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Analysis of ground states of fcc thin film of binary alloy under confinement

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Abstract. In this paper, we have investigated the ground states of a few-layered fcc thin film of binary alloy with two surfaces in the (001) direction under symmetric surface confinement. The phase diagram of the ground states is given according to the energy analysis of binary alloy thin film composed of six atomic layers in the (001) direction. Surface confinement field (SC field) is introduced as a term to describe the confinement on the two surfaces in the (001) direction. Using Monte Carlo simulation, we have found that there are 17 different ground states occurring when both SC field and chemical potential vary from $-\infty$ to $+\infty$. Antiphase boundary(APB) was found in 12 of the 17 ground states, and only nine configurations with different symmetry were found among the 17 ground states.

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1 Introduction

With the development of the study of alloy surfaces [1–14], there has been more and more extensive research on thin films due to their growing technological importance and fundamental scientific interest [15–25]. Interaction between the thin film and its environment will draw atoms of the thin film to its surfaces, which is the so-called surface segregation. The concentration of segregated atoms generally decay exponentially, and approaches to the bulk value when the depth of segregated atoms is more than a specific value(the decaying depth) [2]. If the decaying depth of surface segregation is greater than half of the number of atomic layers of thin film, the thin film will exhibit novel phenomena. When the surface interaction is very large, N-layer thin film systems will display a rather unusual phase diagram with a disordered phase laying between the ordered phase down to zero temperature [22].

Extensive study of thin films is based on the analysis of their ground states, on which there have been many studies [14,26–33]. Most studies consider thin films of only one atomic layer using square and triangular lattices with the Ising method. In Ising model, metal atoms are described as the spin, and the action exerted by the environment are described as a type of field. On a square lattice a well-defined variety of hyperstructures has been found in the possible ground states of an Ising system of spin 1/2 with interactions up to third-nearest neighbours in the presence of an external magnetic field [26]. On the triangular lattice, six ground state spin arrangements occur in the presence of an external magnetic field and only five spin orderings occur according to the relative sizes of the exchange integrals [30]. Ground states of the monolayered thin film with the triangular and square configurations have been also analyzed using Ising model in references [29,33], too. Besides studies on the ground states of monolayered thin films, there has been some research on multilayered thin film [14,31,32]. However, these have only considered systems of many (> 10) or infinite layers. To our knowledge, no work has been done on the ground states of few-layered thin films.

This paper will analyze the phase diagram of the ground states of fcc binary alloy thin film composed of six atomic layers in the (001) direction. Surface effects, such as surface segregation, are described by a surface field, which is called surface confinement field (SC field). It only acts on the atoms in the two outermost atomic layers of the thin film in the (001) direction. We begin with a description of methods in Section 2. The results are give in Section 3. The possible ground states are calculated using Monte Carlo simulation method in Section 3.1. Detailed analysis of the ground states and the phase diagram of the ground states of thin film is given in Section 3.2. Section 4 gives a brief conclusion of the paper.

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2 Method

2.1 Hamiltonian analysis

In this paper, we consider fcc thin film of binary alloy A_xB_{1-x} under surface confinement in the (001) direction and use an Ising-like Hamiltonian to describe the binary alloy thin film on a lattice consisting of N two-dimensional parallel atom layers. The nearest-neighbor and next-nearest-neighbor interactions are included. The Hamiltonian is given as [36]

$$\mathcal{H} = J\sum_{NN} s_i s_j - \alpha J \sum_{NNN} s_i s_j - H\sum_{all} s_i - h\left(\sum_{i\in\{1\}} s_i + \sum_{i\in\{N\}} s_i\right) \quad (1)$$

