

Ferromagnetism and Antiferromagnetism of 3d-Metal Overlayers on Metals

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We report systematic calculations based on the full-potential linearized augmented-plane-wave method for the whole transition-metal series (V,Cr,Mn,Fe,Co,Ni) as overlayers on the Pd(001) surface. An energy analysis shows that Fe, Co, and Ni overlayers favor the ferromagnetic $p(1 \times 1)$ configuration, but V, Cr, and Mn, the antiferromagnetic $c(2 \times 2)$ superstructure. We conjecture that this result is a general trend which should also be found on the (001) surfaces of Pt and the noble metals.

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Surface magnetism has attracted much attention recently, especially the theoretical predictions¹ of magnetic overlayers with greatly enhanced moments and the prospect of studying clean model cases of two-dimensional magnetism. The experimental investigations of these systems are still at an early stage and face tremendous material preparation and characterization problems. For Fe overlayers on Ag(001) the predicted ferromagnetic structure of the overlayer^{1,2} has been confirmed.³ However, a recent study⁴ of V on Ag(001), which has also been predicted¹ to form a ferromagnetic overlayer, did not find any indication of ferromagnetism.

In this Letter we present a systematic series of calculations for all 3d transition metals (V,Cr,Mn,Fe,Co,Ni) as overlayers on Pd(001). This is the first time that the trend for a whole series of overlayers on one particular substrate has been calculated. We believe that this is very important since it clearly reveals the underlying physics and because density-functional theory is most reliable in predicting trends rather than results for isolated cases. Our attention will be focused on the stability of the ferromagnetic $p(1 \times 1)$ phase of the overlayer and its competition with an antiferromagnetic $c(2 \times 2)$ superstructure which is shown in Fig. 1. While our calculations were in progress the possible existence of this antiferromagnetic structure has been shown independently by Freeman and Fu,⁵ who found this configuration to be energetically more stable for a Cr overlayer on Au(001). Our systematic calculations show that on Pd(001),

monolayers of the early transition metals V, Cr, and Mn prefer the antiferromagnetic configuration, whereas the late transition metals Fe, Co, and Ni favor the ferromagnetic state. From these results and the arguments presented below we conjecture that this trend is also valid for the (001) surfaces of the noble metals Cu, Ag, and Au as well as Pt.

The results are obtained with the full-potential linearized augmented-plane-wave method⁶ in a film geometry. Nine-layer (001) films consisting of seven layers of Pd and one 3d-metal monolayer on each surface are considered. To obtain reliable energy differences between the ferromagnetic $p(1 \times 1)$ and antiferromagnetic $c(2 \times 2)$ phase both magnetic structures are calculated with the antiferromagnetic unit cell containing eighteen atoms. A total number of 2×850 symmetrized augmented plane waves is used as variational basis set. It is found that sufficiently accurate Brillouin-zone integrations can be performed with use of ten special k_{\parallel} points⁷ in the irreducible wedge of the 2D Brillouin zone. Inside the muffin-tin spheres, lattice harmonics with angular momentum components $l \leq 8$ are included to describe charge and potential within touching muffin-tin spheres. All states including core states are calculated self-consistently. The calculations apply density-functional theory^{8,9} with use of the local-density approximation of von Barth and Hedin¹⁰ with parameters as chosen by Moruzzi, Janak, and Williams.¹¹

Our calculations show that for all 3d-metal overlayers V, . . . , Ni, both configurations are always stable. As a typical example, Fig. 2 shows the local density of states for the ferromagnetic and the antiferromagnetic structures of a Cr overlayer. In both cases we see a strong splitting of the peak intensities with the main peak at approximately the same energy; thus in first approximation the densities of states are very similar. A closer look shows that the antiferromagnetic subbands are appreciably narrower. This results from the weak overlap between the next-nearest neighbors in the planar lattice of Fig. 1. The hybridization of the nearest-neighbor wave functions belonging to the energy levels located at different energies gives rise to additional small intensities

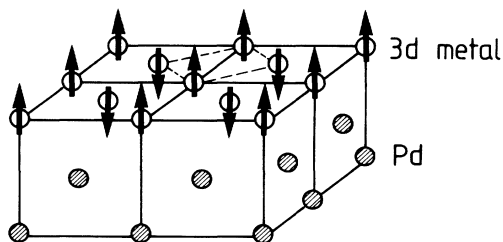


FIG. 1. The antiferromagnetic $c(2 \times 2)$ superstructure of a 3d-metal overlayer on the Pd(001) surface.

