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First-principles studies on the structural and magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers

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Abstract. The structural and magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers with the tetragonal $L1_0$ ordered structure in paramagnetic, ferromagnetic, and three antiferromagnetic states are studied by means of the self-consistent full-potential linearized augmented-plane-wave method. By means of total-energy minimization, the lattice constants for their ground states are estimated. It is found that $L1_0$ ordered Cr/Ag has an AF1-type antiferromagnetic ground state with a large local moment of $3.30\mu_B$ at the Cr site, $L1_0$ ordered Mn/Ag has an AF2-type antiferromagnetic ground state with a large local moment of $3.63\mu_B$ at the Mn site, and the $L1_0$ ordered Fe/Ag monatomic multilayer has a ferromagnetic ground state with an enhanced moment of $2.75\mu_B$ at the Fe site.

1. Introduction

In recent years the magnetic multilayers have attracted considerable attention because of their novel physical properties such as enhanced magnetoresistance, large magnetic moment, perpendicular magnetic anisotropy, and oscillatory interlayer coupling [1]. Among the most extensively studied systems have been the transition-metal–noble-metal one, because this system has the advantage of good lattice matching. Recent developments in thin-film preparation techniques have made it possible to control film growth on the atomic scale. Takanashi *et al* [2] reported that the Fe/Au monatomic multilayers with the tetragonal $L1_0$ ordered structure can be fabricated artificially by alternate deposition of Fe(001) and Au(001) monatomic layers, although the Fe/Au system has a peritectic-type phase diagram and neither an intermediate phase nor an intermetallic compound exists in the equilibrium phase diagram [3]. The $L1_0$ ordered Fe/Au monatomic multilayer is ferromagnetic, and it possesses a large Fe moment exceeding the bulk value, a high Curie temperature, a large uniaxial magnetic anisotropy perpendicular to the Fe and Au atomic planes, and novel magneto-optical Kerr spectra. For this system, we have reported [4] that the $L1_0$ ordered Fe/Au monatomic multilayer has a ferromagnetic ground state with an enhanced moment, $2.76\mu_B$, of Fe, and the lattice constants determined are in good agreement with the experimental data given by Takanashi *et al* [2].

In this paper, we report the structural and magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers with the tetragonal $L1_0$ ordered structure. Existing experimental results for the Cr/Ag superlattice given by Kyuno *et al* [5] and Demuynck *et al* [6] have shown that a Cr/Ag superlattice with a monolayer of Cr can be fabricated artificially by the molecular beam epitaxy (MBE) method, with the Cr monolayer on Ag(001) being antiferromagnetic. Self-consistent calculations on ultrathin Cr films over different substrates and sandwich

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multilayers have predicted that the value of the magnetic moment will be enhanced by as much as a factor of five with respect to the bulk value for a Cr monolayer on a noble-metal substrate [7–11]. As for the magnetic configuration of a Cr monolayer, Blügel *et al* [8, 9] have suggested that the antiferromagnetic configuration is energetically more stable than the ferromagnetic structure. Similar results reported by us [4] show that the $L1_0$ ordered Cr/Au monatomic multilayer has a large local magnetic moment, $3.18\mu_B$, of Cr, and has an antiferromagnetic ground state. For the Mn/Ag superlattice, some experimental results have been reported in references [12–14]. Jonker *et al* [12] have studied experimentally the single-crystal Mn films and coherent Mn/Ag superlattices on Ag(001). They found that the Mn films exhibited a 2.89 Å square surface net, identical to that of Ag(001), and without a significant ferromagnetic contribution at temperatures down to 5 K. They concluded that the Mn atoms are antiferromagnetically coupled. Recently, Schieffer *et al* [14] have also studied the growth of a flat Mn monolayer on Ag(001) and shown the possibility of preparing well-ordered $p(1 \times 1)$ two-dimensional Mn monolayers on Ag(001) by means of photoelectron diffraction. They found that a flat monolayer with a good degree of perfection was actually achieved by deposition at a low rate on a substrate held at 80 K. Low-energy electron diffraction revealed a very sharp $p(1 \times 1)$ chemical cell pattern and it was attributed to in-plane $c(2 \times 2)$ antiferromagnetic order with a large local magnetic moment of Mn of about $4\mu_B$. For the Fe/Ag superlattice, experimental studies have been performed by several groups [15]. Recently, Runge *et al* [16] reported an induced magnetic hyperfine field in Fe(001)/Ag(100) multilayers; Krishnan *et al* [17] and Hicken *et al* [18] reported magneto-optical properties, and Temst *et al* [19] reported magnetic coupling in as-prepared states.