where J is the nearest-neighbor interaction, α is the ratio between the nearest-neighbor and next nearest-neighbor interactions. We only consider antiferromagnetic nearest-neighbor interactions and ferromagnetic next-nearest-neighbor interactions, that is $J > 0$ and $\alpha > 0$ [36]. Since we only consider the Cu-Au thin film, we take $\alpha = 0.2$ [37]. The first sum runs over all the nearest-neighbor atom pairs, the second sum runs over all the next-nearest-neighbor atom pairs, and the third sum runs over all the sites. Spin $s_i = 1$ corresponds to A atom occupying lattice site i and $s_i = -1$ corresponds to B atom occupying lattice site i. The energy parameter H is the chemical potential, while h represents what we call the SC field. It describes the effects of confinement on the surface segregated atoms. Therefore, the last sums in the right-hand side of equation (1) are restricted to the surface sites, *i.e.* to the two outermost layers (layer 1 and layer N) on which the SC field acts. In the following, we will analyze the relation between the ground states and the two energy parameters in equation (1): H and h.

The structure of ordered A_xB_{1-x} thin film can be considered as a stack of three kinds of atom layers along a cubic axis [35]: that is, layers purely of A atoms(denoted as $\mathcal{A}$), purely of B atoms(denoted as $\mathcal{B}$), and of a mixture of equal numbers of A and B atoms(denoted as $\mathcal{C}$). Next, we analyze the effect of the SC field on ground states of the thin film AB_3. If the SC field is weak, the film can be considered as a stack of $\mathcal{BCBC}$..., which is the truncated bulk structure. In this case, the weak SC field has no effect on the ground states. If there is strong surface segregation of B atoms caused by strong SC field in favor of B atoms, the two surfaces of thin AB_3 film should be $\mathcal{B}$ layers. The film can be considered as the stack of $\mathcal{BCBC}$...$\mathcal{CBCB}$. In this case, the SC field has much effect on the ground states of the thin film. If the number of atomic layers of the thin film is even, the film should have the $\mathcal{BB}$ or $\mathcal{CC}$ structure, *i.e.* APB in which the composition of atomic layers alternates. If the number of atomic layers of the thin film is odd, APB will not occur. Therefore in the following, we consider only thin films composed of even number of atomic layers, as their ground states are much more complicated due to the effects of APB on the ground states. The layer number is described as N in the paper. There are more ground states than the ones analyzed above under SC field, and we will give detailed analysis in the following.

2.2 Monte Carlo simulation

In the following, we use Monte Carlo simulation to get all the possible ground states of the thin film on the fcc lattice in a 40 (in the (100) direction) × 40 (in the (010) direction) × 6 (in the (001) direction) geometry according to the Hamiltonian in equation (1). The calculations on other geometries such as 30 × 30 × 6 and 80 × 80 × 6 are also performed and the same results are obtained. (001) direction is set to be the stack direction of the atomic layer of the thin films. We use the periodic boundary conditions in the (100) and (010) directions. In the calculation, we allow the system to anneal down from the disordered state at high temperatures to the ordered state at low temperatures. During the process of annealing, spin flipping mechanism is used to get the configuration with minimal free energy. When temperature approaches zero, the system will be annealed into the ground state. So we can get all the possible ground states under different energy parameters if we allow the system to anneal down to low temperature in all cases.

We use the order parameter in each layer to describe ground states of the thin films. Each layer is divided into two sublattices (denoted as I and II), and the order parameter is defined as

$$m_i = \left|\left(N_{Ai}^{II} - N_{Ai}^{I}\right)\right| / N_1 \quad (2)$$

where N_{Ai}^{I} and N_{Ai}^{II} are the number of A atoms on the two sublattices in layer i, respectively. N_1 is the total number of sites in one layer. In Monte Carlo simulation, N_1 is equal to 40 (in the direction of (010) × 40 (in the direction of (100) = 1600.

3 Results

3.1 Monte Carlo simulation

In our calculation, we consider the annealing process of thin film from high($k_{\rm B}T/J = 2.0$) to low($k_{\rm B}T/J = 10^{-6}$) temperature to get its ground states. In each process, we select different H and h in the step of 1.0, and all possible combinations of H and h are considered. At the temperature of $k_{\rm B}T/J = 10^{-6}$ we can get the ground states of the thin film under different combinations of H and h.

