PHYSICAL REVIEW B **74**, 205402 (2006)

# Short-range order in $AB_3$ binary alloy thin films

I. Zasada,* A. Sukiennicki,† and L. Wojtczak
*Solid State Physics Department, University of Lodz, Poland*

F. L. Castillo Alvarado
*Escuela Superior de Fisica y Matematicas, Instituto Politecnico National, Mexico City, Mexico*

(Received 12 April 2006; revised manuscript received 4 August 2006; published 2 November 2006)

The theory of order-disorder phenomena in binary alloy thin films of $AB_3$ type is considered in the context of long-range and short-range order parameters. The paper is based on the model introduced in connection with the surface melting and surface disordering considerations in the approach to the samples with the restricted dimension when it requires the construction of a thermodynamically inhomogeneous system consisting of homogeneous subsystems whose entropy determination needs then the pair entropy approximation. Among others, two effects seem to be of particularly great interest: namely, the crossover of the site occupancy in the surface layer and the shift of atoms in the surface plane between two kinds of lattice sites. These effects influence the diffuse low-energy electron diffraction, surface melting, or spin-wave resonance conditions.

DOI: 10.1103/PhysRevB.74.205402 PACS number(s): 73.61.At, 68.35.Rh

## I. INTRODUCTION

In the present paper order-disorder phenomena including the distribution of chemical composition are discussed in terms of the long-range order as well as the short-range order in binary alloys and their films whose surfaces play an essential role.

The considerations concerning the long-range order behavior are based on the model applied by Valenta and Sukiennicki[1] which takes into account the Valenta approach[2] to the description of thin films in the form of monoatomic layers parallel to the surfaces and treated in the sense of Néel sublattices. This assumption leads to the single-site entropy term which is factorized with respect to the order parameter in the monoatomic planes. In this case we can apply the approach to the samples with restricted dimension, including thin films, based on a thermodynamic construction of the thermodynamically inhomogeneous system consisting of homogeneous subsystems.[3,4]

The aim of the present paper is to extend the model discussed in Ref. 3 to the case when the short-range order behavior is taken into account. The presented formulation is valid for an arbitrary crystallographic lattice although an example is shown in the case of fcc structure for illustration.

The short-range order behavior is considered in terms of the pair entropy term whose calculations are given for thin films in the present paper in analogy to the approaches discussed by Kikuchi[5] and Morán-López and Falicov[6] as well as López-Chávez and Castillo Alvarado[7] who applied it in the case of bulk materials. The fcc lattices were also considered in this context by Sanchez and de Fontaine.[8]

The model introduced by Valenta and Sukiennicki[1] was applied to the case of the disorder description in dilute alloy ferromagnetic thin films.[9] The influence of structural disorder on the magnetization and the Curie temperature was studied using generalized Valenta equations in Bragg-Williams approximations.[10] However, the critical concentration of disordered binary magnetic alloys was predicted using more advanced methods[11] whose applications were discussed also in, e.g., Refs. 12 and 13 in connection with the surface magnetism existence. An excellent review of theoretical results concerning surface and thickness effects in binary magnetic alloys is presented in Ref. 14. Papers based on differential or the integral operator techniques have also contributed to the description of structurally disordered magnetic media; in particular, the influence of surface amorphization or recrystallization on the magnetic properties of thin films was discussed (e.g., Refs. 15 and 16).

The order-disorder phase transition at the surface of binary alloys structure was studied within the Landau theory for fcc lattice[17] as well as considerations for bcc (110) binary alloy thin films were presented.[18] Moreover, the thermodynamics of finite-size effects was considered.[19] Studies have shown that surfaces can influence the thermodynamic properties in a substantial way by introducing surface-induced order.[20] The order-disorder transition was described in the usual way by subdividing the lattice into two interpenetrating sublattices $\alpha$ and $\beta$ and by determining the lattice order by means of the long-range order parameter.[20,21] In this context the present paper similar to Refs. 17–21 is a continuation of Ref. 3 devoted to the description of binary-alloy thin-film properties and to their discussion in terms of the pioneering work of Ref. 1 which is taken into account as the background of the entropy considerations.

The theory of ordering in fcc lattices was developed for systems with first- and second-neighbor interactions[8] described by the Ising model as well as calculated in the tetrahedron-octahedron approximation of the cluster variation method.[22] The different statistical-mechanics approximations for the study of antiferromagnetism in the fcc lattice were compared and discussed in the context of real characteristics of samples.[23] The cluster variation method was also applied to evaluate the critical temperature for fcc Ising ferromagnets.[24] The method is very effective and relatively convenient for calculations.[25] The paper can be used as an alternative background for the construction of a model containing short-range order correlations in its entropy formulation in contrast to our approach based on pair probability configurations consequently to the approach given in Ref. 1.

Short-range order is explicitly presented in connection with the diffuse scattering experiments of electrons on binary alloys.[26] In this case there is a coincidence with the present paper since our aim consists also in the application of the short-range order correlations found in this paper to diffuse low-energy electron diffraction (DLEED) measurements.

A development in the investigations of order-disorder phenomena in binary alloy thin films,[27] independently of magnetic films behavior,[28] consists, first of all, in the prediction of an interesting phenomenon, i.e., surface disordering, discussed in analogy to the surface melting.[3] Moreover, in this case an interpretation of the disordering kinetics is proposed in connection with the behavior of disorder which appears as a layer-by-layer process starting from the surface planes.

In the present paper we discuss short-range order behavior. Its profile across a film results from the variational principle formulated for the free energy $F$ which consists of the internal energy $U$ and entropy $S$ terms: $F=U-TS$. The paper deals with the pair entropy contribution formulated by means of the pair probability standing for the number of possible configurations for a given distribution of concentration of two kinds of atoms. Each configuration is described by the probability of the nearest-neighboring site occupation with respect to the central site. Then, the particular probabilities allow us to define the long-range order and, first of all, the short-range order parameter which is related to the pair correlations. These probabilities describe also the internal energy term. In particular, the correlations at the surface are interesting from their physical applications in the case of the low-energy electron diffraction considerations. The numerical results collect various situations for the long- and short-range order behavior. Their description and interpretation are summarized in the concluding remarks.

## II. PAIR ENTROPY FORMULATION

In order to calculate the entropy with respect to its pair contribution which is responsible for the short-range order correlations we introduce the cumulant representation (e.g., Ref. 29). Taking into account the expression for the total entropy we can write it in the form (e.g., Ref. 30)

$$S=\sum_{r}\sigma_r+\sum_{\langle rr'\rangle}(\sigma_{rr'}-\sigma_r-\sigma_{r'}) \tag{1}$$

when we neglect the cumulants of the higher order than 2. In this case $\sigma_r$ stands for the single-site entropy while $\sigma_{rr'}$ is the pair entropy contribution per one atom.

We can see from Eq. (1) that the entropy has then two contributions: one of them corresponding to the single-site entropy and the second one describing the pair entropy. The contribution of single-site entropy in homogenous systems, including bulk samples for $n=N$, can be written as

$$S_1=\sum_{r}\sigma_r-\sum_{\langle rr'\rangle}(\sigma_r+\sigma_{r'})=N^2n\sigma_1-\frac{1}{2}N^2n2z\sigma_1, \tag{2}$$

where

$$\sigma_1=k_B\ln g_1, \tag{3}$$

with the probability $g_1$ taking into account all the configurations of atoms and $z$ standing for the nearest neighbors. The contribution of pair entropy in homogenous systems, including three-dimensional bulk $n=N$ samples or two-dimensional plates $n=1$, can be written as

$$S_2=\sum_{\langle rr'\rangle}\sigma_{rr'}=\frac{1}{2}N^2nz\sigma_2. \tag{4}$$

The pair entropy is then given by

$$\sigma_2=k_B\ln g_2, \tag{5}$$

with the probability $g_2$ standing for the number of possible configurations for a given distribution of concentration and a distribution of both the long- and short-range order parameters.