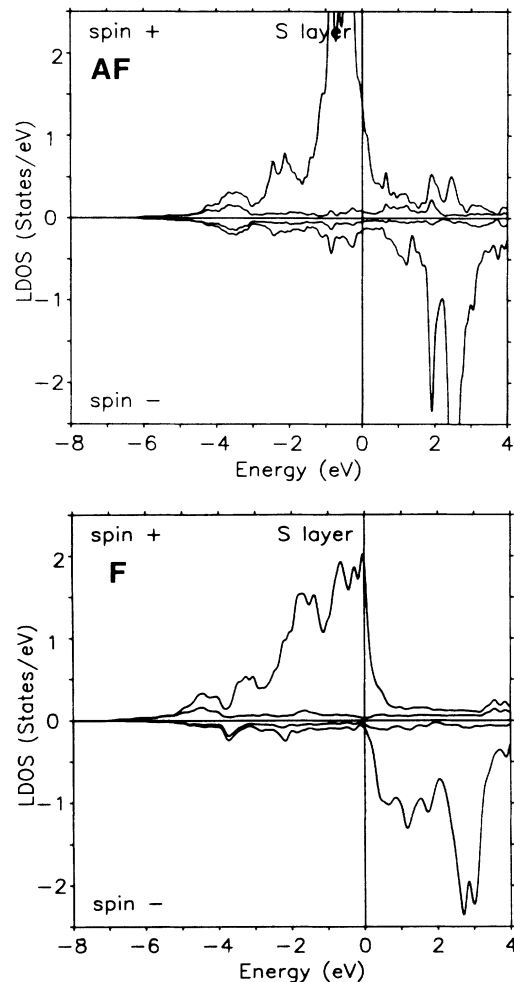


FIG. 2. Local density of states of a ferromagnetic (F) and an antiferromagnetic (AF) Cr overlayer on Pd(001).

appearing at the energy position of the main peak, but for the opposite spin direction, as is well known from bulk band-structure calculations of antiferromagnets.¹²

The calculated local moments for both configurations are listed in Table I. Surprisingly the moments are very similar for both cases. Except for V the antiferromagnetic moments are the same as or slightly smaller than the ferromagnetic ones which is a consequence of the additional humps in the density of states for the opposite spin direction. The moments are also similar in magnitude to the ones calculated for overlayers on Ag or Au (Refs. 1, 2, and 5) and much larger than the corresponding bulk moments. This shows that the hybridization of the overlayers with the *d* band of Pd does not significantly suppress their moments. Table I also lists the results for transition-metal impurities in bulk Pd as calculated by the Korringa-Kohn-Rostoker Green's-function method.¹³ Despite their different geometry and nearest-neighbor coordination, the impurity moments in the bulk are very similar to the overlayer moments. The

TABLE I. Local moments of ferromagnetic (M_F) and anti-ferromagnetic (M_{AF}) overlayers on Pd(001) compared with the local moments (M_I) of impurities in bulk Pd.

	M_F (μ_B)	M_{AF} (μ_B)	M_I (μ_B)
V	0.51	1.39	0.00
Cr	3.87	3.46	3.14
Mn	4.11	4.05	4.13
Fe	3.19	3.20	3.47
Co	2.12	1.99	2.28
Ni	0.89	0.59	0.92

explanation for this rather strange result is that because of the large lattice constant of Pd, the hybridization within the overlayer and with the Pd substrate is strongly reduced so that one approaches an atomlike behavior where the moments saturate and become insensitive to environmental changes. We will discuss this aspect and the similarities with the impurity results in a separate publication.¹⁴

Since both the ferromagnetic and the antiferromagnetic configuration have very similar densities of states and local moments, an experimental distinction by photoemission will be very difficult. Only spin-polarized experiments or magnetometry can identify the ferromagnetic configuration uniquely. On the other hand, the antiferromagnetic configuration could be easily confused with a possible paramagnetic one and a clear distinction seems to be a very difficult problem. A promising way could be the observation of superstructure reflection spots in the LEED pattern. Calculations¹⁵ show that their intensities might be detectable. Another possible method could be spin-polarized photoelectron diffraction in core-level emission which has been recently observed in antiferromagnets.¹⁶

The central result of our paper is shown in Fig. 3. The full line shows the total energy difference $\Delta E = E_{AF} - E_F$ between the antiferromagnetic and ferromagnetic structures of the overlayer. The trend is quite clear: The early transition metals V, Cr, and Mn prefer the antiferromagnetic configuration, whereas Fe, Co, and Ni favor the ferromagnetic structure. The energy difference is sizable, about 0.2–0.4 eV per surface atom. Only for V and Ni is the energy difference much smaller, basically because the moments are small.

