STATISTICAL-THERMODYNAMIC THEORY OF ORDERING IN A BINARY FILM
DEPOSITED ON THE SURFACE OF A MONOCRYSTAL

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The ordering of a binary monolayer deposited on the surface of a monocrystal is studied. In the case when the structure of the film is equivalent to that of the crystal surface, the ordering in the film is qualitatively similar to that in the bulk of the sample: When the ordering energy is positive there exists an order-disorder phase transition at a certain temperature and for a certain concentration interval. If the structure of the film is different from the structure of the surface, then the film is ordered at all temperatures, independently of the sign of the ordering energy. In this case, in addition to the equilibrium ordered state in the region $T < T_*$ (T_* is a certain temperature which is determined by the composition of the alloy and by the magnitude of the energy shift of the atoms of the film in the field of the substrate), there exists a metastable ordered state in which there is a jump-like change in the ordering at the point T_*, analogous to a first-order phase transition. Possible methods of experimental study of the ordering in films are discussed.

1. The wide practical application of film overlays makes the theoretical study of the structure and thermal behavior of multicomponent films deposited on the surface of a crystal an important problem. In the simplest case of a two-component monolayer film consisting of atoms of two kinds (A and B) which can occupy lattice sites of two different types, the problem is quite similar to the ordering in a two-dimensional alloy. However, the presence of the substrate field leads to several features in the structural ordering of films which do not take place in two-dimensional systems.

In the present paper we develop a statistical theory of the ordering in a binary monolayer film (A–B) which adheres to a substrate. We consider the case when the film orders in two sublattices. Interaction with the substrate is taken into account by introducing a coupling energy $E_\alpha^{(i)}$ between an atom of type α (α = A, B) occupying a site on the i-th sublattice and the crystal. A priori there are two possibilities: 1) $E_\alpha^{(1)} = E_\alpha^{(2)}$; 2) $E_\alpha^{(1)} \neq E_\alpha^{(2)}$. These two possibilities obviously correspond to an equivalent and nonequivalent arrangement of film lattice sites of the first and second kinds with respect to the lattice sites of the substrate. The two possibilities are illustrated in Fig. 1 where we show possible structures of films deposited on the [100] and [110] faces of a bcc crystal and on the [111] face of an fcc crystal. It follows from the geometry of the relative arrangement of the sites of the first and second kinds in the film and the sites on the surface of the substrate that for structures a, b, d, f there is no difference in the binding energy of an atom with the substrate when it occupies a site of the first or second sublattice. There is such a difference in the structures for example. The characteristic feature of a film with a nonequivalent arrangement of lattice sites of different types is that it is ordered at any temperature. Physically the situation in this case is similar to the ordering of interstitial atoms over energetically nonequivalent interstices on the surface of a crystal [1]. If

o - type 1 sites
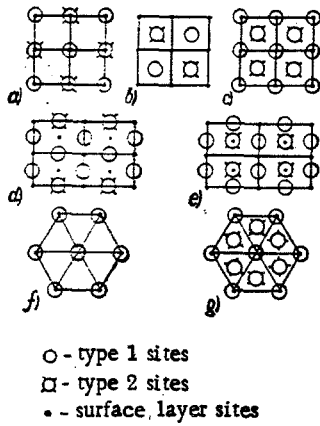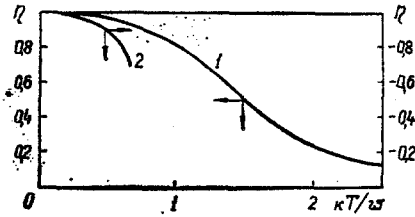□ - type 2 sites
• - surface layer sites

Fig. 1

Fig. 2

Fig. 1. Possible structures of a film on the [100] faces (a, b, c) and [110] faces (d, e) of a bcc crystal and on the face [111] (f, g) of an fcc crystal.

Fig. 2. Temperature dependence of the degree of long-range order in a film with a nonequivalent arrangement of sites of the different sublattices.

the structure of the film is equivalent to that of the substrate, ordering in the film is qualitatively similar to that in a three-dimensional alloy.