Let us now analyze an infinite, in the surface plane, thin film of fcc binary alloy $A_cB_{(1-c)}$ with film thickness of $n$ monoatomic layers having the (111) surface orientation. We divide the film into $n$ monoatomic layers labeled by $i$. Each layer can be considered then as a homogenous sublattice from the thermodynamic point of view although the film is not now a homogenous thermodynamic system. In order to describe the lattice long-range order, the fcc lattice is also divided into two sublattices $\alpha$ and $\beta$. In the perfectly ordered case, all $\alpha$ sites are occupied by $A$ atoms and the $\beta$ sites are occupied by $B$ atoms. In the completely disordered case, the probabilities to find an $A$ atom in $\alpha$ and $\beta$ sites are the same (cf. Ref. 27) and similary the atoms $B$ are situated in the sites $\alpha$ and $\beta$ with the same probabilites.

The lattice order parameter $t(i)$, describing the difference in concentrations between the $\alpha$ and $\beta$ sublattices appearing in the monolayer $i$, is defined by[27]

$$t(i)=p_A^{\alpha}(i)-p_A^{\beta}(i)=p_B^{\beta}(i)-p_B^{\alpha}(i). \tag{6}$$

The symbols $p_C^{\gamma}(i)$ denote the probability of finding C atoms in the $\gamma$ sublattice. These probabilities are normalized by[27]

$$p_A^{\alpha}(i)+p_B^{\alpha}(i)=1,\quad p_B^{\beta}(i)+p_A^{\beta}(i)=1. \tag{7}$$

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

$$x(i)=p_A^{\alpha}(i)F_\alpha+p_A^{\beta}(i)F_\beta, \tag{8}$$

while the concentration of atoms $B$ in the same layer can be written as

$$y(i)=1-x(i)=p_B^{\alpha}(i)F_\alpha+p_B^{\beta}(i)F_\beta, \tag{9}$$

where $F_\alpha$ and $F_\beta$ are the relative numbers of $\alpha$ and $\beta$ 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 $t(i)$: namely,[27]

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

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

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

$$p_B^\alpha(i) = 1 - x(i) + F_\beta t(i). \tag{10}$$

It is worth while to notice that formulas (10) are identical with those used in Ref. 10 Next, we can write[15]

$$g_1^\gamma = \begin{pmatrix} F_\gamma N^2 n \\ F_\gamma N^2 n p_A^\gamma \end{pmatrix} \tag{11}$$

for bulk systems where $n=N$ and

$$g_1^\gamma = \Pi_i g_1^\gamma(i), \quad g_1^\gamma(i) = \begin{pmatrix} F_\gamma N^2 \\ F_\gamma N^2 p_A^\gamma(i) \end{pmatrix} \tag{12}$$

for thin-film geometry.

Using now, as usual, the Stirling formula, we obtain

$$\sigma_1^\gamma = k_B \sum_C F_\gamma p_C^\gamma \ln p_C^\gamma \tag{13}$$

for bulk systems and

$$\sigma_1^\gamma = k_B \sum_i \sum_C F_\gamma p_C^\gamma(i) \ln p_C^\gamma(i) \tag{14}$$

for the considered thin-film system,[27] where the summation over $C$ runs over $A$ and $B$.

The single-site contribution to the entropy given by Eq. (1) is then determined by the relations

$$\sum_r \sigma_r = N^2 \sum_\gamma \sigma_1^\gamma \tag{15}$$

and

$$\sum_{\langle rr' \rangle} (\sigma_r + \sigma_{r'}) = N^2 n \sum_{\gamma\gamma'} \sigma_1^\gamma r_{\gamma\to\gamma'}, \tag{16}$$

where $r_{\gamma\to\gamma'}$ stands for the nearest neighbors of atoms in the position $\gamma'$ when the central atom is situated at the site $\gamma$. Of course, in the case of thin films, we have

$$\sum_r \sigma_r = N^2 \sum_i \sum_\gamma \sigma_1^\gamma(i) \tag{17}$$

and

$$\sum_{\langle rr' \rangle} (\sigma_r + \sigma_{r'}) = N^2 \sum_i \sum_{\gamma\gamma'} \sigma_1^\gamma(i) r_{\gamma\to\gamma'}^i \tag{18}$$

instead of Eqs. (15) and (16), respectively.

When we consider the quantity $g_1$ its factorization (12) with respect to $g_1(i)$ is evident and it is described taking into account the derivation reported in Ref. 1. Unfortunately, the factorization of $g_2$ with respect to $g_2(i)$ is not obvious because of the interactions between the sites localized perpendicularly to the monoatomic layers. Therefore, we need to define properly the two-site probabilities which determine the quantity $g_2$: namely, the following.

(i) The probability $p_{AA}^{\alpha\beta}(i)$ means the conditional probability that site $\alpha$ is occupied by atoms $A$ and site $\beta$ is occupied also by atoms $A$ while both sites belong to the same monoatomic layer $i$.

(ii) The probability $p_{AB}^{\alpha\beta}(i)$ means the conditional probability that site $\alpha$ is occupied by atoms $A$ and site $\beta$ is occupied by atoms $B$ while both sites belong to the same monoatomic layer $i$.

(iii) The probability $p_{BA}^{\alpha\beta}(i)$ means the conditional probability that site $\alpha$ is occupied by atoms $B$ and site $\beta$ is occupied by atoms $A$ while both sites belong to the same monoatomic layer $i$.

(iv) The probability $p_{BB}^{\alpha\beta}(i)$ means the conditional probability that site $\alpha$ is occupied by atoms $B$ and site $\beta$ is occupied also by atoms $B$ while both sites belong to the same monoatomic layer $i$.

Generally, we can formulate the probabilities $p_{CC'}^{\gamma\gamma'}(i)$ for $(\gamma,\gamma') \in (\alpha,\beta)$ and $(C,C') \in (A,B)$ defined in the similar way: namely, the following.

The probability $p_{CC'}^{\gamma\gamma'}(i)$ means the conditional probability that site $\gamma$ is occupied by atoms $C$ and site $\gamma'$ is occupied by atoms $C'$ while both sites belong to the same monoatomic layer $i$.

Moreover, in the case of pair entropy formulation, we can consider the probabilities $p_{CC'}^{\gamma\gamma'}(i,i\pm 1)$ which are defined in analogy to $p_{CC'}^{\gamma\gamma'}(i)$ as follows.

The probability $p_{CC'}^{\gamma\gamma'}(i,i\pm 1)$ means the conditional probability that site $\gamma$ is occupied by atoms $C$ and site $\gamma'$ is occupied by atoms $C'$ while site $\gamma$ belongs to the monoatomic layer $i$ and site $\gamma'$ belongs to the nearest-neighboring monoatomic layer $i\pm 1$.

In order to factorize the pair entropy (14) we consider the position index $r=(i,j)$ where $j$ belongs to the monoatomic plane in which the system is homogenous and $i$ labels the monoatomic planes in the direction of film thickness. Thanks to this description we can see that the probabilities describing the behavior of atoms in the positions in two nearest neighboring planes $p_{CC'}^{\gamma\gamma'}(i,i\pm 1)$ should be factorized in the form

$$p_{CC'}^{\gamma\gamma'}(i,i\pm 1) = p_C^\gamma(i) p_{C'}^{\gamma'}(i\pm 1), \tag{19}$$

which assures the factorization procedure for the entropy.

