Ab initio-Monte Carlo Studies on Magnetic Properties of Tetragonal L1₀ Ordered 3d/Au Superlattices

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3d/Au (3d = V, Cr, Mn, Fe, Co, Ni) superlattices with tetragonal L1₀ ordered structure are studied by means of the self-consistent full-potential linearized augmented-plane-wave method under the generalized gradient approximation. It is shown that the ground state magnetic configuration changes from intra-layer antiferromagnetic to ferromagnetic with increasing 3d electron number from VAu to NiAu. Based on a Heisenberg model with exchange parameters extracted from ab initio calculations, Monte Carlo simulations are carried out to study the finite-temperature properties. Curie temperature and Néel temperature are obtained and discussed in connection with the 3d electrons filling.

Keywords: exchange interaction, spin arrangement, ab initio calculation, magnetic transition, antiferromagnetism

1. Introduction

Over the past nearly quarter century, the molecular beam epitaxy (MBE) technique and vapor deposition techniques made it possible to synthesize high quality metastable ultrathin films in layer by layer mode using different combinations of elements.¹⁻⁷ Experimental studies revealed that the (001) surfaces of fcc noble metals Ag and Au allow good epitaxy because many bcc transition metals such as Cr and Fe are lattice matched to them by a factor of √2, thereby providing a one-on-one match for the atoms at the interface. For example, metastable structures like L₁₀ FeAu²⁻³ monatomic multilayer have been fabricated successfully in the laboratory by using the MBE technique, although these do not exist naturally in the equilibrium phase diagram. Studies of such metastable systems are of great importance from the point of view of applications. Since the growth of thin films can be controlled artificially in the laboratory, one may be able to form many possible multilayers with a control on their properties. Some of the fascinating properties of such systems are enhanced magnetoresistance, large magnetic moment, perpendicular magnetic anisotropy, and oscillatory interlayer coupling, etc.¹⁻¹⁴ These special properties make them good candidates for applications to sensors, communication devices, or recording media.

On the finite-temperature magnetism, several pioneering theoretical works have been successfully performed on the bulk magnetic metals. You et al.¹⁵ calculated exchange parameters of bcc Fe from the selected four types spin arrangements, and estimated the Curie temperature by mean-field theory. Uhl and Küberl¹⁶ investigated the finite-temperature properties of Fe, Co, and Ni by employing an exchange-coupled spin-fluctuation theory. Rosengaard and Johansson¹⁷ calculated the Curie temperatures of ferromagnetic bcc Fe, fcc Co and Ni by using Monte Carlo (MC) simulations with the exchange parameters deduced from ab initio results of total energies for different configurations. Zhou et al.¹⁸ used a similar procedure to study the magnetic phase transitions in fcc Fe and Mn antiferromagnets. More recently, it is shown that such an ab initio-MC method also works well for low-dimensional magnetic systems.¹⁹⁻²¹

In the present paper, we report a systematic study on the finite-temperature magnetism of L₁₀ tetragonal 3d/Au (3d = V, Cr, Mn, Fe, Co, Ni) system based the ab initio-MC approach described above. First, the total energies of the several collinear spin-configurations are calculated by means of the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method²² under the generalized gradient approximation.²³,²⁴ Then, the exchange parameters within a classical Heisenberg model are extracted from the ab initio results. Finally, the finite temperature magnetism is studied using MC simulations with the exchange parameters obtained, and a phase diagram with the Curie temperature (Tc) and Néel temperature (TN) as a function of the 3d electrons filling is given.

