Magnetic coupling in 3d transition-metal monolayers and bilayers on bcc (100) iron

Mirbt, S.; Eriksson, O.; Johansson, B.; Skriver, Hans Lomholt

Published in:
Physical Review B Condensed Matter

Link to article, DOI:
10.1103/PhysRevB.52.15070

Publication date:
1995

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Mirbt, S., Eriksson, O., Johansson, B., & Skriver, H. L. (1995). Magnetic coupling in 3d transition-metal monolayers and bilayers on bcc (100) iron. Physical Review B Condensed Matter, 52(21), 15070-15073. DOI: 10.1103/PhysRevB.52.15070

PHYSICAL REVIEW B VOLUME 52, NUMBER 21 1 DECEMBER 1995-I

Magnetic coupling in $3d$ transition-metal monolayers and bilayers on bcc (100) iron

S. Mirbt, O. Eriksson, and B. Johansson
Condensed Matter Theory Group, Department of Physics, Uppsala University, S-75121 Uppsala, Sweden

H. L. Skriver
Center for Atomic-scale Materials Physics and Physics Department, Technical University of Denmark, DK-2800 Lyngby, Denmark

(Received 19 July 1995)

We have calculated the magnetization profile in the (100) surface of bcc Fe covered by a monolayer or a bilayer of $3d$ transition metals. The calculated trends are explained in terms of the hybridization between the $3d$ states of the overlayer and the Fe substrate.

A combination of new methods for preparing well-defined clean surfaces and techniques for measuring magnetic properties has recently enabled detailed studies of magnetism of surfaces, interfaces, and thin films. Simultaneously, the theory of electronic structure has matured to a stage where questions concerning the magnetic moments and the type of magnetic coupling, i.e., ferromagnetic (FM) or antiferromagnetic (AFM), at an interface may be answered with great accuracy. Of particular interest for practical applications, as well as from a physical point of view, is the modification of the magnetic moments which takes place when an Fe surface is covered by a few layers of a $3d$ transition metal. Apart from the pure Fe system, which has been studied in detail[1-6] some experimental as well as theoretical results exist for V,[7,8] Cr,[9-11] Mn,[12,13] and Ni,[14,15] while Co (Ref. 16) is only studied experimentally. In the cases of Ti and Cu there are neither experimental data nor theoretical results available in the literature. The results we are going to present are in good agreement with both experiments and earlier calculations where they exist.

Here, we present a systematic, theoretical study of the magnetic properties of the (100) surface of ferromagnetic, bcc Fe covered by a monolayer or a bilayer of the $3d$ elements Ti to Cu. In particular, we calculate the magnetic moments through the interface region including that of the topmost Fe layer. In the calculations we considered the size of the magnetic moment and the total energy for different types of magnetic couplings between the surface and subsurface layers. We have thus calculated the total energy of the monolayer covered surface with FM as well as AFM coupling to the Fe substrate. Similarly, in the bilayer calculations, we allowed the surface and subsurface of the two $3d$ overlayers to attain the magnetic coupling to the Fe substrate which gave the lowest total energy. Despite considerable experimental efforts the magnetic moments in the systems under consideration are not too well known and most of the present results are in fact predictions of the unique magnetic behavior one may encounter in thin-film materials with a thickness of a few monolayers.

The calculations were performed by means of the interface Green's function technique, developed by Skriver and co-workers.[17] This method is based on the linear muffin-tin orbitals (LMTO) method[18,19] within the tight-binding,[20-22] frozen core, and atomic-sphere approximations together with the local spin density approximation as parametrized by Vosko, Wilk, and Nusair.[23] The number of $k_{\|}$ points was taken to be 528 special points[24] in the irreducible part of the two-dimensional Brillouin zone. Moreover the Wigner-Seitz radius was chosen to be 2.662 a.u. for all elements involved, which corresponds to the experimentally observed volume of bcc Fe. Although lattice relaxation has been shown to sometimes influence the magnetic properties[13] we neglect, in this systematic study, this effect. At this atomic volume bulk Fe is calculated to have a ferromagnetic spin moment of $2.23\mu_B$. We have studied systems which consist of semi-infinite bcc(100) Fe, on which we add one or two layers of element X before reaching vacuum. For most of the calculations we allowed 8 Fe layers to differ from Fe bulk, although it turned out that 3 Fe layers were sufficient, so for a few calculations we only allowed 3 Fe layers to differ from Fe bulk.

