PHYSICAL REVIEW B VOLUME 61, NUMBER 6 1 FEBRUARY 2000-II

Magnetic properties of thin vanadium films on iron

D. Spišák and J. Hafner
Institut für Materialphysik, Universität Wien, A-1090 Wien, Austria
and Center for Computational Materials Science, A-1060 Wien, Austria

(Received 9 July 1999; revised manuscript received 6 October 1999)

Self-consistent calculations based on real-space tight-binding linear-muffin-tin-orbital formalism have been carried out to study magnetic properties of vanadium adlayers grown on Fe(001) and Fe(103) substrate. The effects of imperfections such as surface steps and interdiffusion have been investigated.

I. INTRODUCTION

The transition metal vanadium is nonmagnetic in its bulk body-centered-cubic structure, although as a single atom it exhibits a magnetic moment of $3\mu_B$ in the ground state. However, the observation of large paramagnetic fluctuations demonstrates that bcc V is very close to the onset of magnetic ordering.[1] The understanding of the magnetic state of vanadium in intermediate geometries with a reduced coordination number is rather controversial. Electron-capture spectroscopy measurements[2] have revealed a ferromagnetic order at the (001) surface of bulk paramagnetic vanadium, which disappears at about 540 K. On the other hand, theoretical approaches predict a paramagnetic surface[3] or a small magnetic moment of $0.2\mu_B$.[4] Another possibility how to reduce the dimensionality is the preparation of ultrathin V layers or small clusters. Epitaxial deposition of thin films on substrates produces films with varying interatomic distances and thus possibly different magnetic behavior. Experimental studies for V monolayers (ML) on Ag(001) reported either no indication of a ferromagnetic ordering,[5,6] or ferromagnetically ordered V layers.[7] The first self-consistent calculations reported ferromagnetic ordering of V ML in V/Ag(001),[8] subsequent calculations found that the ground state of V on Ag(001) is antiferromagnetic.[9]

Recently the magnetic properties of ultrasmall vanadium clusters of up to four atoms have been calculated[10] and it was concluded that the free clusters are ferromagnetic. However, measurements found no evidence of a magnetic behavior of V clusters containing as few as nine atoms,[11] while larger V clusters were found to be magnetic.[12]

No conflicting foundings as regards the magnetic ground state of vanadium layers have been reported for systems in which the V atoms are in a contact with a magnetic partner. Because V is at the edge of the onset of the magnetism, induced magnetic moments on V develop readily. Calculations presented in this paper address the magnetic state of ultrathin V films on (001) and (103) Fe substrates. Both perfect and rough surfaces of V are considered. In addition the variation of the V moments as a function of composition in V_xFe_{1-x} bulk alloys and alloy films is studied. A model study of V ML on several low-index Fe surfaces was undertaken by Vega *et al.*[13] considering the exchange integral as a parameter. They concluded that a V monolayer couples antiferromagnetically with the ferromagnetic Fe substrate, whereas in a V bilayer the top layer couples ferromagnetically with the substrate. Mirbt *et al.*[14] performed self-consistent local-spin-density calculations for the complete series of $3d$-monolayers and bilayers on Fe(001) substrates and confirmed the antiferromagnetic coupling of V monolayers to the substrate. For a 2-ML film however, an almost vanishing V-surface moment and an interface moment aligned antiparallel to the substrate moments was found. The induced magnetic order at 193 K in ultrathin V films on Fe(001) was studied using spin-polarized electron-energy-loss spectroscopy by Walker and Hopster.[15] For a V ML an antiferromagnetic coupling to the Fe surface was detected with a magnetic moment below $1\mu_B$. For a V bilayer the total magnetic moment is aligned parallel to the Fe substrate and for thicker V films the magnetic moment is below the experimental resolution of $0.4\mu_B$. The same trends are observed in spin-polarized secondary-electron emission and spin-polarized Auger-electron spectroscopy studies performed at room temperature.[16] The first ML of V was observed to carry a negative magnetic moment of $-0.3 \pm 0.08\mu_B$, subsequent layers exhibit a positive magnetization decreasing with the thickness of V adlayers.

Before we confront the facts known about the V/Fe(001) system with our results, a concise account of the theoretical approach and some technical information concerning the calculations are given in the next section.

II. CALCULATIONAL PROCEDURE

The results presented here were obtained using the real-space tight-binding linear-muffin-tin-orbital (RS-TB-LMTO) method.[17–19] The local spin density (LSD) exchange-correlation functional of Barth, Hedin,[20] and Janak,[21] the generalized gradient corrections (GGC) of Perdew and Wang[22] were used. The use of the gradient-corrected exchange-correlation functionals is essential, because local-spin-density calculations predict the wrong structural and magnetic ground state for Fe, Mn, and Cr, whereas the correct result is obtained by including GGC's.[23] The frozen-core-electron density was calculated fully relativistically, for the self-consistently iterated valence-electron densities the scalar-relativistic Kohn-Sham equations were solved in the atomic-sphere approximation.

