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Calculation of spin- and angle-resolved photoemission spectra from Pd(100) coated with a monolayer of a magnetic 3*d* metal, Cr or Mn: Comparison between antiferromagnetic and ferromagnetic configurations

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With use of full-potential linearized augmented-plane-wave film potentials, calculations of spin- and angle-resolved photoemission spectra are reported for the Pd(100) system covered with a monolayer of Cr and Mn in a ferromagnetic $p(1\times1)$ configuration. Comparison is made to the antiferromagnetic $c(2\times2)$ configuration and to the ferromagnetic overlayer systems of Fe and Co on Pd(100). The spin-resolved layer-by-layer-like contributions to the photocurrent are used to estimate the hybridization with the Pd host. Also discussed is the occurrence of spin-resolved surface states.

I. INTRODUCTION

In two previous papers[1,2] we discussed spin- and angle-resolved photoemission from Pd(100) coated with a ferromagnetic monolayer of Fe, Co, and Ni (in the following referred to as I) and with an antiferromagnetic monolayer of V, Cr, and Mn (in the following referred to as II). In this paper we will deal with the ferromagnetic ordering of Cr and Mn on Pd(100). According to Blügel *et al.*[3-7] a $c(2\times2)$ antiferromagnetic structure was predicted, contrary to Fe, Co, and Ni, where a stable $p(1\times1)$ structure should be observed. However, until now there is no experimental evidence for the antiferromagnetic prediction stated above, because the experimental verification is a highly nontrivial task. First, the above prediction is only valid for epitaxially grown layers with a thickness of around one monolayer, which requires much skill on the monolayer preparation. For a coverage with two or more layers of Cr and Mn we expect topological antiferromagnetism,[8] while for coverages below one monolayer (ML) (i.e., 0.33 ML in Ref. 9) we expect different magnetic structures due to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Furthermore, depending on the thermal conditions under which the monolayer is going to be prepared, ordered $c(2\times2)$ surface alloys[10] can be formed which also show magnetic structures different from those predicted above. Second, the detection of the two-dimensional antiferromagnetic structure does not show any exchange splitting, and many experimental techniques average over the unit cell. Since the predicted antiferromagnetic structures have not yet been confirmed, we believe that the calculation of the photoemission spectra is of importance to motivate and guide future experimental studies. We will therefore compare the spectra of both magnetic configurations and, since the ferromagnetic configuration cannot *a priori* be ruled out, discuss and investigate how a purely angle-resolved photoemission experiment can distinguish between the two magnetic phases.

The photoemission spectra are calculated in exactly the same manner[11-15] as in I and II, namely, for normal emission and an angle of $\Theta=60°$ with respect to the surface normal for the incident light. The spin-integrated spectra are presented as the sum of the minority- and the majority-spin contributions. The spectra for clean Pd were discussed in I. It should be noted that in the following by Pd peaks we mean hybridized states dominated by the Pd host.

The interpretation is supported by the layer-by-layer decomposition (LLD) of the photocurrent and follows papers I and II.

II. THE FERROMAGNETIC CONFIGURATION OF Cr AND Mn ON Pd(100)

For the ferromagnetic configuration the majority-spin spectra (Fig. 1) of Cr/Pd(100) and Mn/Pd(100) are quite different from each other: only the Mn system can be viewed in line with the Fe and Co systems. This can be understood by looking at the density of states (DOS) of these systems.[3] For Mn/Pd(100) as well as for the Fe and Co systems the majority band is completely filled, while in the Cr system the Fermi energy cuts the majority band at a peak position. The minority-spin spectra (Fig. 3) on the other hand are very similar for all investigated ferromagnetic overlayer systems. This can also be under-