Taking into account the above assumption we can consider the pair entropy (5) only in the planes $i$ while the entropy contribution due to the nearest-neighboring layer interactions is reduced to the single-site entropy term. In order to determine the pair entropy term given by Eq. (14) we can see that $\sigma_{rr'} = \sigma_{jj'}(i)$ does not depend in fact on $j$ and $j'$ due to the homogeneity in the plane $i$. Moreover,

$$g_2^{\gamma\gamma'} = \Pi_i g_2^{\gamma\gamma'}(i) \tag{20}$$

is then factorized with respect to the monoatomic layers $i$ according to Eqs. (12); however now, not only is the long-range order parameter $t(i)$ inhomogeneous with respect to the layers $i$, but also the short-range order parameter $s(i)$ has its distribution perpendicular to the surface.

## III. ORDER PARAMETERS IN TERMS OF THE PAIR PROBABILITIES

Let us now consider the relations between the pair probabilities $p_{CC'}^{\gamma\gamma'}(i)$ and the single-site probabilities $p_C^{\gamma}(i)$. It is easily to notice that the probability $p_A^{\alpha}(i)$ denoting the occupation of the site $\alpha$ by atoms $A$ in layer $i$ is equal to the sum of the pair probabilities $p_{AA}^{\alpha\beta}(i)$ and $p_{AB}^{\alpha\beta}(i)$ which denotes the occupation of site $\alpha$ by atoms $A$ independently of the occupation of site $\beta$ by atoms $A$ or $B$. Thus, we obtain

$$p_{AA}^{\alpha\beta}(i) + p_{AB}^{\alpha\beta}(i) = p_A^{\alpha}(i),$$

$$p_{AA}^{\alpha\beta}(i) + p_{BA}^{\alpha\beta}(i) = p_A^{\beta}(i),$$

$$p_{BB}^{\alpha\beta}(i) + p_{BA}^{\alpha\beta}(i) = p_B^{\alpha}(i),$$

$$p_{BB}^{\alpha\beta}(i) + p_{AB}^{\alpha\beta}(i) = p_B^{\beta}(i), \tag{21}$$

and similarly for other proper combinations of the possible configurations of atoms.

The relations (21) allow us to define the long-range order parameter $t(i)$ in terms of the pair probabilities,

$$t(i) = p_{AB}^{\alpha\beta}(i) - p_{BA}^{\alpha\beta}(i) \tag{22}$$

or

$$t(i) = p_{BA}^{\beta\alpha}(i) - p_{AB}^{\beta\alpha}(i) \tag{23}$$

and to show that the definitions (22) and (23) are equivalent to the definitions (6) introduced by means of the single-site probabilities $p_C^{\gamma}(i)$.

In analogy to the definition of the long-range order parameter we can introduce now the definition of the short-range order parameter $s(i)$ as

$$1 - s(i) = \frac{p_{AB}^{\alpha\beta}(i) + p_{BA}^{\alpha\beta}(i)}{p_A^{\alpha}(i)p_B^{\beta}(i) + p_B^{\alpha}(i)p_A^{\beta}(i)}, \tag{24}$$

which can be interpreted in terms of the correlations which represent its nature from the physical point of view.

Taking into account the general procedure we can calculate $p_{AA}^{\alpha\beta}(i)$, $p_{AB}^{\alpha\beta}(i)$, $p_{BA}^{\alpha\beta}(i)$, and $p_{BB}^{\alpha\beta}(i)$ by means of the relations (10), (22), and (24). Similarly, we can introduce all the probabilities $p_{CC'}^{\gamma\gamma'}(i)$ which are collected in the Appendix in their explicit forms.

We are ready now to construct the pair entropy term. The probability $g_2^{\gamma\gamma'}$ can be expressed by

$$g_2^{\gamma\gamma'} = \binom{F_\gamma N^2}{F_\gamma N^2 p_A^{\gamma}} \binom{F_\gamma N^2 p_A^{\gamma}}{F_\gamma N^2 p_{AA}^{\gamma\gamma'}} \binom{F_\gamma N^2 p_B^{\gamma}}{F_\gamma N^2 p_{BB}^{\gamma\gamma'}}, \tag{25}$$

whose interpretation is the following: the probability $g_2^{\gamma\gamma'}$ determines the conditional probability that the $F_\gamma N^2$ atoms in the position $\gamma$ is divided into two groups gathering $F_\gamma N^2 p_A^{\gamma}$ and $F_\gamma N^2 p_B^{\gamma}$ atoms which have their neighbors of the same type $A$ or $B$, respectively.

Taking into account the Stirling approximation for the Boltzmann entropy representation we obtain

$$\sigma_2^{\gamma\gamma'} = k_B \sum_{CC'} F_\gamma p_{CC'}^{\gamma\gamma'} \ln p_{CC'}^{\gamma\gamma'}, \tag{26}$$

which contributes to the entropy given by Eq. (1) as follows

$$\sum_{\langle rr'\rangle} \sigma_{rr'} = \frac{1}{2} N^2 n \sum_{\gamma\gamma'} \sigma_2^{\gamma\gamma'} r_{\gamma\to\gamma'} \tag{27}$$

in analogy to formulas (15) and (16). The same procedure leads to the expression

$$\sum_{\langle rr'\rangle} \sigma_{rr'} = \frac{1}{2} N^2 \sum_i \sum_{\gamma\gamma'} \sigma_2^{\gamma\gamma'}(i) r_{\gamma\to\gamma'}^{ii} \tag{28}$$

for thin films where

$$\sigma_2^{\gamma\gamma'}(i) = k_B \sum_{CC'} F_\gamma p_{CC'}^{\gamma\gamma'}(i) \ln p_{CC'}^{\gamma\gamma'}(i) \tag{29}$$

in analogy to Eq. (14). Finally, the entropy (1) is given by

$$S = -k_B N^2 \left[ \sum_{i\gamma C} F_\gamma (1 - z_\gamma^i) p_C^{\gamma}(i) \ln p_C^{\gamma}(i) + \frac{1}{2} \sum_i \sum_{\gamma\gamma'} \sum_{CC'} F_\gamma r_{\gamma\to\gamma'}^i p_{CC'}^{\gamma\gamma'}(i) \ln p_{CC'}^{\gamma\gamma'}(i) \right], \tag{30}$$

where

$$z_\gamma^i = \sum_{\gamma'} r_{\gamma\to\gamma'}^i. \tag{31}$$

The entropy (30) corresponds to the case when the system is constructed by homogenous subsystems represented by monoatomic layers $i$. When the system is homogenous all the quantities appearing in Eq. (30) do not depend on $i$; i.e., the system represents the bulk sample.

It is worthwhile to remark that the factorization (19) applied to the entropy derivation in the form (1) in order to obtain Eq. (30) is equivalent to the situation that the nearest neighbors $r_{\gamma\to\gamma'}^i$ are confined to those in the monoatomic layer $i$:

$$r_{\gamma\to\gamma'}^i = r_{\gamma\to\gamma'}^{ii}. \tag{32}$$

In this case, however, the results are not providing the bulk solution. The expression (30) describes very well the bidimensional case when we consider a planar sample. On the other hand, we can understand the numbers $r_{\gamma\to\gamma'}^i$ as those corresponding to the nearest neighbors in three-dimensional space:

$$r_{\gamma\to\gamma'}^i = r_{\gamma\to\gamma'}^{ii} + r_{\gamma\to\gamma'}^{ii-1} + r_{\gamma\to\gamma'}^{ii+1}. \tag{33}$$

In this case both the limiting solutions for three-dimensional and two-dimensional samples are properly achieved.

