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First-principles calculation of the structural and magnetic properties of Fe/Au and Cr/Au monatomic multilayers

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Abstract. The structural and magnetic properties of Fe/Au and Cr/Au monatomic multilayers with the tetragonal $L1_0$ ordered structure in paramagnetic, ferromagnetic, and antiferromagnetic states are studied by means of the self-consistent full-potential linearized augmented-plane-wave method. It is found that the $L1_0$ ordered Fe/Au monatomic multilayer has a ferromagnetic ground state with an enhanced moment of $2.76\mu_B$ of Fe. On the other hand, the $L1_0$ ordered Cr/Au monatomic multilayer has an antiferromagnetic ground state with a large local moment $3.18\mu_B$ of Cr. By total energy minimization, the lattice constants for their ground states are determined.

In recent years magnetic multilayers have attracted considerable attention because of their novel physical properties, such as enhanced magnetoresistance, a large magnetic moment, and perpendicular magnetic anisotropy [1]. Recent developments of thin-film preparation techniques have made it possible to control film growth on an atomic scale. A typical example is that of the tetragonal $L1_0$ ordered structure, which consists of an alternate stacking of two different atomic planes, as shown in figure 1. Some ordered alloys such as AuCu and FePt are known to exist naturally with the tetragonal $L1_0$ ordered structure, which is generally produced by heat treatment of alloy samples below the order–disorder transformation temperature. Recently, Takanashi *et al* [2, 3] reported that the Fe/Au and Fe/Pt monatomic multilayers with the tetragonal $L1_0$ ordered structure can be fabricated artificially by alternate deposition of Fe and noble-metal (Pt or Au) monatomic layers. The Fe/Pt system has natural $L1_0$ ordered structure around an equiatomic composition in the equilibrium phase diagram [4]. On the other hand, the Fe/Au system has a peritectic-type phase diagram, and neither an intermediate phase nor an intermetallic compound exist in the equilibrium phase diagram [4]. Therefore, the tetragonal $L1_0$ ordered Fe/Au monatomic multilayer is of great technological interest, because it adds a new member to the tetragonal $L1_0$ family of ferromagnets.

In this paper, we report the magnetic properties of Fe/Au and Cr/Au monatomic multilayers with the tetragonal $L1_0$ ordered structure. For Fe/Au monatomic multilayers, an experimental result given by Takanashi *et al* [3] shows that the Fe/Au system can be fabricated artificially by depositing alternately monatomic layers of Fe and Au with the tetragonal $L1_0$ ordered structure, and that it is metastable at room temperature. The $L1_0$ ordered Fe/Au monatomic multilayer is ferromagnetic, and it has an Fe moment of about $2.5\mu_B$, a considerable Curie temperature, and a large uniaxial magnetic anisotropy perpendicular to the Fe and Au atomic planes. For this system, a theoretical study has also been performed by Shi *et al* [5]. Their calculations show that this artificial thin film is ferromagnetic, with an enhanced moment $2.75\mu_B$ of Fe. In their calculations, the lattice

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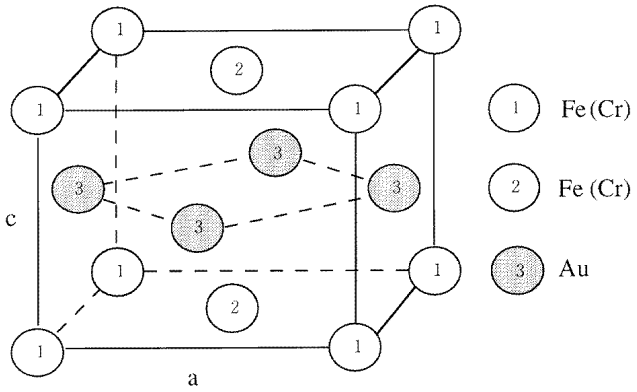

Figure 1. The crystal structure of the tetragonal $L1_0$ ordered structure.

constant was set to $a = a_{\mathrm{Au}} = 4.08$ Å, where a_{Au} is the lattice constant of fcc Au. Therefore, the structure is not fully optimized with respect to the lattice constants a and c. In the present work, we fully optimize the structure of Fe/Au of $L1_0$ ordered structure, and study its magnetic properties.