From Monte Carlo simulation, we have found 17 possible ground states for the six-atomic-layer thin film. They are listed in Table 1, and the structures are shown in Figure 1. If we replace all A atoms by B atoms and all B atoms by A atoms in the thin film, we can get the O_{2a} phase from O_{6c}. In the same way, we can get the O_{6c} phase from O_{2a}. O_{2a} and O_{6c} thus have the same symmetry. No phase has

Table 1. Structure of 17 possible ground states of six-atomic-layer thin film, $\mathcal{A}$ stands for the atomic layer purely of A atoms, $\mathcal{B}$ for the one purely of B atoms and $\mathcal{C}$ for the one of a mixture of equal numbers of A and B atoms.

Phase No.	Surface Segregation	APB	Structure
O_1	No	No	$(\mathcal{A})(\mathcal{A})(\mathcal{A})(\mathcal{A})(\mathcal{A})(\mathcal{A})$
O_{2a}	B atoms	Yes	$(\mathcal{AB})(\mathcal{A})(\mathcal{AB})(\mathcal{A})(\mathcal{A})(\mathcal{AB})$
O_{2b}	No	No	$(\mathcal{A})(\mathcal{AB})(\mathcal{A})(\mathcal{AB})(\mathcal{A})(\mathcal{AB})$
O_{2c}	A atoms	Yes	$(\mathcal{A})(\mathcal{AB})(\mathcal{AB})(\mathcal{A})(\mathcal{AB})(\mathcal{A})$
O_{3a}	B atoms	Yes	$(\mathcal{B})(\mathcal{A})(\mathcal{A})(\mathcal{A})(\mathcal{A})(\mathcal{B})$
O_{3b}	B atoms	Yes	$(\mathcal{AB})(\mathcal{A})(\mathcal{AB})(\mathcal{AB})(\mathcal{A})(\mathcal{AB})$
O_{3c}	A atoms	Yes	$(\mathcal{A})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{A})$
O_{4a}	B atoms	Yes	$(\mathcal{B})(\mathcal{A})(\mathcal{AB})(\mathcal{AB})(\mathcal{A})(\mathcal{B})$
O_{4b}	No	No	$(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})$
O_{4c}	A atoms	Yes	$(\mathcal{A})(\mathcal{B})(\mathcal{AB})(\mathcal{AB})(\mathcal{B})(\mathcal{A})$
O_{5a}	B atoms	Yes	$(\mathcal{B})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{AB})(\mathcal{B})$
O_{5b}	A atoms	Yes	$(\mathcal{AB})(\mathcal{B})(\mathcal{AB})(\mathcal{AB})(\mathcal{B})(\mathcal{AB})$
O_{5c}	A atoms	Yes	$(\mathcal{A})(\mathcal{B})(\mathcal{B})(\mathcal{B})(\mathcal{B})(\mathcal{A})$
O_{6a}	B atoms	Yes	$(\mathcal{B})(\mathcal{AB})(\mathcal{B})(\mathcal{AB})(\mathcal{AB})(\mathcal{B})$
O_{6b}	No	No	$(\mathcal{B})(\mathcal{AB})(\mathcal{B})(\mathcal{AB})(\mathcal{B})(\mathcal{AB})$
O_{6c}	A atoms	Yes	$(\mathcal{AB})(\mathcal{B})(\mathcal{B})(\mathcal{AB})(\mathcal{B})(\mathcal{AB})$
O_7	No	No	$(\mathcal{B})(\mathcal{B})(\mathcal{B})(\mathcal{B})(\mathcal{B})(\mathcal{B})$

the same symmetry as O_{4b}. Not all phases have the same symmetry, but every phase except O_{4b} phase has a counterpart. Therefore, in 17 ground states, there are only nine different symmetries: O_1 O_{2a}, O_{2b}, O_{2c}, O_{3a}, O_{3c}, O_{3b}, O_{4a} and O_{4b}.

