Surface melting and surface disordering in binary alloy thin films

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An interdependence between the surface melting and the surface disordering observed in binary alloy thin films is considered in the context of their mutual relations. The present discussion allows us to extend the diagram of phase transitions to the case when the crystallinity parameter behavior influences the local concentration profiles and the lattice order parameter describing the alloy structure. In particular, the surface-induced disorder is described when the crystal structure is preserved and, in contrast, when the surface melting is expected for partially disordered samples.

I. INTRODUCTION

In the present paper we consider the diagrams describing the phase transitions in binary alloys with thin film geometry. In particular, the surface melting and surface disordering described as phenomena with different origin are discussed in the context of their interdependence. In this case the description requires two independent order parameters. One of them is a characterization of the lattice ordering in the sense of alloy structure while the second one is connected with the crystallinity state.

One of the models reported in Ref. 1 and applied to the description of systems in which more than one density parameter is needed to characterize the ordered state is based on two densities which are (i) the nonordering density identified then with the deviation of the average concentration from stoichiometry and (ii) the lattice order parameter given by the difference of the sublattice concentrations.

This model can be used to describe the order-disorder transition in binary alloy thin films.[1] In the case of short-range forces the order parameter profile at the surface corresponds to the surface induced disorder behavior. Taking into account the long-range interactions the analysis based on this model leads to the description for the surface melting of crystalline films.[1]

It seems to us that the physical nature of melting is extremely different from the lattice disordering behavior. In the second case the lattice structure is preserved while atoms move only around their equilibrium positions. The disorder concerns then the random occupation of the regular sites by the atoms of two different kinds. On the other hand, the melting consists in a destruction of the lattice. The atoms leave the lattice sites and they wonder in space of the sample volume interacting between them. Moreover, the interactions in the liquid phase change their character with respect to the interactions appearing in the crystalline structure.

This physical picture can be a source of a new aspect announced in Ref. 2 for the relation between the surface melting and surface-induced disordering state. In fact, it is simply an interdependence of these phenomena.

In the light of the interpretation presented above the considered model should be extended by introducing an addi-

tional order parameter, the so-called (iii) crystallinity order parameter which can characterize the deviation from the crystal structure. It can be defined, e.g., by the change of the densities of a sample in its crystalline and liquid stats. In this case the interactions between two atoms occurring in the free-energy construction for alloys depend now on the density and change their values when the solid-liquid phase transition takes place.

The structure of a binary alloy sample with thin film geometry of film thickness $d=na$ consists in a superposition of n monoatomic layers labeled by i and parallel to the surfaces localized at $i=1$ and $i=n$ while a means the distance between neighboring planes. The system is infinite and homogeneous in the surface plane directions.

The ordered state is characterized by three parameters and their profiles across a film: (i) the stoichiometric concentration $c(i)$ which satisfies the constrain condition $\Sigma_i c(i)=nc$ for an average concentration c of one component of the considered alloy, (ii) the lattice order parameter $t(i)$ which reflects the occupation of the different lattice sites by the same kind of atoms in a considered alloy, (iii) the crystallinity parameter $m(i)$ which determines the sample crystallinity degree by means of the density dependent interactions $V(\rho)$ for $\rho=\rho_l+(\rho_c-\rho_l)m$ with ρ_c and ρ_l standing for the crystal and liquid phase densities, respectively. Thus, $m=1$ means the solid phase, while $m=0$ corresponds to the liquid phase. The transition from $m=1$, or more precisely $m\neq 0$, to $m=0$ describes the melting effect.

In context of the present model the analogy between the surface melting of binary alloy thin films and their surface disordering can be considered in two extreme cases: (1) from the position of melting when the crystallinity parameter m achieves its value characteristic for the fluid phase $m=0$ at the temperature T_{sm} when the considered alloy is homogeneous [$c(i)=c$] and completely disordered $t=0$ at the temperature $T_{st} < T_{sm}$, (2) from the position of disordering when the crystallinity parameter m keeps its value close to $m=0$. In this case we obtain the profiles of the lattice order parameter $t(i)$ and the surface disordering phase at $T_{st} > T_{sm}$, which exhibits its behavior of the first order transitions. An interme-

diate case $T_{st} \approx T_{sm}$, leads to the interdependent relation between surface melting and surface disordering which is a basic subject of the present considerations.

II. BASIC CONCEPTS

The thermodynamic considerations in the case of thin films concern of course the systems in which the role of finite size effects in the rigorous definitions of the thermodynamic functions should be taken into account. The formulations reported by Hill[3] in the context of small particles can be applied to the film structure when we treat a thin film as a system divided into subsystems equivalent to two-dimensional monoatomic layers parallel to the surfaces.[4] The film thickness d is then the characterization of a sample and it can be expressed by the number n of monoatomic layers $d=na$, with a standing for the average spacing between the neighboring layers. In real films the separations between layers at the surfaces change with respect to their values inside a sample. This effect can be introduced by the surface energy terms usually appearing in the current models of thin films.[5] Thus, the thermodynamic functions which describe the relations for the considered thin film structure are not rigorously extensive, i.e., they are not proportional to the number of elements, but they satisfy the relations including size effects. According to the considerations presented by Hill[3] an arbitrary thermodynamic function G can be written in the form

$$G = N^2 n \left(\bar{G} + \frac{1}{n} G' \right), \qquad (1)$$

where N^2 stands for the number of atoms in the plane while n is the number of monoatomic layers. $\bar{G}$ and G' refer to the mean value of G when the system is homogeneous and to the difference between the two-dimensional and three-dimensional average value of G, respectively.[3]