The role of factorization is evident in the case of calculations of the internal energy. The interactions between the nearest neighbors are then divided into those considered in plane $i$ and those between the layers $i$ and $i \pm 1$. Thus we can write

$$U = -\frac{1}{2}\sum_{i}\sum_{\gamma\gamma'}\sum_{CC'} F_{\gamma} r^{ii}_{\gamma\to\gamma'} p^{\gamma\gamma'}_{CC'}(i) V_{CC'} - \frac{1}{2}\sum_{i}\sum_{\gamma\gamma'}\sum_{CC'} F_{\gamma} p^{\gamma}_{C}(i) \times [r^{ii+1}_{\gamma\to\gamma'} p^{\gamma'}_{C'}(i+1) + r^{ii-1}_{\gamma\to\gamma'} p^{\gamma'}_{C'}(i-1)] V_{CC'}, \tag{34}$$

where we use the relation (19) which introduces the decupling of the second term in Eq. (34).

The free energy of binary alloy thin films, namely,

$$F = U - TS, \tag{35}$$

where $U$ is given by Eq. (34) and $S$ is given by Eq. (30) with respect to the $p^{\gamma}_{C}(i)$ and $p^{\gamma\gamma'}_{CC'}(i)$ dependent on $t(i)$ and $s(i)$ defined by Eqs. (22) and (24), is a functional whose minimization leads to the distribution of the long- and short-range order parameters as well as to the distribution of the concentrations $x(i)$ or $y(i)$ given by Eq. (8) or (9), respectively.

## IV. PAIR CORRELATIONS

The physical interpretation of the introduced pair probabilities $p^{\gamma\gamma'}_{CC'}(i)$, collected in the Appendix, refers to the physical correlations which, first of all, play an important role for the description of the diffuse low-energy electron diffraction.[31,32] The correlations are determined by

$$\langle p^{\gamma}_{C}(i) p^{\gamma'}_{C'}(i)\rangle = p^{\gamma\gamma'}_{CC'}(i) - p^{\gamma}_{C}(i) p^{\gamma'}_{C'}(i); \tag{36}$$

hence, due to the definition (24), we can express the correlations of the alloy components by the single-site occupation probabilities $p^{\gamma}_{C}(i)$ and the short-range order parameter $s(i)$.

The surface correlations determined by Eq. (36) for $i=1$ are responsible for the surface scattering of electrons in disordered systems. The surface reflects electrons by the diffuse scattering potential which depends on the interaction between surface and the substrate due to its modification by the short-range order. This property can be observed in the diffuse LEED intensity expressed in terms of (i) the form factor, which contains physical information about the geometrical arrangement of surface atoms and their position with respect to the substrate atoms, and (ii) the structure factor, which depends on the statistical distribution of surface atoms at the bidimensional surface lattice sites.

The last term is determined by means of the Fourier transform of pair correlation functions taking their form (36) in the case of binary alloy surfaces. We can see from Eq. (36) that the scattering intensity is expressed by the short-range order parameter whose symmetry can be checked experimentally.

The present approach leads to two pictures. First of all, the correlations have the bidimensional symmetry below some critical value of the crossover film thickness. In this case the correlations perpendicular to the surface are marked in fact by the short-range order parameter profile—more precisely, by its gradient when the number of neighbors is given by Eq. (32). The second case corresponds to the three-dimensional radial symmetry when the nearest neighbors are taken in the form (33). Thus, symmetry of the correlations is proper for the films sufficiently thick, above the crossover thickness. The correlations are then of the spherical symmetry and they behave properly close to the case when the space is isotropic.

The transition from the region where the symmetry is of bidimensional character to the region where the symmetry is of three-dimensional behavior can be evaluated by means of the critical film thickness parameter found from the minimization approach with respect to the critical value of the thickness. The problem is of general nature and its experimental verification is one of the forthcoming tasks discovered due to the pair energy contribution being taken into account.

## V. NUMERICAL RESULTS

As an example we will consider a thin film of the $AB_3$ alloy ($Ni_3Fe$) with (111) surface orientation. Permalloy is chosen for illustration in analogy to the paper by Valenta and Sukiennicki[1] where the interactions are also confined to the case of a lattice order parameter description only. In this case the $\alpha$ sublattice consists of all corner sites and the $\beta$ sublattice consists of all the face-centered sites. All $\alpha$ sites have six $\beta$ sites as nearest neighbors in the plane while all $\beta$ sites have two $\alpha$ sites and four $\beta$ sites as nearest neighbors in the plane. In the next plane, all $\alpha$ sites have three $\beta$ sites as nearest neighbors while all $\beta$ sites have one $\alpha$ site and two $\beta$ sites as nearest neighbors. The quantities $F_{\gamma}, r_{\gamma\to\gamma'}$ appearing in the relation for internal energy $U$ and entropy $S$ for bulk sample take the values

$$F_{\alpha} = \frac{1}{4}, \quad F_{\beta} = \frac{3}{4}, \quad r_{\alpha\to\alpha} = 0, \quad r_{\alpha\to\beta} = 12,$$
$$r_{\beta\to\alpha} = 4, \quad r_{\beta\to\beta} = 8,$$

while in the case of thin films they take the following values:

$$F_{\alpha} = \frac{1}{4}, \quad F_{\beta} = \frac{3}{4}, \quad r^{ii}_{\alpha\to\alpha} = 0, \quad r^{ii}_{\alpha\to\beta} = 6,$$
$$r^{ii}_{\beta\to\alpha} = 2, \quad r^{ii}_{\beta\to\beta} = 4,$$
$$r^{ii\pm1}_{\alpha\to\alpha} = 0, \quad r^{ii\pm1}_{\alpha\to\beta} = 3, \quad r^{ii\pm1}_{\beta\to\alpha} = 1, \quad r^{ii\pm1}_{\beta\to\beta} = 2.$$

The considered system is described by the pairwise lattice interactions in the nearest-neighbor approximation. The lattice interactions are defined by three parameters $V_{AA}$, $V_{BB}$, and $V_{AB} = V_{BA}$. We also define (cf. Ref. 27) the quantity $V = V_{AB} - \frac{1}{2}(V_{AA} + V_{BB})$ which takes a positive value for ordering alloy and a negative value for the segregating one. We confine our considerations to the case off ordering for which we discuss here the long-range order together with the short-range order and the concentration distribution in thin films. In order to relate our calculations to the case of $Ni_3Fe$ alloys we assume the value of $V$ which corresponds to the phase transition temperature $T_t$ taken for the bulk sample as an experimental data.

First, we present the case of bulk material. In Fig. 1 we show the temperature dependence of the long-range order

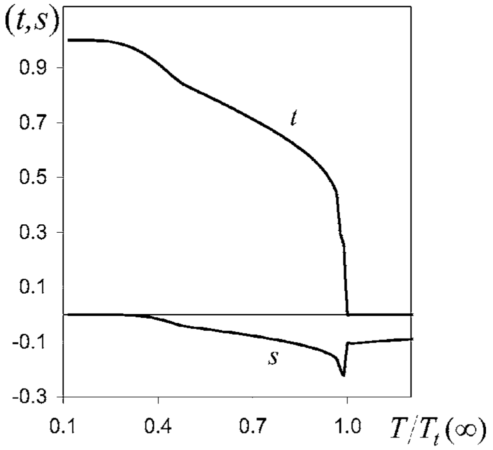

FIG. 1. Temperature dependence of the long-range order parameter $t$ and the short-range order parameter $s$ in the case of bulk.

