

Magnetically Stabilized Surface Alloys

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1 Introduction

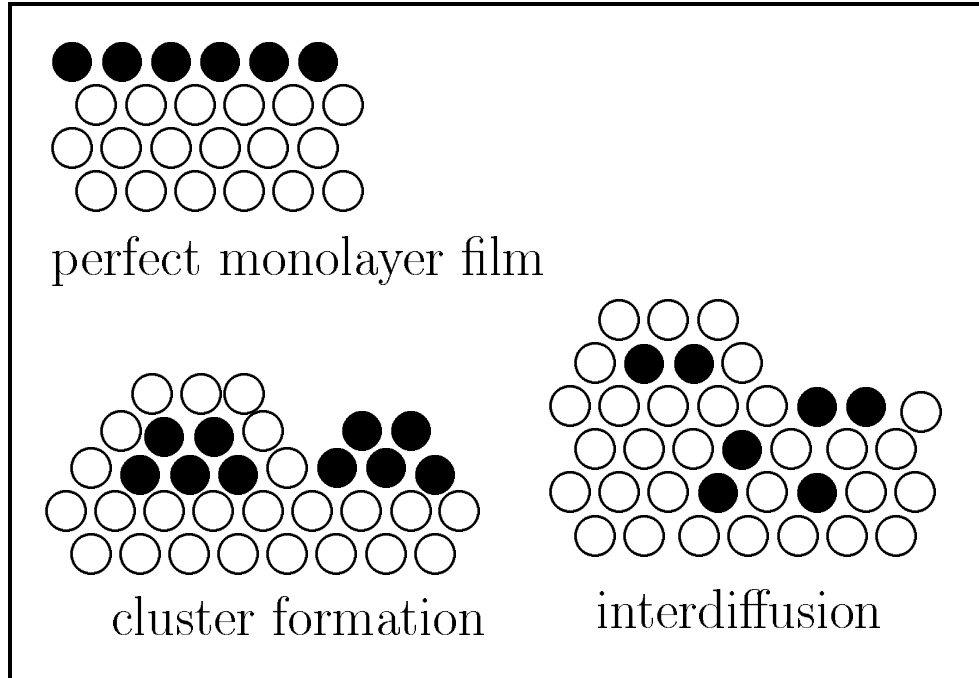
With the evolution of metallic systems from bulk through surfaces, ultrathin films, to linear chains and small atom aggregations the dimensionality, symmetry, and the coordination number, become increasingly important parameters for determining the properties of these systems. Magnetism is a feature which is particularly dependent on those parameters. The simplest low-dimensional system is the isolated atom. It is known that nearly all of the 30 transition-metal (TM) atoms have magnetic moments. In the middle of the transition-metal series the magnetic moments are as large as $5 \mu_B$. On the other hand, one knows that among the 30 transition-metals only five of them remain magnetic in their bulk crystalline phase: Co and Ni are ferromagnetic, Cr is antiferromagnetic, and Mn and Fe are ferromagnetic or antiferromagnetic, depending on their crystal structure. Low-dimensional transition-metals should fall between these two extremes, and one may envisage a magnetic material which is nonmagnetic as a bulk metal but magnetic as an ultrathin film or as a nanostructure.

Furthermore, it is well-known that the formation of local magnetic moments plays an important role in the structure of metals and stability of alloys. Os and Ru, for example, crystallize in hcp bulk phases, but due to the magnetism, Fe crystallizes in bcc structure, although all three are isoelectronic. With the increase of local moments in low-dimensional metallic systems, the importance of magnetism for the structure and stability of these nanosystems should become increasingly more important. Recently, we have investigated this aspect for ultrathin magnetic films at one monolayer range. We have investigated the importance of the magnetism for the stability of these films and have come to an interesting conclusion that in certain cases magnetism stabilizes (ordered) two-dimensional surface alloys.

In the past, almost all *ab initio* investigations published on ultrathin magnetic films on diverse substrates described the ideal pseudomorphic ultrathin film with atoms located in the hollow sites formed by the adjacent substrate atoms. These investigations described well the electronic and magnetic properties of pseudomorphically grown films, within one surface terrace of at least 15 atoms across.

In general, however, it is experimentally very difficult to achieve pseudomorphic growth conditions. This is particularly true for transition–metal films grown on noble metal substrates. According to the conventional wisdom in this field, these types of films are thermodynamically unstable and are prepared in a metastable state. That means, they are kinetically stabilized, because the activation energy needed for diffusion is too high. Generally, the film is affected by: (i) by the surface diffusion of film atoms across the surface, which may well lead to cluster formation, and (ii) the interdiffusion of the film atoms into the substrate, which may well lead to the formation of bulk alloys or clusters of film atoms covered by substrate atoms. To illuminate both scenarios, schematically illustrated in Fig. 2, we start with a gedanken experiment of an ideal and perfect film at 0 K temperature. This film might be highly metastable and by increasing the temperature, one may finally reach the activation energy for the surface diffusion. Thus film atoms may diffuse along the surface which may then lead to the clustering of these atoms. After a further increase of the temperature one may finally reach the activation barrier for the substrate interdiffusion. Film atoms may diffuse into the substrate forming a bulk alloy or *vice versa* substrate atoms may wet the clustered film atoms.

Figure 2:



The above reasoning is supported by thermodynamic arguments where the surface free energy, γ , enters. Typically, the surface free energy of the 3d transition–metal film atoms,

γ_{3d} , is larger than the surface free energy of the noble metal substrate atoms, γ_{Cu} , γ_{Ag} , γ_{Au} , and a metastability of such films is anticipated. Despite the intensive study of 3d transition–metal monolayers on noble metal substrates, these arguments have hardly been questioned.

Experimentally, it is rather difficult to precisely determine absolute surface free energies. Usually, one measures the heat of vaporization and substitutes it into an empirical relation [1] to determine the surface free energy. It is clear, that transition–metal atoms forming ultrathin films are in a very different state than transition–metal surface atoms.