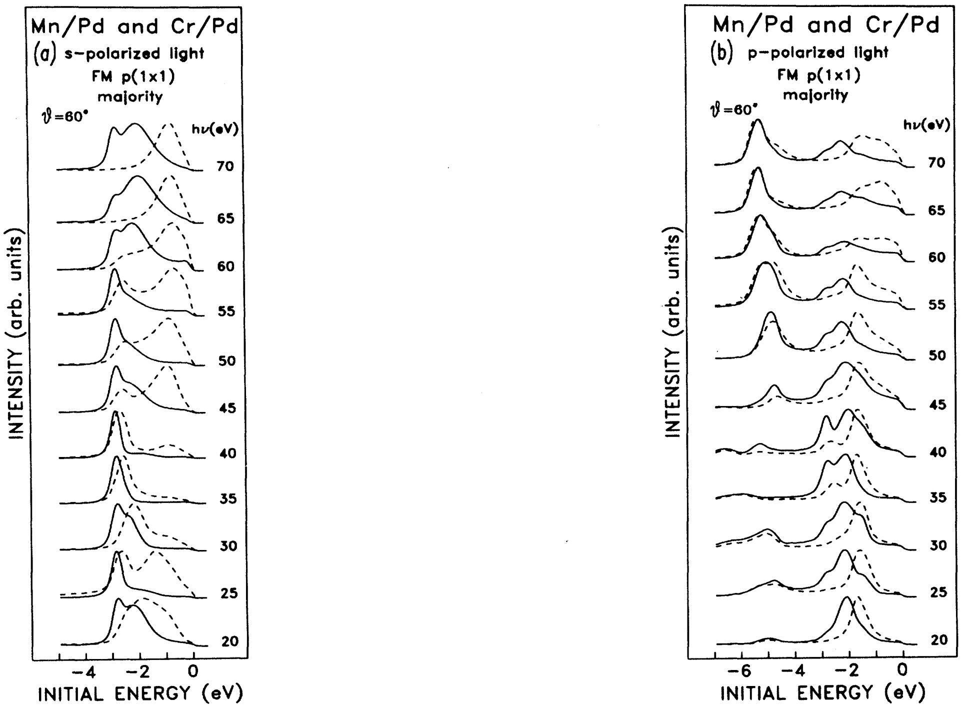

FIG. 1. Majority-spin spectra for Mn (solid) and Cr (dashed): (a) *s*-polarized and (b) *p*-polarized light.

stood by looking at the minority DOS of these systems shown in Ref. 3. For Cr and Mn there is essentially no difference for the DOS of the minority-spin *d* electrons over the entire energy range. Only close to the Fermi energy small differences are visible. These differences close to the Fermi energy become larger for Fe and Co which is in line with the results presented in I.

A. Majority-spin direction

For Cr/Pd(100) and *s*-polarized light [Fig. 1(a)] the Pd Δ_5-like peak is shifted less than in the antiferromagnetic case and gains Cr contributions only for high photon energies, where the intensity decreases rapidly. For photon energies above 40 eV the dominant peak at about -0.8 eV binding energy can be attributed solely to Cr. This Cr surface state has also a shoulder which shows some Pd contribution. In the case of *p*-polarized light [Fig. 1(b)] the spectra differ from the Pd spectra only for photon energies above 40 eV. The lowest Pd Δ_1-like peak, the Pd surface resonance, and the Pd Δ_1-like peak show the same behavior as in the antiferromagnetic case, however, all peaks are less shifted than in the antiferromagnetic case II. The dominant peak at about -1.7 eV binding energy can be attributed to a hybridized Cr-Pd state. At about -0.8 eV binding energy the same peak as in the case of *s*-polarized light emerges. The corresponding LLD is displayed in Fig. 2(a).

