PHYSICAL REVIEW B VOLUME 32, NUMBER 9 1 NOVEMBER 1985

Theory of surface effects in binary alloys with fcc crystal structure: A Landau approach

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(Received 15 April 1985)

The interplay of surface segregation and ordering in binary alloys with face-centered-cubic structure is studied within the Landau theory of phase transitions. In contrast to the bulk first-order transition, the surface may disorder in a continuous manner. We find that the surface disorders at the temperature at which a bulk-ordered and a surface-disordered phase coexist. A mechanism for the bulk first-order phase transition is discussed.

I. INTRODUCTION

In previous publications[1–4] we have studied surface effects in binary alloys A_xB_y $(y=1-x)$ that undergo order-disorder[1–3] and magnetic[4] second-order transitions. Those theories were developed to study the interplay of spatial order, magnetism, and segregation in (i) flat[1–4] and stepped[3] surfaces of ordering alloys which can be described by two equivalent interpenetrating sublattices, like FeCo, CuZn, AuCd, AlNi, NiZn, LiTl, etc. and (ii) face-centered-cubic clustering alloys,[2,5] like CuNi, AuNi, AuPt, etc.

Systems equally important in catalytic processes[6] and metallurgy are ordering alloys with face-centered-cubic structure, like[7] PtNi, PtCo, FeNi, AuCu, etc. The main characteristic of these alloys is that the spatial order-disorder transition is of first order.[8–10] Therefore, the theories mentioned above do not hold for these systems.

Additional interest in the fcc binary alloys is given by the prediction[11,12] that semi-infinite systems with a bulk first-order transition may show a second-order phase transition at the surface and that near the bulk transition temperature T_0 a disordered surface region of macroscopic dimensions is formed. In that study the free energy was evaluated in a Landau expansion of a continuous order parameter and the equilibrium state at the surface was obtained for various situations.

Here, we present a theory, where in addition to the minimization of the free energy with respect to the order parameters, the constraint on the particle conservation imposes the minimization of the free energy with respect to the surface concentration. The additional constraint leads to new results, some of them discussed recently,[13] which provide, among other features, a mechanism of bulk first-order phase transitions.

It is well known that to obtain the correct phase diagram of fcc binary alloys it is necessary to calculate the configurational entropy at least in the tetrahedron approximation.[9,10] The Bragg-Williams (BW) approximation[14] yields a phase diagram with a maximum at $x=0.5$, the value at which the transformation becomes of second order. In this paper we investigate the general effects on the phase transformation caused by the surface, by performing a Landau expansion of the entropy calculated in the BW approximation.

A similar study in the tetrahedron approximation of the (001) surface and its application to the CuAu system has been carried out recently.[15–17] It is found that the phase transitions taking place in a surface with that geometry differ considerably from the results obtained here for the (111) surface. In particular, for the A_3B alloy, Sánchez and Morán-López[17] found that in most cases the surface layer disorders through a second-order phase transition, while the rest of the solid follows the first-order transition in the bulk.

In Sec. II we outline the theory and calculation for the bulk and for the surface with planes parallel to the (111) direction. The results for various situations are presented and discussed in Sec. III.

II. THEORY AND CALCULATION

A. Bulk properties

The order-disorder phase transition is described[18] by subdividing the lattice into two nonequivalent sublattices α and β such that the number of α and β sites are $\frac{3}{4}$ and $\frac{1}{4}$ of the total number of sites N, respectively. An α site has four α sites and eight β sites as nearest neighbors. On the other hand, a β site has twelve α sites as nearest neighbors. Thus, there are four different single-site probabilities, p_I^ρ $(\rho=\alpha,\beta;\ I=A,B)$, and the phase transformation is described by the order parameter

$$\eta=p_A^\alpha-p_A^\beta\ . \qquad (2.1)$$

By assuming that the contributions to the internal energy U are only the nearest-neighbor pair energies ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}, the free energy can be written in the form

$$f=f/N=u(0)-\tfrac{3}{8}W\eta^2+k_BT/4\left[3\sum_I p_I^\alpha \ln p_I^\alpha+\sum_I p_I^\beta \ln p_I^\beta\right], \tag{2.2}$$

where

$$W=\epsilon_{AA}+\epsilon_{BB}-2\epsilon_{AB}\ . \tag{2.3}$$

The main features of the free energy are kept if we take the Landau expansion up to the fourth order[19]