As far as we know, there have been no theoretical and experimental studies on the $L1_0$ ordered Cr/Au monatomic multilayer. Like Fe/Au, the Cr/Au system has a peritectic-type phase diagram, and neither an intermediate phase nor an intermetallic compound exist in the equilibrium state [4]. The solubility limit is very low around room temperature. However, the lattice matching in the plane for this 45° geometry between bcc Cr and fcc Au is almost perfect. i.e., $a_{\mathrm{Au}}/\sqrt{2} = 2.8836$ Å and $a_{\mathrm{Cr}} = 2.8839$ Å. This suggests that it is possible to artificially fabricate the ordered Cr/Au monatomic multilayer with $L1_0$ ordered structure. Previously, a number of studies have been made on ultrathin Cr films over different substrate and sandwich multilayers [6–10]. Self-consistent calculations predict that the size 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 [6–10]. As for the magnetic configuration of a Cr monolayer, Blügel *et al* [7, 8] suggest that the antiferromagnetic configuration is energetically more stable than the ferromagnetic structure. Similar results were also obtained by Oguchi and Freeman [10] for the Cr/Au superlattice, where the Cr magnetic moment may be as large as $2.94\mu_B$, and the in-plane AFM coupling is more stable than the FM coupling. In the present work, we fully optimize the structure of Cr/Au in the $L1_0$ ordered structure, and study its magnetic properties.

In order to study exactly the magnetic properties of the $L1_0$ ordered Fe/Au and Cr/Au monatomic multilayers, the calculations are performed for the three different cases, a paramagnetic (PM), a ferromagnetic (FM), and an antiferromagnetic (AFM) state.

All of the calculations reported in this paper are performed using the self-consistent full-potential linearized augmented-plane-wave method (FLAPW) [11]. The FLAPW method is well known to enable accurate calculations to be made of the electronic structure and magnetic properties of crystals [12]. The crystal structure of Fe/Au and Cr/Au is the tetragonal $L1_0$ ordered structure, as shown in figure 1. The $L1_0$ structure can be reduced to the primitive structure, which is regarded as a tetragonally distorted B_2-type structure, but in the present study we adopted the $L1_0$ structure without reduction. In this structure the number of inequivalent atoms is three, which are numbered 1, 2, 3 as shown in figure 1. The unit cell includes four atoms, at $(0, 0, 0)$, $(a/2, a/2, 0)$ for Fe (Cr), and at $(a/2, 0, c/2)$,

Table 1. Lattice parameters, magnetic moments (μ_B), and relative energies (mRyd) for Fe/Au and Cr/Au systems in paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AFM) states. $\Delta E = E_{\mathrm{AFM}} - E_{\mathrm{FM}}$. For $\Delta E < 0$, the AFM state is more stable than the FM state.

		Lattice parameter (Å)				
System	State	a	c	c/a	Moment (μ_B)	Relative energy (mRyd)
Fe/Au	PM	3.97	3.41	0.86		86
	FM	3.97	3.57	0.90	2.76	0.0
	AFM	3.97	3.49	0.88	2.22	60
	FM [3]	3.99	3.83	0.94	2.5	
	FM [5]	4.08	3.53	0.865	2.75	
Cr/Au	PM	4.02	3.54	0.88		100
	FM	4.02	3.62	0.90	2.52	84
	AFM	4.02	3.70	0.92	3.18	0.0
	FM [10]				2.94	10.9
	AFM [10]				3.0	0.0
Au_4Cr	AFM [14, 15, 16]			0.62	3.2	

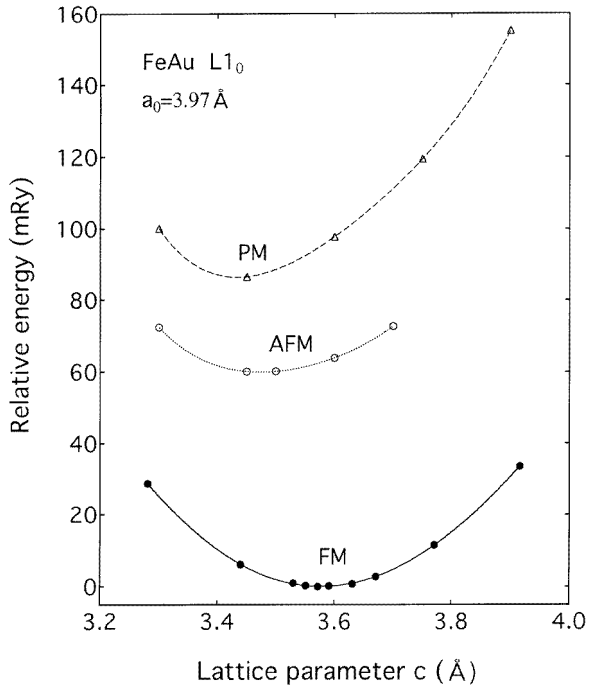

Figure 2. The relative total energy as a function of the lattice parameter c for the $L1_0$ ordered FeAu alloy in the paramagnetic, ferromagnetic, and antiferromagnetic states, where $a = 3.97$ Å. The total energy minimum is set to zero.

