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Magnetism of alloyed models of $\mathrm{Cr(Mn)_xV_{1-x}}$ and $\mathrm{Mn_xCr_{1-x}}$ overlayers on V (001) substrates

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Abstract. The magnetism is calculated for substitutional alloyed of $\mathrm{Cr}_x(\mathrm{Mn}_x)\mathrm{V}_{1-x}$ monolayers (MLs) and $\mathrm{Cr}_x\mathrm{Mn}_{1-x}$ on V (001) surface with a variety of concentrations ($x = 0.25$, 0.50 and 0.75). The substitutional surface alloys were treated by an artificial super cell construction. Parallel magnetic ordering is obtained for all the considered structures. The surface net magnetization increases in terms of Cr (Mn) concentration in $\mathrm{Cr}_x(\mathrm{Mn}_x)\mathrm{V}_{1-x}$/V (001) system, while no serious variations occur in $\mathrm{Cr}_x\mathrm{Mn}_{1-x}$/V (001). Vanadium atoms at the interfacial layers acquire appreciable magnetic moments antiferromagneticly (AF) coupled with the surface moments.

PACS. 75.70.Ak Magnetic properties of monolayers and thin films

1 Introduction

Transition metals are considered to be well-promising candidates as constituents of synthetic magnetic structures due to their favorable properties. Intensive theoretical and experimental studies are devoted to investigate the magnetism of such structures. One of the exciting aspects of surface science is the discovery of unexpected magnetic behavior at surfaces and ultrathin films.

Although bulk Cr exhibits an antiferromagnetic (AF) behavior with magnetic moment 0.59 μ_B, the (001) surface exhibits a Ferromagnetic (F) structure as it was predicted theoretically using the tight-binding approximation with local magnetic moment of 2.8 μ_B [1]. This prediction is in agreement with the value obtained using spin-fluctuation theory [2], and full-potential linearized augmented plane-waves (FLAPW) method [3]. Experimentally Klebanoff *et al.* confirmed these values with a moment of 2.4 μ_B [4]. The exciting theoretical predictions concerning the magnetism of Cr surfaces have stimulated experimentalists to test a number of substrates such as Al, V, Fe, Co, Ag, Nb, W and Au for the growth of Cr ultrathin films, which have attained different success [5]. Furthermore, Zhang *et al.* [6] have observed a self-organized nanostructure on the Cr/Pt (111) system and Albrecht *et al.* [7] have discussed the growth and structure of Cr on Ru (0001). Ultrathin Cr films with a thickness less than 3 monolayers (MLs) appear to be face-centered-cubic (fcc) when grown on Pd (100) substrate. Blügel *et al.* [8] have reported on the magnetic properties of a Cr ML on Pd (001). Within FLAPW method in film geometry they have shown that Cr on the Pd (001) substrate orders in a $c(2\times2)$ AF structure favored by 24.5 mRy below the ferromagnetic configuration. The calculations of Cr slabs on Pd (001) substrate were extended by semi-emperical tight-binding method by Khalifeh [9], and these investigations have shown an in-plane AF structure and interlayer AF coupling in such structures. Overlayers of Cr were studied extensively, they exhibit $p(1\times1)$ and $c(2\times2)$ configurations when they are deposited on Fe and Ag, respectively [10–13].

The magnetic moment of Cr overlayer in Cr/V (001) system is found to be seriously larger than the bulk value and is AF coupled with an induced moment on V atoms at the interface [14]. In addition, V/Cr system was investigated using generalized gradient approximation and an appreciable magnetic moment of 2.1 μ_B was obtained on V overlayer, whereas the Cr moment was surprisingly reduced to 0.6 μ_B at the interface [15].

The magnetic moments of Mn overlayers up to three monolayers adsorbed on Cr substrates are studied in recent publications for different crystallographic orientations [16,17]. The magnetism in a magnetic/magnetic system is found to be less favorable in the (011) orientation with in-plane AF coupling. The onset of magnetism depends on the faces considered. A sizable induced moment appears in the Cr interface layer. The calculations show ferromagnetic sheets of both metals for the orientations (001) and (111) and a sort of $c(2\times2)$ configuration for the (011) orientation. Furthermore, $\mathrm{Cr_n}$/Mn systems show interesting magnetic properties associated with AF interlayer coupling in (001) and (111) orientations, while for

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(011) orientation, in-plane AF coupling between Cr moments occurs in the overlayers and continues in the interface layers.