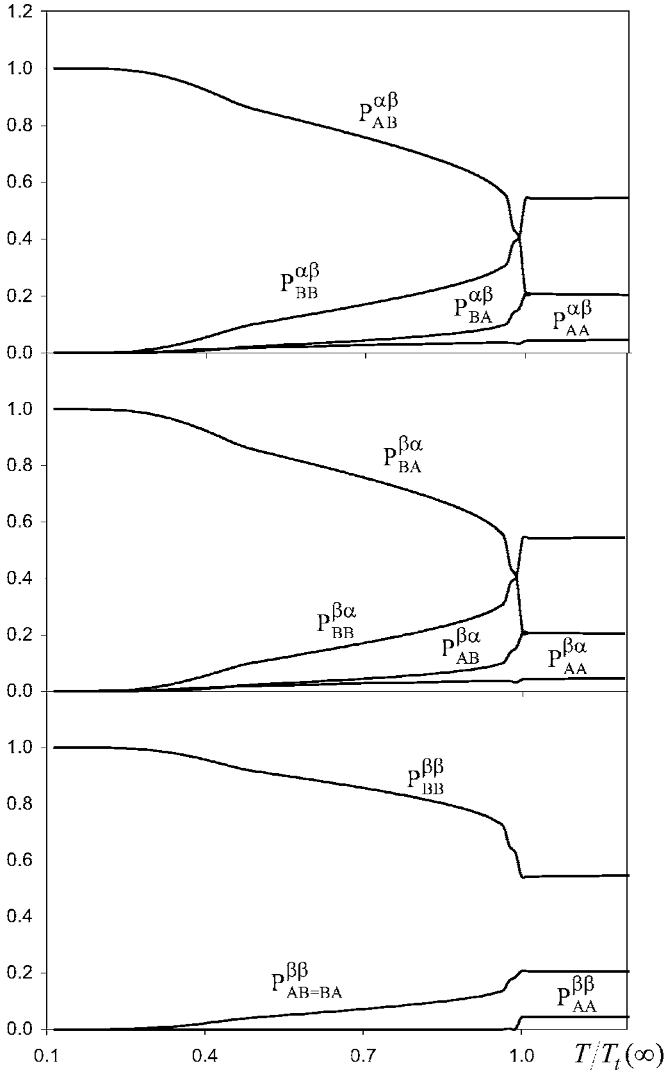

FIG. 2. Two-site probabilities calculated from Eqs. (A1)–(A3) in the case of bulk.

parameter $t$ and the short-range order parameter $s$. At the lattice order-disorder phase transition temperature $(t=0)$ we can clearly see the discontinuous slop of the short-range order parameter but it does not drop to zero. Using now these dependences we can calculate all the two-site probabilities given in explicit form in the Appendix. Figure 2 presents these probabilities in three graphs, each of them for a different pair of sites. In the low-temperature region the probabilities showing the stoichiometric arrangement have the highest values. With increasing temperature we observe smooth continuous changes in all probabilities until the order-disorder phase transition temperature when a jump is seen. The most probable local arrangement of atoms above this phase transition temperature is *B*-*B* at all types of sites lying in the nearest-neighbor distances. We can also see that all probabilities of finding together atoms *A*-*B* or *B*-*A* are the same as well as that the finding of pair *A*-*A* is the least probable situation. In Fig. 3 we present the correlation functions calculated from expression (36) for all possible arrangements with respective to Fig. 2.

The temperature dependence of the long- and short-range order parameters as well as the concentration of *A* components in the case of a thin film constructed with five monoatomic layers is shown in Fig. 4. From all curves we can draw a very clear conclusion that there are three temperature intervals with different specific behavior of these parameters. The first one pronounced the most in the concentration curves is placed between $T/T_t=0.48$ and 0.59. The second one, evidently seen in the short-range order curves, takes place between $T/T_t=0.69$ and 0.75, while the last one is connected with the order-disorder phase transition occurring at a given temperature $T_t$. These different regions are connected with different distributions of alloy components in the direction perpendicular to the film surface. In the insets we present the distribution across the film thickness for $T/T_t=0.54$, 0.71, and 0.83. For the long-range order parameter we observe that disordering begins at the film surfaces in all cases although for higher temperatures its difference between the surface and the rest of the sample is larger. For the *A* concentration we can see that the distribution changes its character. For the temperatures from the first mentioned interval there are more *A* components in the surface layer while for the rest of the temperatures this relation is inversed and we additionally observe the oscillations in concentration. Thus, we can conclude that migration of elements forming the thin film takes place. For the short-range order parameter we can also see the different character of its distribution across a film but the interpretation of this fact is not so easy. In order to make it clear we have to calculate all two-site probabilities (see the Appendix) using values of all three parameters for a given temperature. Figures 5 and 6 present these probabilities in the graphs first for the different pairs of sites and second for different pairs of components for all monoatomic layers composing the film. We can seen now that all of the above-mentioned temperature intervals are connected with specific characteristics for nearest-neighbor site occupation. Thus, it is sufficient to take into account only the probability behavior for an interpretation of the short-range order parameter and of the concentration distribution.

First of all, we can see that the probability curves show different behavior between these curves in the surface layers and those situated deeper in the sample while the differences

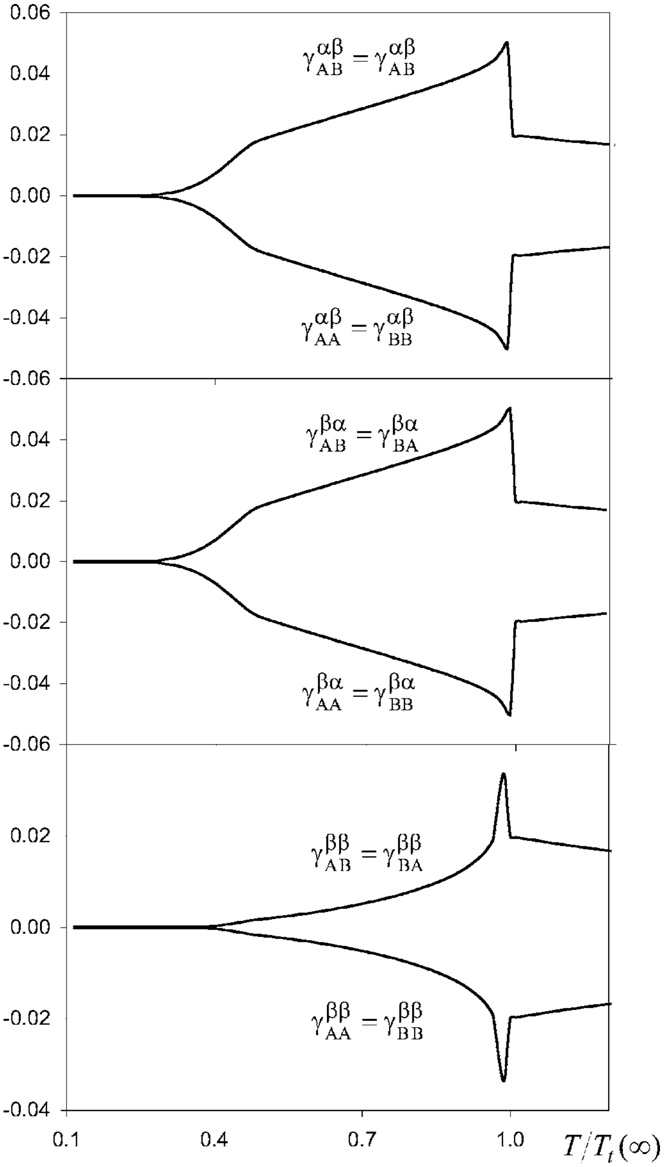

FIG. 3. Correlation functions calculated from (36) for all possible atoms arrangements.