The spin-polarized local densities of state were calculated by means of the recursion method.[24] The calculations were

0163-1829/2000/61(6)/4160(7)/$15.00

performed for about 1100 atoms in clusters with periodic boundary conditions in lateral directions and free boundary conditions in the direction of the surface normal. The lattice parameter of bulk Fe ($a=2.87$ Å) was used, no lattice relaxation was taken into account. Three layers of empty spheres were considered to account for the spilling-out of charge into the vacuum. Between the Fe interface and the Fe bulk the magnetic moments were allowed to change in three layers. Calculations of the density of state were performed with 15, 20, and 45 levels of the continued fraction for s, p, and d states, respectively.

For a good resolution of the density of states calculated by a recursion method sufficiently large atomic models must be used. In such a large cluster a realistic random distribution or a some kind of partial order of atomic species can be achieved by means of a random number generator. The concentration dependence of the magnetic moments in bulk and thin-film V_xFe_{1-x} random substitutional alloys was obtained for a cluster with 1458 or 2000 atoms, in which the correlation functions of the first shell were checked to vanish. The calculations were restricted to a single-site approximation, in which the response of the surrounding host atoms is treated in an average way. Choosing a starting recursion vector with random complex phases distributed over a given component's orbitals allows to compute the averaged component-projected densities of state. From the moments of the partial Fe and V densities of states, new potential parameters are derived and the procedure is repeated until self-consistency has been achieved on average. Local quantities such as the magnetic moments on individual sites are calculated in a single non-self-consistent run. The results presented below were obtained as an average over three random starting vectors.

Finally, we have briefly investigated the influence of a possible structural relaxation of the adsorbed monolayer and of the interface by performing a multilayer structural optimization using the projector-augmented wave (PAW) method[25,26] implemented in the Vienna *ab initio* simulation program VASP (Ref. 27) using the same gradient-corrected functionals.

III. RESULTS AND DISCUSSION

A. Thin vanadium films on Fe(001)

The magnetic moments of one to four monolayers of V on Fe and the Fe magnetic moments near the interface are shown in Table I. Obviously the V magnetic moment is due to polarization by the Fe substrate. In the monolayer limit a rather large induced magnetic moment of $-1.85\mu_B$ is accompanied by a significant reduction of the magnetic moment in the adjacent Fe layer. By inspecting the layer-resolved densities of the state in Fig. 1 this behavior can be explained by a strong hybridization of the V majority-spin and the Fe minority-spin $3d$ states resulting in the charge transfer from surface V atoms to the Fe atoms and the antiferromagnetic coupling follows. Although the calculated V magnetic moment is almost a factor of two larger then that found in experiment,[15] only a slightly lower value of about $-1.75\mu_B$ was obtained by Mirbt *et al.*[14] The difference between this value and our V-moment of $-1.85\mu_B$ can be attributed to the GGC we included in the exchange-correlation potential. We note that our attempts to stabilize a magnetic moment in the V monolayer oriented along the Fe magnetic moment or even an improbable $c(2\times2)$ in-plane antiferromagnetic order in the V monolayer failed. In contrast, for a 2-ML film we get two magnetic solutions: one with parallel and the other with antiparallel V moments, the latter being of about 27 meV/atom lower in the energy. Therefore the total magnetic moment of 2-ML V films is much smaller than it was in a single V ML and it points along the Fe magnetization, what is exactly what has been deduced from the experiment.[15] The same observation of an increased surface and a reduced interface V moment was obtained in the semi-empirical calculations of Vega *et al.*[13] Actually, putting their free parameter (the exchange coupling) to the value 0.6 eV leads to quantitative agreement with our results for both V monolayer and bilayer. The magnetic moments for a V bilayer reported in Ref. 14 are much

TABLE I. Magnetic moments in V/Fe(001) films with up to four monolayers of V in μ_B. The results within TB-LMTO approach using gradient corrections.

ML	1	2_1	2_2	3	4
V(4)					-0.06
V(3)				0.40	-0.02
V(2)		0.95	-0.48	-0.01	0.00
V(1)	-1.85	-0.55	-0.35	-0.47	-0.45
Fe(1)	1.81	1.81	1.72	1.66	1.53
Fe(2)	2.58	2.46	2.47	2.49	2.50
Fe(3)	2.33	2.34	2.36	2.34	2.32
Fe(4)	2.39	2.36	2.36	2.33	2.35
Fe(5)	2.32	2.31	2.31	2.31	2.31

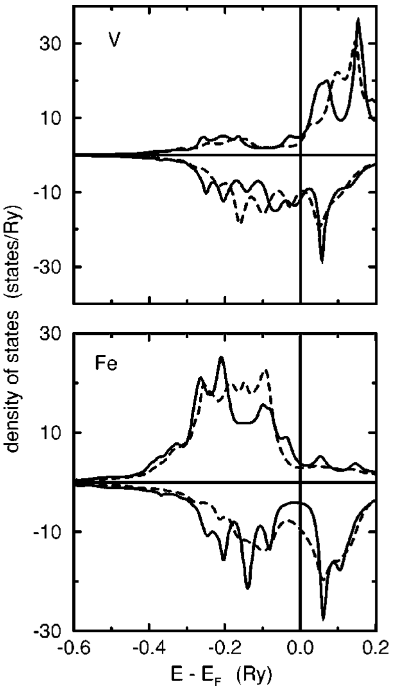

FIG. 1. Layer- and spin-resolved density of states in the topmost V and first Fe layer in 1 ML-V/Fe(001) (solid lines) and 1 ML-V/Fe(103) (dashed lines) systems.