In Fig. 1 we present the calculated magnetic moment of the overlayer both for a monolayer and a bilayer coverage. In the monolayer case it is seen that the magnetic moment of

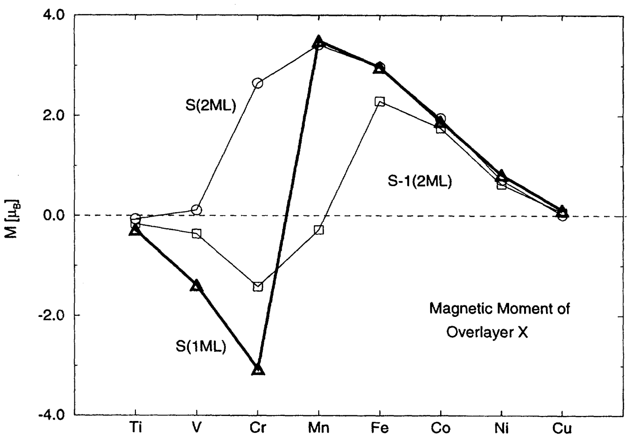

FIG. 1. The magnetic moment for the bcc(100) Fe surface covered by monolayers and bilayers of $3d$ transition metal X where X = Ti,...,Cu. The triangles correspond to the magnetic moment of the surface layer, S (1 ML), of the monolayer covered surface. The circles and squares correspond to the surface, S (2 ML), and subsurface, $S-1$ (2 ML) of the bilayer covered surface.

0163-1829/95/52(21)/15070(4)/$06.00

the added layer is antiparallel to that of the Fe substrate for the earlier transition-metal elements and parallel for the later elements. This is reminiscent of the coupling exhibited by a $3d$ impurity in bulk Fe.[25,26] The effect is a consequence of the change in hybridization between the $3d$ states of the substrate and those of the overlayer which takes place as one proceeds through the transition-metal series. In the early transition metals the $3d$ states are positioned at higher energies than those of Fe. Since the Fe $3d$ states have an appreciable exchange splitting such that the spin-down Fe $3d$ states have moved up in energy and therefore are closer to the $3d$ states of the overlayer, the hybridization of the $3d$ states of the early transition metal with the spin-down Fe $3d$ states is stronger than the hybridization with the Fe $3d$ spin-up states. As a result, the fraction of spin-down $3d$ states of the early transition metal found in the energy region of the Fe $3d$ states is increased and since the Fermi level is situated in this region an AFM coupling follows. For the late transition metals the situation is reversed and the coupling to the substrate is therefore FM. Moreover, due to the induced polarization from the Fe substrate and the band narrowing at the surface the magnitude of the moment on the monolayer atoms is substantially enhanced with respect to the moment in the corresponding bulk transition metal. In fact, Ti and V are nonmagnetic as bulk metals, whereas as monolayers on Fe they are found to have an appreciable magnetic moment, which in case of V was verified experimentally.[12] The largest enhancement is found in Mn, which is quite close to being completely saturated with almost all of its five d electrons in the spin-up band. The calculated enhancement is in excellent agreement with both an earlier calculation[13] and experiment.[8]

For the bilayer covered surface the situation is more involved, especially as regards the coupling to the underlying Fe substrate. Thus, the magnetic moment in the surface layer is found to be oriented parallel to the Fe moments whereas the subsurface $3d$ moments show a behavior similar to that found in the monolayer calculations and in calculations of $3d$ impurities in Fe, i.e., AFM for the early $3d$ elements and FM for the late $3d$ elements. The magnetic coupling of the subsurface $3d$ atoms, which are in direct contact with the Fe atoms, may be understood from the same arguments as outlined above for the monolayer moments. However, it is interesting to note that the magnitude of the magnetic moment of the subsurface layer is substantially smaller than that of the surface layer in the monolayer calculation. This is a direct consequence of the fact that the subsurface atoms of the bilayer interact and hybridize with eight nearest-neighboring atoms, as opposed to the surface atoms which have a reduced coordination number.