$(0, a/2, c/2)$ for Au. To keep the close-packed arrangement as an FCC-like structure, the muffin-tin radii of Au and Fe (Cr) are set to $r_{\mathrm{Au}} = (\sqrt{2}a)/4$, $r_{\mathrm{Fe}} = \sqrt{a^2 + c^2}/2 - r_{\mathrm{Au}}$ in

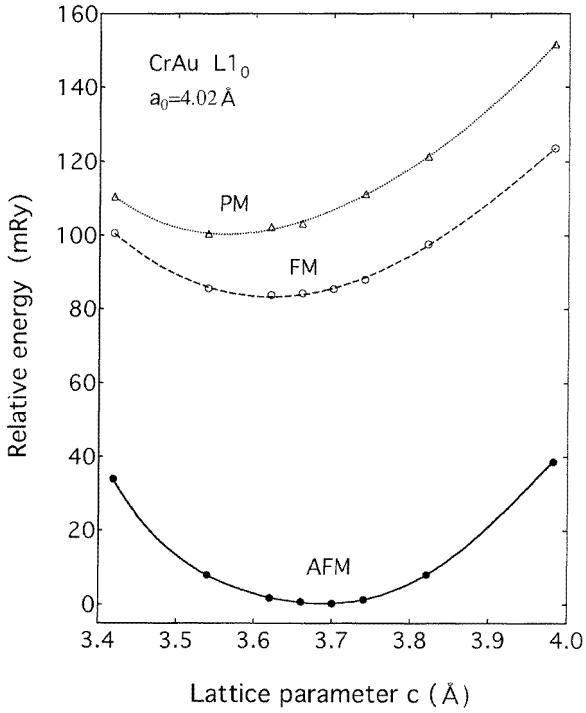

Figure 3. The relative total energy as a function of the lattice parameter c for the $L1_0$ ordered CrAu alloys in the paramagnetic, ferromagnetic, and antiferromagnetic states, where $a = 4.02$ Å. The total energy minimum is set to zero.

the present calculations.

In the present calculations, the Moruzzi–Janak–Williams exchange–correlation functions [13] are used. The Brillouin zone sampling is performed using 1000 special-k-point meshes, which yielded 90 points in the irreducible Brillouin zone. In the spin-polarized calculations we set a starting moment for Fe (Cr). The spin configurations of Fe are $[Ar]3d^44s^1$ for up spins and $[Ar]3d^24s^1$ for down spins. The spin configurations of Cr are $[Ar]3d^34s^{0.5}$ for up spins and $[Ar]3d^24s^{0.5}$ for down spins. For the ferromagnetic case, the moment on site 1 is set parallel to the moment on site 2. For the antiferromagnetic case, the moment on site 1 is set antiparallel to the moment on site 2.

In order to find the most stable ground-state structures of these systems, the total energy as a function of the volume is calculated. In the first step, we set the in-plane lattice parameter a to 3.99 Å corresponding to the experimental value [3], and the lattice parameter c is obtained by energy minimization. In the next step, the lattice parameter c is fixed, and then the lattice parameter a can be obtained. In this way, the structure geometries of $L1_0$ ordered Fe/Au and Cr/Au monatomic multilayers are determined. The self-consistent calculation is stopped when the total energy convergence achieves 0.01 mRyd/unit cell.

The calculated total energy as a function of the lattice parameter c for the tetragonal $L1_0$ ordered Fe/Au monatomic multilayers is shown in figure 2, where a is fixed as 3.97 Å. We can see that the FM state is energetically more favourable than the AFM state. By total energy minimization, lattice parameters of the ferromagnetic ground state are estimated to be $a = 3.97$ Å, $c = 3.57$ Å ($c/a = 0.90$), and the estimated Fe magnetic moment is $2.76\mu_B$;

see table 1. The present numerical results for the tetragonal $L1_0$ ordered Fe/Au monatomic multilayers are similar to those in reference [5]. From table 1, we can see that the energy differences for PM, FM, and AFM states are fairly large (several 10 mRyd).

For the $L1_0$ ordered Cr/Au monatomic multilayer, three magnetic states are obtained. In figure 3 the relative total energies as functions of the lattice parameter c in the tetragonal $L1_0$ ordered Cr/Au monatomic multilayer are shown, where a is fixed at 4.02 Å. The AFM state has lower energy than the FM state, and it is energetically more stable than the FM state. For the antiferromagnetic state, the lattice parameters are estimated to be $a = 4.02$ Å, $c = 3.70$ Å ($c/a = 0.92$).