smaller (the surface V moment almost vanishes) than our values and they predict an antiferromagnetic coupling of the total moment of the V film and the Fe substrate, in disagreement with experiment. Because of the disagreement between our results and those of Mirbt *et al.*,[14] we repeat the calculations using the spin-polarized PAW scheme. For a 1-ML film moments of $\mu(\mathrm{V}) = -1.93\mu_B$ and $\mu(\mathrm{Fe}) = 1.88\mu_B$ are obtained at the surface and at the interface, assuming an unrelaxed geometry. Under the same assumption we find for the bilayer case $\mu(\mathrm{V}_1) = 0.72\mu_B$, $\mu(\mathrm{V}_2) = -0.54\mu_B$, $\mu(\mathrm{Fe}) = 1.80\mu_B$. Considering the difference between an ASA for the potential and a full potential calculation, this can be considered as a very satisfactory agreement. To check whether the discrepancy between our results and those of Mirbt *et al.* is eventually to be attributed to the neglect of gradient correction, we repeated the TB-LMTO calculation in the LSDA. The results $[\mu(\mathrm{V}_1) = 0.73\mu_B,\ \mu(\mathrm{V}_2) = -0.42\mu_B,\ \mu(\mathrm{Fe}) = 1.71\mu_B]$ confirm that the GGA leads to a general enhancement of the magnetic moment, but do not resolve the existing discrepancy. The important point is that the bilayer-results obtained by two different techniques demonstrate the tendency to an antiferromagnetic coupling between neighboring V layers, in agreement with experiment.[15]

As can be seen from Table I, in a 3-ML film of V/Fe(001) only the surface and the interface V layers carry magnetic moments. Because the magnetic moment in the sub-surface layer would like to couple antiferromagnetically to the moments in both neighboring V layers, and the resulting orientation parallel to the substrate moments is in conflict with the antiferromagnetic coupling of the V adatoms with the Fe substrate, it is quenched. The surface layer with a relatively large magnetic moment is magnetically only weakly coupled to the deeper layers. Therefore it is conceivable that an in-plane $c(2\times2)$ antiferromagnetic order similar to that obtained for a V monolayer on Ag(001) might appear. However, our efforts to stabilize such a configuration were not successful. The antiferromagnetically stacked V layers turned out to be unstable as well.

In a 4-ML V/Fe(001) film no substantial magnetic polarization except at the V/Fe interface survives and the surface of the V film resembles the surface of a paramagnetic V. The magnetic moments in Fe covered by V undergo a large reduction (up to -34% of the bulk value) just at the interface, followed by a slight enhancement in the second layer from the interface. The magnetic state deeper in the Fe substrate is affected only marginally. This behavior is opposite to what is obtained for a (001) Fe surface, where the surface moment increases by 34%.[28] The interface magnetic moments on the V side stay nearly constant ($\mu \approx -0.5\mu_B$) for 2–4 V ML and it is very probable that the both Fe and V interface moments will not change for thicker V films.

The formation of V moments and the reduction of the Fe-moments at the interface goes hand-in-hand with a rather pronounced charge redistribution. At the free surface, conduction electrons relax into the vacuum, so that in a 3-ML V/Fe(001) film, for example, the first layer of vacuum spheres contains about 0.41 electrons/sphere. The first V ML looses electrons not only to the vacuum, but also to the V subsurface layer where charge is increased to 5.21 electrons/atom. In the V interface layer the charge is reduced to 4.85 electrons/atom, 0.15 electrons/atom being transferred to the first Fe layer. The resulting very pronounced changes in the local densities of states are illustrated in Fig. 2. It is remarkable that the V layer at the free surface shows a very large density of states at the Fermi level for the majority spins. In the subsurface and interface layer we observed the strong bonding/antibonding splitting in the *d* band and the deep density-of-states minimum at E_F characteristic for the body-centred transition metals with a less than half-filled *d* band. The charge-redistribution effects at the free surface and at the V/Fe interface are almost independent of film thickness, except for the V monolayer, where the charge transfer from V to Fe is enhanced to 0.31 electrons/atom.