Mn/Pd(100) shows the same features as the Fe and Co overlayers on Pd(100). In the case of *s*-polarized light [Fig. 1(a)] the lowest peak as well as the peak at about -2.2 eV are strongly developed. For *p*-polarized light the LLD [Fig. 2(b)] indicates that the peaks due to the lowest Pd Δ_1-like band and the Pd surface resonance show considerable Mn contribution. The next two peaks refer to hybridized Pd-Mn initial states, the lower one with Δ_5, the higher one with Δ_1 symmetry. At 20–45-eV photon energies the shoulder has mainly Pd character. For photon energies above 55 eV this weak feature refers again to a hybridized Pd-Mn state. In the case of Cr/Pd(100) this shoulder is covered by the much stronger Cr-Pd Δ_1-like state.

B. Minority-spin direction

For *s*-polarized light [Fig. 3(a)] only the relative intensities of the Cr and Mn induced peaks differ from each other. Due to the cutoff at the Fermi energy in the case of Mn/Pd(100) the surface state near the Fermi energy is stronger than for Cr/Pd(100). The lower peak probably originates from an enhanced Pd surface resonance since in the LLD the contribution of the first Pd layer is dominant. The intensity of this peak decreases from Cr to Ni and accordingly we find a larger Pd contribution in the LLD for Cr/Pd(100). The surface state on the contrary gains intensity as going from Cr to Ni.

The spectra for *p*-polarized light are presented in Fig. 3(b). Up to 40 eV only the surface state just below the Fermi energy has contributions from the 3*d*-metal overlayer. For higher photon energies all the peaks lose intensity except for the Pd related Δ_1 *s*-band peak. The different occupation of the minority-spin band reflects the trend from Cr to Co: in the case of Cr/Pd(100) the surface state is only weak and gains some strength for

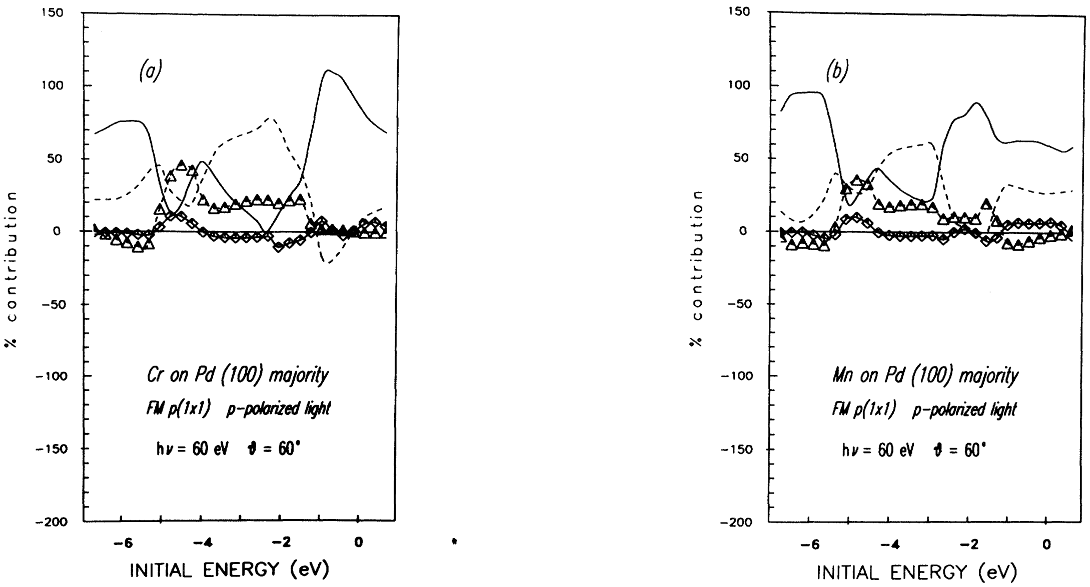

FIG. 2. Layer-by-layer distribution of the photocurrent (LLD) for p-polarized light for the ferromagnetic configuration and for the majority-spin direction for 60 eV: (a) Cr/Pd(100) and (b) Mn/Pd(100). Solid line, layer 1 ($3d$-metal); dashed line, layer 2 (first Pd layer); triangles, layer 3; diamonds, layer 4.