In particular, it is known from the work of the past years [2, 3, 4] that transition–metal atoms, constituting ultrathin films on noble metal substrates, show large magnetic moments, in most cases significantly larger than transition–metal surface atoms. The magnetic moments follow Hund’s first rule and are largest at the center of the transition-metal series (cf. Table 2). Various magnetic phases exist, with the $c(2 \times 2)$ antiferromagnetic phase being closest in energy to the $p(1 \times 1)$ ferromagnetic phase. In most cases both phases exist and the local moments are of a very similar size. A general trend has emerged: V, Cr and Mn monolayer films on noble metals are $c(2 \times 2)$ antiferromagnetic, and Fe, Co, and Ni are $p(1 \times 1)$ ferromagnetic. The energy difference between these two phases is in the order of 300 meV, which is a sizable energy on the scale of the formation energy of alloys.

Table 2: Local magnetic moments in μ_B /atom for 3d transition–metals as ferromagnetic (F) and antiferromagnetic (AF) 3d monolayers (ML) on Ag(001) [3], Pd(001) [5] and on Cu(001) [4]; “0” indicates that the calculated moment was smaller than the numerical accuracy estimated to be about $0.02\mu_B$ /atom. “?” indicates a system, for which the calculation was not carried to self-consistency.

			Ti	V	Cr	Mn	Fe	Co	Ni
ML	on Ag(001)	F	0.34	2.09	3.78	4.04	3.01	2.03	0.65
		AF	0	2.08	3.57	4.11	3.06	?	0
ML	on Pd(001)	F	0	0.51	3.87	4.11	3.19	2.12	0.89
		AF	0	1.39	3.46	4.05	3.20	1.99	0.59
ML	on Cu(001)	F	0	0	0	2.97	2.61	1.76	0.33
		AF	0	0	2.52	2.92	2.35	?	0

Since the magnetic energy is proportional to the square of the local magnetic moment, we expect sizeable additional contributions to the surface free energy of transition–metal film atoms, due to large magnetic moments. It is this additional gain of magnetic energy of a 3d metal atom, constituting the ultrathin film, which modifies the energy balance for the structure and stability of the ultrathin films, beyond the conventional arguments of surface free energies. This argument, that the change of the magnetism provides an additional contribution to the surface free energy, has been totally neglected in the past. We shall show that indeed magnetism has a considerable impact on the stability and structure of ultrathin films, and new magnetically stabilized ultrathin systems ought to be expected.

The following simple d band model (cf. Fig. 1) provides some key ideas as to what extent the formation of large magnetic moments will modify the structural stability of ultrathin films. For simplicity, we consider a transition–metal atom at half band filling (e.g. Mn). We first discuss the nonmagnetic state. The local density of majority and minority states are degenerate. All bonding states are occupied, all antibonding states are unoccupied. For atoms within the ultrathin film, due to the reduction of the coordination number, the local density of states (LDOS), $n(\varepsilon)$, is narrower than for atoms in the crystal. Since the cohesive energy (in this model the band energy $\int_0^{E_F} \varepsilon n(\varepsilon) d\varepsilon$) increases with the bandwidth, cohesive energy is gained when film atoms increase their coordination number. Therefore, the scenario of transition–metal atoms, around half band filling forming (hypothetical) nonmagnetic films, is determined by increasing their coordination number to gain maximum cohesive energy. This favors the interdiffusion of film atoms, and even more so the clustering of $3d$ metal atoms, either after interdiffusion or after diffusion along the surface. The latter $3d$ metal clusters will most likely be wetted by the substrate atoms.

In the second step we allow now the formation of local magnetic moments M . Magnetic energy $E_M = -\frac{1}{2}IM^2$ is gained. On the other hand, one loses kinetic energy and formerly occupied minority bonding states become unoccupied, while formerly unoccupied majority antibonding states become occupied, reducing the gain of the cohesive energy. Thus a new energy balance is found with a total energy lower than for the nonmagnetic case (otherwise no local moment could be stabilized and the system would remain nonmagnetic). For a $3d$ atom in an ultrathin film this energy balance will be different from that of a $3d$ atom in a bulk crystal. As compared to the bulk atoms, the film atoms encounter a reduction of the coordination number, which is accompanied by a narrowing of the LDOS, and a relative loss of the cohesive energy, but at the same time with an increase of the exchange splitting, and the local moment, respectively, which is accompanied by an additional gain of magnetic energy. That means, for the magnetic cases, transition–metal atoms encounter a competition between a rearrangement such as to obtain large coordination numbers to gain maximum cohesive energy, and an arrangement with a small coordination number to gain maximum magnetic energy. Consequently, magnetism tends to stabilize ultrathin films on noble metal substrates and to prevent transition–metal atoms from interdiffusion. This stabilization will be the stronger the larger the magnetic moments. However, from these qualitative arguments we are not able to give quantitative estimates for real systems.

In the following sections we present an analysis, carried out by means of *ab initio* total energy calculations, of the relationship between magnetism and structure, and stability of $3d$ transition–metal monolayers (TM) (TM = V, Cr, Mn, Fe, Co, Ni) on Cu(001). The analysis is subdivided into several steps: (i) first we show that $3d$ metal monolayers are not energetically stable against wetting by the Cu substrate atoms (cf. Sect. 3), (ii) the Cu(001) $c(2\times 2)$ TM substitutional surface alloys (one–monolayer–thick alloy films of Cu and $3d$ atoms, with a checkerboard structure of $3d$ atom and Cu sites (cf. Fig. 4)) is postulated in Sect. 4, (iii) the magnetic properties are discussed in Subsect. 4.1. The energetic