2. First-principles Calculations on the Structure and Exchange Interaction

The crystal structure of 3d/Au superlattices used here is a tetragonal L₁₀ ordered structure, which also can be reduced to a tetragonally distorted B₂ type structure with a 45° rotation in the (001) plane as shown in Fig. 1. In order to find the most stable magnetic states and the equilibrium lattice parameters, the total energy as functions of the volume and lattice distortion c/a ratio are calculated for one ferromagnetic (FM) and five antiferromagnetic (AF) spin configur-
tions as reported in our previous paper. The lattice distortion $c/a$ ratio is changed from 0.672 to 1, over bcc ($c/a = 1/\sqrt{2}$ or $c_0/a_0 = 1)$ and fcc ($c/a = 1)$ lattice structures. Here, $c$ and $a$ are the out-plane and in-plane lattice parameters of the fcc-like $L_{10}$ ordered superlattices; $c_0 = c$ and $a_0 = a/\sqrt{2}$ are lattice parameters of the bcc-like $B_2$ type structure. The radii of the muffin-tin spheres are set to 0.127 nm for 3d magnetic elements and 0.138 nm for Au, respectively. The cutoff energy is set to 12 Ry. In the case of going from the single (FM, AF1, AF4) to the doubled (AF2, AF3, AF5) unit cell, to gain the same accuracy, the number of $k$ points in the irreducible Brillouin zone is set to be 45–156, keeping the same density. Coverage of the total energy and the charge is carefully checked throughout this calculation.

In Fig. 2, as an example, the calculated total energies for MnAu are shown as the functions of volume and $c/a$ ratio, respectively. It is interesting to note that the most stable state on fcc side is AF2, similar to $L_{10}$ MnAg system reported in our previous paper; On bcc side, the most stable states are AF4 and AF3, being consistent with the experimental findings. According to present results shown in Fig. 2(a), $B_2$ structure is energetically more stable than $L_{10}$ one, however, the energy of $L_{10}$ MnAu is only 0.1 mRy higher, indicating that it might be fabricated artificially like $L_{10}$ FeAu superlattice as reported by Takanashi et al. By total energy minimization, the lattice constants are estimated to be $a_0 = 0.3183$ nm, $c_0 = 0.3283$ nm for $B_2$ MnAu with AF4, which is very close to $d_0 = 0.318$ nm, $c_0 = 0.328$ nm of the experimental values; and $a = 0.407$ nm, $c = 0.3928$ nm for $L_{10}$ with AF2 magnetic states. The calculated magnetic moments on Mn sites are about 3.86 and 3.93 $\mu_B$ for $L_{10}$ and $B_2$ MnAu, respectively, close to 4.0 $\mu_B$ of experimental values.

In order to understand the stability of the spin configurations, the energy difference between the AF and FM energies, $\Delta E_i = E_{AF} - E_{FM}$ are given in Fig. 3 as a function of the number of valence electrons (3d4s) for $L_{10}$ 3d/Au superlattices. We see that the increment in the number of valence electrons leads to the stabilization of FM ordering for (Fe, Co, Ni)/Au, but a decrease tends to stabilize the AF configuration in (V, Cr, Mn)/Au. The change of sign of $\Delta E_i$ 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 overlayer on Ag (001) showed by Blügel et al. MnAu locates at the crossing point between the FM and AF ordering, exhibiting a competing behavior. It is suggested that the ground magnetic state in such systems has close relation to the 3d electron filling: anti-ferromagnetism occurring for nearly half-filled d-shells and ferromagnetism for larger d-band fillings.

In Fig. 4, the exchange parameters $J$ are shown as functions of the number of valence electrons. We consider here the nearest neighbor and the next nearest neighbor interaction for the in-plane ($J_1$ and $J_2$) pairs and the interaction between the first three inter-layer ($J_{1L}$, $J_{2L}$, $J_{3L}$) pairs. These parameters are deduced from following equation by counting number of antiparallel pairs in one unit cell in the five AF states:

\[
\begin{pmatrix}
 8 & 0 & 0 & 16 & 0 \\
 8 & 0 & 4 & 16 & 16 \\
 0 & 0 & 4 & 16 & 16 \\
 4 & 8 & 0 & 8 & 16 \\
 4 & 8 & 4 & 8 & 0 \\
\end{pmatrix} \begin{pmatrix}
 J_1 \\
 J_2 \\
 J_{1L} \\
 J_{2L} \\
 J_{3L} \\
\end{pmatrix} = \begin{pmatrix}
 E_{AF1} - E_{FM} \\
 E_{AF2} - E_{FM} \\
 E_{AF3} - E_{FM} \\
 E_{AF4} - E_{FM} \\
 E_{AF5} - E_{FM} \\
\end{pmatrix}.
\]