2. Let the film contain N_A atoms of type A and N_B atoms of type B, distributed over N_1 sites of the first kind and N_2 sites of the second kind. We take $N_1 = N_2$; similar results are obtained in the case $N_1 \neq N_2$. We consider only interactions between nearest neighbors in the film. We then obtain the following expression for the configurational energy of the film

$$E_{\text{conf}} = \sum_{\alpha=A,B} \sum_{i=1} E_\alpha^{(i)} N_\alpha^{(i)} - \sum_{\alpha,\beta=A,B} N_{\alpha\beta}^{(12)} v_{\alpha\beta}, \tag{1}$$

where $N_\alpha^{(i)}$ is the number of atoms of type α on sites of the i-th sublattice; $N_{\alpha\beta}^{(12)}$ is the number of pairs of neighboring atoms in which atom α occupies a site of the first kind and atom β occupies a site of the second kind; $v_{\alpha\beta}$ is taken to have the opposite sign of the energy of the pair α–β. The thermodynamic probability of a state with the energy (1), calculated in the quasichemical approximation, is given by

$$W = \frac{N!}{[(N/2)!]^2} \cdot \frac{(N_A^{(1)}! \ N_B^{(1)}! \ N_A^{(2)}! \ N_B^{(2)}!)^{z-1}}{N_{AA}^{(12)}! \ N_{BB}^{(12)}! \ N_{AB}^{(12)}! \ N_{BA}^{(12)}!}, \tag{2}$$

where z is the number of nearest neighbors. Calculating the free energy of the film F = E − κT ln W, and minimizing it with respect to the numbers of atoms of different kinds on different sublattices and the numbers of pairs of different types, we obtain the following equilibrium equations:

$$(z-1) \ln \frac{N_A^{(1)} N_B^{(2)}}{N_A^{(2)} N_B^{(1)}} = \frac{\Delta E}{\kappa T} + z \ln \frac{N_{AB}^{(12)}}{N_{BA}^{(12)}},$$

$$\ln \frac{N_{BB}^{(12)} N_{BA}^{(12)}}{N_{AA}^{(12)} N_{BB}^{(12)}} = \frac{w}{\kappa T}. \tag{3}$$

Here

$$\Delta E = E_A^{(2)} - E_A^{(1)} + E_B^{(1)} - E_B^{(2)}, \quad w = 2v_{AB} - v_{AA} - v_{BB}. \tag{4}$$

Expressing the quantities $N_\alpha^{(i)}$ and $N_{\alpha\beta}^{(12)}$ in terms of the degree of long-range order η and the correlation parameter ε_{AB} in analogy with the procedure for three-dimensional alloys [2], we obtain in place of (3):

$$(z-1)\ln\frac{\left(c_A+\dfrac{\eta}{2}\right)\left(c_B+\dfrac{\eta}{2}\right)}{\left(c_A-\dfrac{\eta}{2}\right)\left(c_B-\dfrac{\eta}{2}\right)}=\frac{\Delta E}{\kappa T}+z\ln\frac{c_Ac_B+\dfrac{\eta^2}{2}+\varepsilon}{c_Ac_B-\dfrac{\eta^2}{4}+\varepsilon},\tag{5}$$

$$\varepsilon_{AB}^{(12)}=\frac{1-\left(2c_Ac_B+\dfrac{1}{2}\eta^2\right)y-\sqrt{(c_A-c_B)^2+4c_Ac_B(1-y)-\eta^2y(1-y)}}{2y},\tag{6}$$

$$y=1-e^{-\omega},\quad\omega=\frac{w}{\kappa T}.\tag{7}$$

For a film with an equivalent arrangement of sites of the first and second kinds $\Delta E=0$ and (5) and (6) reduce to the equations for a three-dimensional alloy [2]. It follows from these equations that when the ordering energy is positive, there is a temperature

$$T_0=-\frac{w}{\kappa}\frac{1}{\ln\left(1-\dfrac{z-1}{z^2c_Ac_B}\right)}\tag{8}$$

at which an order-disorder phase transition occurs in the film. In the approximation where correlations are neglected, this case has been considered in [3].

