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Electronic structure of an antiferromagnetic chromium layer adsorbed on the (001) silver surface

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The electronic structure of a chromium layer adsorbed on the silver (001) surface is calculated in the tight-binding approximation. The ground state is found for a $c(2\times2)$ antiferromagnetic structure with a magnetic moment close to 3.6 Bohr magnetons. The two-dimensional energy-dispersion curves are also calculated for a nine-layer slab as a function of the wave vector parallel to the surface. The overall agreement with the experimental values measured by angle-resolved photoemission is not convincing enough to confirm that a chromium monolayer can be deposited on a silver (100) substrate.

I. INTRODUCTION

In recent years, the study of surface and interface magnetism has rapidly developed owing to its many applications, in magnetic recording for example. Among transition metals, the chromium surface has the most interesting properties. Calculations have shown that the magnetic moment in the (100) surface plane is strongly enhanced.[1,2] This has also been confirmed by photoemission spectroscopy.[3] This magnetic moment enhancement is due to a bcc (100) surface state which occurs close to the chromium Fermi level. One would also expect a still larger effect for a free Cr monolayer and effectively a value close to 3.8 Bohr magnetons has been calculated.[4] When the Cr monolayer is adsorbed on top of the Au (100) surface or sandwiched between two Au layers, its magnetic moment is reduced. However, this reduction is small as the magnetic moments remain respectively equal to 3.7 and 3.5 Bohr magnetons.[4] This is due to a rather small coupling between the Cr and Au *d* states as their energy difference is close to 5 eV. One must remember that the common Fermi level at a Cr/Ag interface is close to the middle of the *d* band for bulk Cr, whereas it is far above the top of the *d* band in the case of Ag and Au.

The main experimental problem is to grow a sample. Silver is a good candidate for epitaxial growth of a Cr monolayer as the lattice constants of the bulk materials are close. However, its surface energy is rather small compared to the Cr one.[5] Such a difference generally leads to a growth of three-dimensional Cr islands on a Ag substrate. However, under peculiar conditions, it seems that a Cr monolayer can be deposited on the (100) Ag surface.[6,7]

Under such conditions, the low-energy electron diffraction (LEED) pattern of the adsorbed layer shows a strong $p(1\times1)$ structure together with a very weak $c(2\times2)$ diffraction pattern which could be due to exchange scattering. On the other hand, angle-resolved photoemission clearly shows a $c(2\times2)$ dispersion behavior. There is experimental evidence that a perfect monolayer is deposited.[6,7] Several self-consistent total-energy calculations have been done for this system.[4,8] They show that a Cr monolayer adsorbed on a Au or Ag substrate is antiferromagnetic but a comparison of the calculated two-dimensional dispersion curves with the experimental results is also needed to support the existence of a Cr monolayer.

In Sec. II we explain how the tight-binding method is used to calculate the electronic structure of the Cr monolayer adsorbed on the Ag (100) substrate. The main difficulty is to fix the Cr and Ag band parameters. Then the decimation technique is used to accurately calculate the atomic charges.[9] Orbital charge neutrality is assumed to evaluate the self-consistent potential close to the surface.

In Sec. III the method is applied to the free Ag (001) surface and to the adsorbed Cr monolayer. As in the preceding calculations, the antiferromagnetic state is found to be the most stable. Then using the self-consistent potential near the Ag surface, a slab with eight Ag layers and one Cr layer adsorbed on one side is built to calculate the two-dimensional dispersion curves measured by angle-resolved photoemission.

II. TIGHT-BINDING PROCEDURE

As the magnetic properties we study mainly depend on the *d*-band states, the tight-binding method seems appropriate to calculate the surface electronic structure. However, *s* and *p* states must also been included as we are interested in energy dispersion. According to symmetry, *d* states are modified by *s*-*d* interaction and this notably occurs near the Cr Fermi energy. The Ag nearest and next-nearest tight-binding parameters have been fitted to Korringa-Kohn-Rostoker (KKR) results[10] and are given in Table I. The Ag *d* band is rather narrow. Its *d*-band width is equal to 60% of the Fe *d* band, whereas for chromium we would expect *d*-band parameters close to the Fe or Co ones.[11] In fact, even if the Ag and Cr lattice parameters are quite close, the Cr intralayer next-nearest-neighbor interactions must be reduced in order to fit the two-dimensional (2D) experimental bandwidth. This has been done at the Γ point where we have found that the d_{xy}, d_{yz}, and d_{zx} levels are not modified by the interaction with the Ag substrate states. So this easily fixes the magnitude of the next-nearest-neighbor interactions. The mean value of the Ag (Table I) parameters and of the Fe (Ref. 11) ones gives a good agreement with the experimental values. The same procedure has been extended to the first-nearest-neighbor interactions. Even though they are not directly used in the calculation, these band parameters are necessary to evaluate the hopping integrals between the Cr and the Ag atoms $\beta_{\text{Ag-Cr}}$ which have been taken as usual equal to $(\beta^*_{\text{Ag-Ag}}\beta_{\text{Cr-Cr}})^{1/2}$ where $\beta_{\text{Ag-Ag}}$ and $\beta_{\text{Cr-Cr}}$ are, respectively, the tight-binding parameters for a bulk Ag and the Cr monolayer.