Mn/Pd(100). In the case of the Fe and Co overlayers two dominant surface states develop just below the Fermi energy I.

C. Spin-integrated spectra and comparison of the majority with minority-spin direction for the ferromagnetic configuration

The spin-integrated spectra are presented in Figs. 4 and 5. The differences with respect to the different overlayers are mainly caused by the majority-spin contribution. For both cases, Cr and Mn, the deviations from clean Pd are small up to 40 eV photon energy. For higher photon energies there is almost no minority-spin contribution in the case of Cr/Pd(100). For Mn/Pd(100) the surface state at the Fermi energy is rather weak. The local density of states (LDOS) of Blügel[3] reflects those findings and explains also the trend from the Cr- and Mn- to the Fe- and Co-overlayer systems where this surface

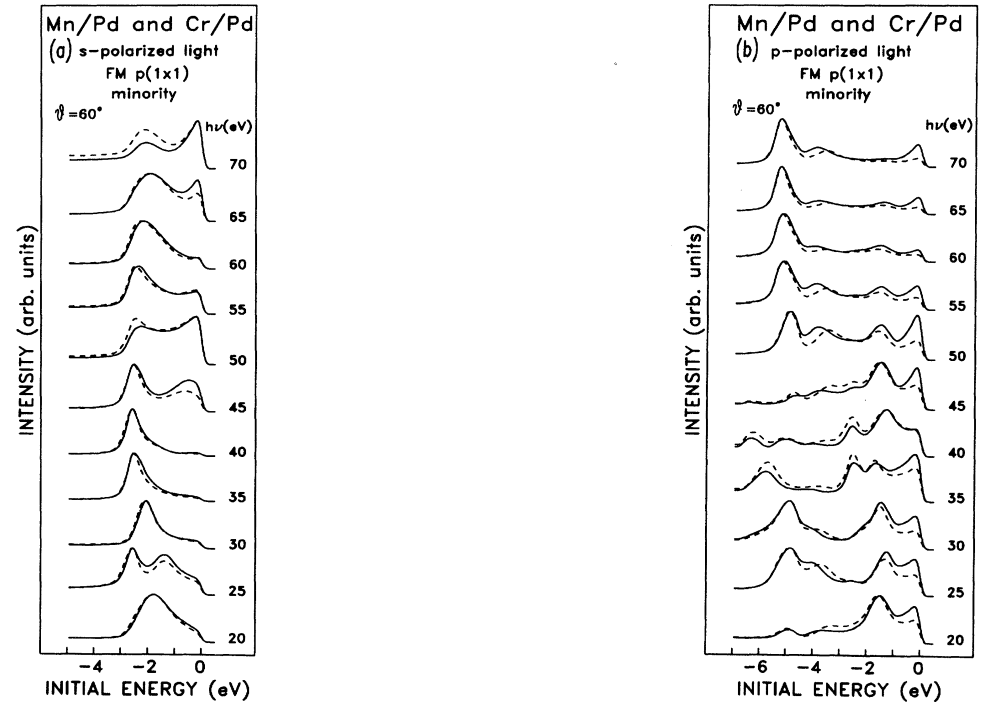

FIG. 3. Minority-spin spectra for Mn (solid) and Cr (dashed): (a) s-polarized and (b) p-polarized light.