$$f=f(0)+a\eta^2/2-b\eta^3/3+c\eta^4/4\ , \tag{2.4}$$

where

$$a=\tfrac{3}{4}(k_BT/4xy-W),\quad b=\tfrac{3}{64}(1/y^2-1/x^2)k_BT\ ,$$
$$c=\tfrac{7}{256}(1/y^3+1/x^3)k_BT\ , \tag{2.5}$$

and

$$f(0)=6W[x^2+(\Delta-1)x+\epsilon_{BB}/W]+k_BT(x\ln x+y\ln y)\ , \tag{2.6}$$

with

$$\Delta=(\epsilon_{AA}-\epsilon_{BB})/W\ . \tag{2.7}$$

The equilibrium values of the order parameter are obtained by minimizing f with respect to η, which yields the equation

$$\eta(c\eta^2-b\eta+c)=0\ . \tag{2.8}$$

Thus, $\eta_1=0$ is a solution as well as the roots of the second-order equation

$$\eta_{2,3}=[b\pm(b^2-4ac)^{1/2}]/2c\ . \tag{2.9}$$

The order-disorder transition occurs at a temperature T_o where the energy of the disordered phase ($\eta=0$) and the ordered phase ($\eta=\eta_0$) coincide. In our approximation T_o and η_0 are given by

$$[\tfrac{3}{2}-\tfrac{1}{7}(x^2-y^2)^2/(x^3+y^3)]k_BT_o=6Wxy \tag{2.10}$$

and

$$\eta_0=\tfrac{8}{7}xy(x^2-y^2)/(x^3+y^3)\ , \tag{2.11}$$

respectively.

Two other transition temperatures might be considered:[20] (i) the temperature of metastability limit of the disordered phase, T_{md}, at which the smaller root of Eq. (2.9) is zero,

$$k_BT_{md}=4Wxy \tag{2.12}$$

and

$$\eta_{md}=3\eta_0/2 \tag{2.13}$$

and (ii) the temperature of metastability limit of the ordered phase T_{mo}, at which the discriminant in Eq. (2.8) is zero,

$$k_BT_{mo}=112xy(x^3+y^3)W/(25x^2-22xy+25y^2) \tag{2.14}$$

and

$$\eta_{mo}=3\eta_0/4\ . \tag{2.15}$$

B. Surface properties

We consider now the [111] direction of the fcc lattice. We subdivide the crystal into planes parallel to the surface. The geometry of these planes is similar to the bulk and the number of α and β sites at each plane is $\frac{3}{4}$ and $\frac{1}{4}$ of the total number of sites per plane $N_{\|}$. We introduce four site probabilities per plane i: $p_{I,i}^\rho$ ($\rho=\alpha,\beta$; $I=A,B$; $i=0,1,\ldots$). In a way similar to the bulk order parameter η we define at each plane an order parameter[21]

$$\eta_i=p_{A,i}^\alpha-p_{A,i}^\beta,\quad i=0,1,2,\ldots\ . \tag{2.16}$$

In terms of these order parameters the free energy can be written as

$$f=f(0,0,\ldots)+\sum_i\left[\frac{a_{ii}\eta_i^2}{2}-\frac{3W\eta_i\eta_{i+1}}{16}-\frac{b_{ii}\eta_i^3}{3}+\frac{c_{ii}\eta_i^4}{4}\right], \tag{2.17}$$

where

$$a_{ii}=\frac{3}{8}\left[\frac{k_BT}{2x_iy_i}-W\right],$$
$$b_{ii}=\frac{3}{64}\left[\frac{1}{y_i^2}-\frac{1}{x_i^2}\right]k_BT\ , \tag{2.18}$$
$$c_{ii}=\frac{7}{256}\left[\frac{1}{y_i^3}+\frac{1}{x_i^3}\right]k_BT\ ,$$

and

$$f(0,0,\ldots)=3W\sum_i[x_i^2+x_ix_{i+1}+\tfrac{1}{2}(\Delta-1)(3x_i+x_{i+1})+k_BT(x_i\ln x_i+y_i\ln y_i)]\ . \tag{2.19}$$

To take into account segregation effects we have written the concentration at the ith plane as x_i.

