Stabilities of spin configuration and exchange interactions in (Cr, Mn, Fe)/Ag monatomic multilayers

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(Received 26 November 1997; revised manuscript received 12 November 1998)

Ab initio calculations on the structural and magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers with tetragonal $L_1_0$ ordered structure in paramagnetic, ferromagnetic, and antiferromagnetic states are performed by means of the self-consistent full-potential linearized augmented-plane-wave method. By fitting the ab initio results to an Ising model, we have extracted exchange interactions in these systems and discuss general behaviors of the exchange interactions with respect to lattice relaxation and 3d electron filling. Finally, a zero-temperature phase diagram is given to describe the stabilities of the magnetic configurations.

[S0163-1829(99)03110-0]

I. INTRODUCTION

In recent years 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. The experimental studies revealed that the (001) surfaces of fcc noble metals Ag and Au allow for good epitaxy because many bcc transition metals such as Cr and Fe are lattice matched to them by a factor of $\sqrt{2}$, thereby providing a one-on-one match for the atoms at the interface. Recent technical progress makes it now possible to synthesize high quality artificial ultrathin films with stable or metastable lattice geometries in a layer-by-layer mode. In fact, the stable or metastable alloys such as $L_1_0$ FeAu (Ref. 2) and $L_1_0$ FePt (Ref. 2) can be fabricated artificially by alternate deposition of Fe and noble-metal (Au, Pt) monatomic layers. Although the $L_1_0$ FePt alloy exists naturally around equilibrium phase, FeAu system, on the other hand, has a peritectic-type phase diagram and neither intermediate phase nor intermetallic compound exists in the equilibrium phase. Therefore, the tetragonal $L_1_0$ ordered FeAu monatomic multilayer is of great interest because it adds a new member to the tetragonal $L_1_0$ family of ferromagnets.

A lot of experimental and theoretical works on the 3d/Ag superlattices have been performed, revealing the complicated ground state configurations of different systems. Existing experimental and theoretical results on CrAg superlattices showed that Cr/Ag with monolayer of Cr can be fabricated artificially by using the molecular-beam epitaxy method, and Cr monolayer on Ag(001) is antiferromagnetic with a large local moment. As for the magnetic configuration of Cr monolayer, Blügel et al. suggested that the in-plane antiferromagnetic configuration $c(2 \times 2)$ is energetically more stable than the ferromagnetic structure. For Mn/Ag superlattice, several experimental results have already been reported in Refs. 10–12, and it is concluded that Mn atoms are antiferromagnetically coupled. Low-energy electron diffraction reveals a very sharp $p(1 \times 1)$ chemical cell pattern and it is attributed to an in-plane $c(2 \times 2)$ antiferromagnetic order with a large local magnetic moment of about $4 \mu_B$ per Mn atom. For the Fe/Ag superlattice, experimental studies have also been performed by several groups. Recently, Runge et al. reported the interface induced magnetic hyperfine field in Fe(001)/Ag(100) multilayers; Krishnan et al. and Hicken et al. reported the magneto-optical properties, and the magnetic coupling in as-prepared states has been reported by Temst et al. In our recent papers, we also gave some fundamental studies on the superlattice of CrAu, FeAu, and FeCu. These theoretical works have given a good understanding to relevant experimental results. Although many theoretical works have already been done, a systematic study of the general behavior of exchange interactions and the stabilities of spin configurations does not exist to our knowledge. The aim of the present paper is to discuss general behaviors of the exchange interaction with respect to lattice relaxation and the number of valence electrons and to study the stabilities of spin configurations for $L_1_0$ ordered (Cr, Mn, Fe)/Ag systems.