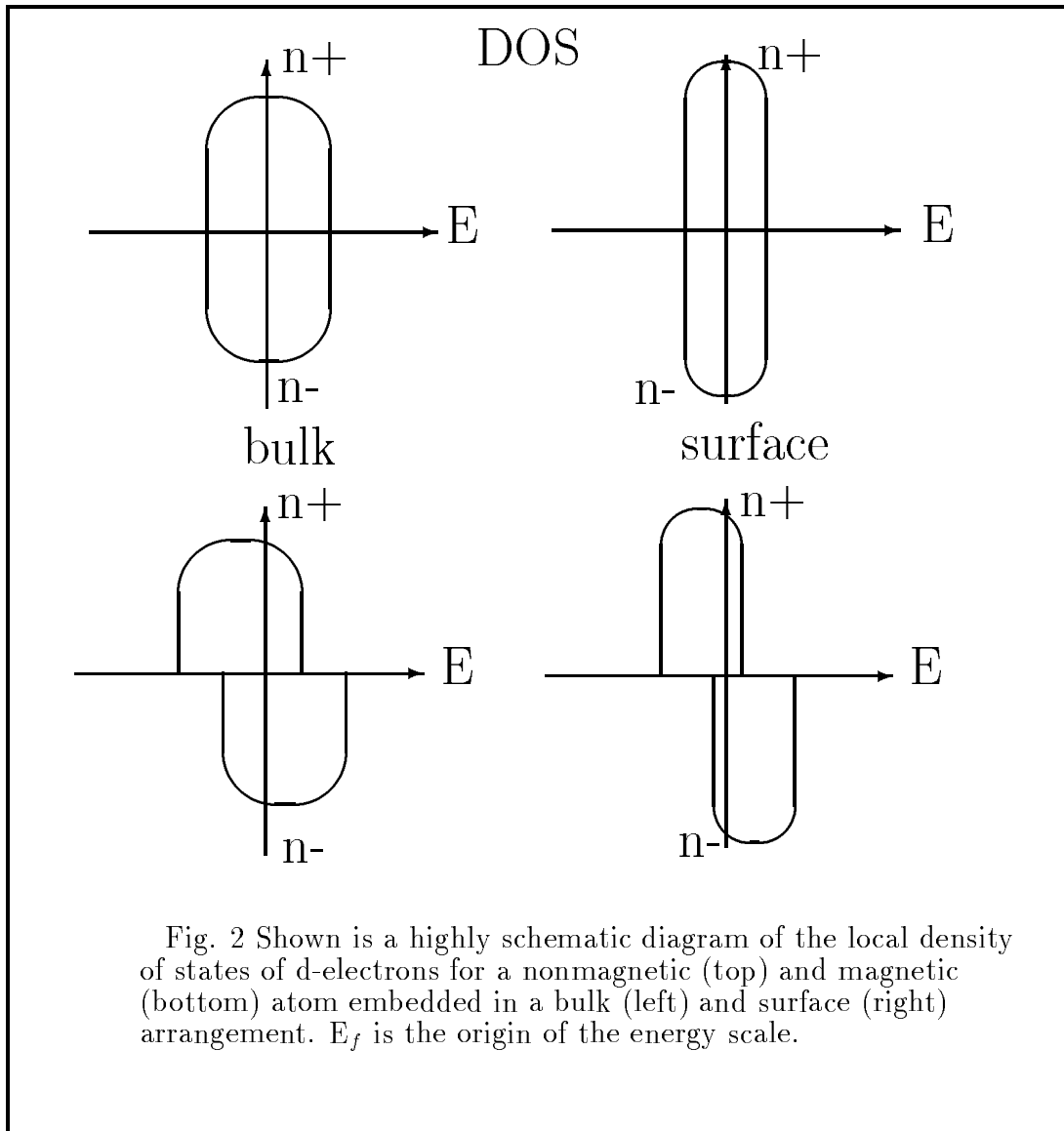


Fig. 2 Shown is a highly schematic diagram of the local density of states of d-electrons for a nonmagnetic (top) and magnetic (bottom) atom embedded in a bulk (left) and surface (right) arrangement. E_f is the origin of the energy scale.

stability of the transition-metal atoms constituting the $\text{Cu}(001)c(2 \times 2)\text{TM}$ surface alloys, against (v) interdiffusion and (vi) clustering, is investigated in Subsects. 4.2 and 4.3, respectively, and finally we comment on the underestimation of the magnetism by the local density approximation and discuss recent results obtained by the generalized gradient approximation.

2 Computational Details

All calculations were based on density functional theory in the local spin density approximation (LSDA). We used the exchange-correlation potential of von Barth and Hedin [6], but with the parameters as chosen by Moruzzi, Janak, and Williams [7]. The results for the $3d$ monolayers as overlayers and as interlayers, and the $c(2 \times 2)\text{TM}$ alloy film as overlayers and interlayers, were obtained with the full-potential linearized augmented-

plane-wave method (FLAPW) in film geometry [8, 9]. The unit cell contained typically 14 to 18 atoms. The lattice constant of Cu was determined by means of a total energy minimization with a bulk FLAPW code.

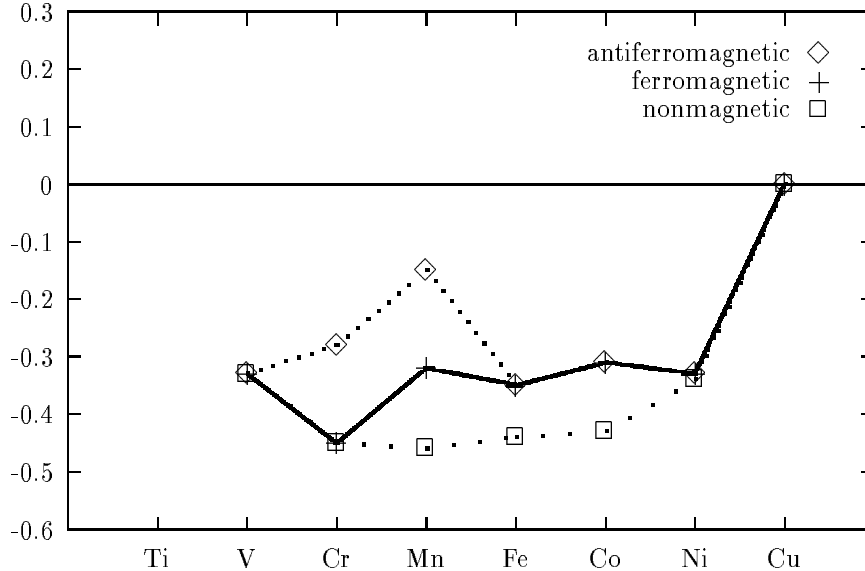
Recently, we have completed our new film and bulk FLAPW program [10], having the flexibility of calculating forces exerted on the atoms, which are used for a structural optimization of the atom positions, and which also includes the generalized gradient (GGA) approximation, in conjunction with the implementation of the appropriate fast Fourier transform (FFT)-methods, quasi-Newton methods to accelerate the convergence of the charge density. We have also explored possibilities of iterative and perturbational approaches to handle large systems. Thus the structure of some of these films have been determined by total energy [11] as well as by force calculations [12], and the calculations have been extended to include the GGA [13]. We used the versions by Perdew and Wang [14] and Perdew [15].