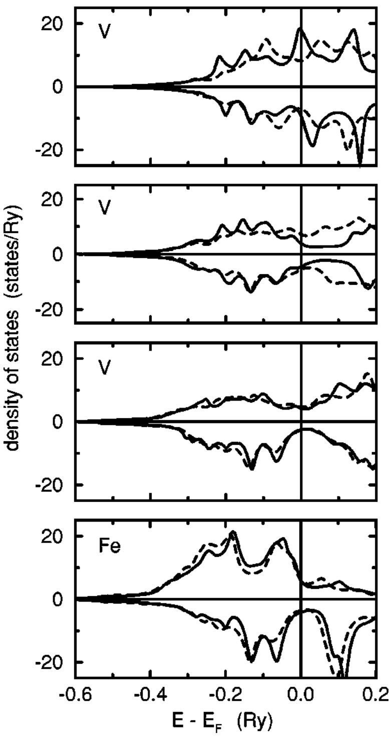

FIG. 2. Layer- and spin-resolved density of states in the four topmost layers in 3 ML-V/Fe(001) (solid lines) and 3 ML-V/Fe(103) (dashed lines) systems.

B. Stepped vanadium films on iron

The real-space approach can conveniently be employed for a treatment of systems with a lowered symmetry. In this section we investigate the surfaces with terraces and steps. The surface roughness can be responsible for a profound alteration of the magnetic arrangement if some kind of antiferromagnetism is present on the surface. A (001) surface with one-atom high and two-atoms wide terraces is just the (103) crystallographic surface. A side view of the (103) surface with three layers of adsorbed adatoms is sketched in Fig. 3. If only the lowest adsorption sites V1 are occupied, this corresponds to the coverage 0.63 compared to a monolayer on the (001) surface (measured in terms of atoms per unit surface area). At this low-coverage only the sites at the inner edge of the step are occupied. The V-Fe coordination number is four, like on the planar (001) surface, but the V-V coordination number is reduced from four to two. In this configuration, for the topmost substrate atoms the Fe-Fe nearest-neighbor coordination is the same, but the next-

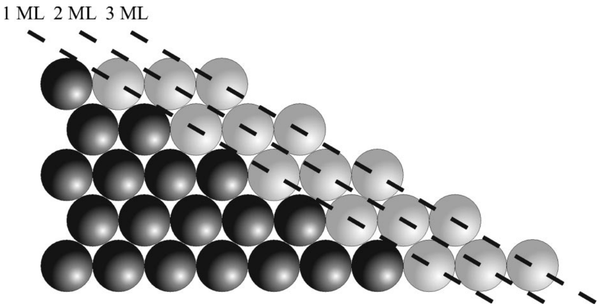

FIG. 3. Structure of a V film on Fe(103).

nearest-neighbor coordination is reduced. These conditions lead to a narrowing of the Fe-*d* band in the top layer (cf. Fig. 1), and to an increased Fe-V hybridization favoring a large magnetic moment on the Fe sites and a strong induced magnetization of the adsorbed V atoms, see Table II. The moment of the V atom is aligned antiparallel to the substrate, its magnitude is with $-2.13\mu_B$ nearly as large as for a V impurity on an Fe surface (cf. Ref. 29 and below).

With the occupation of the second layer of possible adsorption sites, a full coverage of the terraces is achieved. The V atoms forming the outer edges of the steps now have four V and only two Fe neighbors. The V atoms immediately at the interface have now four V and four Fe nearest neighbors (NN). Under these conditions, there is a competition between the NN Fe-V interactions inducing a negative moment in both V layers, and the NN V-V interactions tending towards an antiferromagnetic alignment of the induced moments. As a consequence, the V moments are strongly reduced. We note that our result is at invariance with TB calculations of Vega *et al.*[13] leading to small, but antiferromagnetically aligned V moments. In our calculations, this antiferromagnetic solution turned out to be unstable. Essentially the same result is obtained for a V trilayer on Fe(103)—in contrast to the flat trilayer, the V surface is now practically nonmagnetic. The layer-resolved electronic density of states for 3-ML V/Fe(103) is included in Fig. 2. Compared to the flat 3-ML V/Fe(001) we find a reduced density of states in the top layer, a less pronounced bonding/antibonding splitting in the subsurface layer, but only rather small changes at the interface.

As further study of rough surfaces we have calculated the magnetic profile of 1V/Fe(001) covered by one half-filled V ML forming strips along the ⟨010⟩ direction. Always two V atoms alternate with two unoccupied sites along ⟨100⟩ direction. The distribution of magnetic moments is sketched in Fig. 4. The magnetic moments are slightly lower than in the completed V adlayers but the overall trends are unchanged. Despite of decrease of the bonds to the nearest neighbors in the top half-filled layer, the magnetic moment drops to about one half of the value found on the top of 2V/Fe(001). This is consistent with the picture that the V magnetic moments are mainly induced by a magnetic substrate and not by reduction of the coordination number. Our calculations also demonstrate that a layered magnetic configuration is favored for V adlayers.

TABLE II. Magnetic moments in V/Fe(103) films with up to three monolayers of V in μ_B. The results within TB-LMTO approach using gradient corrections.