These experimental studies revealed that the (001) surface orientation promises a good epitaxy because many bcc transition metals such as Cr and Fe are lattice matched with the fcc noble metals Ag and Au by a factor of $\sqrt{2}$, thereby providing a one-to-one match for the atoms at (001) interfaces. According to these theoretical and experimental studies, it seems possible to artificially fabricate (Cr, Mn, Fe)/Ag monatomic multilayers with the tetragonal $L1_0$ ordered structure. In this paper, we give a detailed study of the structural and magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers with tetragonal $L1_0$ ordered structure by means of the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method [20], and discuss the numerical results obtained in connection with some experiments and previous theoretical studies.

2. Computational details

All of the calculations reported in this paper are performed using the FLAPW method, which is well known to enable accurate calculations of the electronic structures and magnetic properties of a wide range of crystals [21] to be made. The crystal structures of Cr/Ag, Mn/Ag, and Fe/Ag are tetragonal $L1_0$ ordered structures as shown in figure 1. Although the $L1_0$ structure can be reduced to the primitive structure which is regarded as a tetragonally distorted B_2-type structure, in the present study we adopt the $L1_0$ structure without reduction. To keep the close-packed arrangement as a FCC-like structure, the muffin-tin radii of Ag and Cr (Mn, Fe) are set to

$$R_{\mathrm{Ag}} = (\sqrt{2}a)/4 \qquad \text{and} \qquad R_{\mathrm{Cr}} = \sqrt{a^2 + c^2}/2 - R_{\mathrm{Ag}}$$

in the present calculations.

For $L1_0$ ordered structure, five AF models have been proposed by Pál *et al* [22]. In order to study exactly the magnetic properties of the $L1_0$ ordered Cr/Ag, Mn/Ag, and Fe/Ag

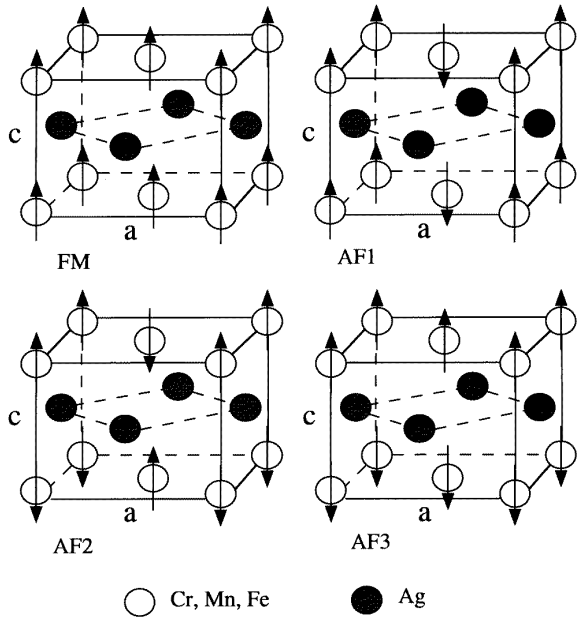

Figure 1. The magnetic structure in the tetragonal $L1_0$ ordered lattice for (Cr, Mn, Fe)/Ag monatomic multilayers. The open circles represent magnetic atoms, the filled ones Ag. The arrows represent the directions of the magnetic spins.

monatomic multilayers, the present calculations are performed in detail for paramagnetic (PM), ferromagnetic (FM), and the three simplest antiferromagnetic (AF1, AF2, and AF3) states, as shown in figure 1 (the other two AF states are higher in energy, and the results for these are not shown here). In the present calculations, for the PM, FM, and AF1 cases, a four-atom magnetic cell is used, and for the AF2 and AF3 cases an eight-atom magnetic cell (two stacked $L1_0$ cells) is used.

In spin-polarized calculations, the Moruzzi–Janak–Williams exchange–correlation function [23] is used. The Brillouin zone sampling is performed by using 1000 and 1800 special-k-point-meshes, which yielded 90–156 points in the irreducible Brillouin zone. In the case of going from the single (PM, FM, AF1) to the doubled (AF2, AF3) unit cell, the density of k-points in reciprocal space has been kept almost constant, in order to reach the same accuracy level. The energy cut-off parameter $R_{MT}K_{max} = 8.0$ (in au) is fixed in our calculations.