3 Energetic Stability of 3d Monolayers against Wetting by the Substrate

In order to investigate the energetics of wetting, we compare the total energies of monolayers, buried as interlayers (E_I) in bulk Cu(001), with the total energies of monolayers deposited as overlayers (E_S) on the Cu(001) substrate. The role which magnetism plays in modifying the stability of the 3d transition-metal films is elucidated by including calculations for p(1×1) ferromagnetic, c(2×2) antiferromagnetic, and (hypothetical) nonmagnetic monolayers.

The results of the energy differences $\Delta E_W = E_I - E_S$ – and I call this energy difference the wetting energy – are summarized in Fig. 4. We find, for all 3d transition-metal monolayers, irrespective of their magnetic state, that $\Delta E_W < 0$, which means that monolayers buried as interlayers in Cu(001) constitute the energetically preferred state. Consequently, the monolayer film on Cu(001) is in a metastable state, and an additional wetting by Cu atoms is thermodynamically favorable. The wetting energy for the (hypothetical) nonmagnetic 3d monolayers follows a parabola shaped curve, reflecting the d band filling, with an energy gain at maximum (0.47 eV per atom) for Mn at half band filling. On the other hand, one finds, in agreement with the simple model presented in Fig. 1, that magnetism tends to stabilize the monolayer films. The reduction of the wetting energy gain due to magnetism is largest for Mn monolayers (0.32 eV per atom), for which also the largest magnetic moment was found. Besides the local moment, the magnetic structure of the monolayer plays also a crucial role for the wetting energy. For Mn one observes a big difference for the wetting energies between the ferromagnetic and the c(2×2) antiferromagnetic states. For the ferromagnetic state the magnetic energy gain amounts to 0.15 eV per atom, as compared to 0.32 eV for the antiferromagnetic state. For Cr the ferromagnetic state does not exist and it is degenerate with the paramagnetic one. For Fe and Co the c(2×2) antiferromagnetic configuration is energetically unfavorable, and has not been

Figure 4: Wetting (or interdiffusion) energy $\Delta E_W = E_I - E_S$ in eV per transition–metal atom calculated for nonmagnetic (squares connected by widely spaced dotted line), ferromagnetic (crosses connected by full line), and $c(2 \times 2)$ antiferromagnetic (diamonds connected by dotted line) $3d$ monolayer films on Cu(001). The solid line connects the magnetic ground state solutions. For $\Delta E_W < 0$ (> 0), wetting by the Cu substrate or interdiffusion into the Cu substrate, respectively, is energetically preferred (prohibited). The results are obtained from calculations neglecting any atom relaxation (all atoms are positioned at the sites of the perfect Cu lattice).



calculated. For Ni this configuration is degenerate with the nonmagnetic one. Although magnetism tends to stabilize the monolayer films, the strength of this effect is too weak.

4 Cu(001) $c(2 \times 2)$ $3d$ Surface Alloys

In a further attempt to reduce the coordination number of transition–metal film atoms in order to increase their magnetic moments, with the prospect of obtaining magnetically stabilized ultrathin films, we make at this point an *ad hoc* postulation of a new class of ultrathin magnetic films: the $c(2 \times 2)$ substitutional surface alloys – actually more accurately of the $c(2 \times 2)$ substitutional surface compounds. This type of ordered phase, schematically illustrated in Fig. 4, can be thought of as a checkerboard type monolayer film consisting of $3d$ metal atoms, where every second transition–metal atom is substituted by a substrate atom, Cu in this particular example. The surface unit cell is classified by the notation $c(2 \times 2)$ and we call these surface alloys $c(2 \times 2)\text{CuTM}/\text{Cu}(001)$ or $\text{Cu}(001)c(2 \times 2)\text{TM}$, respectively.

Within the surface compound layer the $3d$ transition–metal atoms are not nearest neighbour atoms, as for monolayer films, but next nearest neighbour atoms. Thus the overlap between the $3d$ wavefunctions is substantially reduced. This is the effective reduction of the coordination number mentioned above. As we shall see below, due to this reduction of the $3d$ overlap, each $3d$ transition–metal atom within the surface compound can, at least

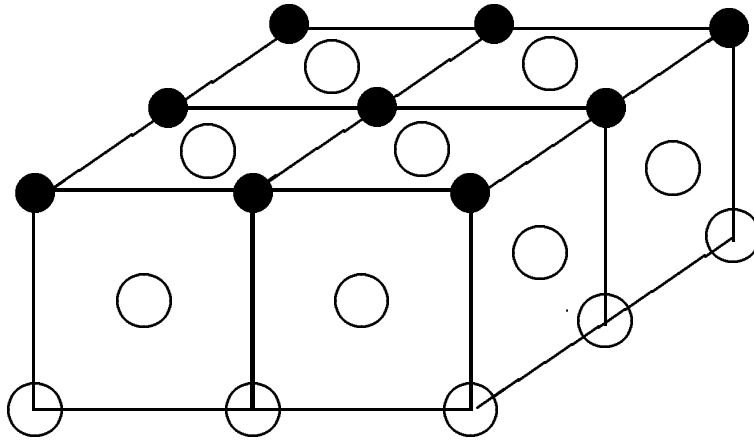


Fig. 4 Schematic representation of a substitutional $(001)c(2 \times 2)$ TM surface compound film of one monolayer thickness (black dots indicate the transition metal grown as overlayer on a fcc (001) substrate (open circles)).

from the viewpoint of the local magnetic moments, be considered in the first approximation as a $3d$ surface impurity in the surface of $\text{Cu}(001)$. Therefore, the interpretation of the $c(2 \times 2)$ surface compound in terms of an ordered, two-dimensional lattice of surface impurities, provides an additional aspect of this new class of films.