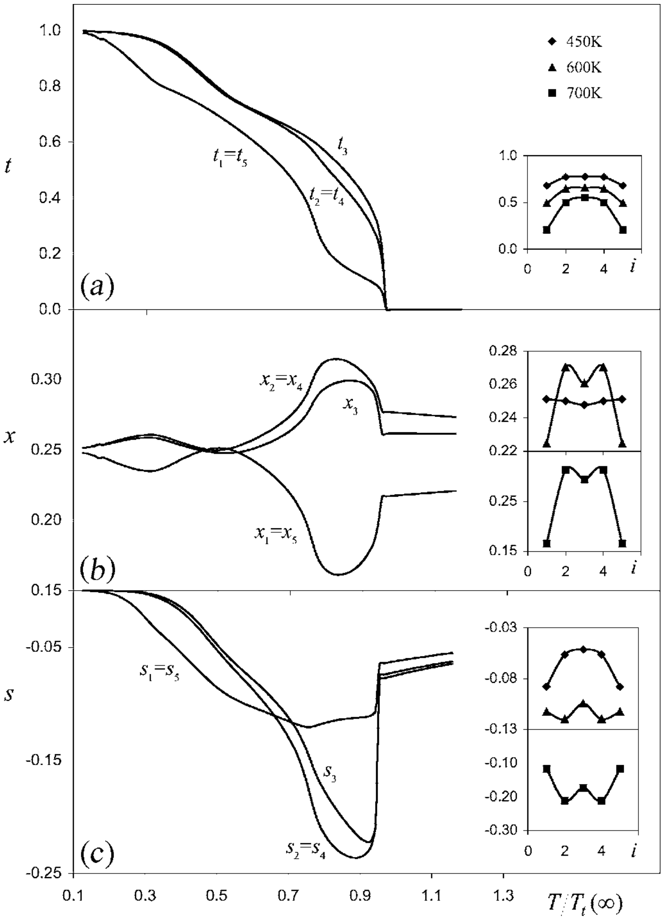

FIG. 4. Temperature dependence of the long-range order, short-range order parameters, and the concentration of $A$ components in the case of a thin film constructed with five monoatomic layers. The insets present the distributions across the film thickness for $T/T_t=0.54$, 0.71, and 0.83.

between the second and third layers are only connected with values keeping the same character of the main behavior. Analyzing the probability curves at the first layer from the point of view of the given pair sites occupancy (Fig. 5) we can see the following.

(i) The crossover between $A$-$B$ type and $B$-$B$ type of occupancy for $\alpha\beta$ sites appears at lower temperature ($T^*$) than the phase transition temperature ($T/T_t=1$) while it is at the same temperature ($T^*=T_t$) in the internal layers;

(ii) There is no evident difference in the case of $\beta\beta$-site occupancy. The points $T^*$ and $T_t$ are almost equivalent.

The same kind of analysis can be applied from the point of view of nearest-neighboring pairs of atoms occupying different sites. In this case, we can see (Fig. 6) that the pairs $B$-$B$ are favorite in the interval ($T^*,T_t$), i.e., above the crossover temperature $T^*$. The same character can be seen for the behavior of the $A$-$A$ pair distribution. The $A$-$A$ pair number at $\alpha\beta=\beta\alpha$ sites decreases above $\tilde{T}$ while its number increases at $\beta\beta$ sites. From the point of view of the physical mechanism the above fact is equivalent to the shift of a part of $A$-$A$ pairs from $\alpha\beta$ sites to $\beta\beta$ positions.

Thus we can see that two new effects can be observed at the surface of binary-alloy thin films: (i) the crossover effect which consists in perturbation of the stoichiometric distribution of $A$-$B$ and $B$-$B$ pairs of atoms in the temperature interval close to the phase transition and (ii) the shift of $A$-$A$ pairs of atoms from the $\alpha\beta$ and $\beta\alpha$ sites to the $\beta\beta$ positions. These effects appear at the surface layer in the temperature interval close to the phase transition point. The crossover temperature $(T^*/T_t)=0.77$ is higher than the shift temperature $(\tilde{T}/T_t)=0.59$. It is worthwhile to notice that these temperatures are just below the intervals seen in the Figs. 4(a) and 4(b). Both of them do not exist in fact in the internal layers. More precisely speaking the crossover temperature interval $(T^*,T_t)$ is reduced to zero while the shift interval drastically approaches the phase transition temperature.

In Figs. 7 and 8 we present the cross section of the parameters in the direction perpendicular to the film surface for different thin-film thicknesses calculated in two cases men-

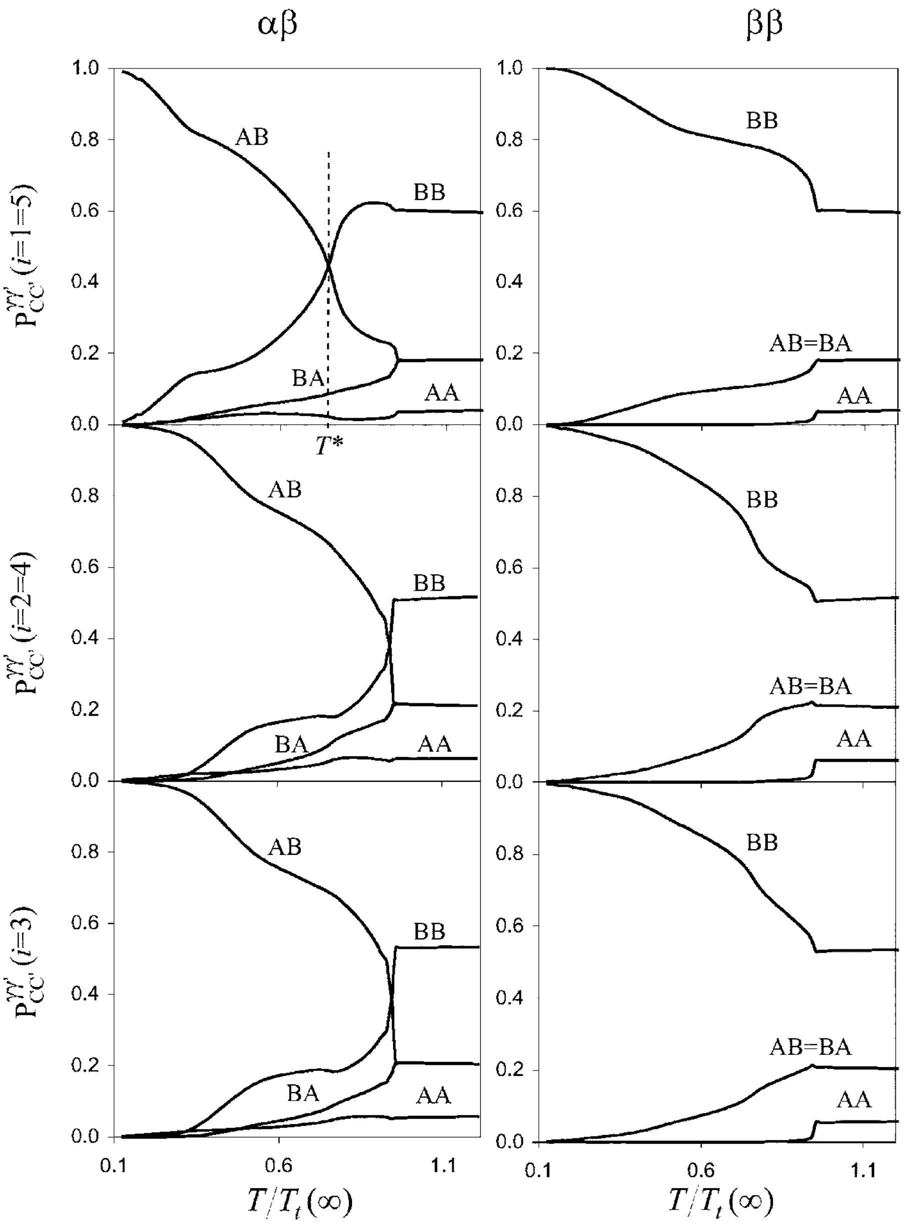

FIG. 5. Two-site probabilities for different pairs of sites in the case of a thin film constructed with five monoatomic layers.