This paper is organized as follows: Section 2 is devoted to the calculation method, Section 3 contains the results and discussion and Section 4 contains the summary.

2 Calculation method

The magnetic structures of the present systems are calculated using a self-consistent real space tight-binding method in the Hartree-Fock approximation of the Hubbard Hamiltonian. Our calculations in this method are based on the local density of states (LDOS) of the d-band. Using the recursion method [18] we can determine $n_i(\varepsilon)$, which is the LDOS of the ith site. The spin polarized local density of states (SPLDOS) with spin σ of the ith site, $n_{i\sigma}(\varepsilon)$, is determined by using the Hubbard Hamiltonian for d-electrons, which proved to be successful for most transition elements, where its diagonal terms are given by [19]:

$$\varepsilon_{i\sigma} = \varepsilon_d^o + U\Delta N(i) - \frac{1}{2}\sigma J\mu(i) \tag{1}$$

for the atomic site i with spin σ and intrasite exchange and direct Coulomb integrals J and U respectively. The number of d-electrons $N(i)$ and the local magnetic moment $\mu(i)$ at the site i are given by:

$$N(i) = \langle n_{i\uparrow}\rangle + \langle n_{i\downarrow}\rangle \tag{2}$$

$$\mu(i) = \langle n_{i\uparrow}\rangle - \langle n_{i\downarrow}\rangle \tag{3}$$

which are determined using the spin polarized density of states $n_{i\sigma}(\varepsilon)$, it is calculated within the recursion method [18], by requiring

$$\langle n_{i\sigma}\rangle = \int_{-\infty}^{\varepsilon_F} n_{i\sigma}(\varepsilon)\mathrm{d}\varepsilon. \tag{4}$$

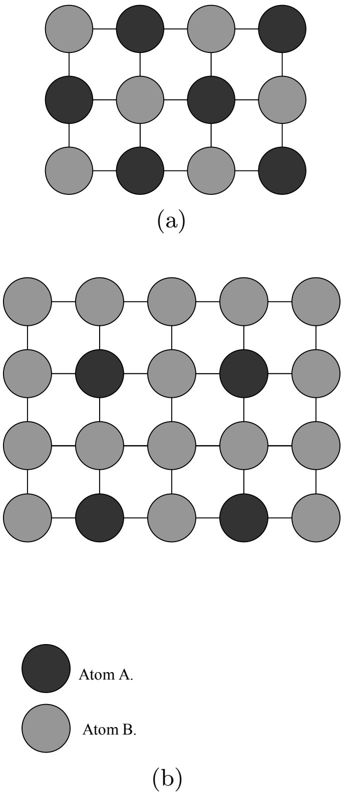
The charge transfer between different sites is given by:

$$\Delta N(i) = N(i) - N_d \tag{5}$$

where N_d is the average number of d-electrons at each site, *they are taken to be 4, 5, and 6 for V, Cr, and Mn, respectively.* If we impose local charge neutrality ($\Delta N(i) = 0$) by considering shifts Ω_i in the diagonal terms $\varepsilon_{i\sigma}$, then the term $U_i\Delta N(i)$ in equation (1) is replaced by Ω_i. This type of approximation has been successfully applied by Victora and coworkers [10,20]. We use the canonical tight-binding parameters that result from the atomic sphere approximation of Andersen [21]. In this model the hopping parameters are spin-independent and restricted to d-type electrons. They are given explicitly [22] as the inverse fifth power of the interatomic distance R_j between jth neighboring atoms

$$dd(\sigma,\pi,\delta)_j = (6,-4,1) \times (dd\delta)_1(R_1/R_j)^5 \tag{6}$$

and they are chosen in order to recover the d-band width of Varma and Wilson [23]. Equations (1, 3) are solved self-consistently and the procedure is stopped when the μ (output) $-\mu$ (input) is less than 10^{-4}.