To find the most stable ground-state structures of these systems, the total energy as a function of the volume is calculated. By means of total-energy minimization, the structure geometries of $L1_0$ ordered (Cr, Mn, Fe)/Ag monatomic multilayers are determined. The self-consistent calculation is stopped when the total-energy convergence achieves 0.01 mRyd/unit cell.

3. Results

The calculated total energy as a function of volume for the tetragonal $L1_0$ (Cr, Mn, Fe)/Ag monatomic multilayers is shown in figure 2, where the volume is given by $V = a^2c$; the lattice constant $a = 4.08$ Å for Cr/Ag, in figure 2(a), and Mn/Ag, in figure 2(b), and

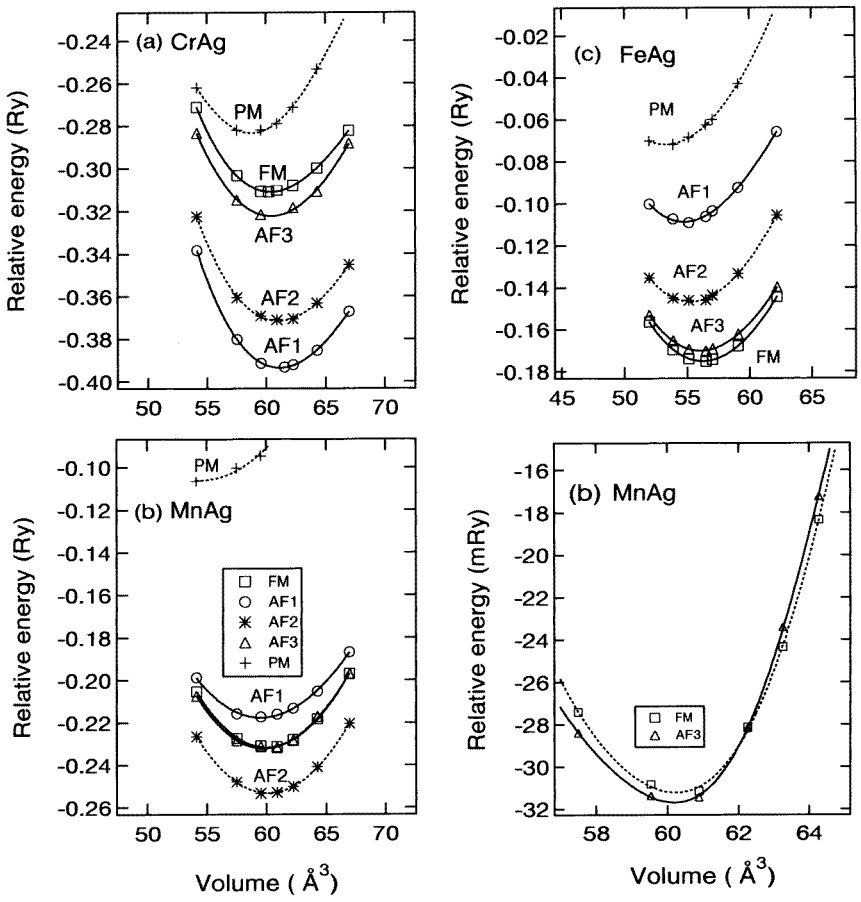

Figure 2. The relative total energy as a function of the volume V for $L1_0$ ordered (Cr, Mn, Fe)/Ag monatomic multilayers in paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AF1, AF2, and AF3) states. The volume is given by $V = a^2c$; the lattice constant $a = 4.08$ Å in (a) Cr/Ag and in (b) Mn/Ag, and $a = 3.97$ Å in (c) Fe/Ag.

$a = 3.97$ Å for Fe/Ag, in figure 2(c). From these curves we found the minimum of the energy for the magnetic states considered here, and determined the equilibrium volume or lattice constants.

For the $L1_0$ Cr/Ag monatomic multilayer, as shown in figure 2(a), three antiferromagnetic states are obtained; their energy curves lie below the equilibrium FM and PM states. Among the antiferromagnetic states, the AF1 state has lower energy than the AF2 and AF3 states, and it is energetically the most stable state. On the other hand, for the $L1_0$ Mn/Ag monatomic multilayer, as shown in figure 2(b), the antiferromagnetic states behave differently to those of Cr/Ag. The FM energy curve lies below the AF1 state, but above the AF2 state, and very close to the AF3 state (there is a first-order phase transition from the AF3 to the FM state as the volume is expanded). For the $L1_0$ Fe/Ag monatomic multilayer, as shown in figure 2(c), the energy of the FM state is lower than those of the three antiferromagnetic states, and therefore the FM state is the most stable one.