tioned in Sec. III by relations (32) and (33), respectively. The results are obtained for the temperature $T^*/T_t$=0.76 which corresponds to the region close to the phase transition. The square points in Fig. 7 represent the values of parameters $t$, $s$, and $x$ calculated for one monoatomic plane—i.e., the pure two-dimensional (2D) situation—while square points in Fig. 8 represent the values of these parameters calculated for the nearest neighbors in three-dimensional space. The value for parameter $t$ is not visible in Fig. 7(a), being zero for the considered temperature. We can see in Fig. 8(a) that the value of the long-range order parameter in the middle layer is going towards the bulk value when the film thickness increases. In the case of the short-range order parameters [Figs. 7(b) and 8(b)] we observe that their values tend to a single plane value or bulk value when the film thickness decreases or increases in the case of 2D or 3D, respectively. The situation is different in the case of the $A$-component concentration distribution. Their values for the limiting situations are the same and they are equal to 0.25. For both cases the value of the concentration parameter in the middle layer goes towards this mean value when the film thickness is increased. For all the above parameters their distribution across a film thickness is more pronounced in the case of a three-dimensional approach than in the case of a two-dimensional treatment.

The numerical experience[33] shows that there is no evident numerical limitations in our case of performed calculations for fcc (001) surfaces ($Cu_3Au$) in order to obtain a qualitative agreement with the experimental data[34,35] reported in Ref. 36. However, the construction of the functional presented here depends on the geometry (bulk 3D or films 2D) when short-range order $s(i)$ is introduced [cf. Eq. (24)]. It means that the construction of the correlations is confined to the definition of $s(i)$ which is well established only for homogeneous sublattices equivalent to layers parallel to the surfaces. The transversal correlations remain at the mean-field approximation level due to the Néel concept of inhomogeneous thermodynamics.[37] In this context the breakdown of

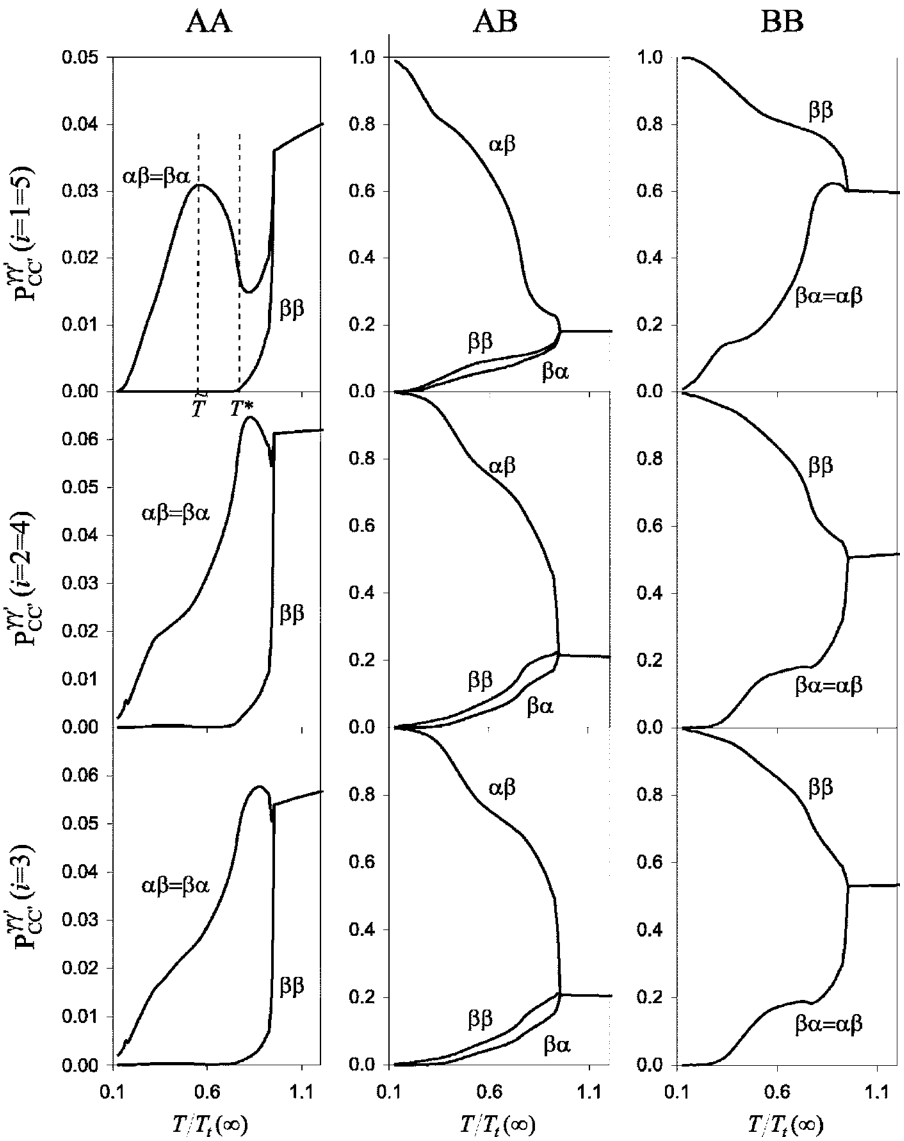

FIG. 6. Two-site probabilities for different pairs of components in the case of a thin film constructed with five monoatomic layers.

mean-field theory as compared with the cluster variation method and explained in a model with first- and second-neighbor interactions[26] should be analyzed more precisely. Moreover, a more general approach to the description of ordering effects in alloys and to determine phase diagrams is reviewed in the book by Ducastelle.[38] Many real fcc structures are marvellous examples of the Ising model in the context of its applicability and justification of its use in an effective form. This evaluation is very stimulating to continue the discussion of alloy properties in terms of the mean-field approximation. The structural and phase stability of alloys is also considered in Ref. 39.

However, it is worthwhile to notice that the pair approximation applied, even in the case of bulk fcc binary systems, has some limitations due to more basic reasons; e.g., the stability of various ordered structures found experimentally in fcc and bcc binary alloys can only be demonstrated by using higher than the nearest-neighbor pair interactions.[24] The analysis of the calculations allows us to conclude then that the results for bcc structure are well established in the pair approximation while the fcc bulk structure description is in this case of poorer quality. The bulk phase diagram for fcc binary alloys is not well described when compared with the Monte Carlo calculations reported in Ref. 22. This kind of limitation appears in any of similar formulations containing the pair approximation.[5,8] The same level of accuracy concerns the results obtained in the present paper for thin films.

## VI. CONCLUDING REMARKS

We present a theory of order-disorder phenomena in binary alloy thin films of $AB_3$ type. The paper is an extension of our approach to the surface melting and surface disordering description in binary alloys thin films based on the thermodynamic approach to small particles when they should be treated as thermodynamically inhomogeneous systems.[4] Our extension consists in the introduction of the short-range order parameter whose determination needs calculations of the entropy in terms of the pair entropy approximation.

The particular calculations concern the $Ni_3Fe$ alloys, showing various kinds of the order parameter behavior.

