $5-10 \times 10^{-10}$ mbar at rates of 1.5 and 0.2 Å/min, respec-

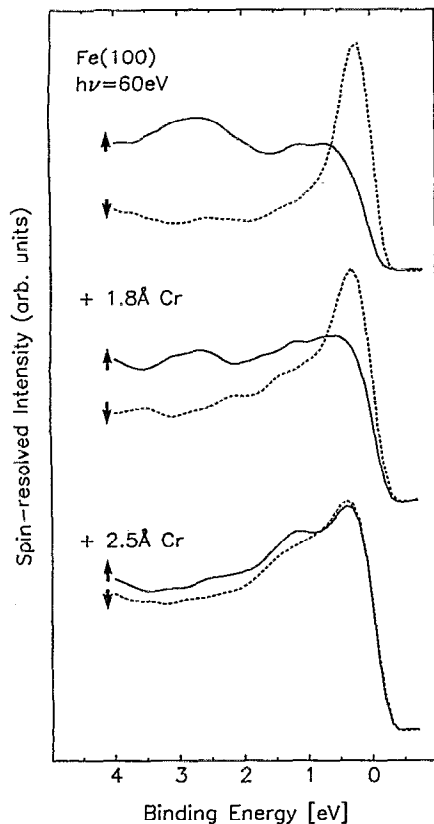


FIG. 1. Spin-resolved valence band spectra taken with 60 eV photons for α -Fe(100), 1.8 Å Cr on Fe(100), and 2.5 Å Cr on Fe(100).

tively. The evaporation rates were measured by a quartz oscillator placed at the position of the sample. Cr coverages derived from this rate and from the Cr 3p to Fe 3p intensity ratios in the photoemission spectra (using 5 to 7 Å escape depth) were in agreement. All data were taken on freshly prepared surfaces within the first 2.5 h after preparation; within this interval no signs of contamination could be detected.

For reference, we checked the clean Fe(100) surface before deposition of Cr for the well-known polarization features arising from the ferromagnetism of Fe. For the (100) surface of α -Fe at normal emission and *s*-polarized light of 60 eV energy the Γ'_{25} minority state leads to a narrow region of negative polarization at the Fermi level E_F .¹⁴ We used this feature as a criterion for a well prepared Fe substrate, and as a reference spectrum to calibrate the spin analyzer. The spectrum in Fig. 1 obtained before Cr deposition shows a large minority peak at the Fermi level (within experimental resolution), and the two majority states ($\Gamma_{12}\uparrow$ and $\Gamma'_{25}\uparrow$) at 1.2 and 2.5 eV binding energy (BE).

Valence band spectra taken under the same conditions after deposition of Cr always show a reduction of the polarization. Figure 1 shows two examples with 1.8 and 2.5 Å coverage. The reduction of polarization is clearly seen in the most prominent features, the Γ'_{25} majority state at 2.8 eV binding energy and the Γ'_{25} minority state at E_F . An overlayer may reduce the polarization by spin-flip scatter-

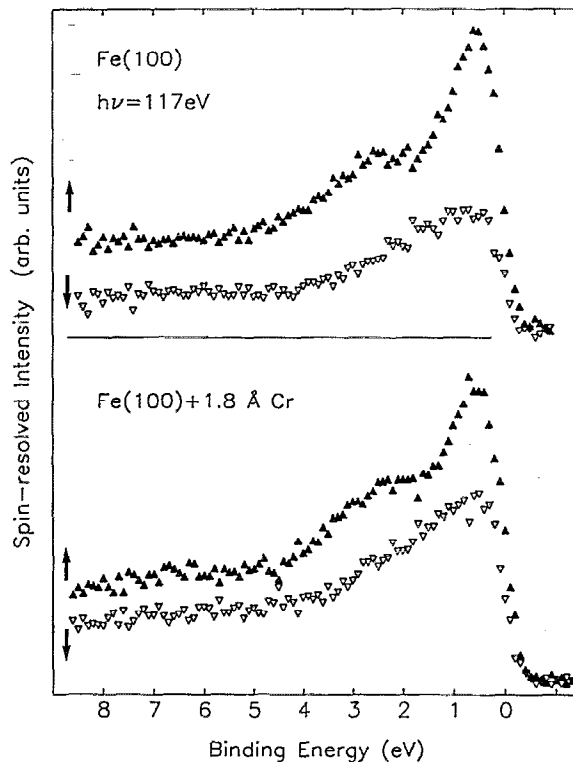


FIG. 2. Spin-resolved valence band spectra taken with 117 eV photons for Fe(100) and 1.8 Å Cr on Fe(100).