In Fig. 2 we show the calculated magnetic moment of the Fe atoms in the atomic layer closest to the interface with the $3d$ overlayer. Note that we show the Fe interface moment both for the monolayer and bilayer geometries as well as for different types of magnetic couplings (ferro and antiferro). As can be seen in Fig. 2 the Fe moment depends very delicately on the number of coating transition-metal layers, the atomic number of the coating material, as well as on the magnetic coupling. The observed quite complicated trends cannot be explained by simple models involving for instance rigid Fe d bands, with a constant exchange splitting and with different band filling (Slater-Pauling curve), depending on the coating. As a matter of fact we calculate a rather constant d occupation in the Fe interface layer, with only a small charge transfer between the interface and the coating atoms ($\sim$ 0.1 electron), where as a rule of thumb, charge is transferred from the lighter element, which has broader bands to the heavier element, which has narrower bands.

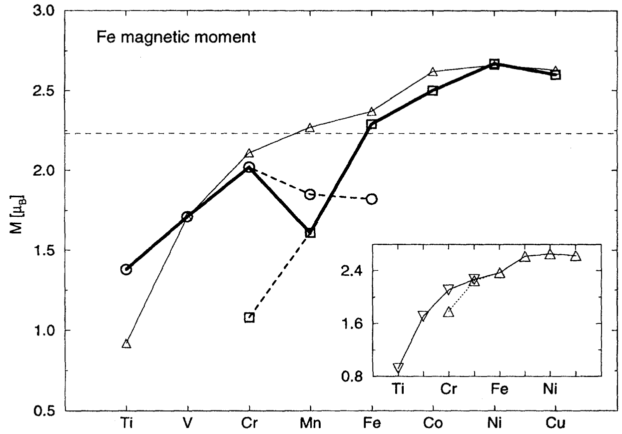

FIG. 2. Calculated magnetic moment of Fe at the interface with X. The bold solid line corresponds to the calculated ground-state moment for the monolayer situation. The broken lines indicate metastable solutions. Circles denote an AFM coupling and squares a FM coupling between the Fe and the overlayer X. The thin line (triangles) corresponds to the Fe interface moment for the bilayer situation. In the inset the Fe interface moment for the bilayer coverage is shown again. The broken line indicates the metastable solutions. Triangles pointing up indicate a FM coupling, triangles pointing down indicate an AFM coupling at the interface.

Despite the quite intricate behavior of the interface moment, shown in Fig. 2, certain trends are distinguishable. For instance, both for the monolayer and bilayer geometry a coating with an early transition metal produces a reduced Fe interface moment whereas a late transition-metal coating produces an increased Fe interface moment. This behavior is again reminiscent of what is found for $3d$ impurities in Fe. In impurity calculations of the spin moment of the Fe atoms around a $3d$ impurity, it was found that for an early $3d$ impurity the nearest-neighboring Fe atoms show a decreased moment, whereas for late $3d$ impurities the moment is enhanced.[26] However, unlike the impurity calculations we observe a drastic reduction of the Fe interface moment when Fe is covered with a monolayer of Mn. Moreover, for the monolayer coating we observe that if a particular type of magnetic coupling is imposed in the calculations, the interface moment behaves more regular. For instance, for the AFM coupling the Fe interface moment is initially increasing, reaches a maximum for Cr, and decreases smoothly for Mn and Fe. Similarly, for the FM coupling the curve is initially increasing, reaches a maximum at Ni and decreases for Cu. The dramatic jump in the Fe interface moment is, as seen in Fig. 2, at least partly due to that the system here changes from an AFM to a FM coupling. We will describe this in more detail below. Also, for the bilayer geometry the dependence of the Fe moment on the coating material is much smoother and the interface moment is much less influenced by the type of magnetic coupling (see the inset of Fig. 2).