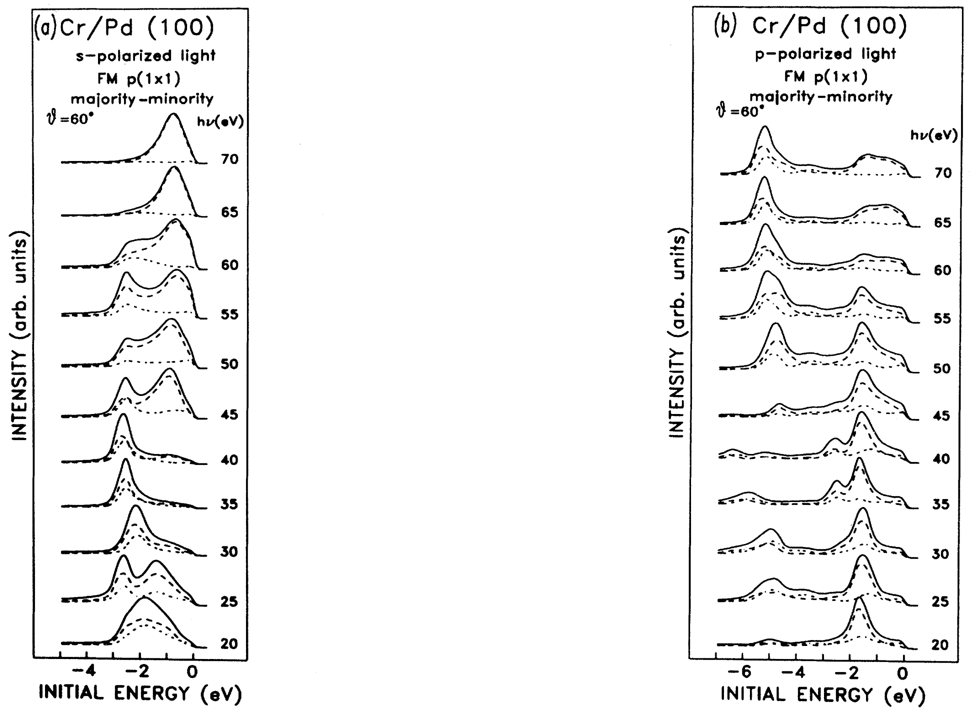

FIG. 4. Spin-integrated spectra (solid lines) together with the minority- (dotted lines) and majority- (dashed lines) spin contributions for Cr/Pd(100) in the ferromagnetic configuration. (a) *s*-polarized light and (b) *p*-polarized light.