ing or by superimposing an unpolarized (or an oppositely polarized) spectrum over a polarized substrate spectrum. Spin-flip scattering should be accompanied by an energy loss roughly equal to the exchange splitting of the overlayer. The depolarization of the majority peak at 2.8 eV does not proceed via the appearance of a peak in the opposite spin channel, so it is probably not caused by spin-flip scattering. As the Cr *d* density of states is expected to be low in this region,⁶ the most likely cause for the quenching of this peak is interaction (formation of an interface state) with the Cr overlayer. In contrast to that, the peak at E_F is always present, and the suppression of its polarization is accompanied by the occurrence of a mirror peak in the other spin channel. For bulk Cr and also for Cr monolayers on Ag or Au the *d* states are concentrated within about three eV below the Fermi level.¹⁵⁻¹⁷ A likely explanation for the change in this region is the occurrence of unpolarized or oppositely polarized Cr states. To determine the magnetic state of the Cr overlayer from spectra of this type it would be necessary to find an exchange split state and determine the sign of the splitting relative to Fe. As this can be a rather lengthy procedure, we concentrated in our experiment on valence band spectra taken at higher photon energy, where the spin-integrated spectra are already very similar to spectra taken in the XPS regime.

Valence band spectra for 117 eV photon energy are shown in Fig. 2. The polarization is positive throughout, and decreases as a consequence of the Cr deposition. For clean Fe the overall valence band polarization is +37%. The effective moment μ per Fe atom is given by the differ-

ence of the numbers of majority and minority spins, $n\uparrow$ and $n\downarrow$. If all d bands are considered to contribute with a probability equal to their occupancy to the spectrum, then the integral polarization should be $P = \mu/n_d$, where n_d is the total number of d electrons. With $n_d = 7.2$, the bulk moment yields a polarization of $+31\%$.¹⁸ At 117 eV photon energy and $\approx 5^\circ$ angular resolution one integrates over about 50% of the Brillouin zone. One may expect that of those states which do contribute to the spectrum under these conditions both the majority and minority portions enter with similar weights. The enhanced polarization may result from an enhanced surface magnetic moment as has been predicted by theoretical calculations,¹⁸ but more experiments are needed to settle this point.

The spectra with Cr on the surface are very similar in shape to the spectrum of clean Fe(100), as can be seen in the lower half of Fig. 2 for 1.8 Å Cr coverage. The most significant change is a reduction of polarization both in the primary valence band emission as well as in the secondary background at binding energies larger than 5 eV. We also note that the secondary background has increased after deposition of Cr, showing a more efficient electron-electron scattering. This supports an earlier idea that additional scattering at the interface is the reason for the high magnetoresistance observed for Cr/Fe layer systems.¹

To separate out the Cr contribution from a valence band spectrum, we subtract from the spectrum for Cr/Fe(100) the spectrum of clean Fe, reduced by a factor $e^{-d/\lambda}$, where d is the thickness of the Cr overlayer, and λ is the mean free path of the photoelectrons.¹⁹ For λ we used 5 Å, and d was determined consistently from the deposition parameters and the core level intensities. The resulting spin-integrated spectrum for 1.8 Å coverage is shown in Fig. 3. The Cr states are distributed over ≈ 3.5 eV below E_F , with a peak at E_F . Overall, the shape of the spectrum is similar to that of clean Fe, indicating that there is a strong hybridization between the Cr and Fe d states.

The reduction of the valence band polarization shown in Fig. 2 may be caused by the magnetic moment of the Cr overlayer being oriented antiparallel to the Fe moment. To obtain a more detailed picture of the Cr-related states of this overlayer system, we look at the Cr-induced changes individually in each spin channel. Figure 3 shows such spectra again for 1.8 Å Cr coverage. The majority curve (referred to Fe) is ≈ 3 eV wide, and has a plateau between E_F and 2 eV BE. The minority curve is peaked at E_F and has slightly larger width (4 eV measured at the base). The overall polarization in this spectrum should be negative, since the total polarization of the valence band is reduced by the Cr. This is indeed the case; the area under minority curve is larger than that under the majority curve, yielding an overall polarization of -18% (negative with respect to Fe). With 5 Cr $3d$ electrons, one finds a moment of $0.9 \mu_B$, again with some caution due to incomplete Brillouin zone sampling, cross sections, and escape depth.