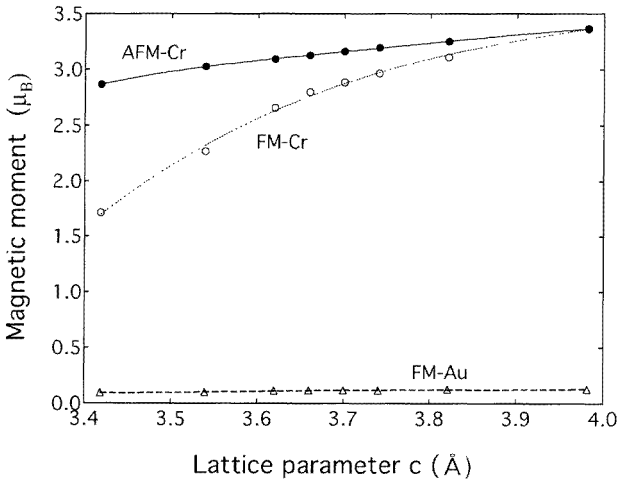

Figure 4. The calculated magnetic moments of Cr and Au in the $L1_0$ ordered CrAu alloys as functions of the lattice parameter c, where $a = 4.02$ Å.

In figure 4 the magnetic moments of Cr and Au in the $L1_0$ ordered Cr/Au monatomic multilayers as functions of the lattice parameter c are shown, where a is fixed at 4.02 Å. As the lattice parameter c increases from 3.41 Å to 3.99 Å, for the FM state, the magnetic moment of Cr increases quickly from 1.71 to 3.36 μ_B, while the Au has a smaller magnetic moment, which increases from 0.092 to 0.126μ_B. For the AFM state, the local moment of Cr shows a large value, and increases slowly from 2.86μ_B to 3.36μ_B with the lattice parameter c increasing from 3.41 Å to 3.99 Å, but the moment of Au is very small. In the AFM ground state with the lattice parameters $a = 4.02$ Å, $c = 3.70$ Å, the local magnetic moment of Cr is 3.18μ_B.

In figure 5 the total electronic density (DOS) and the partial electronic density of states of Cr in the AFM state for the $L1_0$ ordered Cr/Au are shown. The spin-up and spin-down DOS peaks at around the energy of -5 eV are mainly due to the d band of Au, lying far below E_F. In the vicinity of E_F, the spin-up and spin-down DOS peaks at around the energies of -1.5 eV and 1.5 eV are mainly due to the 3d band of Cr. Their corresponding bands are occupied as shown in the band structure of figure 6. The total electronic densities of the up spins and the down spins have equal occupation, so the total moment of $L1_0$ ordered Cr/Au is zero. The partial densities of states of Cr are shown in figure 5. The spin-up and spin-down DOS are shown in the upper and lower panels, respectively, for site 1 and site 2. Between the spin-up and spin-down DOS there is a large split of opposite direction on site 1 and site 2, which gives the larger local moment of Cr, and indicates that

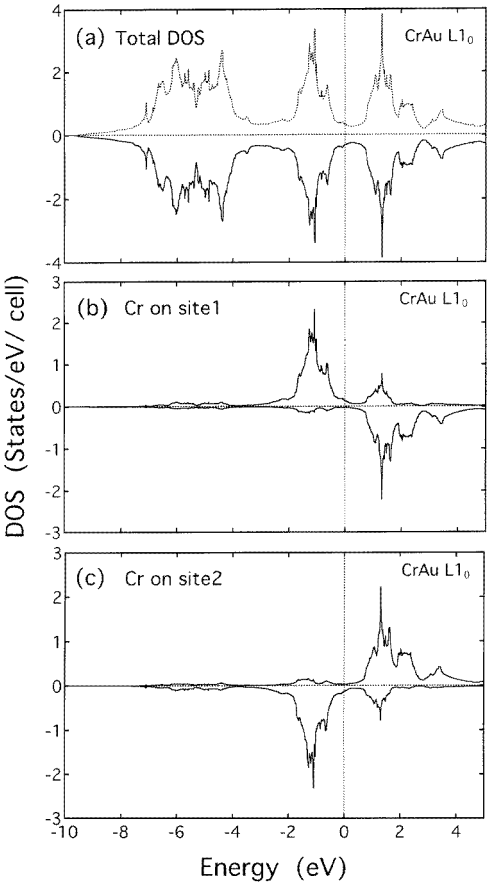

Figure 5. (a) The total electronic DOS of up spins and down spins for the tetragonal $L1_0$ ordered CrAu alloy in the antiferromagnetic ground state with the lattice parameters $a = 4.02$ Å, $c = 3.70$ Å. (b) The 3d electronic DOS of Cr on site 1. (c) The 3d electronic DOS of Cr on site 2.

there is an antiferromagnetic coupling in the Cr layer with a large moment.