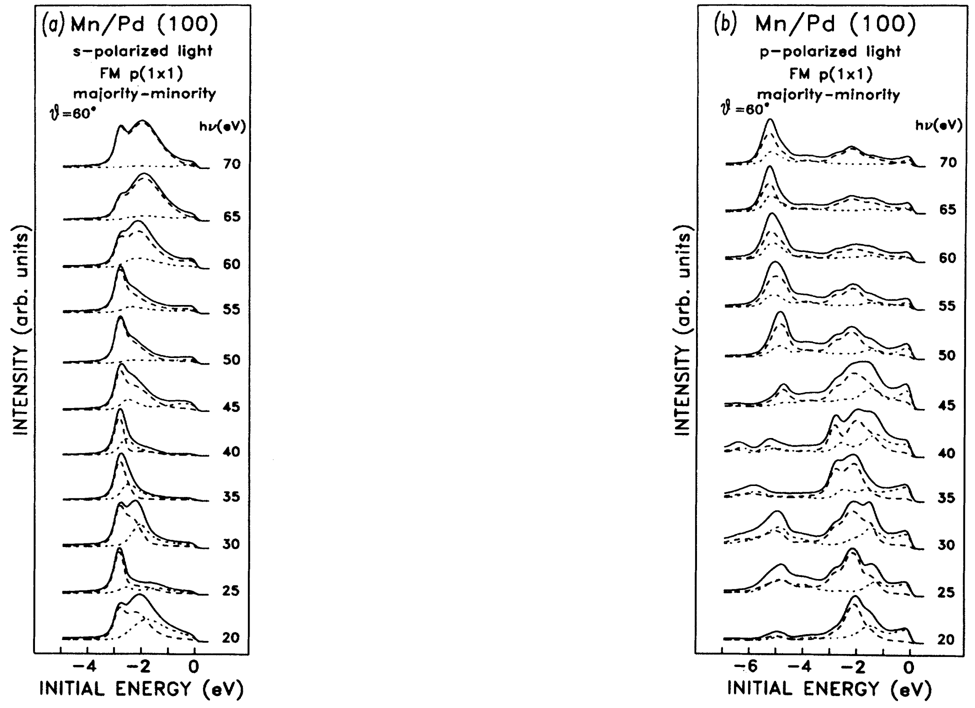

FIG. 5. Spin-integrated spectra (solid lines) together with the minority- (dotted lines) and majority- (dashed lines) spin contributions for Mn/Pd(100) in the ferromagnetic configuration. (a) *s*-polarized light and (b) *p*-polarized light.

state shows increasing intensity I.

Extreme caution has to be used in trying to extract the "exchange splitting" from photoemission. From the spin-integrated spectra alone this is simply impossible, since splitted peaks do not necessarily have different spin orientations. For reasons given in I the spectra for 70-eV and *s*-polarized light are probably best suited.

For the ferromagnetic configuration of Cr and Mn on Pd(100) the minority-spin contribution is so weak that the spin-integrated spectra (for high photon energies) show basically only majority-spin contributions. From the individually normalized majority- and minority-spin spectra we find an "exchange splitting" of 0.5 eV for the two Cr surface states and 0.1 eV for the hybridized Pd-Cr Δ_5-like state. For the Mn overlayer we cannot compare the two surface states since the two corresponding states are above the Fermi level. The splitting of the hybridized Δ_5-like peaks is about 0.6 eV. In the case of Fe/Pd(100) one can compare the Δ_5 majority peak, which exhibits hardly any Pd influence, to the respective minority state. The corresponding splitting, as well as the equivalent one for Mn/Pd(100), is about 1.8 eV. In the case of Mn/Pd(100) it is likely to be even larger, since the center of gravity for the minority state is above the Fermi level.

The influence of the various overlayers and of the hybridization is stronger in the case of the majority-spin direction. Both effects are to be expected from the results of Blügel,[3–7] since for the ferromagnetic case the trends from Cr to Ni can be explained partly by the filling-up of the minority band.

III. SUMMARY AND COMPARISON BETWEEN ANTIFERROMAGNETIC AND FERROMAGNETIC CONFIGURATIONS

Generally, except for a small shift toward higher binding energies and a broadening of peaks in the antiferromagnetic case, there is hardly any difference between the ferromagnetic and antiferromagnetic Cr overlayer spectra. In the case of *s*-polarized light these differences are negligible. In the case of *p*-polarized light (Fig. 6) the main difference is found for the surface state below the Fermi energy. In the antiferromagnetic case this state has a binding energy of about -1 eV. In the ferromagnetic case it is cut off by the Fermi energy for the minority-spin direction, while the corresponding state for the majority-spin direction is a weak Cr Δ_5 state at about -0.7 eV. The Pd surface resonance at about -4.5 eV is much more affected in the antiferromagnetic configuration where it is a separate peak.

Considering the spectra for *s*-polarized light the Mn Δ_5-like surface state at -3.6 eV binding energy in the antiferromagnetic configuration is lost in the ferromagnetic phase, where the hybridized Pd-Mn Δ_5 states and the surface resonance dominate. The surface state near the Fermi level is found for the minority-spin direction and in the antiferromagnetic configuration (Fig. 7).

For *p*-polarized light the majority-spin spectra are very similar to the antiferromagnetic ones: as in the case of Cr there is almost no shift in peak positions and the general trends are similar. Minor differences are found for the

