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Magnetic nature of (100) surfaces of bcc RuV, RhV, and PdV binary alloys

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Based on *ab initio* calculations we predict that the (100) surfaces of the RuV, RhV, and PdV binary alloys in the bcc structure are magnetic over a broad concentration range although they are nonmagnetic in the bulk and the metals V, Ru, Rh, and Pd are nonmagnetic in the bulk and at the surface. We find that the magnetic moment is basically located at the V site in the surface plane of the alloys and the V moment can be as large as about $1\mu_B$ for an alloy with 75% V concentration. The origin of the surface magnetism is traced back to a surface state of V(100), which becomes occupied due to alloying. Additional nonmagnetic alloys with magnetic surfaces are suggested. [S0163-1829(98)51018-1]

It is well known that up to now itinerant magnetism has been restricted to metals, compounds and alloys made out of basically five elements of the periodic table. These are Co and Ni, which are ferromagnetic as plain bulk metals, Cr, which is antiferromagnetic, and Mn and Fe, which are ferromagnetic or antiferromagnetic depending on the crystal structure. One of the long-lasting aims in the field of surface magnetism and ultrathin films is to find new magnetic materials. This aim was evoked by the fundamental observation, that isolated transition-metal atoms have large magnetic moments governed by Hund's rule. Thus transition-metal atoms placed at surfaces or in ultrathin films have less nearest transition-metal neighbor atoms, or in other words a smaller coordination number, than in the bulk and thus should approach the atomic limit with enhanced magnetic moments or provide even new magnetic systems nonmagnetic in the bulk.

In the past decade, we witnessed an extensive search after these new magnets by many groups. At first the search focused on the magnetism at surfaces of transition metals. Indeed enhanced magnetic moments at the surfaces of the bulk magnets Cr, Fe, Co, and Ni (for a review see, e.g., Ref. 1) have been predicted and experimentally confirmed, but no magnetism was found at any low-index surface of a nonmagnetic bulk metal. In particular, for hot candidates such as V(100),[2] Rh(100),[3–6] and Pd(100) (Ref. 7) no magnetism was found experimentally or theoretically. Then, the interest moved on to ultrathin films on noble metals being a realization of two-dimensional magnets with a further reduced coordination number of transition-metal atoms. The extensive search of the last years can be summarized as follows: The magnetic moments of the classical bulk metals are even larger than at the surface and indeed a few other ferromagnetic systems have been found. These are at one monolayer (ML) range: V ($0.5\mu_B$) on Pd(100),[8] V ($2.1\mu_B$) on Ag(100),[9] Ru and Rh on Ag(100) ($1.7\mu_B$, $1.0\mu_B$), and Au(100) ($1.7\mu_B$, $1.1\mu_B$).[7,10] At 2 ML film thickness the magnetic moments are already largely supressed, e.g., the surface moments of 2 ML Ru, Rh, or Pd (Ref. 11) on Ag(100) (Ref. 12) are $0.03\mu_B$, $0.33\mu_B$, and $0.17\mu_B$, respectively.

Unfortunately, from the structural point of view Ru and Rh films are rather delicate systems. Ru and Rh films on noble metals are thermodynamically very unstable and any clustering[12] of the film atoms, alloying[13] with the substrate or wetting[14] of the films by the substrate atoms leads to a rapid quench of the magnetic moments. On the other hand V monolayers form a $c(2\times2)$ antiferromagnetic ground-state phase[15] with zero macroscopic magnetic moment.

In this paper we suggest another class of magnetic materials: the surfaces of alloys. We predict that the surface of certain bulk alloys can become magnetic with rather large magnetic moments although the alloy is *nonmagnetic* in the bulk phase. We demonstrate this effect for the (100) surfaces of three substitutionally disordered binary alloys in the bcc structure: RuV, RhV, and PdV. All three alloys are nonmagnetic in the bulk phase. None of the constituent atoms of these alloys are magnetic either as pure bulk metals or at their low index surfaces. We show that $\mathrm{Ru}_x\mathrm{V}_{1-x}(100)$, $\mathrm{Rh}_x\mathrm{V}_{1-x}(100)$, and $\mathrm{Pd}_x\mathrm{V}_{1-x}(100)$ are magnetic over a broad concentration range of $0.1<x<0.5$, $0.05<x<1.0$, and $0.05<x<1.0$, respectively. The local magnetic moment is essentially confined to the V atoms located in the surface layer with the largest magnetic moments of $1.0\mu_B$ for $x_{\mathrm{Ru}}=0.25$, $1.1\mu_B$ for $x_{\mathrm{Rh}}=0.25$, and $2.15\mu_B$ for $x_{\mathrm{Pd}}=0.9$. The magnetism survives an inward surface relaxation as large as 8% for RhV and PdV.