For a Cr monolayer on Fe(100), Victora and Falicov⁶ calculated that the Cr moments are ordered antiparallel to the moments of the underlying Fe, with a moment of $3.63 \mu_B$. For the first Fe layer these authors find a reduction of

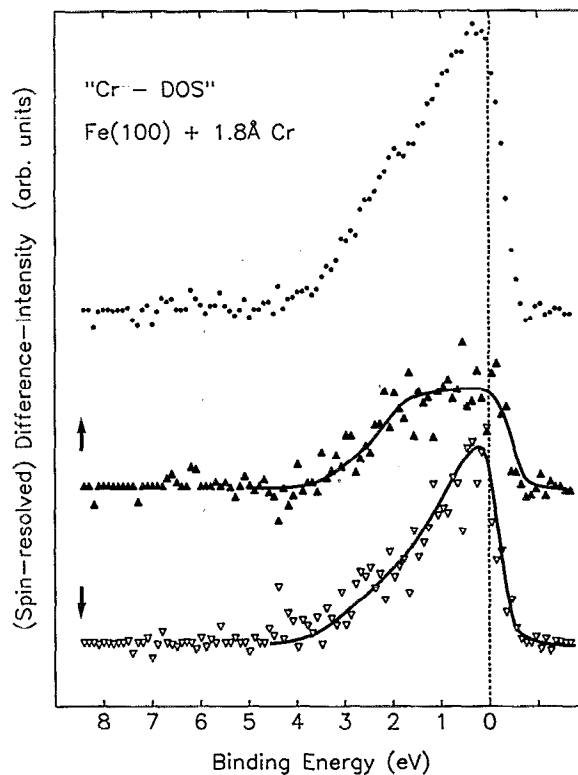


FIG. 3. Spin-integrated (points) and spin-resolved (triangles) Cr-induced valence states for 1.8 Å Cr on Fe(100). Full triangles pointing upwards represents spin parallel to the majority spin of the Fe substrate.

the moment to $1.95 \mu_B$, which is a relatively small effect if compared to the bulk moment ($2.22 \mu_B$), but a drastic one compared to the calculated Fe surface moment of $2.98 \mu_B$.^{5,6,18} We expect a decrease of the polarization of the valence band spectrum, both because of the reduction of the Fe moment and the antiparallel alignment of the Cr moments. How much it should go down depends on the mean free path of the photoelectrons which determines the relative weight of the individual layers in the spectrum.

In principle, the reduction of polarization which is evident in the valence band spectra shown above can have two causes: so far we have only discussed that the Cr moments are oriented antiparallel to those of Fe, so that the measured spectrum is a superposition of two spectra with opposite polarization. It is, however, also possible that the Cr overlayer gives rise to a depolarizing scattering of the photoelectrons coming out of the Fe substrate, without contributing intrinsically to the polarization. As a final criterion for the existence of a net magnetic moment on the Cr overlayer atoms we use core level spectra, which can also be expected to be spin polarized if the valence states have a magnetic moment: The $3p$ core level spectra of the ferromagnetic $3d$ transition metals are spin polarized, with the leading edge being of minority character. For illustration, we show in Fig. 4 a spin-resolved spectrum of the Fe $3p$ line obtained with 117 eV photons. The peaks of the minority and majority EDCs are separated by an exchange splitting of the order of 0.5 eV. The integral polarization is quite large and negative. A characteristic feature of the Fe

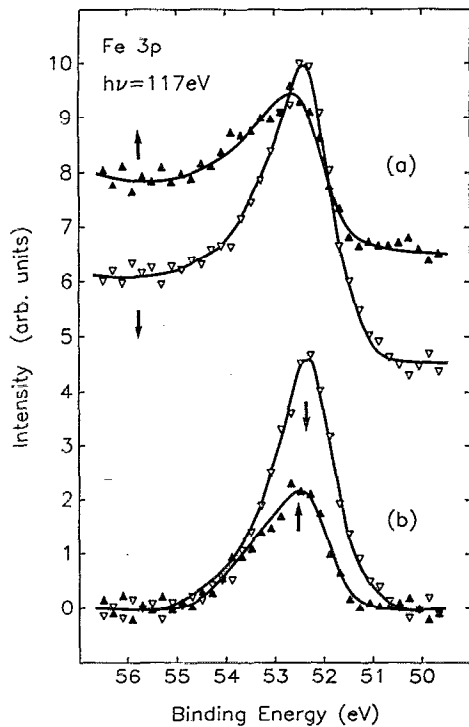


FIG. 4. Spin-resolved spectrum of the Fe 3p level for 117 eV photon energy. (a): original data; polarization of secondary background at 50 eV binding energy is +18%. (b): spin-resolved spectra after removal of background; Fe 3p polarization is -32%.