II. COMPUTATIONAL DETAILS

All the calculations reported in this paper are performed by using the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method in a scalar relativistic version without spin-orbit coupling. It is one of the most accurate schemes for the electronic structure calculations and magnetic properties of crystals. For the tetragonal $L_1_0$ ordered structure, which will be considered in this work, five antiferromagnetic (AF) configurations have been proposed by Pål et al. Although primitive results have been obtained for limited configurations, in order to study the
exchange interactions, we have to know the magnetic properties of all the collinear spin configurations (see Fig. 1), so that we have performed the ab initio calculation for AF4 and AF5 configurations. In spin-polarized calculations, we adopt the Moruzzi-Janak-Williams exchange-correlation function. The Brillouin-zone sampling is performed using 90–156 special \( k \) points in the irreducible Brillouin zone. The muffin-tin radii of Ag and Cr (Mn, Fe) are set to \( R_{\text{Ag}} = (\sqrt{2}a)/4 \) and \( R_{\text{Cr}} = \sqrt{a^2 + c^2}/2 - R_{\text{Ag}} \). The energy cutoff parameter is fixed that \( R_{\text{MT}} K_{\text{max}} = 8.0 \) in the present calculations. To find the ground state structures of these systems, the total energies are fully minimized with respect to lattice constants \( a \) and \( c \). The obtained total energies and magnetic moments (integrated within the muffin-tin spheres) have been shown in Figs. 2 and 3 as functions of the \( c/a \) ratio with \( a \) fixed at 3.97 Å for Fe/Ag and 4.08 Å for (Cr,Mn)/Ag systems. Although the local spin-density approximation procedure is usually believed to underestimate the equilibrium lattice constants, we do not think that it seriously affects the results discussed in this work.

**III. RESULTS AND DISCUSSION**

It is well known that the magnetic properties of the 3\( d \) metallic alloys with large moments can qualitatively be explained by Moriya’s rule, antiferromagnetism occurring for nearly half-filled \( d \) shells and ferromagnetism for larger \( d \) band fillings. In order to understand the present results, we fit the obtained total energy \( (E_T) \) to the following Ising exchange model:

\[
E_T = E_{\text{PM}} + \sum_i E_{M} - \frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j
\]

to describe the stability of the spin configurations, where, \( E_{\text{PM}} \) is the total energy in the paramagnetic (PM) state, \( E_{M} \) is the single ion magnetizing energy, \( \sigma \) is the projection of the unit vector in the spin direction, \( J_{ij} \) is exchange integral, and the sum runs over all pairs of lattice sites \( (i,j) \). We consider here the nearest-neighbor (NN) and next-nearest-neighbor (NNN) for the in-plane \( (J_1 \) and \( J_2 \) ) pairs and between interlayer \( (J_{1L} \) and \( J_{2L} \) ) planes, and estimate these reduced parameters by least-squares fitting to the following equations according to counting the number of antiparallel pairs in one unit cell in the five AF states:

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**FIG. 1.** Magnetic configurations for the tetragonal \( L1_0 \) ordered (Cr, Mn, Fe)/Ag monatomic multilayers. The arrows represent the directions of the magnetic spins.

**FIG. 2.** Total energies as functions of the \( c/a \) ratio for the \( L1_0 \) ordered (Cr, Mn, Fe)/Ag superlattices in paramagnetic (PM), ferromagnetic (FM), and five antiferromagnetic (AF1, AF2, AF3, AF4, and AF5) states, plotted for the lattice constant \( a \) fixed at 4.08 Å for (Cr,Mn)/Ag, and 3.97 Å for Fe/Ag.
In the case of Fe/Ag, the $J$ values are obtained without $\Delta E_1 = E_{\text{AF1}} - E_{\text{FM}}$, since AF1 state is a low spin state (see Fig. 3), and $E_M$ could be obtained accordingly.

Figure 4 shows the magnetization energies ($E_M$) as a function of the $c/a$ ratio. It is clear that the magnetization energies of Cr, Mn, and Fe are decreasing functions of the volume, so that the magnetic states are more stable than the PM ones with the equilibrium volumes being expanded compared with those in PM states. We also note that the magnetization energy exhibits an atomic character. For instance, for Fe, the same behavior is found in other systems such as $L1_0$ FeCu, $B_2$ FeCu superlattices and bcc Fe. The same is true in the behavior of CrAu.

On the contrary, exchange interactions in Fe/Ag show different behavior compared to Cr/Ag system. The exchange parameters $J_1$, $J_2$, and $J_1L$ are mostly positive, so that FM coupling between the Fe atoms are preferred. One can also confirm from Fig. 2 that the FM and AF3 states with in-plane FM coupling have lower energies than other AF configurations. The fact, that the energy difference between FM and the dominating interaction is the antiferromagnetic coupling between in-plane nearest neighbors. This character is clearly seen from Fig. 2 that for Cr/Ag system all the states with in-plane AF couplings (AF1, AF2, AF4, AF5) are energetically lower than those with in-plane FM couplings (AF3, FM). The same is true in the behavior of CrAu.