Here, $E_{AF}$ and $E_{FM}$ are the total energy of the AF and FM magnetic states as given in Fig. 3. It is shown that in-plane nearest neighbor coupling $J_1$ have large value (except MnAu) and the other coupling parameters $J_2$, $J_{1L}$, $J_{2L}$ and $J_{3L}$ are all relatively small. This fact indicates that the dominating interaction is in-plane nearest neighbors coupling, so that as the 3d electron filling increase from V to Ni, the $J_1$ varies from negative to positive, and magnetic state changes from AF to FM. For MnAu, all of the exchange parameters are smaller and close to each other, so that MnAu exhibits a competing behavior.
3. Monte Carlo Simulation of Phase Transition

Using the exchange parameters given in Fig. 4, classical MC simulations with system size \( N \times N \times N \) (\( N = 16, 24 \)) were performed to 3000 MC steps. For ferromagnetic system, the magnetization \( M \), the specific heat \( C = \frac{(E^2) - \langle E^2 \rangle}{k_B T^2} \), and the susceptibility \( \chi = \frac{(M^2) - \langle |M|^2 \rangle}{k_B T} \) are calculated as functions of the temperature. We extrapolate these calculations to the thermodynamic limit using standard finite-size scaling theory. In principle, Curie temperature \( T_c \) can be estimated from the peak of the specific heat, or from the magnetic susceptibility according to the Curie-Weiss’ law. While the actual values of the specific heat and magnetic susceptibility depend on the number of the system sizes, the fourth-order cumulant

\[
U_L = 1 - \frac{(M^4)_L}{3(M^2)_L^2}
\]

are used in order to accurately determine the transition temperature. Theoretical results indicate that for \( T < T_c \), \( U_L \) tends to 2/3, and for \( T > T_c \), \( U_L \) decreases towards zero.\(^{30}\) This behavior of the cumulant makes it very useful to obtain

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**Table 1** Calculated lattice parameters (\( a \) or \( a_0 \), \( c \) or \( c_0 \)), magnetic moment (\( \mu_B \)), and Curie temperature (\( T_c \)) or Néel temperature (\( T_N \)) for \( L1_0 \) 3d/Au superlattices. For comparison, some of the experimental data for \( L1_0 \) 3d-Pd and 3d-Pt are also listed.