The evident example confirming the Hill procedure is connected with the behavior of the order-disorder phase transition temperature $T_t=T_t(d)$ (Refs. 2,6) as well as the melting temperature $T_m=T_m(d)$ with respect to their thickness dependences[7] which has been clearly demonstrated by experiments.[8] Moreover, the application of Hill's procedure to the van der Waals equation of state was a subject of calculations leading to the relation T_m in terms of reduced variables with the reducing parameter dependent on the sample thickness.[9] By this fact we can state that the Hill procedure for the phase transition temperature leads to the result which is qualitatively equivalent to that obtained by means of the approach in terms of molecular field approximation used for the description of thermodynamic subsystems and interactions between them. This approach is frequently applied in thin films physics. Originally introduced by Valenta,[4] from the physical point of view based on the Néel sublattices idea, the model was successfully used by Valenta and Sukiennicki[6] in order to calculate the lattice order-disorder phase transition temperature. Let us notice that the expected dependence of the order-disorder temperature on the film thickness can be then obtained due to the boundary conditions, first of all, given by the lack of nearest neighbors for the surface atoms

and secondly by the appearance of the surface roughness reflected by surface potential.[5] The thermodynamic relation

$$F(d) = U(d) - TS(d) \qquad (2)$$

between the thermodynamic potential F, the internal energy U, and the entropy S are apparently the same in the case of thermodynamic limit and for the systems with restricted dimensions. In particular, this relation is satisfied for each subsystem $i \in (1,n)$, i.e., $F_i = U_i - TS_i$. Therefore, the thermodynamic potential $F(d)$ as one of the thermodynamic functions $G(d)$ given by Eq. (1) can be calculated on the standard way by means of Eq. (2).[5] However, for the sake of simplicity, it is convenient to consider sometime the thermodynamic potential $F(d)$ in its total form, not separated into two parts U and S. This fact takes its place for the description of melting phenomena in terms of the Landau-Ginzburg model for inhomogeneous systems.[5] For these reasons, assuming constructions the most frequently used in literature for given phenomena we take into account different description in the case of ordering and melting effects. We describe the ordering in terms of the internal energy U and the entropy S when calculated with respect to the boundary conditions. The melting is described in terms of the thermodynamic potential F considered in the most convenient form of two intersecting parabolas.[7]

Let us now analyze an infinite thin film of fcc binary alloy AB_3 with a film thickness of n monoatomic layers with the $L1_2$ ordered structure. In order to describe the lattice long-range order, the fcc lattice is divided into two sublattices α and β. In the perfectly ordered case, all α sites are occupied by A atoms and the β sites are occupied by B atoms. In the completely disordered case, the probabilities to find an A atom in α and β sites are the same.

The lattice order parameter $t(i)$, describing the difference in concentrations between the α and β sublattices is defined by[2]

$$t(i) = p_A^\alpha(i) - p_A^\beta(i) = p_B^\beta(i) - p_B^\alpha(i). \qquad (3)$$

The symbol $p_C^\gamma(i)$ denotes the probability of finding an C atom in the γ sublattice. These probabilities are normalized by[2]

$$p_A^\alpha(i) + p_B^\alpha(i) = 1, \quad p_B^\beta(i) + p_A^\beta(i) = 1. \qquad (4)$$

The concentration of atoms A in the monoatomic layer i is given by

$$x(i) = p_A^\alpha(i)F_\alpha + p_A^\beta(i)F_\beta \qquad (5)$$

while the concentration of atoms B in the same layer is written as

$$y(i) = 1 - x(i) = p_B^\alpha(i)F_\alpha + p_B^\beta(i)F_\beta, \qquad (6)$$

where F_α and F_β are the relative numbers of α and β sites, respectively.

With all these definitions it is possible to write the layer dependent probabilities as functions of the layer dependent concentration $x(i)$ and the lattice order parameter $t(i)$:

$$p_A^\alpha(i) = x(i) + F_\beta t(i),$$

$$p_A^\beta(i) = x(i) - F_\alpha t(i),$$

$$p_B^\beta(i) = 1 - x(i) + F_\alpha t(i),$$

$$p_B^\alpha(i) = 1 - x(i) - F_\beta t(i). \qquad (7)$$

The equilibrium values of $t(i)$ and $x(i)$ are obtained by minimizing the free energy F given by Eq. (2) for our system with respect to $t(i)$ and $x(i)$:

$$\frac{\partial F}{\partial t(i)} = 0, \quad i = 1, 2, \ldots, n,$$

$$\frac{\partial F}{\partial x(i)} = \lambda, \quad i = 1, 2, \ldots, n \qquad (8)$$

with λ standing for Lagrange factor which assures the condition

$$\sum_i x(i) = nc, \qquad (9)$$

where c denotes the average concentration of the atoms A in stoichiometric composition of the alloy.