In figure 3, the energy differences between the AF and FM minimum energies,

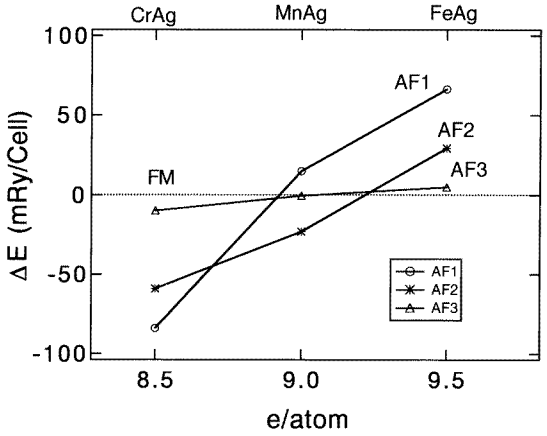

Figure 3. The total-energy difference $\Delta E_i = E_{\mathrm{AF}i} - E_{\mathrm{FM}}$ $(i = 1, 2, 3)$ as a function of the valence electron number.

$\Delta E_i = E_{\mathrm{AF}i} - E_{\mathrm{FM}}$ $(i = 1, 2, 3)$, are shown for CrAg, MnAg, FeAg as functions of the valence electron number. From this figure, we can see that the ground state has been changed from an AF state (Cr/Ag) to a FM state (Fe/Ag) as the number of 3d electrons was increased.

The main results, i.e. lattice constants, atomic magnetic moment, and relative energy of the FM, AF1, AF2, and AF3 states are summarized in table 1, together with the previous results. According to these results, we conclude that the $L1_0$ ordered Fe/Ag monatomic multilayer has a ferromagnetic ground state with an enhanced moment, $2.75\mu_B$, of Fe. On the other hand, $L1_0$ Cr/Ag and Mn/Ag are antiferromagnetic: Cr/Ag has an AF1-type antiferromagnetic ground state with a large local moment of $3.30\mu_B$ at the Cr site; Mn/Ag has an AF2-type antiferromagnetic ground state with a large local moment of $3.63\mu_B$ at the Mn site.

4. Discussion

The present numerical results for $L1_0$ Cr/Ag and Fe/Ag monatomic multilayers are very close to those for $L1_0$ Cr/Au and Fe/Au given in our previous paper [4]. For the Cr/Ag monatomic multilayer, $\Delta E_{1,2,3} < 0$, the three AF states are more stable than the FM state. The AF1 state is the most stable state, since the total energy favours the AF1 state by 83 mRyd/unit cell (measured by ΔE_1). In the AF1 ground state, Cr shows a large local moment of $3.30\mu_B$, and the lattice constants are estimated to be $a = 4.04$ Å, $c = 3.71$ Å. The local moment, $3.30\mu_B$, is close to the value $3.2\mu_B$ for an antiferromagnetic Au_4Cr alloy [24]. The lattice constant a is close to 4.08 Å, the lattice constant for fcc Ag, and $c = 3.71$ Å, which is in agreement with the experimental value of ∼3.78 Å for the [Cr 1 ML/Ag 10 ML] superlattice given by Kyuno *et al* [5]. For the Fe/Ag monatomic multilayer, $\Delta E_{1,2,3} > 0$, since the FM state is more stable than the AF states. $L1_0$ Fe/Ag shows a ferromagnetic ground state with an enhanced Fe moment of $2.75\mu_B$, which is close to the value $2.75 \pm 0.25\mu_B$ [2] for $L1_0$ Fe/Au given by Takanashi *et al*. In the ferromagnetic ground state, the lattice constant a is calculated to be 3.97 Å, which agrees with the experimental value of 3.99 Å [2], while c is 3.57 Å, which is close to the experimental value of 3.83 Å for the $L1_0$ Fe/Au superlattice [2]. The calculated results for Cr/Ag and Fe/Ag are very close to those for

Table 1. Calculated lattice parameters, magnetic moments (μ_B), and relative energies (mRyd) for $L1_0$ ordered (Cr, Mn, Fe)/Ag monatomic multilayers in paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AF1, AF2, and AF3) states.