Our predictions rely on the density functional theory in the local spin density approximation of Vosko, Wilk, and Nusair.[16] The scalar-relativistic all-electron calculations were performed using the tight-binding linear muffin-tin orbital method[17] in the atomic sphere approximation. The substitutional randomness was described within the single-site coherent potential approximation while the surface of the semi-

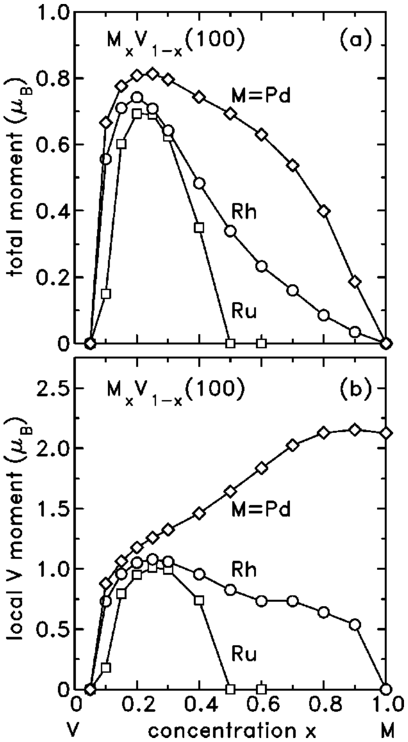

FIG. 1. (a) shows the total magnetic moment of the semi-infinite (100) Ru_xV_{1-x}, Rh_xV_{1-x}, and Pd_xV_{1-x} alloy as function of the $4d$ transition-metal concentration x. (b) shows the local V magnetic moment in the Wigner-Seitz sphere of a V atom located in the surface layer of the (100) surface of these alloys.

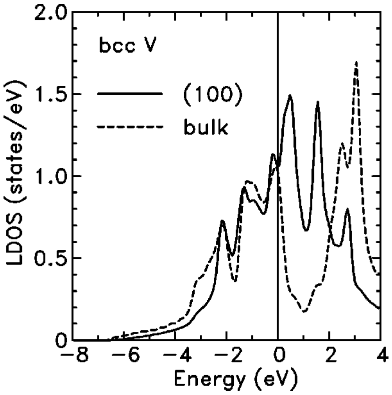

FIG. 2. LDOS per spin for a nonmagnetic V atom located in bulk V and at the V(100) surface. The Fermi energy coincides with the origin of the energy scale.

infinite solid was treated using a surface Green's-function technique.[18] The results presented below were obtained with equal Wigner-Seitz radii for both alloy components and with a complete neglect of lattice relaxations in the bulk and at the surface. This is a reasonable approximation for alloys consisting of species with nearly equal atomic volumes like the present systems, leading to small charge transfer effects in the bulk (smaller than 0.06 electrons in the V-rich region of the studied alloys). The atomic volume for a given alloy composition was set according to Vegard's law with respect to the experimental atomic volumes of pure constituents. Self-consistency of charge and spin densities was pursued in a finite region comprising seven atomic layers and three layers of empty spheres of an otherwise unperturbed solid-vacuum interface. The angular momentum cutoff $\ell_{max}=2$ was used, and the two-dimensional Brillouin zone was sampled with 45 $\mathbf{k}_{\parallel}$ points in the irreducible wedge.

The central results of our work are summarized in Fig. 1. Fig. 1(a) shows the total magnetic moment of the semi-infinite alloys. All three systems exhibit magnetism over a broad concentration range which is unexpected taking into account that all those bulk alloys are nonmagnetic and V, Ru, Rh, and Pd are nonmagnetic in the bulk and at the surface. The largest total moments of $0.7\mu_B$, $0.75\mu_B$, $0.8\mu_B$ were found for $Ru_{0.2}V_{0.8}(100)$, $Rh_{0.2}V_{0.8}(100)$, and $Pd_{0.25}V_{0.75}(100)$. A closer analysis reveals that the primary contribution to the magnetism is due to the large local moments of V in the surface layer. These are shown in Fig. 1(b). For RuV and RhV we find peak V moments of about $1\mu_B$ at about 25% Ru or Rh concentration. We observe an interesting trend, in that the range of concentration for which surface magnetism occurs increases from the RuV to the RhV and PdV alloy. We will come back to this point below. Opposite to the V moments in RuV or RhV alloys, the V moment in the surface of the PdV alloys increases monotonically until it reaches a maximum of $2.15\mu_B$ at 10% V concentration and remains nearly constant for any V concentration below that value. In line with this finding are recent results of Stepanyuk *et al.*[19] who calculated the magnetic moments of adatoms on the Pd(100) and the Pt(100) surface. For V on fcc Pd(100) a moment of $2.8\mu_B$ was found very similar to our value of $2.1\mu_B$ determined for the low V concentration limit in the surface of the bcc PdV(100).