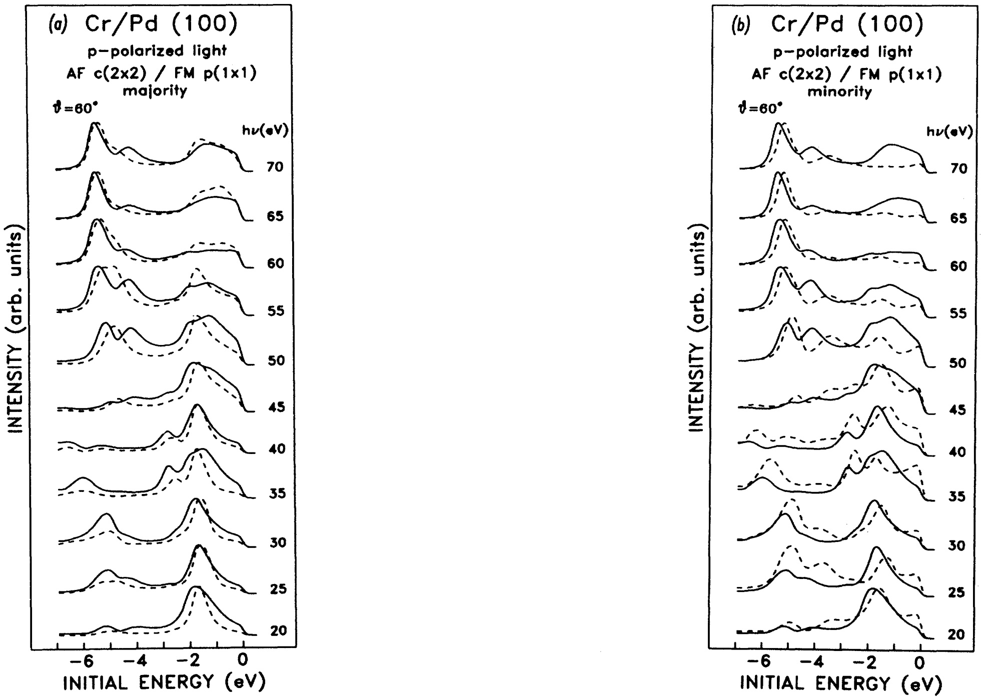

FIG. 6. Comparison of the antiferromagnetic (solid lines) and the ferromagnetic (dashed lines) configuration of Cr/Pd(100) for *p*-polarized light for (a) majority spin and (b) minority spin.