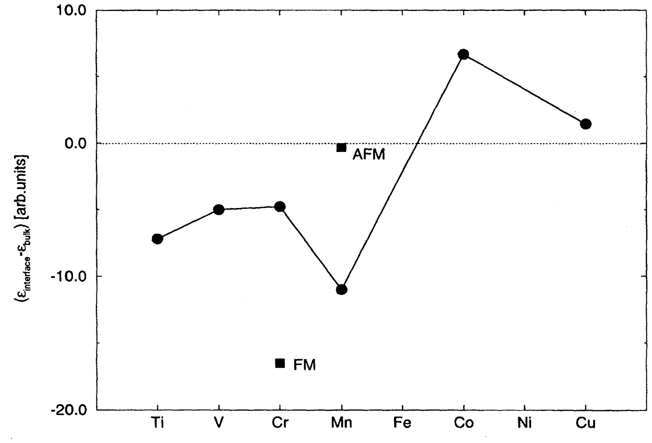

FIG. 3. Calculated exchange coupling of the Fe interface layer according to Eqs. (2)–(4). The solid line corresponds to the calculated ground state, the squares indicate metastable solutions.

Let us now provide a couple of simple arguments explaining some of the calculated trends displayed in Fig. 2. First, we focus on the peculiar dip at Mn, found in the monolayer calculations. Due to hybridization with the overlayer d band the Fe d band will shift in energy by an amount δ:

$$C_{\text{Fe}}^{\text{interface}}=C_{\text{Fe}}^{\text{bulk}}+\delta. \tag{1}$$

In Eq. (1) C is the center of the d band. The exchange splitting ϵ in bulk Fe is equal to $\epsilon_{\text{bulk}}=(C_{\text{Fe}}^{\uparrow}-C_{\text{Fe}}^{\downarrow})$, whereas the exchange splitting of the interface Fe layer after hybridizing with the overlayer may be written

$$\epsilon_{\text{interface}}=\epsilon_{\text{bulk}}+\delta^{\uparrow}-\delta^{\downarrow}. \tag{2}$$

Equation (2) states that if the energy shift of the Fe spin-up band is larger (smaller) than the energy shift of the Fe spin-down band, then the exchange splitting of the Fe interface is increased (decreased) compared to Fe bulk. In order to obtain a quantitative result for the interface moment we thus need to calculate the shift in energy due to the interface-overlayer hybridization. If the two energy levels are sufficiently separated in energy one may obtain a simple expression for this shift.[27] However, in the present study the energy levels are for some cases almost degenerate and to calculate a simple expression for the hybridization induced shift of these levels becomes a difficult task. To avoid this problem we observe that in our calculations the energy shift may be approximated by the following proportionality relations:

$$\delta\sim(C_X-C_{\text{Fe}})^{-1}\frac{(d_X-d_{\text{Fe}})}{|d_X-d_{\text{Fe}}|} \tag{3}$$

for $|d_X-d_{\text{Fe}}|\geqslant 1$ and

$$\delta\sim(C_X-C_{\text{Fe}})^{-1}(d_X-d_{\text{Fe}}) \tag{4}$$

for $|d_X-d_{\text{Fe}}|\leqslant 1$.

In the equation above d_X (d_{Fe}) is the d-band occupation of the interface metal X (bulk Fe). In Fig. 3 we show the exchange splitting, $\epsilon_{\text{interface}}$, which we calculated using Eqs. (2)–(4). For Fe, we used, both for the center of band C_{Fe} and the d-band occupation d_{Fe}, the bulk values, whereas for the covering metal we used the interface values for both parameters. This is of course not quite correct, because the interface values already include the effect of hybridization. Nevertheless, with the exception of Fe and Ni, it is sufficient to use the interface values as a crude approximation. (The Fe and Ni overlayers hybridize very strongly so that the interface value for C_X has changed significantly.) As can be seen in Fig. 3 we reproduce the trend of the interface Fe magnetic moment very well with this simple calculation. In particular we obtain the dip in the Fe interface moment when Fe is covered with a monolayer of Mn. Moreover, the Fe moment increases for Co and Cu and decreases for the early transition metals in accordance with our self-consistent calculations (Fig. 2). Note also in Fig. 2 that for any monolayer coating, the Fe interface moment never is larger than the Fe (100) surface moment of $2.97\mu_B$. This further increase of the magnetic moment at the Fe surface is understandable in terms of band narrowing (due to reduced coordination).