(a)

(b)

Fig. 1. Top view of alloyed MLs V (001) substrates. (a) $\mathrm{A_{0.5}B_{0.5}}$ MLs on V (001) substrates ($c(2 \times 2)$ structure), (b) $\mathrm{A_{0.25}B_{0.75}}$ MLs of on V (001) substrates where $A(B) = Cr$, Mn, V.

3 Results and discussion

In this study we investigate the magnetism of substitutional alloyed monolayers (MLs) of Cr_x (Mn_x) V_{1-x} on V (001) substrates and also alloyed MLs of $\mathrm{Cr}_x\mathrm{Mn}_{1-x}$ on V (001) surface with different concentrations ($x = 0.25$, 0.50 and 0.75). Figure 1 represents top views of the periodic structure of the overlayers for a $c(2\times 2)$ structure (a), and alloyed structures of concentrations $x = 0.25$ and 0.75. Bulk Cr is known to be AF with a magnetic moment 0.59 μ_B so its exchange integral is adjusted to recover this value, however, Mn has a complex behavior of AF and F phases. These two phases were investigated in a previous work and the AF ground state was found to be more stable [16], so it is considered as the ground state of the present calculations and the exchange integral is the one used in previous publications [16,24,25]. With regard to bulk V it has a paramagnetic ground state and the exchange integral is obtained from LMTO calculations [26]. The lattice constants are 4.45 a.u., 4.40 a.u. and 5.71 a.u. for Cr, Mn and V, respectively [27].

The local magnetic moments of the substitutional alloyed overlayers of $\mathrm{Cr}_x\mathrm{V}_{1-x}$ ML on V (001) substrate are shown in Table 1. The local magnetic moment of Cr is 3.07 μ_B at the concentration $x = 0.25$, 2.89 μ_B at $x = 0.5$

Table 1. The magnetic moments, in units of μ_{B}, for Cr and V surface atoms (μ_{S}), the net magnetization of the surface moments (Net μ_{S}), V moments at the sublayers, ($\mu_{\mathrm{S}-1}$) and ($\mu_{\mathrm{S}-1}$), in $\mathrm{Cr}_x\mathrm{V}_{1-x}$/V (001) substitutional alloyed overlayer system, X refers to the concentration of Cr.

X	0.25	0.50	0.75	1.00
μ_{S}	3.07(Cr) 0.61(V)	2.89(Cr) 0.96(V)	3.00(Cr) 1.37(V)	3.13
Net μ_{S}	1.22	1.93	2.59	3.13
$\mu_{\mathrm{S}-1}$	−0.24	−0.44	−0.71	−0.94
$\mu_{\mathrm{S}-2}$	0.01	0.03	0.13	0.17

Table 2. The magnetic moments, in units of μ_{B}, for Mn and V surface atoms (μ_{S}), the net magnetization of the surface moments (Net μ_{S}), V moments at the sublayers, ($\mu_{\mathrm{S}-1}$) and ($\mu_{\mathrm{S}-1}$), in $\mathrm{Mn}_x\mathrm{V}_{1-x}$/V (001) substitutional alloyed overlayer system, X refers to the concentration of Mn.

X	0.25	0.50	0.75	1.00
μ_{S}	3.33(Mn) 0.40(V)	3.30(Mn) 1.44(V)	3.32(Mn) 1.63(V)	3.32
Net μ_{S}	1.13	2.37	2.90	3.32
$\mu_{\mathrm{S}-1}$	−0.21	−0.52	−0.86	−1.24
$\mu_{\mathrm{S}-2}$	0.04	0.03	0.20	0.35