3p line is a large step of the inelastic background which has to be removed for determining the overall polarization. This step is not as obvious in spectra taken at lower energies, because then the background under the 3p line is much higher to start with. The lower half of Fig. 4 shows the Fe 3p line after subtraction of background, which was determined in the usual manner by integrating over the peaks. The "pure" Fe 3p spin-polarized spectra so obtained are then used to determine the polarization, yielding -32%. This number is larger than the polarization given e.g., by Sinkovic *et al.*⁹ Because of the step-like background of the 3p core spectrum the polarization always depends to some degree on how this background is removed. The step-like background is more apparent in the spectra when a higher photon energy is used, because at low photon energy the background is much higher (typically five to ten times the signal) and steeply rising towards lower kinetic energy. At high photon energy (250 eV) the background ($\approx 1/3$ of the Fe 3p signal) is flat on either side of the peak, and one obtains a polarization of $\approx -40\%$.¹³ It is difficult to determine experimentally whether there is any real change with photon energy in the shape of the spectra and/or the polarization which is not explainable by the change of the background.

A typical spectrum of a Cr-covered Fe surface is shown in Fig. 5. The polarization of the background and of the Fe 3p spectrum is slightly reduced by Cr, but apart from that the spectrum is qualitatively similar to that of Fe. The Cr 3p line at 41.8 eV BE is similar to that of bulk

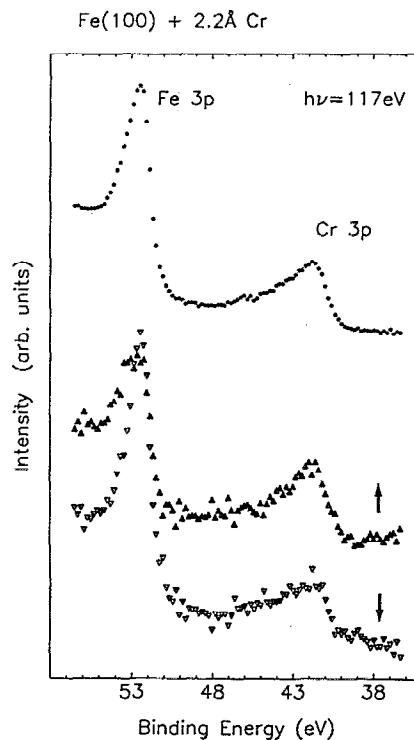


FIG. 5. Spin-integrated and resolved spectrum of Fe 3p and Cr 3p region for 2.2 Å Cr on Fe(100).

Cr, although for low coverages the tail on the high BE side gets more intensity. In the spin-resolved spectra, the Cr 3p emission has more intensity in the majority channel of Fe, and the peak itself is sharper.

Figure 6 shows the Cr 3p line in more detail after subtraction of background. The majority intensity (with respect to Fe) is larger than that in the minority channel; the integral polarization is 12%. The full widths at half maximum are 2.7 and 3.3 eV, although the peaks are at the same energy.

For other coverages we find qualitatively similar behavior. To summarize our results we have collected in Fig. 7 the polarization of the Cr 3p spectrum as a function of Cr coverage. The general trend is a decrease of polarization with Cr coverage. For Cr coverages up to about 2 ML there is always a *positive* polarization with respect to the Fe valence band states. This polarization is *opposite* to that of the Fe 3p spectrum, and demonstrates that there is a net magnetization of Cr *opposite* to that of Fe. For the lowest coverage investigated the polarization is between +20 and +30%, and decreases with increasing Cr coverage. A natural explanation for the decrease of polarization would be the onset of antiferromagnetism within the Cr, as more than one monolayer is present.