		Lattice parameter (Å)				
System	State	a	c	c/a	Moment (μ_B)	Relative energy (mRyd)
Cr/Ag	PM	4.08	3.52	0.86		111
	FM	4.08	3.63	0.89	3.28	83
	AF1	4.08	3.67	0.90	3.29	0
		4.04	3.71	0.92	3.30	
	AF2	4.08	3.67	0.90	3.25	22
	AF3	4.08	3.65	0.89	3.23	72
Mn/Ag	PM	4.08	3.35	0.82		147
	FM	4.08	3.60	0.88	3.61	22
	AF1	4.08	3.60	0.88	3.63	36
	AF2	4.08	3.61	0.88	3.63	0
		4.05	3.63	0.90	3.63	
	AF3	4.08	3.63	0.89	3.64	22
Fe/Ag	PM	3.97	3.39	0.83		104
	FM	3.97	3.57	0.90	2.75	0
	AF1	3.97	3.48	0.88	2.33	66
	AF2	3.97	3.51	0.88	2.70	28
	AF3	3.97	3.56	0.90	2.76	5
PdMn ($L1_0$)	AF [22, 25]	4.07	3.58		4.4	
PtMn ($L1_0$)	AF [22, 26]	4.0	3.67		4.3	
FeAu ($L1_0$)	FM [2]	3.99	3.83		2.75	

Cr/Au and Fe/Au, because fcc Ag and fcc Au have the same lattice constant (about 4.08 Å), and similar electronic properties.

On the other hand, for the $L1_0$ Mn/Ag monatomic multilayer, as compared with those of Cr/Ag and Fe/Ag, some distinctive properties exist around the equilibrium states. First, $\Delta E_1 > 0$, i.e. the FM phase is more stable than the AF1 phase, and $\Delta E_{2,3} < 0$, i.e. the AF2 and AF3 states are more stable than the FM phase, and the total energy favours the AF2 state by 22 mRyd/unit cell (measured by ΔE_2). In the AF2 ground state, Mn shows a large local moment of $3.63\mu_B$, which is close to the experimental value of $4.0\mu_B$ for a Mn monolayer on Ag(001) [14], and the lattice parameters are estimated to be $a = 4.05$ Å, $c = 3.63$ Å. The calculated magnetic moment and lattice parameters are similar to those for $L1_0$ Mn-based alloys such as MnPd [22, 25] and MnPt [22, 26] as shown in table 1. We also note that experimentally no materials with the $L1_0$ ordered structure are found to have the AF2-type magnetic configuration, but similar magnetic structures exist in other FCC-based alloys such as Mn_3Pt (Cu_3Au structure) [22, 26] and in BCC-based alloys such as RhFe (CsCl structure) [27]. In view of the above, we consider that the ground state of the $L1_0$ Mn/Ag superlattice is AF2-type antiferromagnetic.

Incidentally, we appreciate that the LSDA adopted here might lead to an underestimation of the magnetic energy. However, since the competing magnetic phases studied here have roughly equal local magnetic moments (see table 1), their relative energies should have been well estimated by the present calculations, so the main results obtained here may not be compromised by the problems of the LSDA.

5. Summary

In summary, the structural and magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers with the tetragonal $L1_0$ ordered structure in paramagnetic, ferromagnetic, and antiferromagnetic states have been studied by means of the self-consistent full-potential linearized augmented-plane-wave method. It is found that the $L1_0$ Fe/Ag monatomic multilayer has a ferromagnetic ground state with an enhanced moment of $2.75\mu_B$ at the Fe site. On the other hand, $L1_0$ Cr/Ag has an AF1-type antiferromagnetic ground state with a large local moment of $3.30\mu_B$ at the Cr site, and $L1_0$ ordered Mn/Ag has an AF2-type antiferromagnetic ground state with a large local moment of $3.63\mu_B$ at the Mn site.

These theoretical explorations of the magnetic structure in the tetragonal $L1_0$ (Cr, Mn, Fe)/Ag monatomic multilayers have provided a plausible guide for experimental studies. One interesting point is the unusual magnetic properties in the Mn/Ag system, where the AF2 state is energetically more stable than the AF1 and FM states, since for most $L1_0$ Mn-based alloys, the AF1 state is the more stable experimentally. Experiments to verify this magnetic structure would be interesting.

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