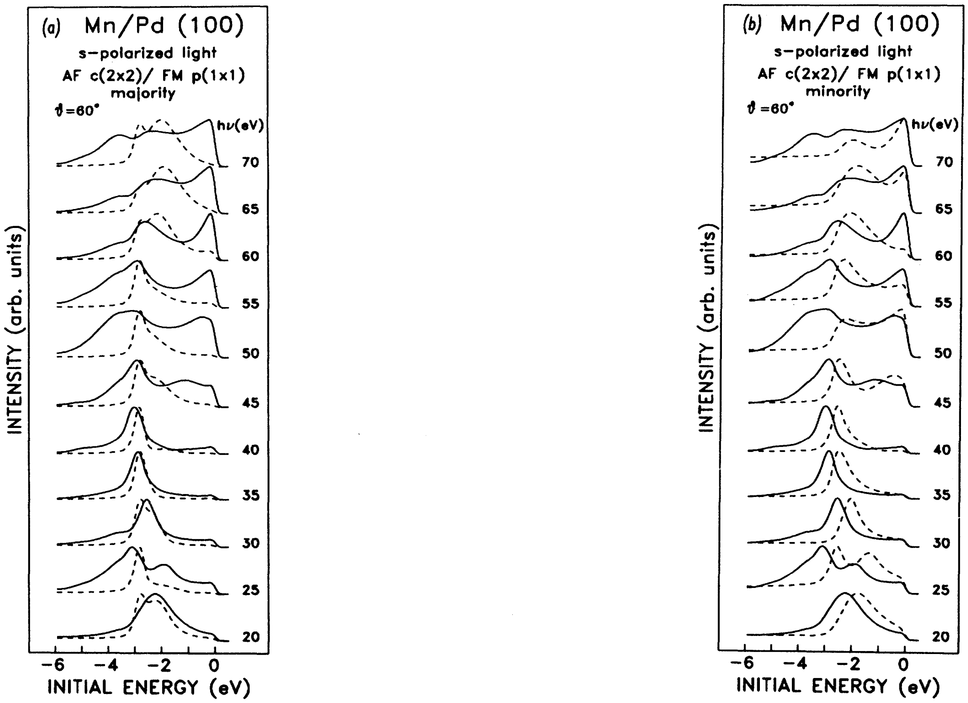

FIG. 7. Comparison of the antiferromagnetic (solid lines) and the ferromagnetic (dashed lines) configuration of Mn/Pd(100) for *s*-polarized light for (a) majority spin and (b) minority spin.

surface state at the Fermi level, which is more pronounced in the antiferromagnetic case, and the hybridized peaks around -2 to -3 eV binding energy, which are not as well resolved in the antiferromagnetic case as in the ferromagnetic one. Only the Pd Δ_1 peak, which is found as a shoulder of the Pd-Mn hybridized peaks for photon energies below 45 eV in the ferromagnetic case, lacks in the antiferromagnetic spectra.

Comparing the antiferromagnetic spectra to the minority-spin spectra differences are found especially for low photon energies where the shift for Pd-Mn hybridized features is large. The most obvious difference is due to the surface state near the Fermi energy. In the antiferromagnetic spectra this state is probably shifted above the Fermi level, whereas in the ferromagnetic case it is well resolved.

It is probably impossible to distinguish these two configurations for Cr/Pd(100) without a spin-polarized experiment. In the ferromagnetic configuration a large positive spin polarization has to be expected, since the minority contribution is almost zero in particular for photon energies above 40 eV where the Cr contributions are dominant. For Mn/Pd(100) and *s*-polarized light the antiferromagnetic surface states should provide the possibility to distinguish the two configurations even for spin-integrated spectra (non-spin-resolved experiment), whereas using *p*-polarized light the configuration can be determined only in a spin-polarized experiment.

IV. COMPARISON WITH SIMILAR SYSTEMS

The pure Cr(100) surface was investigated by Klebanoff *et al.*[16,17] with angle-resolved photoemission spectroscopy (ARPES). They interpreted their results in terms of antiferromagnetic coupling between the layers starting with a ferromagnetic surface layer. Fu *et al.*[18] and Hasagewa[19] calculated ferromagnetic "exchange splittings" of about 1.8 and 1.2 eV, respectively. Zajac *et al.*[20] performed an ARPES investigation of $p(1\times1)$ Cr on Au(100). They found a strong relationship to the spectra of pure Cr(100) in Refs. 16 and 17. Two states at -0.8 and -0.15 eV binding energy are reported. The agreement is interpreted as an already bcc-like surface electronic structure for one monolayer. The bulk *d*-like DOS of Cr is moved to higher binding energies. This was already noted as a general trend for 3*d* overlayers on Pd(100) by Blügel *et al.*[7] In a full-potential linear augmented-plane-wave method (FLAPW) calculation for Cr on Au(100),[21,22] the surface magnetic moment was found to be $3.7\mu_B$ (Ref. 21) and an antiferromagnetic ordering was lower in energy and showed a somewhat reduced but still large magnetic moment.[22] This is also in line with the results of Blügel *et al.*[8] Newstead *et al.*[23] obtained enhanced magnetic moments of Cr on Ag(100) in the submonolayer regime of 0.33 ML, which was confirmed by Johnson *et al.*[9] In the multilayer regime (3.3 ML) no magnetism at all was found, likely due to the fact that their method averages over terraces with different spin directions. Tian *et al.*[10] studied Mn on Pd for which they observed half order LEED spots. However, LEED analysis showed that they are not due to the magnetic superstructure[24] but due to the formation of a $c(2\times2)$ surface alloy. Nevertheless, by changing the growth condition, monolayer growth of Mn on Pd seems possible.

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