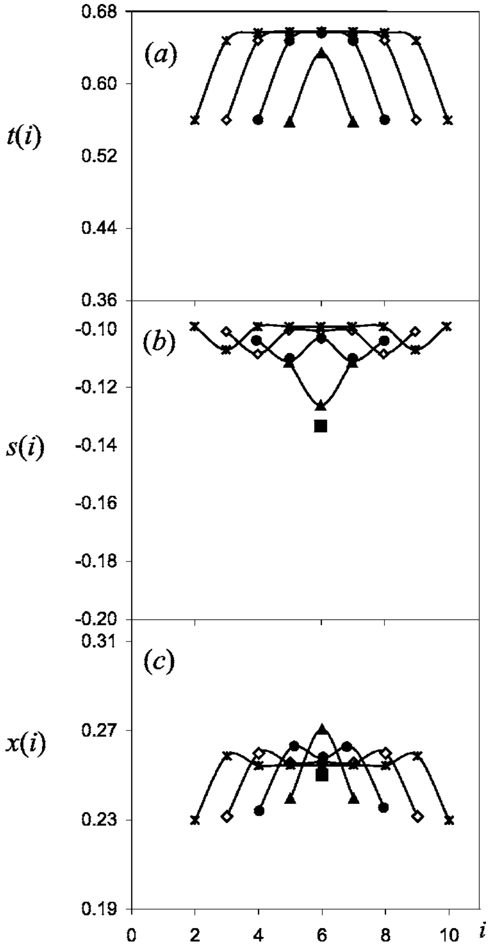

FIG. 7. Cross section of the parameters $t$, $s$, and $x$ in the direction perpendicular to the film surface for different thin-film thicknesses calculated in the case described by relation (32).

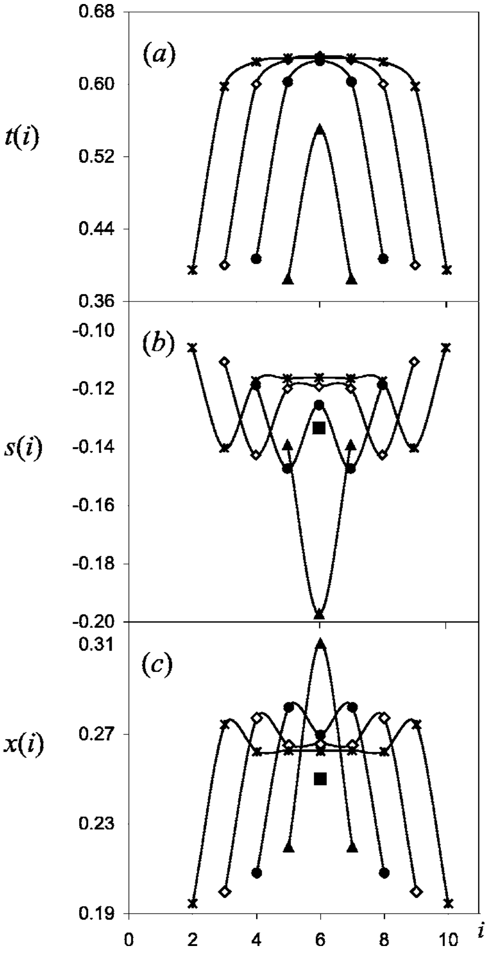

FIG. 8. Cross section of the parameters $t$ and $s$ in the direction perpendicular to the film surface for different thin-film thicknesses calculated in the case described by relation (33).

Among others, two effects seem to be of great interest, particularly in the case of diffuse low-energy electron diffraction applications. There are the crossover of the site occupancy at the surface layer and the shift of atoms from one type of lattice sites to another type in the surface plane. Their physical significance discussed in Sec. V shows their applicability in the case of diffuse LEED measurements. The correlation effects connected with different surface textures are used in DLEED calculations in order to determine the local structure of the disordered surface.

Diffuse LEED illustrates the role of boundary conditions introduced by the surface and its texture which is of particular importance in the dynamics of standing waves in the film thickness direction. This situation can be observed in the case of the spin-wave resonance (SWR) whose conditions depend on the surface state determined by the texture of magnetic samples, e.g., $Ni_3Fe$, which is a Permalloy material. In the considered example, we can distinguish at least two areas in temperature values. The low-temperature condition is described by the low-temperature distribution of the alloy components. In the high-temperature region, but below the Curie point, the boundary conditions relate to the texture modified due to the shift effect. The spin-wave resonance picture is expected then to be changed with respect to that in the low-temperature region.

The boundary conditions, similarly to the case of diffuse LEED as well as of SWR, play an essential role also in the surface melting description. Taking into account the discussion presenting the surface melting and the surface disordering as phenomena of different origins[3] we consider their interdependence for three surface orientations.[40] The local surface melting temperature and the thickness dependence of the global melting temperature have been then found. In this context the different textures discussed here bring new situations which enrich examples of different conditions, similarly to the different surface orientations, for the surface melting.

It is worthwhile to notice that the conditions for DLEED and SWR are of static character contrary to the conditions for surface melting which exhibits a dynamical nature of the process with respect to the temperature dependence.

Finally, we would like to underline that the most original point of the present paper is related to the methodological aspect of the theory and its simplicity. The approach containing the short-range order parameter is introduced in its effective form and evaluated by means of a numerical treatment.

## APPENDIX

A list of pair probabilities in their explicit forms:

$$p_{AA}^{\alpha\beta}(i) = p_A^{\alpha}(i) - [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] - \frac{1}{2}t(i),$$

$$p_{AB}^{\alpha\beta}(i) = [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] + \frac{1}{2}t(i),$$

$$p_{BA}^{\alpha\beta}(i) = [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] - \frac{1}{2}t(i),$$

$$p_{BB}^{\alpha\beta}(i) = p_B^{\alpha}(i) - [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] + \frac{1}{2}t(i), \tag{A1}$$

$$p_{AA}^{\beta\alpha}(i) = p_A^{\beta}(i) - [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] + \frac{1}{2}t(i),$$

$$p_{AB}^{\beta\alpha}(i) = [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] - \frac{1}{2}t(i),$$

$$p_{BA}^{\beta\alpha}(i) = [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] + \frac{1}{2}t(i)r,$$

$$p_{BB}^{\beta\alpha}(i) = p_B^{\beta}(i) - [1 - s(i)]\left[x(i)[1 - x(i)] + \frac{1}{4}t(i)[1 - 2x(i)] + \frac{3}{16}t^2(i)\right] - \frac{1}{2}t(i), \tag{A2}$$

$$p_{AA}^{\beta\beta}(i) = p_A^{\beta}(i) - [1 - s(i)]\left[x(i)[1 - x(i)] - \frac{1}{4}t(i)[1 - 2x(i)] - \frac{1}{16}t^2(i)\right],$$

$$p_{AB}^{\beta\beta}(i) = [1 - s(i)]\left[x(i)[1 - x(i)] - \frac{1}{4}t(i)[1 - 2x(i)] - \frac{1}{16}t^2(i)\right],$$

$$p_{BA}^{\beta\beta}(i) = [1 - s(i)]\left[x(i)[1 - x(i)] - \frac{1}{4}t(i)[1 - 2x(i)] - \frac{1}{16}t^2(i)\right],$$

$$p_{BB}^{\beta\beta}(i) = p_B^{\beta}(i) - [1 - s(i)]\left[x(i)[1 - x(i)] - \frac{1}{4}t(i)[1 - 2x(i)] - \frac{1}{16}t^2(i)\right]. \tag{A3}$$

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*Electronic address: izasada@mvii.uni.lodz.pl

†Deceased.

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