The values of the V moments decrease rapidly from the surface into the bulk. In the subsurface layer they are already significantly smaller and amount to a maximum of $-0.15\mu_B$, $-0.2\mu_B$, $-0.4\mu_B$ for $Ru_{0.25}V_{0.75}(100)$, $Rh_{0.3}V_{0.7}(100)$, and $Pd_{0.6}V_{0.4}(100)$, respectively. The V moments in the subsubsurface layer can be safely ignored. Also the local magnetic moments of the Ru, Rh, or Pd atoms are negligible at the surface and any layer below the surface and negligible for any alloy concentration. The largest moments for $4d$ metal atoms were found in the surface or subsurface layer with the maximum moment of $0.12\mu_B$, $0.06\mu_B$, $0.04\mu_B$ for RuV(100), RhV(100), and PdV(100), respectively. We can safely say that the surface magnetism of the alloys is confined to the two top atomic layers at the surface. Although the magnetic moments of V atoms decrease rapidly into the bulk, the direction of the moments show a clear oscillatory behavior from layer to layer along the surface normal.

In order to understand the origin of the surface magnetism of these alloys and to understand the concentration dependent trends in going from Ru to Rh and Pd observed in Fig. 1 we turn to the discussion of the local density of states (LDOS). As said above the V(100) surface was one of the candidates to show surface magnetism of an otherwise nonmagnetic solid, but failed to become magnetic. This failure can be understood in terms of the simple Stoner model, in which ferromagnetism should occur if the Stoner criterion, $In(E_F)>1$, is satisfied, where $n(E_F)$ is the nonmagnetic density of states at the Fermi energy E_F and I is the exchange integral. From Fig. 2, which shows the LDOS of a V atom at the surface and in the bulk, we see that (i) both have roughly the same $n(E_F)$ and surface magnetism of V is not

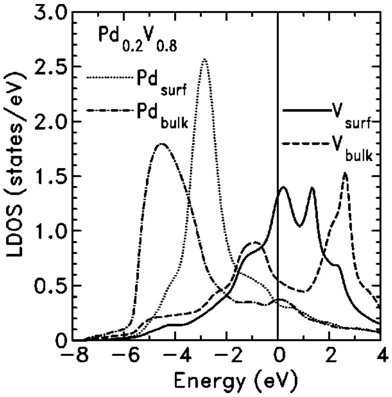

FIG. 3. LDOS per spin for a V and Pd atom located in the bulk and at the surface of the nonmagnetic $Pd_{0.2}V_{0.8}$ alloy.

more likely than magnetism in the bulk and (ii) a few tenths of an eV above E_F we find a strong peak in the LDOS due to the d_{z^2} Tamm-like surface state located in the pseudogap separating bonding from antibonding states typical for bcc metals. The main effect of alloying is now to broaden this peak due to the scattering of electrons in the random alloy. In Fig. 3 we show the LDOS for Pd and V atoms for the $Pd_{0.2}V_{0.8}$ alloy in the bulk and at the surface. Most significant is the large LDOS at E_F for the V atom in the surface, which is larger than for the pure V(100) surface, satisfies the Stoner criterion and is clearly the driving force for the surface magnetism of the alloy. The sum of Pd and V LDOS at E_F is at a minimum for the bulk alloy which makes ferromagnetism impossible, but is the origin of a dominating antiferromagnetic susceptibility along the [100] direction normal to the surface and the origin of the layered antiferromagnetic oscillations of V moments into the bulk. The hybridization between V and the 4d element decreases in the sequence from Ru to Rh and Pd, which explains the slight increase of the total moments and the concentration dependent trends discussed above.