ML	1	2	3
V(4)			
V(3)			0.04
V(2)		−0.15	−0.18
V(1)	−2.13	−0.52	−0.43
Fe(1)	2.24	1.63	1.58
Fe(2)	2.12	2.09	2.11
Fe(3)	2.40	2.47	2.47
Fe(4)	2.46	2.43	2.40
Fe(5)	2.35	2.35	2.36

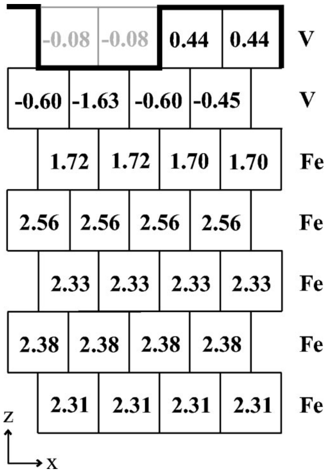

FIG. 4. Distribution of magnetic moments in the 1V/Fe(001) system covered by periodic two-atoms wide strips of V atoms to simulate a rough (001) surface: triangles, Fe moments; circles, V moments; squares, average moments.

C. Influence of interdiffusion in V/Fe(001)

Before we switch to the discussion of the influence of interdiffusion in V/Fe(001) films we briefly discuss the composition dependence of the magnetic moments in random bcc V_xFe_{1-x} alloys in Fig. 5. The Wigner-Seitz radii of V and Fe were kept at their experimental values, corresponding to a linear variation of the atomic volume with composition. We find a nearly linear decrease of the average magnetic moment as vanadium is added to iron in excellent agreement with

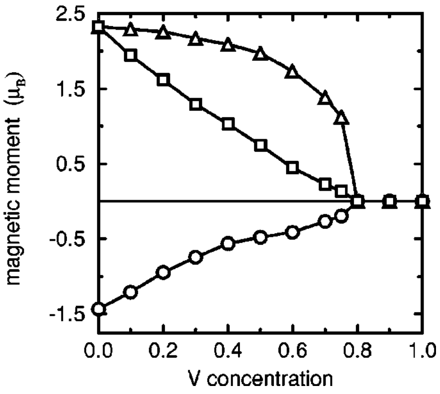

FIG. 5. Individual and average magnetic moments plotted as a function of the concentration in a random V_xFe_{1-x} alloy.

TABLE III. Magnetic moments of Fe and V atoms in bulk V_xFe_{1-x} alloy as a function of number of the like nearest-neighbors n in μ_B. μ_{calc} is average magnetic moments obtained from single-site approximation and $\overline{\mu}=\Sigma_{n=0}^{8}P(n,8)\mu(n)$ is the average magnetic moment calculated as a weight sum over all possible local configurations given in the table. The results within TB-LMTO using gradient corrections.

x	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$\overline{\mu}$	μ_{calc}
					Fe sites						
0.1	1.83	1.95	2.03	2.11	2.17	2.21	2.23	2.31	2.34	2.31	2.29
0.2	1.91	1.97	2.14	2.07	2.11	2.16	2.21	2.25	2.31	2.23	2.26
0.3	1.83	1.91	1.94	2.02	2.09	2.13	2.17	2.21	2.25	2.15	2.17
0.4	1.67	1.79	1.89	1.96	1.98	2.07	2.13	2.18	2.27	2.08	2.09
0.5	1.60	1.73	1.79	1.88	1.97	1.99	2.11	2.11	2.24	1.95	1.97
0.6	1.40	1.51	1.65	1.71	1.84	1.90	1.97	2.05	2.14	1.76	1.73
0.7	1.12	1.26	1.35	1.49	1.56	1.65	1.77	1.85	1.96	1.40	1.38
					V sites						
0.1	-1.29	-1.18	-1.17	-0.96	-0.93	-0.67	-0.56	-0.43	-0.32	-1.22	-1.21
0.2	-1.14	-1.04	-0.90	-0.81	-0.65	-0.53	-0.43	-0.32	-0.24	-0.96	-0.95
0.3	-0.98	-0.89	-0.76	-0.68	-0.57	-0.45	-0.35	-0.25	-0.19	-0.73	-0.75
0.4	-0.90	-0.80	-0.67	-0.58	-0.51	-0.40	-0.31	-0.27	-0.18	-0.58	-0.56
0.5	-0.78	-0.76	-0.67	-0.56	-0.48	-0.41	-0.30	-0.28	-0.17	-0.49	-0.48
0.6	-0.75	-0.66	-0.63	-0.55	-0.49	-0.37	-0.27	-0.25	-0.14	-0.40	-0.41
0.7	-0.54	-0.52	-0.45	-0.43	-0.38	-0.26	-0.25	-0.17	-0.10	-0.26	-0.27

earlier calculations in the coherent-potential approximation and discussed previously.[30,31] The V impurity in Fe bears the moment $-1.44\mu_B$ if GGC are included, or $-1.23\mu_B$ if the LSD approximation is not gradient corrected. The moments collapse at $x_C=0.8$ whether or not GGC is used. Table III collects the magnetic moments of V and Fe atoms as a function of the nearest neighbors of the same type and for different concentrations. The resulting trends, the decrease of the Fe magnetic moment if surrounded with more V atoms and the decrease of the V moments with increasing V nearest neighbors, are not surprising. Large local environment effects are distinguishable for the V atoms, on which magnetic moments of V having no or eight V nearest neighbors at the same alloy composition differ by a factor of 5. The average magnetic moments, however, agree very well with weighted averages of the moments calculated for fixed partial coordination numbers. The weighting factor $P(n,m)=x^n(1-x)^{(m-n)}m!/n!/(m-n)!$ gives the probability to find n neighbors among the $m=8$ nearest neighbors on a given site in an bcc alloy with concentration x.