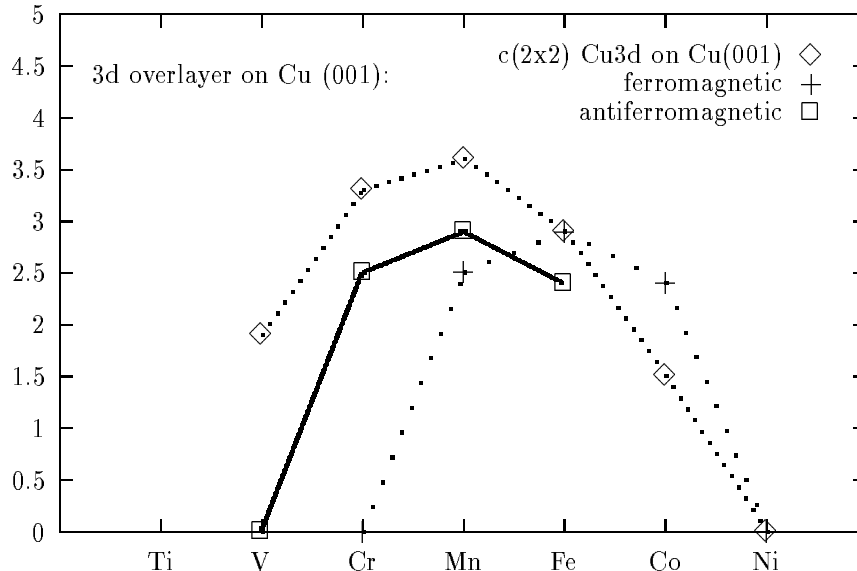
4.1 Local Magnetic Moments of $c(2 \times 2)$ Surface Alloys

The local magnetic moments of the $3d$ transition-metal atoms incorporated in the $\text{Cu}(001)-c(2 \times 2)$ TM surface compounds are shown in Fig. 6, together with the local magnetic moments for the $p(1 \times 1)$ ferromagnetic and $c(2 \times 2)$ antiferromagnetic phase of the $3d$ transition-metal monolayers. Indeed, we find that the reduction of the coordination number increases the magnetic moments of the transition-metal atoms within the surface alloy film. This is particularly true for the transition-metal atoms around the center of the $3d$ series: V, Cr, Mn. For V monolayers on $\text{Cu}(001)$ no magnetism was found, while for $\text{Cu}(001)c(2 \times 2)\text{V}$ the V moment is close to $2 \mu_B$. For Cr and Mn the magnetic moments increase by $0.8 \mu_B$ and $0.7 \mu_B$, respectively, in comparison to the moments of the $c(2 \times 2)$ antiferromagnetic phase of the full coverage monolayers on $\text{Cu}(001)$.

4.2 Stability of $c(2 \times 2)$ Surface Alloys against Interdiffusion into the Substrate

After the above *ad hoc* postulation of a $c(2 \times 2)$ substitutional surface compound as a new class of thermodynamically stable, two-dimensional magnetic films on noble metal substrates, we discuss in this subsection the stability of the transition-metal atoms within the surface alloy against an interdiffusion into the substrate, by comparing total energies (E_S) of $c(2 \times 2)\text{CuTM}$ films deposited on $\text{Cu}(001)$ to interlayer films buried in $\text{Cu}(001)$

Figure 6: Local magnetic moments in units of μ_B calculated for $c(2 \times 2)$ ferromagnetic $\text{Cu}(001)c(2 \times 2)3d$ surface compounds [16]. Results are compared with the local moments of $p(1 \times 1)$ ferromagnetic (plus signs connected by widely spaced dotted line) and of $c(2 \times 2)$ antiferromagnetic (empty squares connected by solid line) full coverage $3d$ monolayers on $\text{Cu}(001)$ [4].

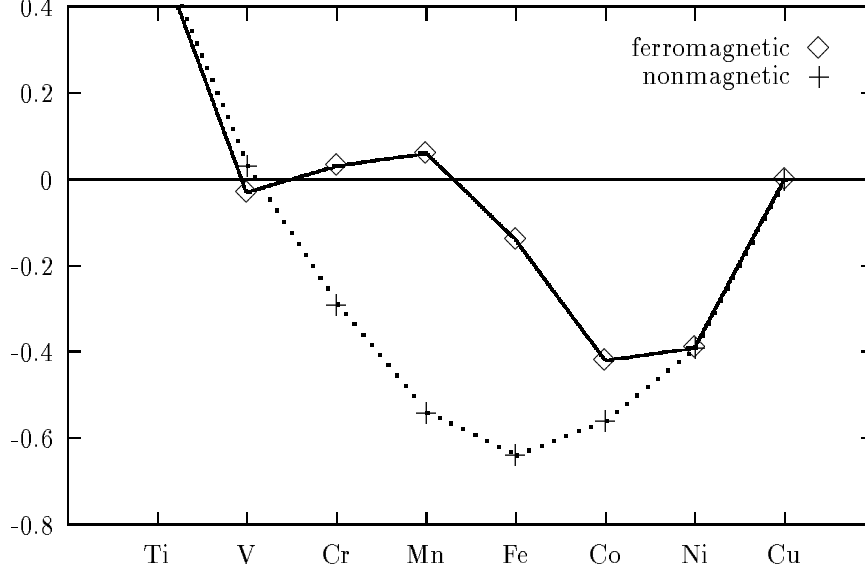


(E_I). Since the monolayer compound film is in first approximation representative of a two-dimensional lattice of impurities, the energy difference between the surface and the bulk layer is indeed close to the energy difference between a $3d$ impurity in the surface and in the bulk, and the energy difference may be called the interdiffusion energy or the segregation energy, depending on the sign of the energy difference. The impact of magnetism for the stability of the surface alloy films is analyzed by performing spin-polarized calculations as well as non-spin-polarized calculations of (hypothetical) nonmagnetic $c(2 \times 2)\text{CuTM}$ monolayer films for both structural configurations. The spin-polarized calculations have been carried out subject to the constraint, that only the ferromagnetic phase within the $c(2 \times 2)$ films was taken into account.

Fig. 7 shows the energy difference $\Delta E_I = E_I - E_S$. We first discuss the interdiffusion energy for the hypothetical nonmagnetic compound monolayers. Except for $\text{Cu}(001)c(2 \times 2)$ V and $\text{Cu}(001)c(2 \times 2)$ Ti, the energy difference ΔE_I is negative ($\Delta E_I < 0$), which means that the transition-metal atoms Cr, Mn, Fe, Co and Ni gain energy by interdiffusion, and for Ti and V interdiffusion is energetically prohibited. The interdiffusion energy follows a similar parabola as the wetting energy of the monolayers on $\text{Cu}(001)$, which are in both cases a result of the d band filling, just as expected from the simple model introduced above.