3.2 Hamiltonian analysis

Surface segregation is caused by the SC field. If the SC field is strong enough, there will be APB in ground states of the thin film. If the SC field is too weak, no APB will be found in the ground states. In that case, surface segregation makes no effect on the ground states of the thin film. The effect of SC field for A and B atoms is opposite. If SC field h_0 causes surface segregation of A atoms, SC field of -h_0 will cause surface segregation of B atoms. So we have two different APB in the thin film of even atomic layers. In the thin film, the concentrations of A and B atoms in the ground states will differ if we use different chemical potentials. So H is used to alter the concentrations of A and B atoms.

In the following, we give an analysis of the energies of all the ground states. We need only consider the unit cell with two atoms in each layer; hence, 12 atoms are included in the selected unit for a six-layer thin film. In the unit cell we can calculate the average number of nearest neighbors and next-nearest neighbors of AA, BB and AB atom pairs, A and B atoms in the two surfaces. For O_{2a} phase, there are 36 nearest neighbors and 23 next-nearest neighbors of AA atom pairs, 28 nearest neighbors and 2 next-nearest neighbors of AB atom pairs, 0 nearest neighbors and 7 next-nearest neighbors of BB atom pairs, 2 A

Table 2. Total energy per unit of 17 possible ground states of thin film composed of six atomic layer.

Phase No.	Total energy per unit
O_1	$64J - 32\alpha J - 12H - 4h$
O_{2a}	$8J - 28\alpha J - 6H$
O_{2b}	$-32\alpha J - 6H -$ 2h
O_{2c}	$-28\alpha J - 6H -$ 4h
O_{3a}	$32J - 24\alpha J - 4H + 4h$
O_{3b}	$-8J - 28\alpha J - 4H$
O_{3c}	$-8J - 28\alpha J - 4H - 4h$
O_{4a}	$-8J - 24\alpha J + 4h$
O_{4b}	–24J
O_{4c}	$-8J - 24\alpha J -$ 4h
O_{5a}	$-8J - 28\alpha J + 4H + 4h$
O_{5b}	$-8J - 28\alpha J + 4H$
O_{5c}	$32J - 24\alpha J + 4H - 4h$
O_{6a}	$-28\alpha J + 6H + 4h$
O_{6b}	$-32\alpha J + 6H + 2h$
O_{6c}	$8J - 28\alpha J + 6H$
O_7	$64J - 32\alpha J + 12H + 4h$