Thus we observe for the overlayers the same tendency which is also known from the bulk. After all, Fe, Co, and Ni are elemental ferromagnets, whereas Cr and Mn prefer antiferromagnetic structures. The moments occurring in the bulk are so different, e.g., $0.59\mu_B$ for bulk Cr versus $3.5\mu_B$ or $3.9\mu_B$ in the overlayer, and interaction energies are consequently so much smaller that this might be considered as accidental. However, this is not the case. Even for diatomic molecules it is known that Fe_2 , Co_2 , and Ni_2 prefer configurations with ferromag-

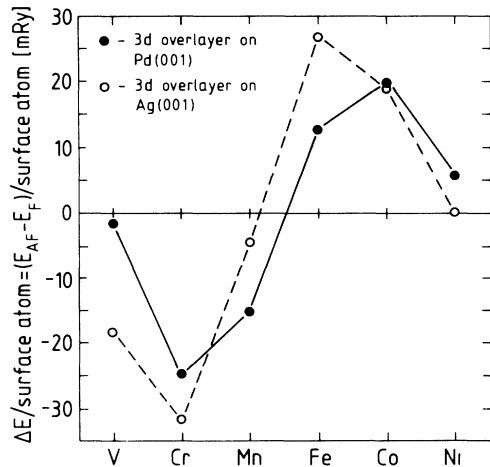


FIG. 3. Energy difference $\Delta E = E_{AF} - E_F$ between the antiferromagnetic and ferromagnetic configurations of the overlayers. For $\Delta E > 0$ ($\Delta E < 0$) the ferromagnetic (antiferromagnetic) configuration is stable.

netic couplings,¹⁷ whereas Cr_2 and Mo_2 couple strongly antiferromagnetically.¹⁸ In this case the interaction energy is even much larger than in the overlayers, since the equilibrium separation is appreciably smaller. The closest analogy to the overlayer is the interaction of $3d$ -metal impurities in bulk. Recent calculations^{13,19} for the interaction of magnetic impurity pairs in Cu and Ag show that on nearest-neighbor sites Fe and Co impurities favor the ferromagnetic coupling (Ni impurities are nonmagnetic), whereas Mn, Cr, and V prefer the antiferromagnetic configuration. Preliminary calculations indicate the same trend for the interaction of Fe pairs (ferromagnetic) and Mn pairs (antiferromagnetic) in a Pd host.¹⁹ If we take the calculated impurity interaction energies for the Ag host (for the Cu host the interaction energies are larger, since the nearest-neighbor distance is about 10% smaller) and assume a nearest-neighbor Ising model for the interaction in the overlayer, with the exchange constant fitted to the impurity interactions, we obtain for the energy difference ΔE of the overlayer the dashed curve in Fig. 3. This not only shows that the same trends should also be observed for Ag(001), but also that the differences between overlayers on Ag(001) and Pd(001) are minor. The biggest effect is a shift of the ΔE curve to the left, which can be understood as arising from the hybridization of the d electrons in the overlayer with the Pd d band. In total, however, the trend and the magnitude of the interaction are very similar. From these results and the experience with impurity interactions we conjecture that V, Cr, and Mn overlayers order also antiferromagnetically on the (001) surfaces of Pt as well as on the noble metals Cu, Ag, and Au, whereas Fe, Co, and Ni form ferromagnetic layers on these surfaces. This is in agreement with the recent result of Freeman and Fu for Cr on Au(001).⁵

Finally, we will briefly speculate about magnetic overlayers on the (011) and (111) surfaces. From the discussion above we expect for the close-packed (111) surface the nearest-neighbor interaction to be dominant. For Fe, Co, and Ni this would lead to ferromagnetic overlayers. In the antiferromagnetic case (V, Cr, or Mn) the situation is, however, more complex since the triangular planar lattice gives rise to frustration so that very complicated configurations could occur as has, e.g., been studied for the planar x - y model.²⁰ The rectangular atomic arrangement on the (011) surface leads to two different coupling constants between first and second neighbors. While the dominating nearest-neighbor interaction should show the same trend as discussed above (Fig. 3), the weaker next-nearest-neighbor interaction could have a different sign, since Ruderman-Kittel-Kasuya-Yosida-type interactions could become important. Therefore, also for this surface more complicated structures could occur. Thus a wealth of interesting and exciting magnetic structures could be found on these surfaces.