In Fig. 5, the exchange parameters $J$ are shown as functions of the $c/a$ ratio. We found that in the case of Cr/Ag, the in-plane NN coupling $J_1$ shows a very large negative value over the whole $c/a$ range, and the other coupling parameters $J_2$, $J_1L$, and $J_2L$ are all relatively small. This fact indicates that the dominating interaction is the antiferromagnetic coupling between in-plane nearest neighbors. This character is clearly seen from Fig. 2 that for Cr/Ag system all the states with in-plane AF couplings (AF1, AF2, AF4, AF5) are energetically lower than those with in-plane FM couplings (AF3, FM). The same is true in the behavior of CrAu.

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AF3 is very small, can help us to understand the oscillatory behavior of the interlayer coupling via noble metals (Au, Ag) within systems such as Au/Fe/Au/Fe/Au(001) sandwiches.  

The most complicated system is Mn/Ag. The in-plane exchange parameters \( J_1 \) and \( J_2 \) of the \( L1_0 \) Mn/Ag are both negative and close to each other, which would lead to frustration for the in-plane spin configuration. The two interlayer interactions show opposite values. All exchange values are smaller than those of the Cr/Ag and Fe/Ag cases. As shown in Fig. 2, energetically \( L1_0 \) Mn/Ag favor the AF2-type magnetic configuration than the other five configurations. However, due to the competing nature of the above shown interactions, exact determination of the ground-state spin configuration in the \( L1_0 \) Mn/Ag case should go beyond the present calculation to a much larger planar unit cell.

Considering the competitions between those exchange interactions, we have drawn a zero-temperature spin-configuration phase diagram in Fig. 6, to describe all magnetic solutions corresponding to those proposed by Pál et al. The positions of Cr/Ag, Mn/Ag, and Fe/Ag with data corresponding to the equilibrium volumes have been indicated in this figure. We find that the Cr/Ag and Fe/Ag systems locate at the middle of the AF1 or FM phase regions far away from the boundary, implying such configurations might be quite stable. On the other hand, the Mn/Ag system locates near the phase boundary of AF2 and AF4. This fact suggests that exact equilibrium configuration might be closer to the present AF2 and AF4 configurations [in fact, the ordered compound MnAu has a \( \rho 3 \) antiferromagnetic structure with ferromagnetic sheets lying normal to the short axis (like AF4) of its tetragonal distorted CsCl-type cell].

Finally, we represent the energy difference between the AF and FM minimum energies, \( \Delta E_{L1_0} = E_{AF} - E_{FM} \) as a function of the number of valence electrons (3d4s) for (Cr,Mn,Fe)/Ag in Fig. 7. We see that the increase in the number of valence electrons leads to the stabilization of FM ordering (as in Fe/Ag), but a decrease tends to stabilize the AF configuration (as in Cr/Ag). Mn/Ag locates at the crossing point between the FM and AF ordering, exhibiting a competing behavior. The change of sign of \( \Delta E_{L1_0} \) (from AF to FM) occurs around 7.4 of the valence electron number (nuclear charge \( Z \sim 25.4 \)), which agrees very well with Moriya’s result on the 3d alloys and for the 3d overlayers on Ag (001) showed by Blügel et al.  

IV. SUMMARY

From the first-principles calculation on the magnetic properties of (Cr, Mn, Fe)/Ag monatomic multilayers with the tetragonal \( L1_0 \) ordered structure by the FLAPW method within the local spin-density-functional theory, we have studied the general behavior of both in-plane and interplanar stabilities of several spin configurations. It is shown that generally the Cr/Ag system favors strong in-plane AF coupling, the Fe/Ag system favors a FM coupling, while Mn/Ag system is a frustrated system. The ground state magnetic structure changes from AF to FM with increasing the 3d electron number from Cr/Ag to Fe/Ag, similar to the 3d overlayers on Ag (001) and also agrees very well with Moriya’s result on 3d alloys. An other important issue is that similar results also hold for the Au cases as obtained here for the Ag (001) superlattices because of the similarities in the electronic structures of Au and Ag.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research No. 00101930, from the Japanese Ministry of Education, Science, Sports and Culture. The authors would like to thank Professor P. Blaha, Professor K. Schwarz, Professor P. Dufek, and Professor R. Augustyn for offering us their first-principles program WIEN95. They also wish to express their sincere thanks to the Materials Information Science Group of the Institute for Materials Research, Tohoku University, for their continuous support of the HITAC S-3800/380 supercomputing facility. J.-T. Wang would like to thank the JSPS for financial support.