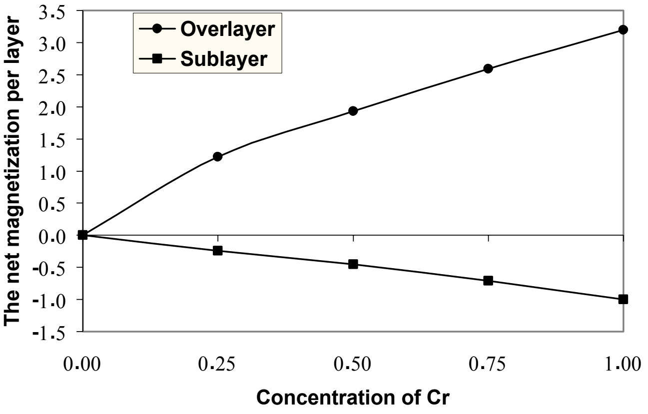


Fig. 2. The net magnetization per atom, in units of μ_{B}, for the $\mathrm{Cr}_x\mathrm{V}_{1-x}$ ML and V interfacial layer in terms of Cr concentration.

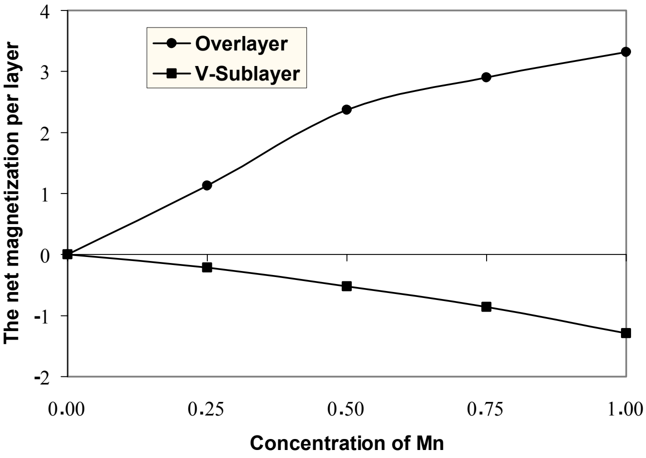


Fig. 3. The net magnetization per atom, in units of μ_{B}, for the $\mathrm{Mn}_x\mathrm{V}_{1-x}$ ML and V interfacial layer in terms of Mn concentration.

and 3.07 μ_{B} at $x = 0.75$. These values are close to that of Cr moments in the case of complete Cr monolayer on V (001), which is found to be about 3.13 μ_{B}. They are slightly affected by the presence of V atoms on the overlayer, however, appreciable induced magnetic moments are acquired by V atoms due to the hybridization of their d-bands with those of Cr atoms, 0.61 μ_{B} at $x = 0.25$, 0.96 μ_{B} at $x = 0.5$ and 1.37 μ_{B} at $x = 0.75$. The moments of both Cr and V at the surface are ferromagnetically coupled. Vanadium interfacial atoms also acquire appreciable magnetic moments, which are AF coupled with the net magnetization at the surface. Figure 2 displays the net magnetization of the overlayer in terms of Cr concentration, where it increases as the concentration increases. This figure reflects the AF coupling between the net magnetization and the magnetic moments of V interfacial atoms. The same behavior appears in the case of substitutional alloyed $\mathrm{Mn}_x\mathrm{V}_{1-x}$ ML on V (001) substrate, the magnetic moments of Mn surface atoms are almost constant are almost constant about 3.33 μ_{B} for all concentrations (Tab. 2). The induced magnetic moments on V surface atoms increase from 0.4 μ_{B} at $x = 0.25$ to 1.63 μ_{B} at $x = 0.75$. The net surface magnetization increases in terms of Mn concentration which and they are slightly larger than those of the previous system (Tab. 1) owing to the larger magnetic moment in bulk Mn [16]. There is also a slight increase in the induced magnetization of V interfacial induced moments and an interlayer AF coupling (Fig. 3).

The moments of surface atoms of substitutional alloyed $\mathrm{Cr}_x(\mathrm{Mn}_x)\mathrm{V}_{1-x}$ overlayers adsorbed on V (001) substrate exhibit parallel magnetic configuration unlike our previous studies using Pd (001) substrates [25,28]. In these recent studies we obtained a ferrimagnetic structure with

Table 3. The magnetic moments, in units of μ_B, for Mn and Cr surface atoms (μ_S), the net magnetization of the surface moments (Net μ_S), V moments at the sublayers, (μ_{S-1}) and (μ_{S-1}), in Mn_xCr_{1-x}/V (001) alloyed overlayer system, X refers to the concentration of Mn.