Next, we focus on the magnetization profile when one penetrates the monolayers and bilayers from the surface. It is known that the magnetic moment of Fe oscillates as a function of the distance from the surface. However, it has been predicted that this oscillation disappears when Fe is coated with a metal.[28] We find in our calculation, Fig. 4, that in some cases, the Fe magnetic moment oscillates around the Fe bulk magnetic moment, in other cases, the Fe magnetic moment decreases smoothly towards the bulk value. The first situation occurs for those cases where the number of Fe majority electrons by far exceeds the number of the overlayer majority electrons, i.e., for all cases of AFM coupling between the Fe and overlayer metal. The second situation oc-

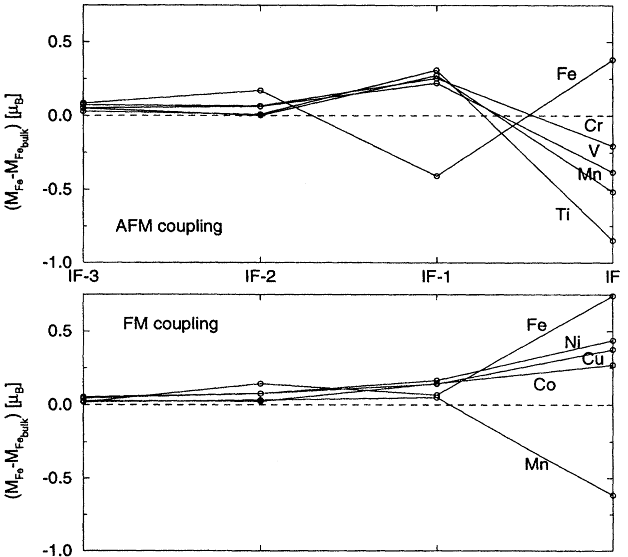

FIG. 4. The Fe magnetic moment profile for monolayer coverages with metal X. In the upper (lower) figure the Fe profiles are shown for an AFM (FM) coupling between the overlayer X and Fe. IF denotes the Fe interface layer, IF-1 the next layer down and so on. For the system Fe on Fe the interface layer moment is identical with the magnitude of the surface layer moment.

curs if the number of Fe majority electrons and the number of overlayer majority electrons are about the same, i.e., for all cases of FM coupling with the exception of Cr.[29] This different behavior of the Fe magnetic moment, i.e., in one case oscillating and in the other case smoothly decreasing, is understandable in terms of spin-dependent scattering. The Fe majority electrons experience a strong scattering if the overlayer metal, compared to Fe, contains far less majority electrons. Thus the Fe magnetic moment oscillates in this case. If the number of Fe and overlayer majority electrons is about the same, the Fe majority electrons experience a very weak scattering which causes the Fe magnetic moment to decrease smoothly towards the bulk value. Because the spin-dependent scattering takes place at the interface, we predict the oscillation behavior of the Fe magnetic moment to be independent on the thickness of the overlayer. It is of interest to compare the results displayed in Fig. 4 with the calculated moment of the different Fe shells surrounding a $3d$ impurity.[26] In the calculations of Drittler *et al.* it was found that the nearest-neigboring shell had the same dependence as shown in Fig. 4, a reduced Fe moment for early $3d$ impurities, and an enhanced Fe moment for the late $3d$ impurities. However, in the impurity calculations the change in the Fe moment is smaller than in the present study. Also, the impurity calculations show a less pronounced oscillatory behavior compared to the data in Fig. 4.