Due to charge oscillations near the surface, a self-consistent potential must be added to the orbital energies near the surface. We assume that this potential is not zero only in the six surface layers close to the surface. There are two contributions to this potential. One is due to exchange splitting and has been considered only in the Cr surface plane. To explore an antiferromagnetic state, on the two atoms of the surface unit cell, it has been taken to be plus or minus $J(n_{\text{up}}-n_{\text{down}})/2$ where J is the exchange integral and $(n_{\text{up}}-n_{\text{down}})$ is the difference between the spin occupations on a given Cr site. It has been neglected in the Ag layers as the spin oscillation is very small in the substrate layers. The J value has been taken equal to 0.49 eV in order to reproduce the experimental results. This is slightly smaller than the estimated bulk value [equal to 0.6 eV (Ref. 1)] but here also the monolayer bandwidth is smaller than the bulk one. The second part of the potential is due to Coulomb electronic repulsion. The d electrons are more localized than the s or p ones. The corresponding d intra-atomic Coulomb integral is larger than the s one. We have also assumed different potential values for the d and the $s(p)$ electrons. We have calculated these potentials such as they ensure a local orbital charge neutrality. This means that each atom not only remains neutral but also that the s-d charge transfer on a surface atom is the same as in the bulk materials. This approximation is also completely justified by the strong localization of the d states and has also been used in preceding calculations.[11]

TABLE I. Tight-binding band parameters for the Ag substrate and the Cr adsorbed layer (in eV).

	Cr layer	Ag substrate
E_s	8.772	9.383
E_p	18.107	17.392
E_{de_g}	1.010	2.714
$E_{dt_{2g}}$	0.877	2.611
$(ss\sigma)_1$	−0.789	−0.565
$(sp\sigma)_1$	1.564	1.127
$(sd\sigma)_1$	0.873	0.553
$(pp\sigma)_1$	3.455	2.716
$(pp\pi)_1$	0.615	1.383
$(pds)_1$	1.139	0.736
$(pd\pi)_1$	−0.216	−0.154
$(dd\sigma)_1$	−0.566	−0.423
$(dd\pi)_1$	0.285	0.210
$(dd\delta)_1$	−0.039	−0.038
$(ss\sigma)_2$	−0.605	−0.463
$(sp\sigma)_2$	0.857	0.618
$(sd\sigma)_2$	0.000	0.000
$(pp\sigma)_2$	1.874	1.706
$(pp\pi)_2$	−0.156	0.469
$(pd\sigma)_2$	0.000	0.000
$(pd\pi)_2$	0.000	0.000
$(dd\sigma)_2$	0.000	0.000
$(dd\pi)_2$	0.000	0.000
$(dd\delta)_2$	0.000	0.000

The local atomic charges have been calculated by a Green-function technique. For a given wave vector parallel to the surface, the resolvent matrix elements of a semi-infinite Ag substrate are determined by the decimation technique.[9] Then using the Dyson equation, five Ag layers and a Cr one are adsorbed on this substrate. The self-consistent potential is assumed to vary only within these six surface layers. The local densities of states are obtained by summation over ten special points[12] in the reduced surface Brillouin zone. In the decimation technique, a small imaginary part (here 0.1 eV) is added to the energy. After summation over the surface Brillouin zone, the Cauchy relations between the derivatives of the real and imaginary part of the resolvent diagonal matrix elements are used to extrapolate the density of states on the real energy axis. On the other hand, the integration over the energy to get the electronic charges has been made in the complex energy plane along a semicircular infinite contour. Such a procedure ensures a fast and very accurate determination of the charges.

A nine-layer slab (8 Ag + 1 Cr) with two atoms per unit cell has also been used to calculate the two-dimensional energy-dispersion curves along the symmetry directions of the surface Brillouin zone. Such a slab is sufficient to correctly describe the interaction of the Cr states with the substrate.