Except possibly for the lowest Cr coverage, the polarization of the Cr 3p photoemission spectrum is lower than that of the Fe 3p spectrum. One may expect that the polarization of a core level spectrum scales in some way with the moment of the valence electrons. In an atomic picture, the moment of a given *d* configuration is determined by

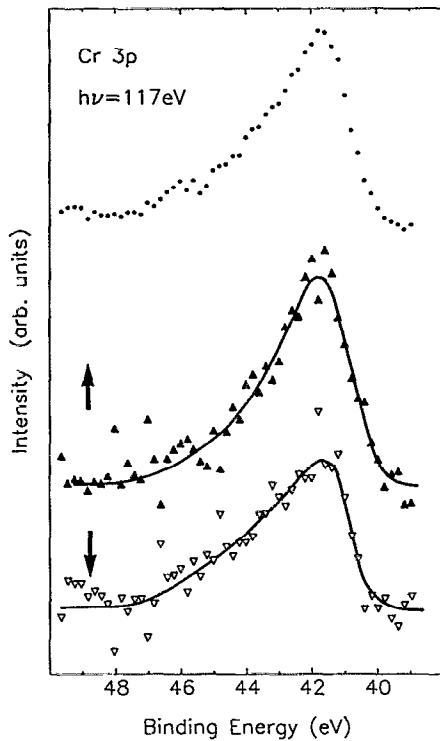


FIG. 6. Spin-integrated and resolved Cr 3p spectrum for 2.2 Å Cr on Fe(100) after removal of background. Cr 3p polarization is 13% opposite to Fe 3p polarization.

Hund's rule, and the leading peak in the core spectrum should always have negative polarization with respect to the majority valence electrons. For Cr with a $3d^5 4s^1$ 7S ground state one expects the 3p threshold to be an 8P state with -75% polarization. To generate a ground state with a moment smaller than the Hund' rule moment one has to include excited states. A model calculation of this type has been performed, and yields for the observed Cr 3p polarization a moment of about $1 \mu_B$.²⁰ However, atomic theory does not give a satisfactory description of the physical situation in a metal. Alternatively, if the polarization is de-

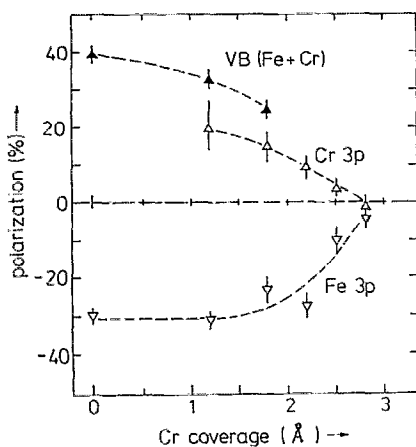


FIG. 7. Total polarization of valence band, Fe 3p, and Cr 3p levels as function of Cr coverage. The sign of the Fe 3p polarization has been reversed.

termined only by the d electron moment, irrespective of how many electrons are present, then one has about $2 \mu_B$ as upper limit by comparing to Fe. Theoretically, it has been predicted that the moment should be as high as $3.6 \mu_B$ for a single monolayer of Cr on Fe(100), so one might expect a polarization even higher than for Fe.

A theoretical description of spin-polarized core level spectra has to account for a net polarization in core level spectra which depends on the level considered: In this investigation, we have made use of the fact that the 3p levels of magnetic 3d systems show quite a large polarization, but the only s level investigated until now (Refs.13 and 21) does not show a significant polarization. Experimentally, one may get a handle on this problem by looking at reference systems in which the Cr moment is known. Unfortunately, there are not many materials suitable for such a comparison. Nevertheless, as the valence band results set an upper limit for the Cr moment, we conclude that the Cr moment is smaller than the Fe moment.

A possible source of the discrepancy between theory and experiment is that in reality the uniform antiferromagnetic alignment with respect to the substrate Fe does not occur. The interactions between Cr atoms are for the distances considered here antiferromagnetic. However, it is impossible to align all Cr moments antiparallel to the substrate and at the same time antiparallel to the nearest neighbor Cr atoms. This may result in a spin arrangement, in which not all the moments are aligned antiparallel to the substrate moment. As more than one monolayer of Cr is deposited, the nearest Cr neighbors to the interface atoms are the atoms in the second layer, and not the surrounding interface atoms. In this situation the energy for a state with all interface Cr moments antiparallel to the Fe is energetically favorable, so that the interface moments may be antiparallel to the Fe moments. Nevertheless, the Cr polarization features will be weaker due to the antiferromagnetic order among first and second layer Cr atoms.