<table>
<thead>
<tr>
<th>Type of magnetic structures, see Fig. 1.</th>
<th>a or ( a_0 ) (nm)</th>
<th>c or ( c_0 ) (nm)</th>
<th>( c/a )</th>
<th>Moment (( \mu_B ))</th>
<th>( T_c ) or ( T_N ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculated Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VAu</td>
<td>0.404</td>
<td>0.390</td>
<td>0.965</td>
<td>AF1</td>
<td>2.13</td>
</tr>
<tr>
<td>CrAu</td>
<td>0.404</td>
<td>0.386</td>
<td>0.955</td>
<td>AF1</td>
<td>3.34</td>
</tr>
<tr>
<td>MnAu</td>
<td>0.407</td>
<td>0.393</td>
<td>0.967</td>
<td>AF2</td>
<td>3.93</td>
</tr>
<tr>
<td>MnAu(B1)</td>
<td>0.318</td>
<td>0.328</td>
<td>1.030</td>
<td>AF4</td>
<td>3.86</td>
</tr>
<tr>
<td>FeAu</td>
<td>0.399</td>
<td>0.375</td>
<td>0.940</td>
<td>FM</td>
<td>2.99</td>
</tr>
<tr>
<td>CoAu</td>
<td>0.396</td>
<td>0.377</td>
<td>0.952</td>
<td>FM</td>
<td>1.84</td>
</tr>
<tr>
<td>NiAu</td>
<td>0.396</td>
<td>0.367</td>
<td>0.927</td>
<td>FM</td>
<td>0.26</td>
</tr>
<tr>
<td><strong>Experimental Data</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrPt(^{36})</td>
<td>0.400</td>
<td>0.367</td>
<td>0.918</td>
<td>AF1</td>
<td>2.24</td>
</tr>
<tr>
<td>MnPt(^{36,38})</td>
<td>0.400</td>
<td>0.367</td>
<td>0.918</td>
<td>AF1</td>
<td>4.30</td>
</tr>
<tr>
<td>MnPd(^{36,38})</td>
<td>0.407</td>
<td>0.358</td>
<td>0.880</td>
<td>AF1</td>
<td>4.40</td>
</tr>
<tr>
<td>FePt(^{36,38})</td>
<td>0.390</td>
<td>0.373</td>
<td>0.956</td>
<td>FM</td>
<td>2.80</td>
</tr>
<tr>
<td>FePd(^{34,36})</td>
<td>0.385</td>
<td>0.372</td>
<td>0.966</td>
<td>FM</td>
<td>3.03</td>
</tr>
<tr>
<td>CoPt(^{36})</td>
<td>0.380</td>
<td>0.370</td>
<td>0.973</td>
<td>FM</td>
<td>2.01</td>
</tr>
<tr>
<td>CrAu(^{36})</td>
<td>0.399</td>
<td>disorder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnAu(B1)(^{25,26,36})</td>
<td>0.318</td>
<td>0.328</td>
<td>1.030</td>
<td>AF4</td>
<td>4.00</td>
</tr>
<tr>
<td>FeAu(^{2,3,33})</td>
<td>0.399</td>
<td>0.383</td>
<td>0.960</td>
<td>FM</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Fig. 3 Total energy differences, \( \Delta E_i = E_{AF_i} - E_{FM} \), as functions of the number of valence electrons (3d4s) for \( L1_0 \) 3d/Au superlattices.

Fig. 4 Exchange parameter, \( J \) for Cr–Cr, Mn–Mn, Fe–Fe, and Co–Co pairs in the \( L1_0 \) ordered 3d/Au superlattices.
estimates of $T_c$ itself which are not biased by any assumptions about critical exponents. In the present study, $U_L$ versus temperature for various system sizes are plotted and $T_c$ are estimated from the common intersection point of the $U_L$ curves.$^{30)}$

In Fig. 5, the magnetization ($M$), the fourth-order cumulant ($U_L$), and the specific heat ($C$) for $L_{10}$ FeAu as the functions of temperature are shown. From the calculated $U_L - T$ curve, $T_c$ for $L_{10}$ FeAu is estimated to be 820 K.$^{31)}$ To our knowledge, experimental report on the $T_c$ value of $L_{10}$ FeAu superlattice is still lacking. However, this value is close to 750 K of $L_{10}$ FePd superlattice,$^{32)}$ which is believed to be similar to the $L_{10}$ FeAu alloy. It is noted that the calculated $T_c$ is larger than $\sim$550 K of the fcc disorder Fe$_{50}$Au$_{50}$ alloy.$^{33)}$

The difference of $T_c$ between the disordered and ordered alloys were also found in FePt and FePd systems.$^{32,34)}$ For instance, $T_c$ for disordered fcc FePt is 530 K with respect to 750 K for ordered $L_{10}$ FePt.$^{34)}$ The reason of the difference in $T_c$ is regarded as that some Fe atoms or clusters may lost their magnetization in the disordered fcc alloys$^{35)}$ due to segregation fluctuation. In Fig. 6, the magnetization ($M$), the fourth-order cumulant ($U_L$), and the specific heat ($C$) for $L_{10}$ CoAu as the functions of temperature are shown. The $T_c$ is estimated to be 790 K, which close to 750 K of $L_{10}$ CoPt superlattice.$^{36)}$