In conclusion, we have calculated the structural and magnetic properties of Fe/Au and Cr/Au monatomic multilayers with the tetragonal $L1_0$ ordered structure by the FLAPW method within the local spin-density functional theory. The main conclusions of this study are summarized in table 1, together with a comparison with previously reported results. For Fe/Au monatomic multilayers, $\Delta E = E_{\mathrm{AFM}} - E_{\mathrm{FM}} > 0$, where E_{AFM} and E_{FM} are the total energies for the AFM and FM states, respectively; the FM state is more stable than the AFM state. $L1_0$ ordered Fe/Au shows a ferromagnetic ground state with an enhanced Fe moment of $2.76\mu_B$, which is larger than the experimental value of $2.5\mu_B$ [3], but is very close to the value $2.75\mu_B$ estimated theoretically by Shi *et al* [5]. In the ferromagnetic ground state, the lattice constant a is calculated to be $a = 3.97$ Å, which agrees with the experimental value of 3.99 Å [3], while c is 3.57 Å, which is larger than the simple average of the values for pure Fe and Au, i.e., $\frac{1}{2}(2.86 + 4.08)$ Å $= 3.47$ Å, but smaller than the experimental value of 3.83 Å [3]. The difference between the experimental and calculated values of c is mainly due to stacking faults [5]. On the other hand, for Cr/Au monatomic

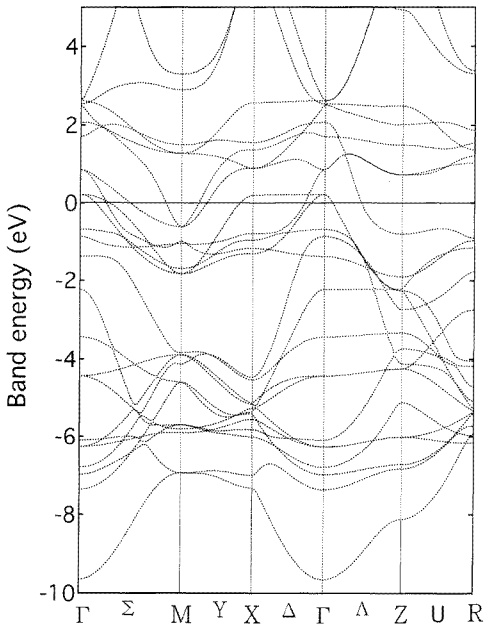

Figure 6. Energy bands for the tetragonal $L1_0$ ordered CrAu alloy in the antiferromagnetic ground state with the lattice parameters $a = 4.02$ Å, $c = 3.70$ Å.

multilayers, $\Delta E < 0$, and the AFM state is more stable than the FM state. The total energy favours the AFM state by 80 mRyd/unit cell. This result is very close to that obtained by Oguchi and Freeman [10] for the [Cr 1 ML/Au 1 ML] superlattice using the spin-polarized LMTO method. They reported that the Cr(001) monolayers are coupled ferromagnetically or antiferromagnetically along the [001] direction, but that the antiferromagnetic coupling is more stable than the ferromagnetic coupling by 10.9 mRyd. In the AFM ground state, Cr shows a large local moment of $3.18\mu_B$, and the lattice parameters are estimated to be $a = 4.02$ Å, $c = 3.70$ Å. The local moment of $3.18\mu_B$ is very close to the value $3.0\mu_B$ given by Oguchi and Freeman [10] for the [Cr 1 ML/Au 1 ML] superlattice and $3.2\mu_B$ for the antiferromagnetic alloy Au_4Cr [14–16]. A recent experimental result for a Cr/Ag superlattice obtained by Kyuno *et al* [17] also shows that the Cr monolayer is antiferromagnetic. Therefore, the Cr/Au monatomic multilayer with the tetragonal $L1_0$ ordered structure has an antiferromagnetic ground state with a large local moment, which is similar to those of other Cr/Au superlattice systems.

As mentioned above, the experimental result shows that the $L1_0$ ordered Fe/Au monatomic multilayer is a ferromagnet with an enhanced magnetic moment, and this is confirmed by the present calculations. It is found that the $L1_0$ ordered Cr/Au monatomic multilayer shows a strong antiferromagnetism. Experiments to verify the magnetic structure would be interesting.

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