A more interesting situation occurs in films with a nonequivalent distribution of sites of different kinds; then $\Delta E\neq 0$. As is evident from (5) and (6), in films of this type $\eta\neq 0$ at any finite temperature and hence the film remains in the ordered state up to the melting temperature. The temperature dependence of η can be obtained by solving the system of equations (5) and (6) numerically using specific values of ΔE and w. However, the main features of the ordering in films of this type can be obtained in the special case of weak correlation. Expanding (5) and (6) in powers of $w/\kappa T$, we obtain in the first approximation:

$$\ln\frac{\left(c_A+\dfrac{\eta}{2}\right)\left(c_B+\dfrac{\eta}{2}\right)}{\left(c_A-\dfrac{\eta}{2}\right)\left(c_B-\dfrac{\eta}{2}\right)}=\frac{\Delta E}{\kappa T}+z\frac{w}{\kappa T}\eta.\tag{9}$$

For an alloy with the stoichiometric composition ($c_A=c_B=0.5$) this equation takes the form

$$\frac{1}{a+2\eta}\ln\frac{1+\eta}{1-\eta}=\omega,\tag{10}$$

where $a=\Delta E/2w$. Equation (10) has a solution for either sign of w, which means that in a film with nonequivalent sites of the different sublattices, ordering exists when the ordering energy is either positive or negative. Physically this is due to the presence of the temperature-independent substrate field, which leads to a different occupation of the two types of positions by the atoms A and B.

When $|a|>1$ the only possible state at all temperatures is the stable ordered state. If $|a|<1$, then in films with $w>0$, below the temperature

$$T_*=\frac{|w|}{\kappa}(a+2\eta_*)\ln\frac{1-\eta_*}{1+\eta_*}\tag{11}$$

[η_* is the value of η at which the function on the left-hand side of (10) reaches an extremum] there occurs a solution corresponding to a metastable ordered state, which exists in addition to the stable ordered state. Unlike the stable equilibrium state, in the metastable state the atoms A and B preferably occupy sites of the "foreign" sublattice. Figure 2 shows $\eta(T)$ for films with $w>0$, for the case $a=0.5$. Curve 1 represents the equilibrium state of the film, corresponding to the absolute minimum in the free energy. Curve 2 gives the temperature dependence of η for the metastable state which exists up to $T_*=0.52\,w/\kappa$ and corresponds to a local minimum in the free energy. The negative values of η on curve 2 mean that $p_A^{(1)}<p_A^{(2)}$ [$p_A^{(i)}$ is the probability that atom A occupies a site on the i-th sublattice]. Hence, in the metastable state the sublattices are reversed.

Because the metastable state cannot exist above the temperature T_*, when the temperature is increased in a film in which this state has been created there is a jump-like change in the degree of long-range order along with a change in its sign. The temperature of this transition depends on the exact heating regime but in any case, it does not exceed T_*.

As noted above, in films with nonequivalent sites of the first and second kinds, ordering exists even when $w < 0$. However, unlike the case of films in which the ordering energy is positive, in this case there is no metastable state. It is interesting that in films with $w < 0$ the correlation parameter ε_{AB} is negative in the presence of long-range order. This is evident from (6). Hence, in films of this type, long-range order coexists with a short-range separation into layers.

One can consider the ordering of a film deposited on the [111] face of an fcc-crystal in a similar way, for the case of the structure shown in Fig. 1d. Using the generalization of the quasichemical method given in [4], we obtain the following equations of equilibrium:

$$(2z - 1) \ln \frac{N_A^{(1)} N_B^{(2)}}{N_A^{(2)} N_B^{(2)}} = \frac{\Delta E}{\kappa T} + z \ln \frac{N_{AA}^{(12)} N_{AB}^{(12)} N_{AB}^{(22)}}{N_{AA}^{(22)} N_{BA}^{(12)^3}},$$

$$\ln \frac{N_{AB}^{(12)} N_{BA}^{(12)}}{N_{AA}^{(12)} N_{BB}^{(12)}} = \frac{w}{2\kappa T}, \quad \ln \frac{N_{AB}^{(22)^2}}{N_{AA}^{(22)} N_{BB}^{(22)}} = \frac{w}{2\kappa T}.$$

(12)

The difference from the previous case is that not only sites of the first and second sublattices are nearest neighbors but also neighboring sites of the second sublattice. Hence, there are pairs of nearest neighbors $N_{AA}^{(22)}$, $N_{BB}^{(22)}$, $N_{AB}^{(22)}$ in which both atoms occupy sites of the second sublattice.