X	0.00	0.25	0.50	0.75	1.00
μ_S	3.13	3.21(Mn) 3.15(Cr)	3.38(Mn) 3.23(Cr)	3.39(Mn) 3.21(Cr)	3.32
Net μ_S	3.13	3.18	3.31	3.30	3.32
μ_{S-1}	−0.94	−1.02	−1.08	−1.15	−1.24
μ_{S-2}	0.17	0.23	0.29	0.28	0.35

a $c(2 \times 2)$-like configuration in the case of substitutional alloyed $V_{0.5}Pd_{0.5}$ overlayers on Pd (001) substrate [25] owing to the FCC geometry, and also it is the case in alloyed $Fe_{0.5}V_{0.5}$, $Fe_{0.5}Mo_{0.5}$ and $V_{0.5}Mo_{0.5}$ overlayers on Pd (001) substrates [28]. Monolayers of Cr (Mn) on Pd (001) substrates exhibit $c(2 \times 2)$ magnetic structures with zero net magnetization [9,24]. The in-plane AF coupling in these structures is ascribed to the fact that the surface atoms set in first neighboring positions. However, the case is different in the present BCC structures since the surface atoms are located in next neighboring positions, thus the net magnetization increases in terms of Cr (Mn) concentration till a $p(1\times1)$ configuration forms for a complete homogeneous ML. The in-plane F coupling was also obtained in Cr MLs adsorbed on stepped V surfaces except for edge-kink atoms that set in first neighboring positions [29] and also in V monolayers adsorbed on Mo stepped surfaces [30]. However, there is a quasi-AF configuration when the Cr ML is on stepped Pd (1 0 k) surfaces ($k > 0$) [31].

The other system investigated is the alloyed Mn_xCr_{1-x} ML on V (001) substrate with $x = 0.25$, 0.50, 0.75 and 1.00. The local magnetic moments are given in Table 3. A parallel magnetic configuration is obtained on the alloyed overlayer for various concentrations unlike the case of Mn (Cr) overlayers on Pd (001) substrates, which display $c(2 \times 2)$ structures [9,24]. This difference can be related to the geometrical structure of the substrate. In the case of Pd substrate, surface atoms are oriented in a FCC structure where they are in first nearest neighboring positions, thus their moments are AF coupled. On the contrary, when a BCC substrate is used such as V, the moments of the surface atoms are AF coupled with those of the interfacial layer, whereas they are F coupled at the surface since they are located in second neighboring positions. The surface net magnetization increases as the Mn concentration increases. This is ascribed to the larger magnetic moment of bulk Mn. Furthermore, it is obvious that magnetism persists with appreciable magnetic moments up to the subinterfacial layer for all the alloyed systems unlike the case of the substitutional alloyed structures.

4 Summary

In this work we used semi-emperical tight-binding method to investigate the magnetism of substitutional alloyed overlayers of Cr (Mn) and alloyed Mn_xCr_{1-x} ML on V (001) substrates. The main points of this study can be summarized as follows:

(i) The magnetic moments of Cr (Mn) atoms in substitutional alloyed overlayers adsorbed on V (001) substrates increase and consequently the surface net magnetization increases with concentration. This could be related to the fact that hybridization between Cr (Mn) *d*-bands with those of V surface atoms becomes less.

(ii) Appreciable induced magnetic moments are acquired by V surface atoms, which are F coupled with those of Cr (Mn) exhibiting a parallel magnetic configuration. In addition, V atoms in the interfacial layer acquire less moments AF coupled with those of surface atoms.

(iii) Alloyed overlayer systems of Mn_xCr_{1-x} MLs on V (001) substrate with $x = 0.25$, 0.5, 0.75 and 1 exhibit also parallel magnetic configurations. However, the local magnetic moments are larger than those of substitutional alloyed overlayers on V (001) substrates. Furthermore, the induced magnetic moments acquired by V surface atoms are larger in this case.

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