III. SILVER-FREE SURFACE AND CHROMIUM ADLAYER DENSITIES OF STATES

The method developed in the preceding section has been applied to the free (100) Ag surface. Due to a reduction of the number of nearest neighbors near the surface, the Ag surface s-, p-, and d-band widths are smaller than the bulk ones. In the absence of a self-consistent potential, this leads to a reduction of the electronic s and p charges in the surface plane. The opposite effect occurs for the d electronic charge. On the contrary to the s and p bands, when a band is nearly filled as the Ag d band, the number of d electrons in the surface layer is increased when the bandwidth is reduced.[13] Both these effects give rise to opposite $s(p)$ and d self-consistent potentials in the surface layer (positive for the d states and negative for the s ones). This gives rise to a large narrow peak close to the top of the d bulk band (Fig. 1). This surface band is rather narrow as the shift of the surface d states still reduces the interaction with the subsurface layers. Then the surface d-band width is for a large part only due to

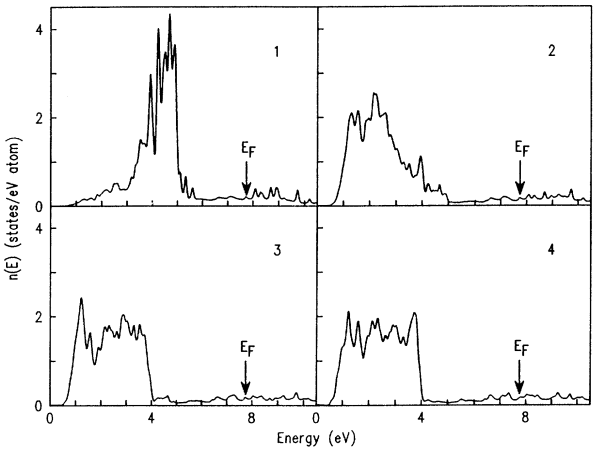

FIG. 1. Local densities of states in the Ag(100) surface layer (1), and in the first (2), second (3), and third (4) subsurface layers.

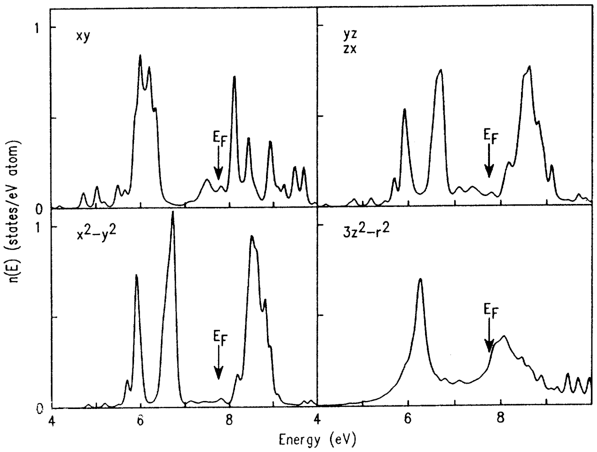

FIG. 3. *d* orbital local densities of states in the Cr adlayer.

the intralayer *d* states interaction.

The same effect is observed in the subsurface layer which is also quite different from the bulk but its bandwidth decrease is smaller. As it is generally observed for *d* bands in transition metals, the local densities of states in the third and fourth planes below the surface are very close to the bulk one.

Then a Cr layer is adsorbed on the Ag surface. An exchange splitting equal to ± 0.88 eV is used to fit the experimental curves. The local magnetic moment is then calculated and is equal to 3.57 Bohr magnetons in good agreement with other calculations[4,8] and measurements.[6] This magnetic moment is quite large as one must remember that its maximum value if we assumed one *s* electron per atom is equal to 5 Bohr magnetons.

The local densities of states on atoms close to the surface are shown in Fig. 2. In the Cr surface layer, two main peaks are observed on both sides of the Fermi level. These peaks roughly correspond to opposite spins. Two Ag layers close to the interface show densities of states slightly different from the bulk one. In the third layer, the density is very close to the bulk result.

In the Cr surface planes, the projected density of states on each *d* orbital shows narrow peaks (Fig. 3). The width of these peaks is close to 0.5 eV. This is only possible if the 2D band dispersion is small. These peaks appear to be in quite good agreement with the 2D experimental dispersion curves.[6] To confirm this point, we have calculated the 2D energy-dispersion curves along the two main symmetry directions of the surface Brillouin zone. The results are given in Fig. 4.