In order to calculate the free energy $F = F(x,t)$ we consider the terms connected with the internal energy $U = U(x,t)$ and the entropy $S = S(x,t)$. In the Bragg-Williams approximation, the internal energy U is given as the average over the energies corresponding to a given long-range order and for the film consisting of n layers can be written as follows:

$$U = -N^2 \sum_{i=1}^{n} \sum_{CC'} [\langle Q_{CC'}\rangle_{ii} V_{CC'}^{ii} + \langle Q_{CC'}\rangle_{ii+1} V_{CC'}^{ii+1}$$

$$+ \langle Q_{CC'}\rangle_{ii-1} V_{CC'}^{ii-1}] \qquad (10)$$

for $C, C' = A$ or B. In the present case, we consider only the nearest neighbors interactions and the mean number of nearest neighbor pairs in a given layer and in the neighboring layers are given by

$$\langle Q_{CC'}\rangle_{ii} = \frac{1}{2}\{F_\alpha p_C^\alpha(i)[r_{\alpha\alpha}^{ii} p_{C'}^\alpha(i) + r_{\alpha\beta}^{ii} p_{C'}^\beta(i)] + F_\beta p_C^\beta(i)$$

$$\times [r_{\beta\alpha}^{ii} p_{C'}^\alpha(i) + r_{\beta\beta}^{ii} p_{C'}^\beta(i)]\},$$

$$\langle Q_{CC'}\rangle_{ii+1} = \frac{1}{2}\{F_\alpha p_C^\alpha(i)[r_{\alpha\alpha}^{ii+1} p_{C'}^\alpha(i+1) + r_{\alpha\beta}^{ii+1} p_{C'}^\beta(i+1)]$$

$$+ F_\beta p_C^\beta(i)[r_{\beta\alpha}^{ii+1} p_{C'}^\alpha(i+1) + r_{\beta\beta}^{ii+1} p_{C'}^\beta(i+1)]\},$$

$$\langle Q_{CC'}\rangle_{ii-1} = \frac{1}{2}\{F_\alpha p_C^\alpha(i)[r_{\alpha\alpha}^{ii-1} p_{C'}^\alpha(i-1) + r_{\alpha\beta}^{ii-1} p_{C'}^\beta(i-1)]$$

$$+ F_\beta p_C^\beta(i)[r_{\beta\alpha}^{ii-1} p_{C'}^\alpha(i-1) + r_{\beta\beta}^{ii-1} p_{C'}^\beta(i-1)]\}. \qquad (11)$$

In the above equations, we have used $r_{\gamma\gamma'}^{ii}$ for denoting the number of the nearest neighbors located at sites γ' of an

atom situated at a site γ in the same layer and $r_{\gamma\gamma'}^{ii\pm1}$ if two neighboring atoms belong to different layers. The boundary conditions for the symmetrical situation at both surfaces requires that

$$\langle Q_{CC'}\rangle_{nn+1} = 0, \quad \langle Q_{CC'}\rangle_{10} = 0. \qquad (12)$$

The entropy S of the state with a given distribution of concentration and the long-range order parameter can by written as

$$S = -k_B N^2 \sum_{i=1}^{n} \sum_{\gamma C} F_\gamma p_C^\gamma(i) \ln p_C^\gamma(i), \qquad (13)$$

where the summation over C runs over A and B and the summation over γ should be taken over α and β.

Let us notice that the summation in Eqs. (10) and (13) concerns the homogeneous subsystem in each plane i and then leads to the factor N^2 when we compare Eqs. (10) and (13) with Eq. (1) while the summation over $i \in (1,n)$ appears instead of n due to the construction for small number n of subsystems.

Usually, in the case of binary alloy theories we assume that the quantities $V_{CC'}^{ii}$ and $V_{CC'}^{ii\pm1}$ appearing in Eq. (10) represent the interaction energies between two atoms. In the Bragg-Williams approximation, they are parameters of the theory characterizing the solid phase in its average density state representation.

In the present model the interpretation of these quantities is extended so that they describe the interaction energies between two atoms embedded in the medium characterized by its crystallinity. This fact can be reflected by introducing the interaction energy dependent on the crystallinity parameter $m(i)$. Thus, in Eq. (10) we should replace $V_{CC'}^{ii}$ and $V_{CC'}^{ii\pm1}$ by $V_{CC'}^{ii}[m(i)]$ and $V_{CC'}^{ii\pm1}[m(i), m(i\pm1)]$, respectively.

Taking into account the model of solid-liquid phase transition discussed in Ref. 10 we can see that in general, the bulk melting behavior can be described by means of van der Waals equation of state in its modified form. In this case $V_{CC'}^{ii}[m(i)]$ and $V_{CC'}^{ii\pm1}[m(i), m(i\pm1)]$ can be treated as the thermodynamic Gibbs free energy functionals with respect to the crystallinity parameter $m(i)$. The most interesting analytical solutions seem to be those reported in Refs. 11,12 in terms of the density $\rho = \rho_l + (\rho_c - \rho_l)m$, where the behavior of $\rho_l(T)$ and $\rho_c(T)$ are determined then by the conditions

$$(1) \quad \text{for } \rho_l \left(\frac{dV_{CC'}^{ii}}{dm}\right)_{m=0} = 0, \qquad (14)$$

$$(2) \quad \text{for } \rho_c \left(\frac{dV_{CC'}^{ii}}{dm}\right)_{m=1} = 0, \qquad (15)$$

and for $V_{CC'}^{ii\pm1}(m)$, respectively.

In order to derive the potentials $V_{CC'}^{ii}(m)$ and $V_{CC'}^{ii\pm1}(m)$ we apply, according to Ref. 10 the method reported by Ref. 13 in the case of the van der Waals equation of state discussion. However, we modify the model by introducing the idea of different mean-field behaviors for solid and liquid

phases.[11,14] The *ab initio* calculations performed for the thermodynamic potentials in the case of aluminium samples confirm their different shape describing both the phases.[15] The idea developed in Ref. 12 is based on the assumption that the liquid phase is well described by the van der Waals equation of state and by the Gibbs energy which corresponds then to this van der Waals equation. The method is applied to determine an effective medium potential for the solid phase.[12] The van der Waals theory is next extended by introducing a modification of the entropy parameters in analogy to the prediction proposed in Ref. 11.