Until now we have discussed the surface magnetism over the entire concentration range of the alloy, irrespective of the existence of the alloys. There are a few points of concern: (i) From bulk phase diagrams[20] it is known that these bulk alloys exist as bcc alloys only in the V-rich regime up to about 25% Ru, 18% Rh, or 30% Pd, respectively. On the one hand this is not a severe limitation since the maximum total moments are just in the range where bulk alloys exist. (ii) On the other hand at the surface the concentration range for which an alloy forms is typically not identical to the bulk alloy. At the surface, the concentration region forbidden for the formation of the bulk alloy could, for example, become accessible by the growth of the 4d atoms on the 4d V bulk alloys with subsequent tempering. Or one can approach the low-V concentration limit of fcc alloys by the growth of V on the Ru, Rh, or Pd(100) surface, which may become magnetic as indicated by the results of Stepanyuk *et al.*[19]

(iii) For a given bulk alloy concentration, the chemical composition of several atomic layers close to the surface differs from the bulk due to surface segregation. This results in a concentration profile, which depends on temperature, bulk concentration and kinetic energies involved. We have investigated the interplay between surface segregation and surface magnetism for alloys with 80% of V, choosing exaggerated concentration profiles. Starting from the homogeneous concentration profile we considered an interchange of 20% of the atoms for both species, but restricted only between the first two surface layers, which leads to the formation of a pure V monolayer either in the top surface layer or in the subsurface one. In general, our calculations show that the segregation of V increases the magnetism and, vice versa, the segregation of a 4d element reduces it. A comparison of total energies reveals a tendency of Rh and Pd to enrich the top surface layer and to extinguish the ferromagnetic state in our exaggerated model. The segregation tendency decreases from Pd to Rh and Ru in full agreement with the trend of surface energies of pure 4d metals.[21] In the $Ru_{0.2}V_{0.8}(100)$ case there is no clear preference of any of the two components to segregate to the surface. Additionally for both exaggerated concentration profiles the surface magnetism was stable. However, it should be stressed that alloys can be realized also out of thermodynamical stability and the segregation profile may be in opposite to those suggested by total energy arguments.

TABLE I. Values of the magnetic moment (in μ_B) for a V atom in the top surface layer as a function of the (inward) relaxation Δz of the surface layer for alloys with 80% of V.

Alloy	$\Delta z = 0\%$	$\Delta z = -5\%$	$\Delta z = -8\%$
$Ru_{0.2}V_{0.8}$	0.99	0.57	0.00
$Rh_{0.2}V_{0.8}$	1.08	0.72	0.36
$Pd_{0.2}V_{0.8}$	1.21	0.85	0.53

(iv) The relaxation of the surface atoms affects the surface magnetism. We tested the effect of the inward relaxation of the top surface layer on the surface magnetism for the three different alloys with 80% V. We included relaxations of $\Delta z = -5\%$ and $\Delta z = -8\%$ of the bulk interlayer distances. These are realistic values in the light of the experimentally determined contraction of the surface to subsurface interlayer distance of 7% with respect to the bulk value for the pure V(100) surface.[22] The results are summarized in Table I. They show that for $Rh_{0.2}V_{0.8}$ and $Pd_{0.2}V_{0.8}$, the magnetism discussed here is strong enough to survive these large surface relaxations.

The setup of the calculations allowed for ferromagnetic and layered antiferromagnetic spin configurations. More complicated spin arrangements such as the $c(2\times2)$ antiferromagnetic one had been ignored. This is reasonable since the nearest-neighbor V atoms are not placed in the surface plane as, e.g., for V monolayers on Ag(100),[15] but in nearest-neighbor layers along the surface normal.

Summarizing, we have investigated the surface magnetism at the (100) surfaces of the binary RuV, RhV, and PdV alloys in the bcc structure over the entire concentration range. Although none of the bulk alloys are magnetic at any concentration, nor are V, Ru, Rh, Pd magnetic in the bulk or at any low-index surface, these alloys become magnetic at the surface over a rather large concentration range. The magnetism is basically due to the large magnetic moment of V in the surface layer. We found local magnetic moments of about 1μ_B for alloys with V concentrations around 75%, which should be possible to prepare according to the bulk phase diagram. The origin of the magnetism was traced back to an unoccupied surface state of the V(100), which becomes occupied due to alloying and causes the magnetic instability. This dominating surface state is strongly connected with the (100) orientation, thus other low-index surfaces of the nonmagnetic alloys, e.g., the (110) or (111) surface, are expected to exhibit a significantly smaller tendency towards magnetism.

Since these arguments are rather general, we think there is a large number of bcc V alloys, e.g., OsV, IrV, PtV, CrV, and NiV, nonmagnetic as bulk alloys, which may become magnetic at the (100) surface. Most of them can be prepared for the magnetically interesting V concentrations of about 75%. Some of these alloys may also become magnetic in the fcc structure at the range of low-V concentrations.

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