Recently an inverse magnetoresistance (MR) has been reported in V_xFe_{1-x}/Au/Co trilayer[32] and it was attributed to the different asymmetry of spin scattering for the two ferromagnetic layers. This asymmetry can be crudely estimated by a ratio of density of states at the Fermi level $n(E_F)$ for the minority- and minority-spin bands, $\alpha=n^{\downarrow}(E_F)/n^{\uparrow}(E_F)$. If one ferromagnetic layer with $\alpha>1$ like Co is used in combination with a magnetic partner with $\alpha<1$, an inverse MR can be expected. The variation of the total and partial Fe and V densities of states in random alloys is shown in Fig. 6. We find that the substitutional disorder influences strongly the majority density of states on the Fe sites: the characteristic peak about 1 eV below E_F is strongly reduced by addition of V. The variation of the spin-asymmetry parameter α with composition is shown in Table IV. We find that for $x=0.2$ α is enhanced to $\alpha=0.62$ and for $x=0.3$ to $\alpha=0.51$, compared to $\alpha=0.27$ for pure Fe. From Table IV is obvious that $\alpha(V_xFe_{1-x})<1$, but it is smallest for pure Fe. However, the experiments by the same group found a normal MR in Fe/Au/Co trilayer system. Therefore, provided the parameter α does not change too much in a thin film, spin-scattering asymmetry cannot be the only mechanism responsible for the

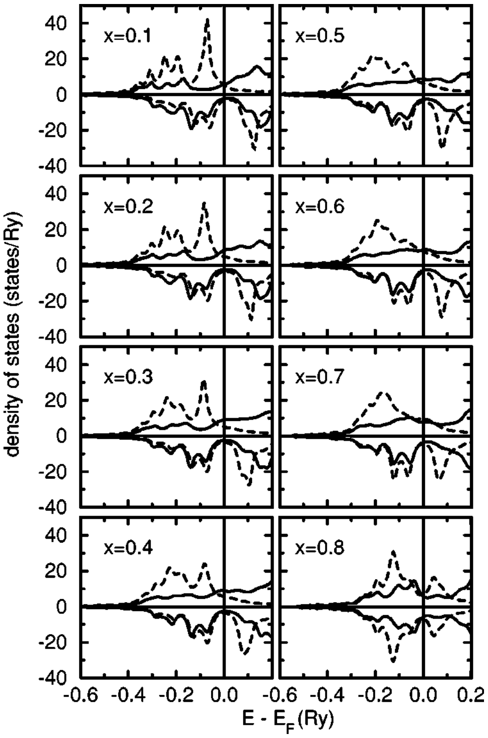

FIG. 6. Total and partial densities of state in V_xFe_{1-x} as a function of concentration.

TABLE IV. The ratio of density of states at the Fermi level for the minority- and majority-spin bands, $\alpha = n^{\downarrow}(E_F)/n^{\uparrow}(E_F)$ in bulk V_xFe_{1-x} alloy.

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
α	0.27	0.61	0.62	0.51	0.45	0.44	0.41	0.46	1.00

inverse MR. The measurements on samples with several thicknesses of V-Fe layer detected a larger inverse MR for thicker layers and hence it was anticipated that bulk-scattering and spin-disorder within the V-Fe layer is responsible for the observed inverse MR.[33]

To find out how a reduced dimension influences the magnetic properties of V-Fe alloys we performed a calculation for 2 ML of substitutionally disordered V_xFe_{1-x} alloy on the top of a Fe(001) substrate. Because the configurational average over 81 atoms in one layer of a total of 1458 atoms in a cluster was accomplished, we performed several trials with various atomic configurations for $x=0.5$. This allows to put the upper confidence limit 6% on the magnitude of magnetic moments. The results are given in Fig. 7, where the individual moments are plotted as a function of the composition. The negative V magnetic moment at the surface decreases with increasing V content of the film and changes sign at about $x=0.5$, indicating that the V-V antiferromagnetic interlayer interaction starts to dominate over the V-Fe antiferromagnetic intralayer interaction. The V moments in the subsurface layer on the other hand are only gradually reduced with increasing V content. The magnetism of Fe both in the adsorbed film and at the interface is also gradually reduced. A single V impurity embedded in the surface layer has an enhanced magnetic moment of $-2.07\mu_B$, which is slightly lower than that found for a V impurity in bulk Fe. This decrease can be explained as a result of lowering the nearest neighboring Fe atoms to one half when going from surface to bulk. The magnetic moment of a V impurity at a subsurface place is $-1.67\mu_B$, a value not differing too much from that found in bulk Fe. While a Fe impurity in a bulk V matrix does not preserve a magnetic character, a Fe atom possesses magnetic moments 2.55 or $-2.35\mu_B$ and $1.58\mu_B$ when put in the top layer or in the subsurface layer in 2V/Fe(001), respectively. The existence of solutions with positive and negative moments for the Fe impurity in the surface indicates that the coupling of the impurity moment to the substrate moment is rather weak. We would like to remind that the impurity in our model corresponds to the smallest possible concentration $x=0.012$.