Expressing the number of pairs $N_{\alpha\beta}^{(i\kappa)}$ in terms of the degree of long-range order η and the correlation parameters $\varepsilon_{AB}^{(12)}$ and $\varepsilon_{AB}^{(22)}$, we obtain from (12):

$$(2z - 1) \ln \frac{\left(c_A + \frac{2}{3}\eta\right)\left(c_B + \frac{1}{3}\eta\right)}{\left(c_A - \frac{2}{3}\eta\right)\left(c_B - \frac{1}{3}\eta\right)} = \frac{\Delta E}{\kappa T} +$$

$$+ z \ln \frac{\left(c_A^2 - \frac{4}{9}\eta^2 - \varepsilon_{AB}^{(12)}\right)\left(c_A c_B + \frac{1}{3}(c_A + 2c_B)\eta + \varepsilon_{AB}^{(22)}\right)\left(c_A c_B + \right.}{\left(c_A c_B - \frac{1}{3}(c_A + 2c_B)\eta + \frac{2}{9}\eta^2 + \varepsilon_{AB}^{(12)}\right)^2 \left(\left(c_A - \frac{2}{3}\eta\right)^2 - \varepsilon_{AB}^{(22)}\right)}$$

$$\frac{\left. \frac{1}{3}(c_A - 2c_B)\eta + \varepsilon_{AB}^{(22)}\right)}{\left(c_A c_B - \frac{1}{3}(c_A + 2c_B)\eta + \frac{2}{9}\eta^2 + \varepsilon_{AB}^{(12)}\right)^2 \left(\left(c_A - \frac{2}{3}\eta\right)^2 - \varepsilon_{AB}^{(22)}\right)}.$$

(13)

$$\varepsilon_{AB}^{(12)} = \frac{1 - \left[2c_A c_B + \frac{1}{3}(c_A - c_B)\eta + \frac{4}{9}\eta^2\right] y_1}{2y_1} -$$

$$- \frac{\sqrt{1 - 2\left[2c_A c_B + \frac{1}{3}(c_A - c_B)\eta + \frac{4}{9}\eta^2\right] y_1 + \eta^2 y_1^2}}{2y_1},$$

$$\varepsilon_{AB}^{(22)} = \frac{1 - 2\left[c_A c_B + \frac{1}{3}(c_A - 2c_B)\eta - \frac{2}{9}\eta^2\right] y_1}{2y_1} -$$

$$- \frac{\sqrt{1 - 4\left[c_A c_B + \frac{1}{3}(c_A - 2c_B)\eta - \frac{2}{9}\eta^2\right] y_1}}{2y_1},$$

$$y_1 = 1 - e^{-\frac{w}{2}}.$$

In the limit of weak correlation, we obtain from (13) the following approximate expression, good to terms of order $0(\omega/2)$ inclusive:

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$$\ln \frac{\left(c_A + \dfrac{2}{3}\eta\right)\left(c_B + \dfrac{1}{3}\eta\right)}{\left(c_A - \dfrac{2}{3}\eta\right)\left(c_B - \dfrac{1}{3}\eta\right)} = \frac{\Delta E}{\kappa T} + \frac{zw}{2\kappa T}\eta,$$

$$\varepsilon_{AB}^{(12)} = \left(c_A^2 - \frac{4}{9}\eta^2\right)\left(c_B^2 - \frac{1}{9}\eta^2\right)\frac{w}{2\kappa T},$$

$$\varepsilon_{AB}^{(22)} = \left[c_A c_B + \frac{1}{3}(c_A - 2c_B)\eta - \frac{2}{9}\eta^2\right]\frac{w}{2\kappa T}. \qquad (14)$$

It follows from the first equation of (14) that for A—B films with nonequivalent lattice sites of different types, ordering exists at all temperatures on the [111] face of an fcc crystal, and the metastable state exists along with the stable ordered state.

3. From the above discussion it follows that films can be divided into three types, depending on the nature of the atomic ordering: 1) films in which long-range order exists in some finite temperature interval, 2) those in which the atomic ordering takes place at all temperatures, and 3) dissociating films having sublattices with equivalent lattice sites and with negative ordering energies. Differences in the ordering in films of the first and second types will show up in those properties of the crystal which are determined by the state of the surface: The temperature dependence of these properties in films of the first type will have anomalous breaks or jumps, whereas in equilibrium films of the second type the dependence will be monotonic. Therefore, the study of properties such as the work function of a crystal in which a film is deposited on the surface, the resistance to high-frequency current, and surface diffusion of the adhesion energy of gases such as hydrogen can be used to indirectly determine the nature of the atomic ordering in the film.

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