Taking into account the equations of state (14) and (15) we can develop the functionals $V_{CC'}^{ii}[m(i)]$ and $V_{CC'}^{ii\pm1}[m(i),m(i\pm1)]$ into series with respect to $(1-m)$, namely,

$$V_{CC'}^{ii}[m(i)] = V_{CC'}(m=1) + \frac{1}{2}\alpha_{CC'}[1-m(i)]^2$$

$$+ \frac{1}{2}\alpha_{CC'}^s[m(i)]^2(\delta_{i1}+\delta_{in}) \qquad (16)$$

for the solid phase of a thin film and into series with respect to m, namely,

$$V_{CC'}^{ii}[m(i)] = V_{CC'}(m=0) + \frac{1}{2}\alpha_{CC'}[m(i)]^2$$

$$+ \frac{1}{2}\alpha_{CC'}^s[m(i)]^2(\delta_{i1}+\delta_{in}) \qquad (17)$$

for the liquid phase of a thin film. The surface contribution (proportional to $\alpha_{CC'}^s$) to the energy given by Eqs. (16) and (17) in both the cases is taken into account in its parabolic form frequently used in literature, first of all, in the paper of Sakai,[7] which is one of the reference works in the field of thin films melting.

Similarly, the interaction energies between the atoms lying in neighboring layers are expressed by

$$V_{CC'}^{ii\pm1}[m(i)] = V_{CC'}^{ii}[m(i)] - \frac{1}{2}J_{CC'}m(i)\Delta m(i),$$

$$\Delta m(i) = m(i+1) + m(i-1) - 2m(i) \qquad (18)$$

for both crystal $V_{CC'}^{ii}[m(i)]$ given by (16) and liquid $V_{CC'}^{ii}[m(i)]$ given by Eq. (17) phases, respectively. The appearance of the second order difference $\Delta m(i)$ reflects the influence of the boundary conditions for $m(1)$ and $m(n)$ introduced by the lack of nearest neighbors at the surface [see (12)]. The term $\Delta m(i)$ corresponds to the gradient term in the Landau-Ginzburg functional and integrated over all the sublattices is equivalent to the term G' in the Hill formulation [see Eq. (1)]. The present forms of Eqs. (16) and (17) correspond to the potentials of two intersecting parabolas which are very well known in literature.[16,17] Moreover, the analysis of this type of the potential shows that it is very convenient for calculations and its results are quite precise.[7] For these reasons we reduce any potential to its parabolic shape when it is described only by parameters $\alpha_{CC'}$ and $\alpha_{CC'}^s$ considered

as the parameters of the theory. Of course, taking into account one of the forms for the van der Waals potential discussed in Ref. 10 we can precisely determine these parameters but it seems that the theory is more flexible when they remain free parameters. The parameters $J_{CC'}$ stand for the material constants characteristic for a given sample describing its bulk, i.e., homogeneous case while $\alpha_{CC'}^s$ correspond to the surface, i.e., $\alpha_{CC'}^s$ appear only at the surface planes ($i=1$ and $i=n$).

In the particular case $\alpha_{CC'}=0$, $\alpha_{CC'}^s=0$ and $J_{CC'}=0$ the present model can be reduced to the standard form of the alloy description in terms of Bragg-Williams approximation for interaction energies which are given by $V_{CC'}(m=1)$. Thus, they can be determined by the low temperature behavior of the energy. In the present version of the model extended to the melting area the relation between the energy $V_{CC'}(m=1)$ in the solid phase and the energy $V_{CC'}(m=0)$ in the liquid phase is given by

$$V_{CC'}(m=0) = V_{CC'}(m=1) + \Lambda, \qquad (19)$$

where

$$\Lambda = L_m\left(1 - \frac{T}{T_m}\right) \qquad (20)$$

is valid for arbitrary temperature T close to T_m from below and above with T_m and L_m standing for the bulk melting point and the latent heat for melting per unit volume, respectively. The relation (19) follows the thermodynamic considerations connected with the phase transition description.[16,17] In this case $V_{CC'}(m=1)$ and $V_{CC'}(m=0)$ belong to the internal energy term (10) while the entropy is given by Eq. (13). However, for the reasons explained above the potentials (16) and (17) contains the terms for $\alpha_{CC'}$ which is a contribution of two kinds. Formally, we can write that $\alpha_{CC'} = \alpha_{CC'}(U) + \alpha_{CC'}(S)$ where $\alpha_{CC'}(U)$ denotes a contribution to the internal energy due to the change of the crystallinity parameter while $\alpha_{CC'}(S)$ is a contribution introduced by the crystallinity parameter to the entropy $S[m(i)]$ (see Ref. 5). Of course, we do not divide the coefficient $\alpha_{CC'}$ into two parts in practice, taking into account the fact that the functional $F[x(i),t(i),m(i)]$ is derived by means of the potentials (16) and (17) with Eq. (18) given in the convenient form of two intersecting parabolas (see Ref. 7). Thus, substituting Eqs. (16) and (17) with Eq. (18) into Eq. (10) we calculate the functional F for which we obtain the condition

$$\frac{\partial F}{\partial m(i)} = 0, \quad i = 1,2,\dots,n \qquad (21)$$

which now, together with the solutions of Eq. (8), leads to the equilibrium values of $m(i)$ with respect to $x(i)$ and $t(i)$ considered simultaneously.