At the center of the Brillouin zone, three levels are found. The upper one corresponds to d_{yz} and d_{zx} states

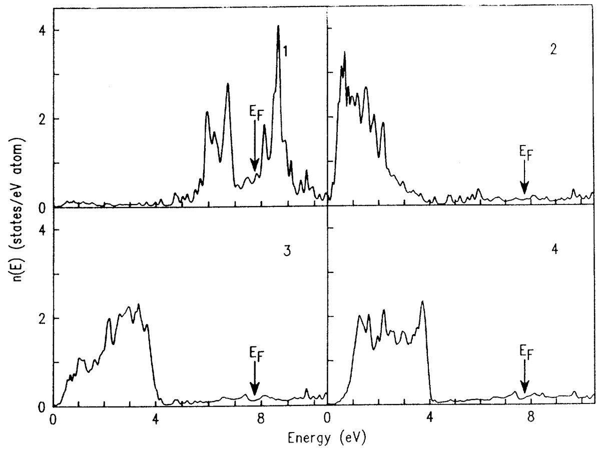

FIG. 2. Local density of states in the Cr adlayer (1) and in the Ag layers close to the interface (2–4). As the energy shift between the *d* Ag and Cr states is close to 5 eV, the coupling between the two bands is small.

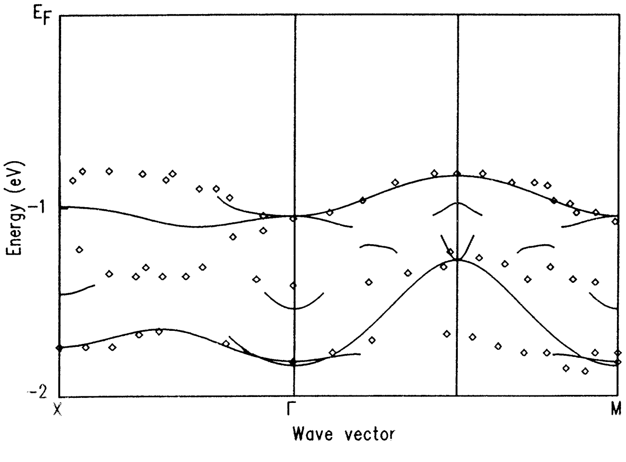

FIG. 4. 2D band dispersion $E(k)$ along the main symmetry directions of the $p(1\times1)$ surface Brillouin zone. The broken lines correspond to *d* states localized in the Cr adlayer. The experimental points (Ref. 6) are also shown for comparison. The origin of the energy is taken at the Fermi level. Due to the $c(2\times2)$ antiferromagnetic structure of the layer, the curves are symmetric between Γ and *M*.

which are energy degenerated. Its energy is not sensitive to the exchange splitting. The lower levels 1.8 eV below E_F correspond to d_{xy} and $d_{x^2-y^2}$ states whose energies are very close. The last level at the middle 1.5 eV below E_F is a $d_{3z^2-r^2}$ state. All these states are in agreement with the photoemission experiment.[6]

Between Γ and M, the upper band shape strongly depends on the exchange splitting and has been used to fit its value. With an exchange splitting given above (0.49 eV) close to the value (0.60 eV) used for bulk chromium, the resulting band shape is in very good agreement with the experimental points as the lower band between Γ and X. All the experimental points 1.5 eV below E_F belong to the same band and would correspond to $d_{3z^2-r^2}$ states which rather interact with the substrate states. Then they are less localized in the surface plane but are, however, obvious in the calculated energy spectrum near X, Γ, and M. One can see in Fig. 4 that these states also agree with the experimental values.

The agreement between theory and experiment is worse for the other states which are a mixing of Cr d states with Ag s states. This could be due to experimental inaccuracy but in fact the disagreement occurs for unambiguous experimental data points. This could also be due to the s-d coupling which is not well described by the tight-binding approximation. This already appears for bulk Ag energy-dispersion curves. Even though the overall agreement is quite good, some small discrepancies appear between the tight-binding calculation and the KKR results for energy curves which strongly depend on the s-d interaction. We have also neglected the electron-electron correlation. Its effect could be important as the width of the Cr d band is quite small. One must introduce a self-energy correction term in order to compare the calculated $E(k)$ to the experimental photoemission results.

IV. CONCLUSION

The electronic structure of a chromium monolayer adsorbed on a (001) silver substrate has been calculated in the tight-binding approximation assuming an atomic charge neutrality near the surface. An antiferromagnetic $c(2\times2)$ ground state has been found with an exchange integral close to 0.5 eV. The energy dispersion of some 2D chromium states agrees very well with the experimental results of angle-resolved photoemission experiments. However, the agreement is not so good for states like the $d_{3z^2-r^2}$ state which strongly interacts with the substrate. The overall behavior does not definitely settle whether a chromium monolayer can be deposited on a silver (001) substrate.

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