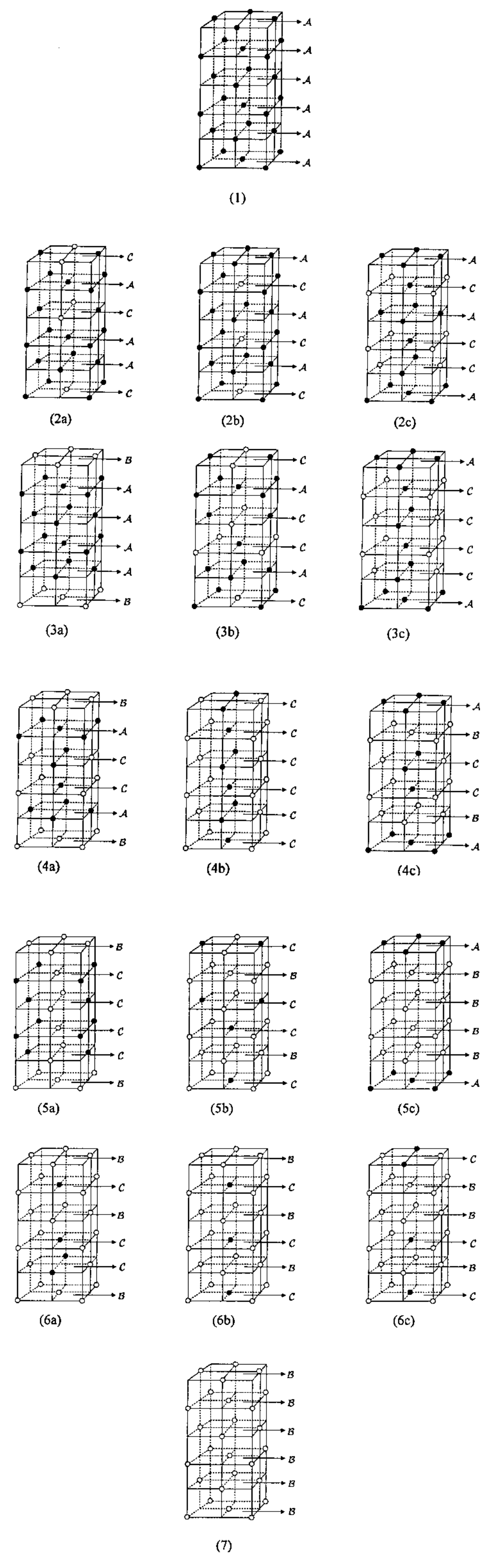

Fig. 1. 17 ground states of six-atomic-layer thin film with two surfaces in the (001) direction from Monte-Carlo simulation, $\mathcal{A}$ stands for the atomic layer purely of A atoms, $\mathcal{B}$ for the one purely of B atoms and $\mathcal{C}$ for the one of a mixture of equal numbers of A and B atoms. (1) O_1. (2a) O_{2a}. (2b) O_{2b}. (2c) O_{2c}. (3a) O_{3a}. (3b) O_{3b}. (3c) O_{3c}. (4a) O_{4a}. (4b) O_{4b}. (4c) O_{4c}. (5a) O_{5a}. (5b) O_{5b}. (5c) O_{5c}. (6a) O_{5a}. (6b) O_{6b}. (6c) O_{6c}. (7) O_7.

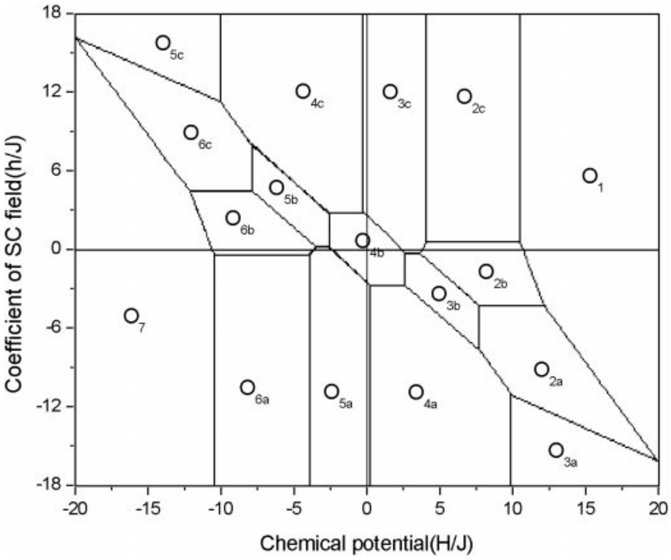

Fig. 2. Phase diagram of ground states for binary alloy thin film of six atomic layers with two surfaces in the (001) direction.

atoms and 2 B atoms in the two surfaces. Thus, the total energy per unit of the thin film is $E_0 = 8J - 28\alpha J - 6H$. In the same way, we can get the total energy per unit of all the other ground phases for the six-atomic-layer thin film in Figure 1. The energies of all possible ground states for the six-atomic-layer thin film are listed in Table 2.

The ground states have the lowest total energy. Comparing the energies of the different ground states (Tab. 2), we get their phase diagram (Fig. 2) [34].

4 Conclusions

In summary, we have studied the ground states of (001) six-layer thin film of binary alloy using the Monte Carlo simulation and Hamiltonian analysis. The phase diagram of the ground states of the thin film under surface confinement is given. There are 17 possible ground states, of which APB has been found in 12. Although not all phases have the same symmetry, every phase except one has a counterpart. Therefore, there are only nine different symmetries among the 17 ground states. The phase diagram of ground states has a symmetry with π rotation about the origin.

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