III. CALCULATIONS AND RESULTS

As an example we will consider the thin film of the AB_3 alloy with (111) surface orientation. In this case the α sublattice consists of all corner sites and the β

sublattice consists of all the face-centered sites. All α sites have six β sites as nearest neighbors in the plane while all β sites have two α sites and four β sites as nearest neighbors in the plane. In the next plane, all α sites have three β sites as nearest neighbors while all β sites have one α site and two β sites as nearest neighbors. The quantities $F_\gamma, r_{\gamma\gamma'}^{ii}, r_{\gamma\gamma'}^{ii\pm1}$ appearing in the relation for internal energy U and entropy S take the following values: $F_\alpha = \frac{1}{4}, F_\beta = \frac{3}{4}, r_{\alpha\alpha}^{ii} = 0, r_{\alpha\beta}^{ii} = 6, r_{\beta\beta}^{ii} = 4, r_{\beta\alpha}^{ii} = 2, r_{\alpha\alpha}^{ii\pm1} = 0, r_{\alpha\beta}^{ii\pm1} = 3, r_{\beta\beta}^{ii\pm1} = 2, r_{\beta\alpha}^{ii\pm1} = 1$.

Our system is described by the pairwise interactions which are defined with the quantities given by Eqs. (12), (14), and (15). The three parameters $V_{AA}(m=1), V_{BB}(m=1)$, and $V_{AB}(m=1) = V_{BA}(m=1)$ considered in the nearest-neighbor approximation are nothing else than the interaction energies used in our previous paper[2] for describing the order-disorder phenomena in binary alloy thin films without taking into account the other phenomena appearing in the sample with temperature changes. In the present considerations the interaction energies are more complicated functions allowing the melting phenomenon and the values of these parameters have to be changed in the way which ensure that the order-disorder phase transition take place at the proper temperature for the considered alloy composition.

We discussed here the properties of the ordering alloys around the two phase transition points. The first one is characteristic for the order-disorder phase transition while the second one is connected with surface melting event. All the characteristics are found by simultaneous minimization of the total free energy with respect to the lattice order parameter, concentration, and crystallinity parameter [see Eqs. (8) and (21)] for the thin film with thickness $n=9$. We also assume that our sample is composed of nickel and iron atoms forming the FeNi$_3$ alloy with the bulk lattice order-disorder phase transition temperature $T_t(\infty) = 779$ K and the bulk melting temperature 1748 K.

A. Lattice disordering temperatures

The lattice order-disorder phase transition means that the distribution of atoms A and B over the sublattices α and β becomes completely random in the temperature T_t well defined for a given crystal. Surface disordering consists in the appearance of a disorder in a surface layer while the rest of a sample is still in the partially ordered state. In thin films the lattice disordering temperatures depend on the film thickness and the surface states similarly to the melting temperatures. The lattice disordering can be interpreted by the random distribution of components (A or B) located in the sites (α or β) of the well regular lattice. The lattice is not destroyed during the disordering process.

Figure 1 shows the temperature dependence of the lattice long-range order parameter $t(i)$. We can clearly see that the disordering state at the surface layer appears at lower temperature T_{st} and it goes as a layer by layer process towards the middle of a film when the temperature approaches T_t. The horizontal line indicates disordering degree in particular layers at the point when the middle layer exercises the discontinuous jump of its order parameter. The dashed lines show the way of the layer order parameters decreasing
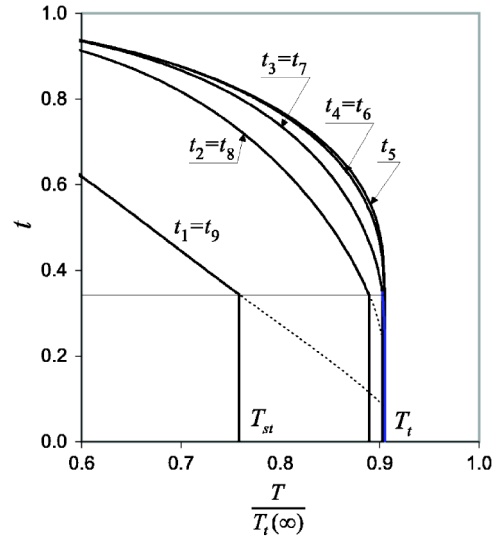

FIG. 1. Layer dependent long-range order parameter $t(i)$ vs reduced temperature for the film with nine layers.

in the interval of temperatures between disordering reached in the first layer and disordering transition for whole sample. Thus the dashed lines represent the solution of the minimizing procedure formulated by Eqs. (8) and (21) in the temperature interval in which the surface layers are disordered while the solutions of Eqs. (8) and (21) in the temperature interval below T_{st} correspond to the partially ordered surfaces. The effect described above for the surface layers in the symmetric case ($t_1 = t_9$) is also observed for the next layers ($t_2 = t_8$) only in the narrower interval of temperature (Fig. 1). In Fig. 2 we demonstrate the lattice long-range order parameter (top graph) and the Fe concentration (bottom graph) as a function of the plane position in the film with nine monoatomic layers for three different temperatures.