When we lift the constraint of nonmagnetism by carrying out spin-polarized calculations, all systems with the exception of the Ti and Ni based systems, become magnetic and we find for $\text{Cu}(001)c(2 \times 2)\text{Cr}$, Mn, and Fe a remarkable change in their interdiffusion energies. For $\text{Cu}(001)c(2 \times 2)\text{Cr}$ and $\text{Cu}(001)c(2 \times 2)\text{Mn}$, ΔE becomes even positive, which means magnetism indeed prevents Cr and Mn from diffusing into the Cu substrate. For

Figure 7: Interdiffusion energy $\Delta E_I = E_I - E_S$ in eV per transition-metal (TM) atom calculated for the $\text{Cu}(001)c(2 \times 2)3d$ monolayer compound films. Crosses connected by a dotted line indicate the nonmagnetic results obtained from non-spin-polarized calculations and diamonds connected by a solid line mark the results for compound films in the $c(2 \times 2)$ ferromagnetic configuration. For $\Delta E_S < 0$ (> 0), interdiffusion is energetically preferred (prohibited). The results are obtained from calculations neglecting any atom relaxation (all atoms are positioned at the sites of the perfect Cu lattice).



Fe and Mn the reduction of the interdiffusion energy amounts to about 0.6 eV and 0.5 eV, respectively. For Fe, this is not sufficient and magnetism cannot prevent Fe from the interdiffusion into the substrate. The effect of magnetism on $\text{Cu}(001)c(2 \times 2)\text{V}$ and Co remains small (~ 0.1 eV) although for V the interdiffusion energy changes sign, but this change is marginal. For Ti and Ni the effect of magnetism is absent, because Ti and Ni remain nonmagnetic in both configurations. To summarize at this point, $\text{Cu}(001)c(2 \times 2)\text{Cr}$ and Mn are promising candidates for magnetically stabilized surface alloys, and Ti may be a candidate for a nonmagnetic surface alloy.

4.3 Stability of $c(2 \times 2)$ Surface Alloys against Cluster Formation: The Formation Energy of Surface Alloys

The second necessary condition for confirming the existence of two-dimensional surface alloys is to prevent the alloy from phase separation. Phase separation of a surface alloy is synonymous with atom rearrangement such as to obtain the clean $\text{Cu}(001)$ substrate surface and the clustering of the former $3d$ transition-metal constituent surface alloy atoms. The clustering is modeled by the formation of monolayer films. The formation of thicker films such as double layer or triple-layer $3d$ metal films is neglected at this point. The stability of the surface alloy against the phase separation or the clustering, respectively, is investigated in terms of the formation energy

$$\Delta E_F(\{M\}, \{\Delta z_M\}) = E_{\text{Cu}(001)c(2 \times 2)TM}(M, \Delta z_M)$$

$$- \frac{1}{2} \left(E_{TM/Cu(001)}(M, \Delta z_M) + E_{Cu(001)}(\Delta z) \right), \quad (1)$$

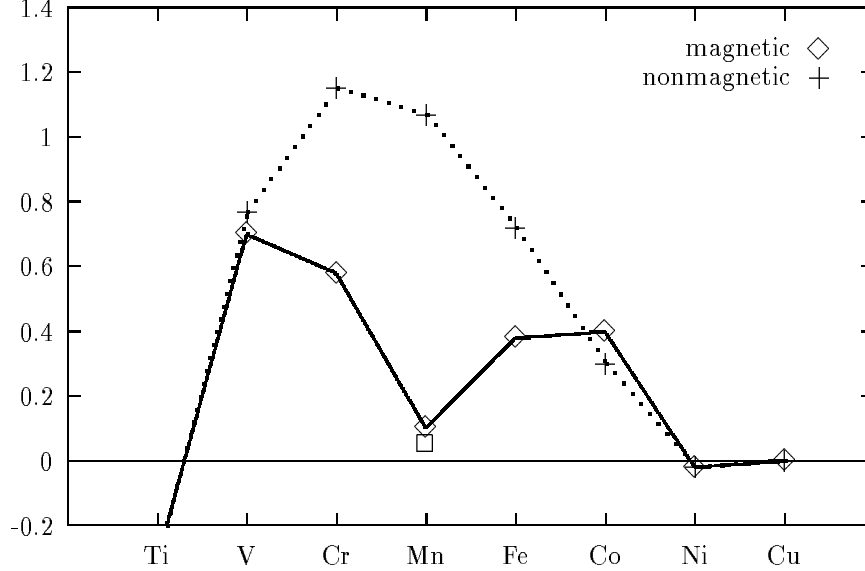
which is determined by the total energy difference between the systems containing the surface alloy ($E_{Cu(001)c(2 \times 2)TM}$) and the average of the total energies determined by the 3d monolayers on Cu(001) ($E_{TM/Cu(001)}$), and the clean Cu(001) surface ($E_{Cu(001)}$). The formation energy depends on the magnetism – (a) the local moments as well as (b) the magnetic ground state structure. The magnetism (M) enters twice, through the total energies of the surface alloys as well as of the monolayers. For each transition–metal constituent atom one has to include the minimum energy ground state magnetic configuration in order to obtain the ground state formation energy ΔE_F . For the surface alloys we included calculations for the nonmagnetic (P) as well as ferromagnetic (F) configuration ($M = P, F$) (possible antiferromagnetic phases are discussed here). For the monolayers on Cu(001) we include calculations for the nonmagnetic (P), the ferromagnetic (F), and the c(2×2) antiferromagnetic state (AF) as discussed above. The formation energy depends also on the atomic positions of the atoms of each of the 3 terms entering Eq. 1. In this work we determined the minimum energy bulk lattice constant of Cu (a_0^{Cu}) and in order to determine the ground state formation energy ΔE_F , one should at least include for each of these 3 terms the minimum energy interlayer relaxation Δz_M of the surface layers, which depend also on the magnetic state. At present, the interlayer relaxation is neglected ($\Delta z = 0$). We shall come back to this point below.