For antiferromagnetic system, the magnetic phase transition temperature $T_N$ can be evaluated easily from the energy correlation which is proportional to the product of the specific heat and temperature square, $CT^2$. In Fig. 7(a), as an

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**Fig. 5** Temperature dependence of the magnetization ($M$), fourth-order cumulant ($U_L$), and specific heat ($C$) for $L_{10}$ ordered FeAu with system size $16 \times 16 \times 16$ and $24 \times 24 \times 24$.

**Fig. 6** Temperature dependence of the magnetization ($M$), fourth-order cumulant ($U_L$), and specific heat ($C$) for $L_{10}$ ordered CoAu with system size $16 \times 16 \times 16$ and $24 \times 24 \times 24$. 

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examples, the energy correlation for MnAu \(^{21}\) as a function of temperature for \(c/a = 0.92\) and \(0.707\) are shown. With all \(T_N\)’s obtained, the phase diagram for magnetic states versus lattice distortion \(c/a\) is presented in Fig. 7(b). It can be seen that \(T_N\) is a decreasing function of \(c/a\) for \(c/a < 1/\sqrt{2}\) over AF3 range; an increasing function for \(c/a > 1/\sqrt{2}\) over AF4 and AF2 ranges. A minima exists at the bcc limit. The increasing of \(T_N\) in AF4 and AF2 regions is governed by the enhancement of intra-plane AF interactions (\(J_1, J_2\)) since intra-plane atomic distance decreases as \(c/a\) increase. \(^{21}\) On the other hand, in AF3 region, the interplane interaction become more important as \(c\) decreases, which explains the decreasing behaviors in this region. Thus between these two region there must be a minimum. \(T_N\) for \(B_2\) MnAu is estimated to be 528 K, which is in fairly good agreement with 513 K of the experimental value; \(^{37}\) \(T_N\) for \(L1_0\) MnAu is about 946 K, which is close to 975 K of \(L1_0\) MnPt ordered superlattice reported by Krén \textit{et al.} \(^{38}\)

In Fig. 8, the calculated \(T_c\) and \(T_N\) are shown as a function of the number of valence electrons (3d4s) in comparison with some experimental data. It is seen that a maximum of \(T_N\) appears around the Cr site due to the strong antiferromagnetic coupling between Cr–Cr atoms.

**Fig. 7 Monte Carlo studies of MnAu superlattices.** (a) Temperature dependence of the energy correlation with \(c/a = 0.92\) and \(0.707\), obtained with system size \(16 \times 16 \times 16\) and with Monte Carlo steps 3000 to 5000. (b) Phase diagram for magnetic states versus the lattice distortion \(c/a\).

**Fig. 8 Phase diagram for magnetic states versus the number of valence electrons (3d4s) for \(L1_0\) 3d/Au superlattices.** The open square are the experimental data of \(L1_0\) (Pd, Pt) alloys.

### 4. Summary

In summary, we have performed first-principles calculations on the \(L1_0\) ordered 3d/Au superlattice. It has been shown that the exchange interactions can be obtained by fitting the calculated total energies for different collinear spin configurations. The resulting exchange interactions show interesting dependence on the 3d electron filling: Cr favors antiferromagnetic coupling, Fe ferromagnetic coupling and Mn is highly frustrated. By using MC simulations with exchange parameters extracted from \textit{ab initio} results, the Curie temperatures and Néel temperature of metastable 3d/Au superlattices are predicted, which hopefully can be verified later by advanced experiments.

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### REFERENCES

31) It is noted that the $T_c$ and $T_N$ can be influenced by the lattice parameters of $a$, $c$, and $c/a$ ratio.