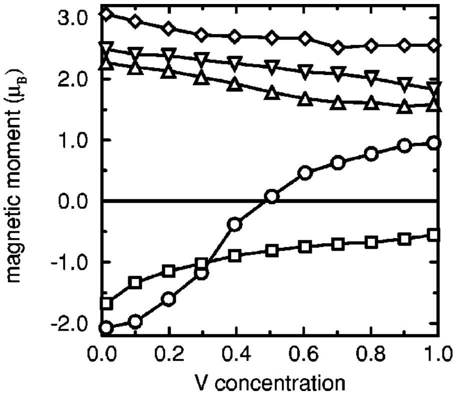

FIG. 7. Individual magnetic moments plotted as a function of the concentration in a 2-ML-thick random V_xFe_{1-x} alloy on the top of Fe(001): circles, V moments at the surface; squares, V moments in the subsurface layer; diamonds, Fe moments at the surface; up triangles, Fe moments in the subsurface layer; down triangles, Fe moments in first substrate layer.

IV. STRUCTURAL RELAXATION

Finally we turn very briefly to the possible influence of surface and interface relaxation on the magnetic properties of thin V films on Fe(001). Due to the larger atomic volume of V (the volume ratio is about 1.06), we would expect an outward relaxation of the V adlayer constrained to the smaller lattice constant of Fe in order to conserve the local atomic volume. However, it is also known that V surface shows a large surface contraction (top layer contractions by -9% [full potential linearized augmented plane-wave (FLAPW) calculation of Ref. 3] or -13.6% (present work, PAW calculations) have been reported) caused by a relaxation of electronic charge into the vacuum. In a bulk transition metal the zero-pressure equilibrium condition is met by a compensation of a *s*-electron pressure favoring expansion and a *d*-electron pressure favoring compression. This equilibrium is changed in the surface layer because the more mobile *s* electrons show a strong spill-out into the vacuum, leading to the inward relaxation because the attractive *d*-*d* interactions now dominate. Hence in V/Fe films there are two competing effects.

The results obtained via LSD+GGA calculation performed using VASP and the projector augmented-wave (PAW) method for a 1 ML V+5 ML Fe slab (allowing the V ML and the two top Fe layers to relax) are compiled in Table V. At zero relaxation we find a good agreement between the PAW and LMTO calculations. Surprisingly, PAW predicts an inward relaxation of the V adlayer by -11.5% and smaller oscillatory relaxations of the substrate layers. As the same technique predicts a relaxation of V(001) surfaces by -13.6% calculated at the theoretical V lattice parameter of 3.00 Å obtained by VASP or by -16.1% calculated at the experimental lattice parameter, the present result differs essentially by the effect expected from the V/Fe lattice mismatch. Due to the relaxation, the V and Fe moments at the surface and interface are reduced to $\mu_V = -1.69\mu_B$ and $\mu_{Fe} = 1.66\mu_B$, but there are only minor changes in the deeper layer.

For the present purpose, the important point is that the magnetic character of V films on Fe substrate undergoes no qualitative change when the film is allowed to relax. However, the predicted relaxation is interesting and deserves further investigation.

V. CONCLUSIONS

In the present paper we report detailed investigations of the magnetic properties of V films on Fe substrates. We demonstrate that in ultrathin V films on Fe(001), the covalent Fe-V interaction at the surface induces a substantial magnetic moment in the V layer at the interface, aligned antiferromagnetically with the moments in the substrate. Further V layers tend to form layered antiferromagnetic configurations. Due

TABLE V. The magnetic moments μ_i in μ_B and relaxations $\delta_i=(d_{i+1}-d_i-d_0)/d_0$ in % calculated using VASP for V(001) surface and for 1-ML V/Fe(001). The magnetic moments in parentheses were obtained for ideal lattice geometry.

	V(001)			1V/Fe(001)	
	$a_{\mathrm{V}}^{exp.}=3.03$ Å	$a_{\mathrm{V}}^{theor.}=3.00$ Å		$a_{\mathrm{Fe}}=2.87$ Å	
	δ_i	δ_i		μ_i	δ_i
V(1)	-16.1	-13.6	V(1)	-1.69 (-1.93)	-11.5
V(2)	-1.0	1.0	Fe(1)	1.66 (1.88)	-3.3
			Fe(2)	2.51 (2.52)	-2.7

to the competition between antiferromagnetic V-V interactions and the more long-ranged Fe-V interactions, magnetism in films with more than two V ML is strongly quenched, except immediately at the interface.

The induced magnetism depends also quite substantially on the surface orientation of the substrate—this is demonstrated for Fe(103) surfaces: in the monolayer limit, the magnetism of V is even enhanced due to suppressed V-V contacts, but it is strongly reduced on increasing film thickness.