In Fig. 8 we compare the ground state formation energy $\Delta E_F(0)$ with the formation energy resulting from non–spin–polarized calculations $\Delta E_F(P, 0)$. We find, that without the formation of local magnetic moments the $\Delta E_F(P, 0)$ is positive for all 3d transition–metal elements with the exception of Ti and Ni. This means, that for all these systems phase separation or clustering, respectively, is expected. Phase separation is suppressed only for Cu(001)c(2×2)Ti and Cu(001)c(2×2)Ni films. The phase separation energy ($-\Delta E_F$) is largest for Cr and Mn with about 1.1 eV/TM atom. This means, hypothetical nonmagnetic Cu(001)c(2×2)Cr and Cu(001)c(2×2)Mn surface alloy films may never be thermodynamically stable and surface alloys may only be expected for Ti and Ni systems. For Ti, since all Ti systems remain nonmagnetic, the formation energy $\Delta E_F(P, 0)$ is equal to the ground state formation energy $\Delta E_F(0)$.

For the magnetic systems, the ground state formation energy $\Delta E_F(0)$ shows a remarkably different behavior. For Cu(001) c(2×2)V, ΔE_F and $\Delta E_F(P, 0)$ are close in energy. Then for Cu(001)c(2×2)Cr and Cu(001)c(2×2)Mn the formation ΔE_F decreases continuously to a minimum for the Mn system with a formation energy of about 100 meV/Mn atom. Then, it increases again for the Cu(001)c(2×2)Fe and Cu(001)c(2×2)Co systems, and for Cu(001)c(2×2)Ni, $\Delta E_F(0)$ and $\Delta E_F(P, 0)$ are nearly identical. Although we again find that, with the exception of Cu(001)c(2×2)Ni and Cu(001)c(2×2)Ti, all formation energies are positive and no surface alloy should be energetically stable, due to the existence of magnetism, there exists a pronounced kink in formation energy for the Mn system, indicative that the clustering process may well be suppressed.

In general one can say, that magnetism reduces the phase separation energy and supports

Figure 8: Shown is the formation energy $\Delta E_F = E_{Cu(001)c(2 \times 2)TM} - \frac{1}{2}(E_{TM/Cu(001)} + E_{Cu(001)})$ in eV per transition-metal (TM) atom for the Cu(001)c(2×2)3d surface compounds. Crosses, connected by a dotted line, indicate the nonmagnetic results yielded by non-spin-polarized calculations. The formation energies marked by diamonds, connected by a solid line, were determined by taking into account the magnetic ground state configuration for the monolayers and the c(2×2) ferromagnetic state for the surface compounds. For $\Delta E_F < 0$ (> 0), surface alloy formation (clustering) is energetically preferred. The results are obtained from calculations neglecting any atom relaxation (all atoms are positioned at the sites of the perfect Cu lattice). The square indicates the formation energy of the fully relaxed Mn system (i.e. including the relaxation for the atoms in the surface layer of the surface compound, the Mn monolayer on Cu(001) and the Cu(001) surface).



the surface alloy formation. This effect is strongest for Cr and Mn and less important for Fe. For Co it is the opposite, and for the V and Ni systems, magnetism remains unimportant. For Cr and Fe the support of magnetism is too weak and only the Mn system has a chance to become a magnetically stabilized surface alloy.

All these results have been obtained neglecting any interlayer relaxation. Since the Cu(001)c(2×2)Mn system is just at the edge of becoming a magnetically stabilized surface alloy, we have improved the investigations by including the interlayer relaxation for all 3 subsystems: ferromagnetic Cu(001)c(2×2) Mn, Cu(001), and the antiferromagnetic Mn monolayer on Cu(001). Including all these energies leads finally to a formation energy for Cu(001)c(2×2) Mn of 40 meV.

From the trend of the formation energy ΔE_F , where magnetism is included, and the absolute value of ΔE_F obtained for Cu(001)c(2×2) Mn, there is a strong indication that magnetism may well support the formation of this surface alloy. We believe that this is the LSDA answer to this problem. As we will see below the LSDA systematically underestimates the magnetism of the Mn/Cu systems. Recently performed calculations [13] including the GGA show a formation energy of about -180 meV (cf. Sect. 4.4).

To summarize the two sets of calculations, we investigated the stability of ultrathin magnetic films against alloying and interdiffusion. We found that all magnetic transition

metal films on Cu(100) at one monolayer range are thermodynamically unstable. The films show a strong tendency towards clustering and wetting by the Cu substrate. This has been confirmed in numerous experiments on Co/Cu(001) and Fe/Cu(001). For Mn, we found that the Mn monolayer is (nearly) unstable against alloy formation, and the Cu(001)c(2×2) Mn surface alloy is stable against interdiffusion, suggesting the existence of a two-dimensional surface alloy. Cr shows a tendency towards clustering, but at the same time it is stable against interdiffusion, if it is incorporated into the surface layer as surface impurity, and may show interesting behaviour at step edges. A Ni film is also unstable against surface alloy formation, but the surface alloy is unstable against interdiffusion, thus Ni will diffuse into the substrate and the Ni film will disappear (depending on the temperature and activation barriers). Ti is nonmagnetic, showing a strong tendency for surface alloy formation, and at the same time, the surface alloy is stable against interdiffusion. Thus Ti/Cu(001) is a strong candidate for a nonmagnetic surface alloy.

4.4 Experimental Evidence

Recently, four systems of this type of surface alloys have been identified, one of which has been realized in Jona’s group: Pd(001)c(2×2)Mn [17] and three of them in Wuttig’s group: Cu(001)c(2×2)Mn [18], Cu(011)c(2×2)Mn [12] and Ni(001)c(2×2)Mn [19]. Due to the thermodynamic stability of these films a very precise structural characterization by I–V LEED [17, 11, 20, 12] and atomically resolved STM [21, 22] became possible. In these STM images (not shown here) one observes very perfect regular arrays of Mn atoms located at c(2×2) positions. The Cu atoms remain typically unresolved. Cu(001)c(2×2)Mn and Ni(001)c(2×2)Mn electronic structure and magnetic properties have been investigated in detail by inverse [23, 24] and spin–polarized photoemission [24], as well as by soft x–ray absorption and magnetic circular dichroism [25, 26] has been carried out. Now, they belong to the best characterized ultrathin magnetic films of all. In particular, since the structure is simple and well defined, they became model systems for the comparison between theory and experiment.