In summary, we have calculated the surface profile of the magnetization of Fe, when covered with a monolayer or a bilayer of a $3d$ transition metal. The change in magnetic coupling and the variation of the magnetic moments across the $3d$ transition series is explained in terms of the hybridization between the Fe $3d$ states and the $3d$ states of the covering metal. We have also shown that it is possible to stabilize different magnetic configurations for these systems, an effect previously also discussed for $3d$ impurities in Fe and Ni.[26] Clearly it would be very interesting to compare our calculations with experimental data. One of few experimental methods capable of measuring a magnetic depth profile is conversion-electron Mössbauer spectroscopy (CEMS).[30] As far as we know there are no CEMS experiments available for the presently investigated systems.

We thank Lars Nordström for helpful discussions. We are grateful to the Swedish Natural Science Research Council for financial support. The support by the Swedish Materials Consortium No. 9 was acknowledged. The Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation.

---

[1] S. Ohnishi, A.J. Freeman, and M. Weinert, Phys. Rev. B **28**, 6741 (1983).

[2] R.H. Victora, L.M. Falicov, and S. Ishida, Phys. Rev. B **30**, 3896 (1984).

[3] E. Tamura, R. Feder, G. Waller, and U. Gradmann, Phys. Status Solidi B **157**, 627 (1990).

[4] A.J. Freeman and R. Wu, J. Magn. Magn. Mater. **100**, 497 (1991).

[5] M. Aldén, S. Mirbt, H.L. Skriver, N.M. Rosengaard, and B. Johansson, Phys. Rev. B **46**, 6303 (1992).

[6] M. Aldén, H.L. Skriver, S. Mirbt, and B. Johansson, Surf. Sci. **315**, 157 (1994).

[7] A. Vega, L.C. Balbás, H. Nait-Laziz, C. Demangeat, and H. Dreyssé, Phys. Rev. B **48**, 985 (1993).

[8] T.G. Walker and H. Hopster, Phys. Rev. B **49**, 7687 (1994).

[9] T.G. Walker, A.W. Pang, H. Hopster, and S.F. Alvarado, Phys. Rev. Lett. **69**, 1121 (1992).

[10] J. Unguris, R.J. Celotta, and D.T. Pierce, Phys. Rev. Lett. **69**, 1125 (1992).

[11] F.U. Hillebrecht, Ch. Roth, R. Jungblut, E. Kisker, and A. Bringer, Europhys. Lett. **19**, 711 (1992).

[12] T.G. Walker and H. Hopster, Phys. Rev. B **48**, 3563 (1993).

[13] R. Wu and A.J. Freeman, Phys. Rev. B **51**, 17 131 (1995).

[14] J.I. Lee, S.C. Hong, A.J. Freeman, and C.L. Fu, Phys. Rev. B **47**, 810 (1993).

[15] J. Vogel, G. Panaccione, and M. Sacchi, Phys. Rev. B **50**, 7157 (1994).

[16] P. Pain and J.P. Eymery, J. Magn. Magn. Mater. **133**, 493 (1994).

[17] H.L. Skriver and N.M. Rosengaard, Phys. Rev. B **43**, 9538 (1991).

[18] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[19] H.L. Skriver, *The LMTO Method* (Springer-Verlag, Berlin, 1984).

[20] O.K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

[21] O.K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed-Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, New York, 1985).

[22] O.K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).

[23] S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1908).

[24] S.L. Cunningham, Phys. Rev. B **10**, 4988 (1983).

[25] M. Akai, H. Akai, and J. Kanamori, J. Phys. Soc. Jpn. **54**, 4257 (1985).

[26] B. Drittler, N. Stefanou, S. Blügel, R. Zeller, and P.H. Dederichs, Phys. Rev. B **40**, 8203 (1989).

[27] O.K. Andersen, W. Klose, and H. Nohl, Phys. Rev. B **17**, 1209 (1978).

[28] S. Ohnishi, M. Weinert, and A.J. Freeman, Phys. Rev. B **30**, 36 (1984).

[29] Cr turns out to have less majority electrons than Fe for both coupling cases, i.e., FM and AFM. The Fe magnetic moment profile for a monolayer coverage of Cr looks about the same for both coupling cases. Therefore we show in Fig. 4 only the profile for the AFM coupling.

[30] J.A. Sawicki and B.D. Sawicka, Hyperfine Interact. **13**, 199 (1983).