B. Melting temperatures

Melting means a transition from the solid phase to the liquid phase of a considered sample at the melting temperature T_m which is well defined for a given crystal. Surface melting consists in the appearance of a thin quasiliquid layer on top of the own solid surface at the temperature T_{sm} below the bulk temperature $T_m (T_{sm} < T_m)$ in the condition of the homogeneous thermodynamic bath without any gradient of temperature. In thin films these two melting temperatures T_m and T_{sm} depend on the film thickness and the surface states.[11] It is worth while to notice from the point of view of ordering in alloys that the crystallinity disorder means the distribution of atoms, independently of their kind (A or B) out of the crystallographic lattice sites (α or β). The atoms wonder in the intersite space or, in other words, the regular lattice construction is destroyed. The phase transition picture is represented in Fig. 3. We show there the behavior of the solid and liquid phase free energies (two solid lines) and their intersection point $T_m(n)$ which determines the melting temperature of a sample with film thickness $n=9$. The dashed line represents the free energy of this thin film when its surface layers are in the liquid phase it means the surface melting is al-
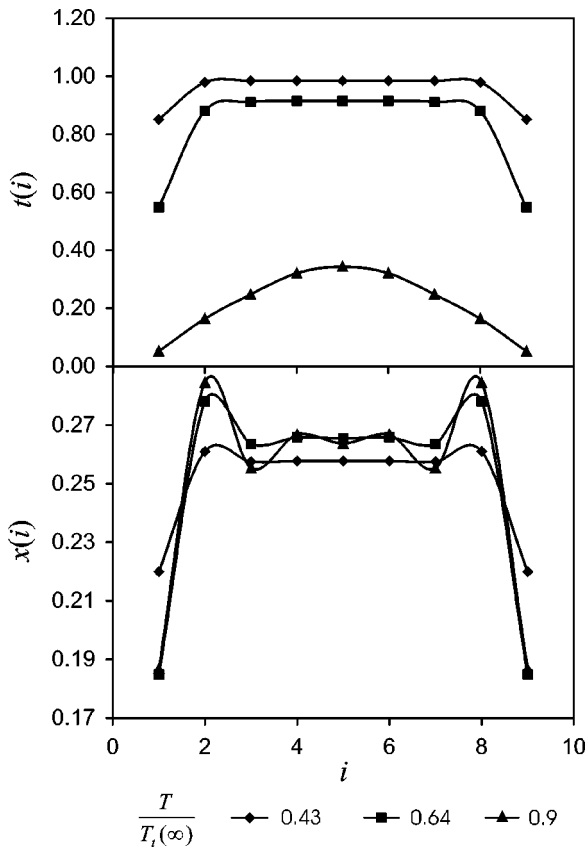
FIG. 2. Cross section of t and x through nine layers calculated for three values of reduced temperature $T/T_t(\infty)$.
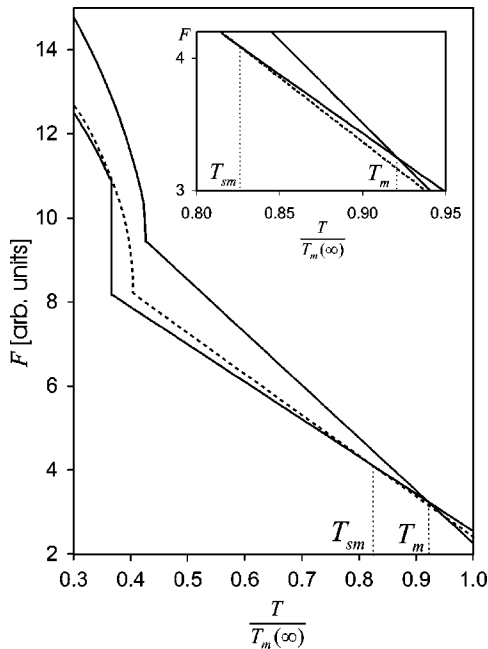

FIG. 3. The free energies for solid and liquid phase (solid lines, respectively) and for the same film when its surface layers are in the liquid phase. The inset shows the intersection region for melting area.
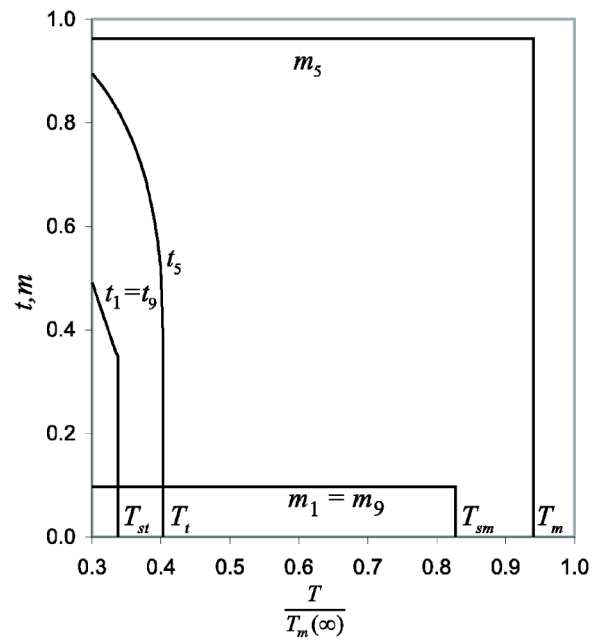

FIG. 4. Layer-dependent long-range order parameter $t(i)$ and crystallinity parameter $m(i)$ vs reduced temperature calculated for the film when its surface layers are in the liquid phase.

lowed and the intersection point between this curve and the solid phase one determines the surface melting temperature T_{sm}. The jumps visible on all three curves in Fig. 3 are connected with the discontinuous order-disorder phase transition taking place in the crystal phase, liquid phase and in the case of surface melting, respectively.