The importance of surface roughness has been investigated for 1.5 ML V/Fe(001) films. These results show that V-moment formation is a rather local phenomenon—the local thickness determines the magnetic structure, but roughness tends to reduce both V and Fe moments at the interface.

Influence of interdiffusion has been tested by performing calculations for 2 ML $\mathrm{V}_x\mathrm{Fe}_{1-x}$ films on Fe(001), and confronting the results with studies of bulk V-Fe alloys. The results for the alloy films confirm the competition between antiferromagnetic V-V and V-Fe interactions leading to a concentration-dependent spin-reorientation of the V-moments in the surface layer.

ACKNOWLEDGMENTS

This work has been supported by the Austrian Ministery for Science and Transport within the project ‘‘Magnetism on the Nanometer Scale’’ and through the Center for Computational Materials Science.

---

[1] T. M. Hattox, J. B. Conklin, Jr., J. C. Slater, and S. B. Trickey, J. Phys. Chem. Solids **34**, 1627 (1973).

[2] C. Rau, C. Liu, A. Schmalzbauer, and G. Xing, Phys. Rev. Lett. **57**, 2311 (1986).

[3] S. Ohnishi, C. L. Fu, and A. J. Freeman, J. Magn. Magn. Mater. **50**, 161 (1985).

[4] G. Yokoyama, N. Hirashita, T. Oguchi, T. Kambara, and K. I. Gondaira, J. Phys. F **11**, 1643 (1981).

[5] M. Stampanoni, A. Vaterlaus, D. Pescia, M. Aechlimann, F. Meier, W. Dürr, and S. Blügel, Phys. Rev. B **37**, 10 380 (1988).

[6] R. L. Fink, C. A. Ballantine, J. L. Erskine, and J. A. Araya-Pochet, Phys. Rev. B **41**, 10 175 (1990).

[7] C. Rau, G. Xing, and M. Robert, J. Vac. Sci. Technol. A **6**, 579 (1988).

[8] C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985).

[9] S. Blügel, B. Drittler, R. Zeller, and P. H. Dederichs, Appl. Phys. A: Solids Surf. **A49**, 547 (1989).

[10] S. E. Weber, B. K. Rao, P. Jena, V. S. Stepanyuk, W. Hergert, K. Wildberger, R. Zeller, and P. H. Dederichs, J. Phys.: Condens. Matter **9**, 10 739 (1997).

[11] D. C. Douglass, J. P. Boucher, and L. A. Bloomfield, Phys. Rev. B **45**, 549 (1992).

[12] H. Akoh and A. Tasaki, J. Appl. Phys. **49**, 1410 (1978).

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

[14] S. Mirbt, O. Eriksson, B. Johansson, and H. L. Skriver, Phys. Rev. B **52**, 15 070 (1995).

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

[16] P. Fuchs, K. Totland, and M. Landolt, Phys. Rev. B **53**, 9123 (1996).

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

[18] H. J. Nowak, O. K. Andersen, T. Fujiwara, O. Jepsen, and P. Vargas, Phys. Rev. B **44**, 3577 (1991).

[19] R. Lorenz and J. Hafner, Phys. Rev. B **54**, 15 937 (1996).

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

[21] J. F. Janak, Solid State Commun. **5**, 53 (1978).

[22] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[23] E. G. Moroni, G. Kresse, J. Hafner, and J. Furthmüller, Phys. Rev. B **56**, 15 629 (1997); M. Eder, J. Hafner, and E. G. Moroni, Surf. Sci. Lett. **43**, L244 (1999).

[24] R. Haydock, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 215.

[25] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).

[26] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[27] G. Kresse and J. Furthmüller, Phys. Rev. B **56**, 11 169 (1996); Comput. Mater. Sci. **6**, 15 (1996).

[28] D. Spišák and J. Hafner, J. Magn. Magn. Mater. **168**, 257 (1997).

[29] B. Nonas, K. Wildberger, R. Zeller, and P. H. Dederichs, J. Magn. Magn. Mater. **165**, 137 (1997).

[30] D. D. Johnson, F. J. Pinski, and J. B. Staunton, J. Appl. Phys. **61**, 3715 (1987).

[31] I. Turek, J. Kudrnovský, M. Šob, and V. Drchal, in *Stability of Materials*, edited by A. Gonis, P. E. A. Turchi, and J. Kudrnovský (Plenum, New York, 1996), p. 431.

[32] J.-P. Renard, P. Bruno, R. Mégy, B. Bartenlian, P. Beauvillain, V. Chappert, D. Dupas, E. Kolb, M. Mulloy, P. Veillet, and E. Vélu, Phys. Rev. B **51**, 12 821 (1995).

[33] J.-P. Renard, P. Bruno, R. Mégy, B. Bartenlian, P. Beauvillain, V. Chappert, D. Dupas, E. Kolb, M. Mulloy, J. Prieur, P. Veillet, and E. Vélu, J. Appl. Phys. **79**, 5270 (1996).