In summary, we have presented the first systematic calculation for all $3d$ transition metals as overlayers on a particular substrate, Pd(001) in this study. In all cases we find both the ferromagnetic $p(1 \times 1)$ and the antiferromagnetic $c(2 \times 2)$ configurations to be stable. The ferromagnetic configuration is more stable for Fe, Co, and Ni overlayers, while V, Cr, and Mn overlayers prefer the antiferromagnetic structure. We find strong similarities with the behavior of $3d$ -metal impurities in the bulk, with respect both to the size of the moments and also to the trend and magnitude of the magnetic interaction. We conjecture that the major trends found here for $3d$ -metal overlayers on Pd(001) are also valid for the (001) surface of Cu, Ag, Au, and Pt. For the (001) and (111) surfaces of these metals, particularly rich and complex antiferromagnetic structures are to be expected.

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¹C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985); A. J. Freeman, C. L. Fu, S. Ohnishi, and M. Weinert, in *Polarized Electron in Surface Physics*, edited by R. Feder, Advanced Series in Surface Physics, Vol. 1 (World Scientific, Singapore, 1985).

²R. Richter, J. G. Gay, and J. R. Smith, Phys. Rev. Lett. **54**,

2704 (1985).

³B. T. Jonker, K.-H. Walker, E. Kisker, G. A. Prinz, and C. Carbone, *Phys. Rev. Lett.* **57**, 142 (1986); B. Heinrich, K. B. Urquhart, A. S. Arrott, J. F. Cochran, K. Myrtle, and S. T. Purcell, *Phys. Rev. Lett.* **59**, 1756 (1987); M. Stampanoni, A. Vaterlaus, M. Aeschlimann, and F. Meier, *Phys. Rev. Lett.* **59**, 2483 (1987).

⁴M. Stampanoni, A. Vaterlaus, D. Pescia, M. Aeschlimann, W. Dürr, and F. Meier, to be published.

⁵A. J. Freeman and C. L. Fu, *J. Appl. Phys.* **61**, 3356 (1987).

⁶E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **24**, 864 (1981); M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26**, 4571 (1982).

⁷D. J. Chadi and Marvin L. Cohen, *Phys. Rev. B* **8**, 5747 (1973); S. L. Cunningham, *Phys. Rev. B* **10**, 4988 (1974).

⁸P. C. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

⁹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A115 (1965).

¹⁰U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

¹¹V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

¹²J. Kübler, *J. Magn. Magn. Mater.* **20**, 107 (1980); A. R. Williams, R. Zeller, V. L. Moruzzi, C. D. Gelatt, and J. Kübler, *J. Appl. Phys.* **52**, 2067 (1987).

¹³A. Oswald, R. Zeller, P. J. Braspenning, and P. H. Dederichs, *J. Phys. F* **15**, 193 (1985).

¹⁴S. Blügel and P. H. Dederichs, to be published.

¹⁵E. Tamura, S. Blügel, and R. Feder, *Solid State Commun.* (to be published).

¹⁶B. Sinkovic, B. Hermsmeier, and C. S. Fadley, *Phys. Rev. Lett.* **55**, 1227 (1985).

¹⁷J. Harris and R. O. Jones, *J. Chem. Phys.* **70**, 830 (1979).

¹⁸B. Delley, A. J. Freeman, and D. E. Ellis, *Phys. Rev. Lett.* **50**, 488 (1983); J. Bernholc and N. A. W. Holzwarth, *Phys. Rev. Lett.* **50**, 1451 (1983).

¹⁹A. Oswald, R. Zeller, and P. H. Dederichs, *J. Magn. Magn. Mater.* **54-57**, 1247 (1986).

²⁰D. H. Lee, J. D. Joannopoulos, J. W. Negele, and D. P. Landau, *Phys. Rev. B* **33**, 450 (1986).