C. Interdependence of melting and lattice disordering temperatures

Figure 4 presents the temperature dependence of the long-range order parameter $t(i)$ and the crystallinity parameter $m(i)$ calculated for the case of thin film with surface melting allowed. The results in this figure clearly indicate that the considered thin film first exhibits surface disordering, then global lattice disordering, next, after the important interval of temperature, the surface melting is observed, and finally the whole sample is melted. As mentioned above, both kinds of phase transitions discussed here depends on surface state. Let us now consider the changes in the surface state after introducing different surface interaction energies than those existing inside the film to our system.

Up to now, all interactions energies were the same for whole sample and the observed surfaces effects were connected exclusively with the boundary conditions (12). In Fig. 5 we show the lattice long-range order parameter (top graph) and the Fe concentration (bottom graph) as a function of the plane position in the film with nine monoatomic layers when the surfaces interactions are enhanced by a factor of 2 with respect to those acting inside the film. We can see that this enhancement leads to an increase of the order at the surface when compared with the inside. In this case we can speak on the surface ordering. The surface is higher ordered than the
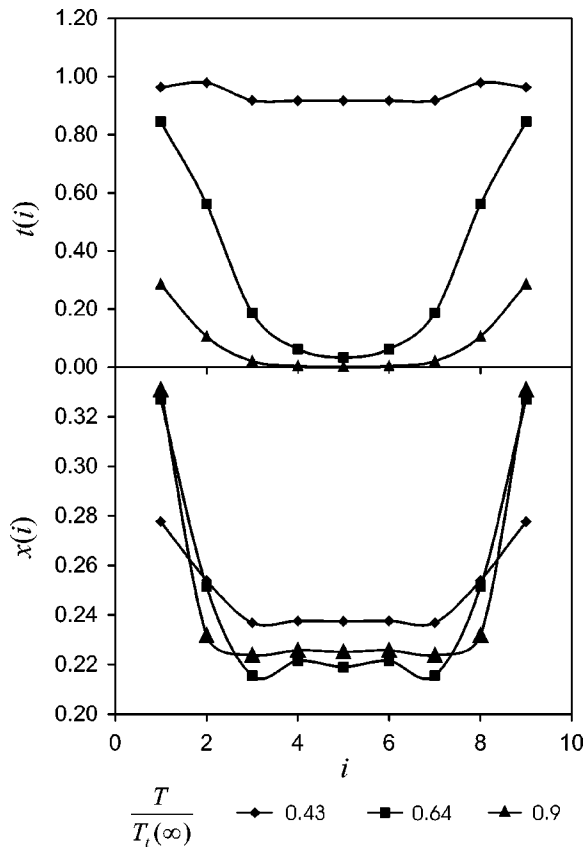
FIG. 5. Cross section of t and x through nine layers with surfaces interactions enhanced calculated for three values of reduced temperature $T/T_t(\infty)$.
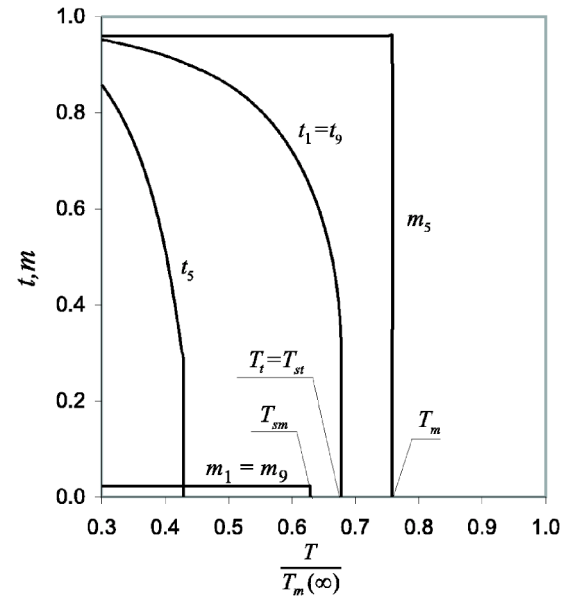

FIG. 6. Layer-dependent long-range order parameter $t(i)$ and crystallinity parameter $m(i)$ vs reduced temperature calculated for the film with surfaces interactions enhanced when their melting is allowed.

middle layers. It is worthwhile to notice that it is closely connected with the concentration distribution which is changed from the one imposing an overstoichiometric concentration of Fe in the middle layers (Fig. 2) to the opposite situation when the surface interactions are enhanced (Fig. 5). We can compare the behavior for $t(i)$ in the thin film, particularly at the surface $[t(i=1)]$ with the case of $[t(i=1)]$ in a semi-infinite crystal. This comparison is possible by taking into account the results found in Ref. 2 for a semi-infinite sample simulated by means of the properly chosen boundary condition at the surface $i=n$.[2] The behavior of $t(i=1)$ is then of analogous form confirming the above interpretation.

In Fig. 6 we present the temperature dependence of the long-range order parameter $t(i)$ and the crystallinity parameter $m(i)$ calculated for the case of a thin film with surface melting allowed. It is clearly seen that the considered thin film exhibits first the middle layer disordering, next the surface melting, and then the surface and global lattice disordering followed by the sample melting. The surface layer melts before being disordered in the sense of the lattice distribution of components. In the considered case we can observe the melting at the surfaces while the lattice disorder is still different than zero.

From the physical picture point of view it means that in the interval of temperature (T_{sm}, T_{st}) we should expect that the surface liquid layer is inhomogeneous composition of the islands consisting the same kind of alloy components. At the

temperature T_{st} the surface liquid layer becomes homogeneous.