Table 3: Structural data obtained by LEED analyses for different ordered surface alloys. Δz is the corrugation, ($z_{Atom\ 1} - z_{Atom\ 2}$) between the coordinates normal to the surface of the two structurally or chemically inequivalent atoms of a c(2×2) plane. Theoretical results (theo) are obtained by total energy or force calculations within the FLAPW-method.

Surface Alloy	Cu(100) c(2×2) Au	Cu(100) c(2×2) Pd	Cu(100) c(2×2) Mn	Ni(100) c(2×2) Mn
Δz [Å]	0.1	0.02 ± 0.03	0.30 ± 0.02	0.25 ± 0.02
Δz [%]	5.5	1.1 ± 1.7	16.6 ± 1.1	13.9 ± 1.1
theo [%]			14.0	11.5

In Table 3 we compile the structural results for ordered surface alloys formed on Cu(001)

and Ni(001) substrates, together with earlier examples of ordered surface alloys with $c(2 \times 2)$ structure, Cu(001) $c(2 \times 2)$ Au [27, 28], and Cu(001) $c(2 \times 2)$ Pd [29, 30]. However, the latter surface alloys are nonmagnetic like the majority of surface alloys known at present [31]. A comparison of the corrugation for the surface layer shows that the two alloys containing Mn have a much larger corrugation of 0.30 Å (MnCu) and 0.25 Å (MnNi) than the CuAu and CuPd surface alloys. The earlier trend in the corrugation of the CuAu and CuPd alloys are in line with the simple argument of Wu *et al.* [29] that the corrugation of the surface alloy layer increases with increasing difference in the atomic radii of the alloy constituents. This statement is consistent with the smaller buckling of the CuPd surface alloy as compared with the CuAu surface alloy, since the atomic radius of Au is larger than the one of Pd. If this tendency would also hold for Mn, one would expect an even smaller corrugation than for the CuPd surface alloy since the atomic radius of elemental Mn is smaller than the one of Pd. On the contrary, the corrugation found for the Mn surface alloy on Cu(001) and Ni(001) is even considerably larger than the corrugation of the CuAu surface alloy. This shows that simple size arguments are insufficient to explain the buckling of surface alloys.

We have performed a structural optimization by total energy minimization [11] and force calculations [12] for ferromagnetic and nonmagnetic Mn/Cu and Mn/Ni surface alloys. In case magnetism is artificially suppressed, the corrugation is practically zero, as expected from atomic radii. However, if we include magnetism, we obtain large outwards relaxations of Mn and slight inwards compression of Cu or Ni, respectively, ending up in corrugations close to experiment (cf. Table 3). Thus this large corrugation is explained in terms of a giant magneto–volume effect, which additionally stabilizes the surface alloys.

Further, the work function change was investigated upon the formation of surface alloys [24]. This was done probing by means of inverse photoemission the binding energy shift of the image potential (surface) state, which is known to be an ideal measure for a work function change. For example, the image state shifts from 4.1 eV for clean Cu to a 0.45 eV lower energy upon alloy formation with Mn. The ferromagnetic calculations yield a lowering of the work function in the same energy range (0.31 eV) going from Cu(001) to $c(2 \times 2)$ Cu/Mn/Cu(001), while calculations for a hypothetical nonmagnetic CuMn/Cu(001) surface alloy lead to a work function change which amounts only to 0.05 eV. Thus we have identified the formation of the high magnetic moments as the basic origin for the large modifications of the electronic structure which causes the work function change.

5 Limit of LSDA

A closer look reveals that the local spin density approximation systematically underestimates the surface magnetism of Mn. (i) The formation energy was found too small. The alloy exists over a large temperature range, but the calculated formation energy is positive, which means the alloy should not form and entropy, not included in the analysis,

should work against the alloy formation. (ii) The corrugation is systematically too small. (iii) The work function change is too small. (iv) The experimentally observed exchange splitting [24] is much larger than the theoretically determined one. Although the exchange splitting is not a ground state property and cannot be expected to be very precisely reproduced within the density functional theory, experience has shown that an agreement between theory and experiment, better than 1 eV, is not uncommon for transition-metal films.

In collaboration with T. Asada [13] we have started to extend the above calculations to the generalized gradient approximation on exchange and correlation of Perdew and Wang [15]. The results look very promising. The trends do not change, but the formation energy for the Mn/Cu surface alloy changes sign ($\sim -180\text{meV}$ instead of $+100\text{meV}$). A more complete analysis will be presented in future.

6 Summary and Outlook

Exemplary for 3d transition metal monolayers on noble metal substrates, detailed calculations for 3d monolayers on Cu(100) have been performed, showing clear trends as follows: i) Magnetism acts against interdiffusion. At low coverage, where the magnetism of Cr and Mn is very large, interdiffusion is suppressed. ii) Magnetism reduces clustering and promotes alloy formation. For Mn we find a strong tendency for alloy formation. From i) and ii) we expect for the case of the Cu substrate a thermodynamically stable, two dimensional surface alloy: Cu(100)c(2 \times 2)Mn. Although in detail, the results depend on the Cu substrate, the trends presented above have an universal character. Therefore, Cu(100)c(2 \times 2)Mn is only an example of a much wider class of magnetic surface alloys. Recently, several of these surface alloys have been found experimentally, in agreement with the trends presented above. We found in addition a nonmagnetic surface alloy Ti/Cu(001), which is not yet confirmed experimentally. Total energy and force calculations are applied to determine the structure of the surface alloys. From the comparison between theory and experiment we conclude that the LSDA underestimates the magnetism of Mn. Recent improved calculations using the GGA look promising.

While in this article we have shown the possibility of magnetically stabilized surface alloys, many questions remain unanswered. For example, do additional magnetic surface alloys exist, that are not based on Mn, but possibly on Cr? What is their magnetic order, how large is their critical temperature T_c for the magnetic transition, which surface alloys at one monolayer range will form multilayer alloy films? Do additional structural phases as a function of the coverage exist? Is there a structural order-disorder transition? What is the termination of the surface alloys at step edges. More questions can easily be asked. I hope we will answer some of these questions in future.

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