The experiments presented here have shown that the first monolayer of Cr deposited on Fe has a magnetic moment antiparallel to that of Fe. This moment appears to be smaller than predicted theoretically. For the substrate Fe, the polarization features are strongly but not completely suppressed with increasing Cr coverage for the range investigated. For coverages of two monolayers of Cr there is apparently no long-range order with a net moment in the Cr overlayer.

¹P. Grünberg, R. Schreiber, Y. Pang, and H. Sowers, Phys. Rev. Lett. 57, 2442 (1986); G. Binasch, H. Grünberg, F. Saurenbach, and W. Zinn, Phys. Rev. B 39, 4828 (1989); P. Grünberg, S. Demokritov, A. Fuss, M. Vohl, and J. A. Wolf, Proc. MMM Conference 1990, San Diego.

²S. S. Parkin, N. More, and K. P. Roche, Phys. Rev. Lett. 64, 2304 (1990); S. S. Parkin, R. Bhadra, and K. P. Roche, Phys. Rev. Lett. 66, 2152 (1991); S. S. Parkin, Phys. Rev. Lett. (in press).

³D. Pescia, D. Kerkmann, F. Schumann, and W. Gudat, Z. Phys. B 78, 475 (1990).

⁴B. Heinrich, Z. Celinski, J. F. Cochran, W. B. Muir, J. Rudd, Q. M. Zhong, K. Myrtle, and J. Kirschner, Phys. Rev. Lett. 64, 673 (1990).

⁵C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. 54, 2700 (1985); C. L. Fu and A. J. Freeman, Phys. Rev. B 33, 1755 (1986).

⁶R. H. Victora and L. M. Falicov, Phys. Rev. B 31, 7335 (1985).

- ⁷S. Blügel, B. Drittler, R. Zeller, and P. H. Dederichs, *Appl. Phys. A* **49**, 547 (1989).
- ⁸C. Carbone and E. Kisker, *Solid State Comm.* **65**, 1107 (1988).
- ⁹B. Sinkovic, P. D. Johnson, N. B. Brookes, A. Clarke, and N. V. Smith, *Phys. Rev. Lett.* **65**, 1647 (1990).
- ¹⁰T. Kachel, C. Carbone, W. Heinen, and W. Gudat, *BESSY Annual Report 1989*, p. 178 (unpublished).
- ¹¹W. Peatman, C. Carbone, W. Gudat, W. Heinen, P. Kuske, J. Pflüger, F. Schäfers, and T. Schroeter, *Rev. Sci. Instrum.* **60**, 1445 (1989).
- ¹²D. Tillmann, R. Thiel, and E. Kisker, *Z. Phys. B* **77**, 1 (1989).
- ¹³F. U. Hillebrecht, R. Jungblut, and E. Kisker, *Phys. Rev. Lett.* **65**, 2450 (1990); F. U. Hillebrecht, L. Wiebusch, W. Wienholt, R. Jungblut, and E. Kisker (unpublished).
- ¹⁴E. Kisker, K. Schröder, M. Campagna, and W. Gudat, *Phys. Rev. Lett.* **52**, 2285 (1984).
- ¹⁵L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, *Phys. Rev. B* **30**, 1048 (1984); *Phys. Rev. B* **31**, 6379 (1985).
- ¹⁶G. Zajac, S. D. Bader, and R. J. Friddle, *Phys. Rev. B* **31**, 4947 (1985).
- ¹⁷D. A. Newstead, C. Norris, C. Binns, and P. C. Stephenson, *J. Phys. C* **20**, 6245 (1987).
- ¹⁸S. Ohnishi, A. J. Freeman, and M. Weinert, *Phys. Rev. B* **28**, 6741 (1983). Here 6.2 *d* electrons are found within the muffin tin sphere, but the total number of electrons is only ≈ 7 . We assume the remaining charge to be *d*-like between the muffin tin spheres.
- ¹⁹For subtraction, backgrounds were removed and remaining total areas were normalized. Then the area for the uncovered Fe was reduced by the appropriate escape depth factor.
- ²⁰F. U. Hillebrecht, R. Jungblut, Ch. Roth, E. Kisker, and A. Bringer (unpublished); and A. Bringer (unpublished).
- ²¹C. Carbone, T. Kachel, R. Rochow, and W. Gudat, *Z. Phys.* **79**, 325 (1990).