Figure 7 illustrates the behavior of the crystallinity parameter as a section across the film thickness in the layer-by-layer melting process. The number of melt layers results, for a given temperature, from the minimizing process described by the conditions (8) and (21). The curves in the top graph were calculated for the homogeneous interaction energies in the film while those in the bottom graph represent the case when interaction energies in the surface layers are enhanced. The three curves visible in both graphs in Fig. 7 represent, looking from the top, the distribution of the melting parameter $m(i)$ for the thin film in the crystal phase, for the same thin film with one liquid layer at the surfaces (to compare with Figs. 4 and 6, respectively), and next with two liquid layers at the surfaces. The presented distributions result from the minimization of the energy for the temperature $T/T_t(\infty)$ $=0.3$, 0.5, and 0.7, respectively. We note that the surface interaction energy enhancement does change the values of the crystallinity parameter but does not change the character of the melting process which in the present case always starts at the surfaces in contrast to the disordering process where it starts in the middle of a sample. The surface interaction energy enhancement influences only the melting temperatures (see Fig. 6).

IV. FINAL REMARKS

A phenomenon of the surface melting has been the subject of quite a number of works for many years.[18–23] This phenomenon relies on the appearance of a liquidlike layer on the surfaces of crystals, between the solid and gas phases. Such a layer exists at the thermodynamic equilibrium below the bulk melting temperature (the triple point). Pluis et al.[16] have

phenomena. In our work the surface melting in the thin film of binary alloys is discussed in terms of the model based on three densities: the crystallinity order parameter which characterizes a topological deviation of the liquid structure from the crystalline one, the lattice order parameter which describes a degree of the ordering of components in alloy, and the nonordering density identified with the deviation of the local concentration in planes parallel to the surface from the average concentration. All three densities have their own temperature-dependent profiles across the film which are calculated and discussed. The important results show the profile of the crystallinity order parameter which decreases from the middle of the film towards the surface layers, showing that when the melting temperature of the material is approached from below, the melting starts at the film surface in such a way that at the beginning only one surface layer melts at each film surface and with the temperature rising the consequent parts of the film melt, layer by layer. The surface melting obtained in our work for thin films of alloys is therefore basically similar to that obtained earlier for one constituent slab.[1] The most significant result concerns the picture of the surface melting which can be obtained even in the cases where the microscopic surface interactions are changed in comparison with the interactions inside the film in such a way that they lead to the surface-induced lattice ordering instead of surface-induced disordering.

It is interesting that a picture of the surface melting obtained by us is to some extent similar to that obtained earlier in models including two densities only, where the lattice order parameter and the nonordering density connected with a concentration profile have been considered.[1] It seems to us, however, that the three densities model is more clear physically: the crystallinity order parameter distribution and a description of melting appears in our approach as the result of a simultaneous minimization of the free energy with respect to all three densities, while in an earlier version the surface melting has been described as a result of the free energy minimization with respect to the lattice order and concentration profiles only. Thus, our approach allows us to discuss the interdependence of melting and lattice disordering, especially in the case where both phenomena appear in the same range of temperature. In particular, a nonzero surface-induced lattice disorder may appear not only if the crystal structure is still preserved but also if the surface layer is already melted.
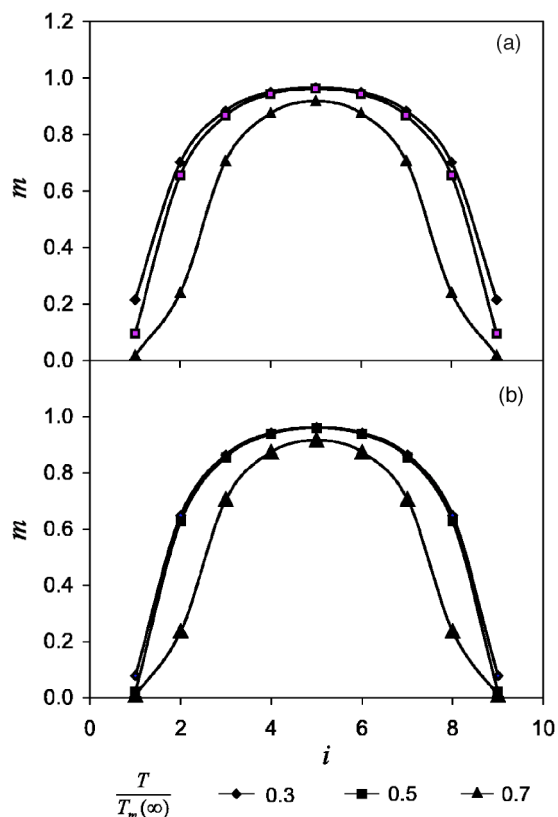

FIG. 7. Cross section of crystallinity parameter *m* through nine layers calculated in two cases (a) for homogeneous interaction energies and (b) for interaction energies in the surface layers enhanced. Three curves in both graphs, looking from the top, represent the film in crystalline phase; with one liquid layer at each surfaces; with two liquid layers at each surface, respectively.

shown that such a phenomenon can be described by using the simple Landau theory and other authors[1,7,24,25] have applied such a theory to thin film or slab geometry. On the other hand, the Landau theory approach has been applied to the surface induced disorder phase transition in binary alloys with fcc structure in Ref. 25 and to thin films in Ref. 26. In the case of thin films of binary alloys with fcc structure the surface melting has been also studied in analogy to the surface induced disordering.[1]

The present paper inspired by Ref. 2 shows the analogy as well as differences and interdependence of the considered

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