The equilibrium values of η_i and x_i are obtained from the two sets of coupled equations:

$$\frac{\partial f}{\partial \eta_i}=0,\quad i=0,1,2,\ldots \tag{2.20}$$

and

$$\frac{\partial f}{\partial x_i}=\frac{\partial f}{\partial x}=\mu,\quad i=0,1,2,\ldots\ . \tag{2.21}$$

The set of equations (2.20) and (2.21) can be written in the form

$$\eta_1=h_1(\eta_0,x_0)\ ,$$
$$\eta_2=h_2(\eta_0,\eta_1,x_1)\ ,$$
$$\vdots$$
$$\eta_n=h_n(\eta_{n-2},\eta_{n-1},x_{n-1}) \tag{2.22}$$

and

$$x_1=g_1(\eta_0,\eta,x_0,x)\ ,$$
$$x_2=g_2(\eta_1,\eta,x_0,x_1,x)\ ,$$
$$\vdots$$
$$x_n=g_n(\eta_{n-1},\eta,x_{n-2},x_{n-1},x)\ . \tag{2.23}$$

By substituting η_1 in η_2, η_2 in η_3, etc., and by applying the boundary condition that $\eta_{n+1}=\eta$ one obtains, instead of Eqs. (2.22), the equation

$$H(\eta_0,\eta,x_0,x_1,\ldots,x)=0\ . \tag{2.24}$$

In a similar way the set of equations (2.23) can be reduced to the equation

$$G(x_0,x,\eta_0,\eta_1,\ldots)=0\ . \tag{2.25}$$

After characterizing the bulk properties, we find the solution of those equations in the following way: (i) We fix $x_0=x_1=\cdots x$; (ii) we find the solution for η_0 from Eq. (2.24); (iii) we substitute this value in Eqs. (2.22) to determine $\eta_1, \eta_2, \ldots, \eta_{n-1}$; (iv) the values obtained for the η_i's are used in Eq. (2.5) to find x_0; (v) we substitute the η_i's and x_0 in Eqs. (2.23) to find $x_1, x_2, \ldots, x_{n-1}$; (vi) we use the new values for the x_i's as input to calculate new values for the η_i's as described in step (i). The loop is carried out until the difference between the input and the output values for the x_i's and the η_i's is smaller than a given tolerance value. Within the range of values allowed for the η_i's and x_i's there is only one solution that fulfills the boundary conditions.

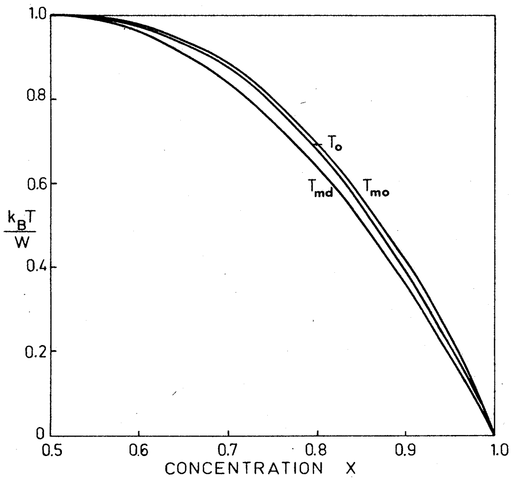

FIG. 1. Bulk phase diagram in the concentration versus temperature parameter space; T_o is the order-disorder transition temperature given by Eq. (2.9); T_{md} and T_{mo} are the temperatures of metastability of the disordered and ordered phases, respectively. The order-disorder transition is of first order in the whole range of concentrations except for $x=0.5$.

III. RESULTS AND DISCUSSION

A. Bulk properties

We show in Fig. 1 the phase diagram for the bulk in the parameter space k_BT/W versus x. The three curves correspond to the transition temperatures T_o, T_{md}, and T_{mo} given by Eqs. (2.10), (2.12), and (2.14). Relative minima for $T_{md}<T<T_0$ with $\eta=0$ and for $T_o<T<T_{mo}$ with $\eta\neq0$ characterize metastable states. As mentioned above, the phase transformation taking place at T_o is of first order except at $x=0.5$. This can be seen clearly in Fig. 2 where the concentration dependence of the order parameter at the transition temperature of η_o is plotted. We show also η_o as obtained by using the full expression of the free energy, Eq. (2.2).

B. Surface with $x_0=x_1=\cdots=x$

First we ignore the chemical potential constraint and study the case of no segregation, i.e., $x_0=x_1=\cdots=x$, which requires the minimization of the free energy only with respect to the order parameters. This case is equivalent to one previously studied within the continuous Landau theory.[11]

After solving the set of equations (2.20) and assuming 50 layers different from the bulk, we find that the surface disorders through a second-order phase transition. We show in Fig. 3 the temperature dependence of η_i for $i=1,\ldots,6$ and of the bulk η_b for an alloy with $x=0.75$.

To find our the order of the surface phase transition we studied the solutions for η_i very near T_o. In Fig. 4 we show, in the upper part, results for the surface profile of the long-range-order parameter at temperatures

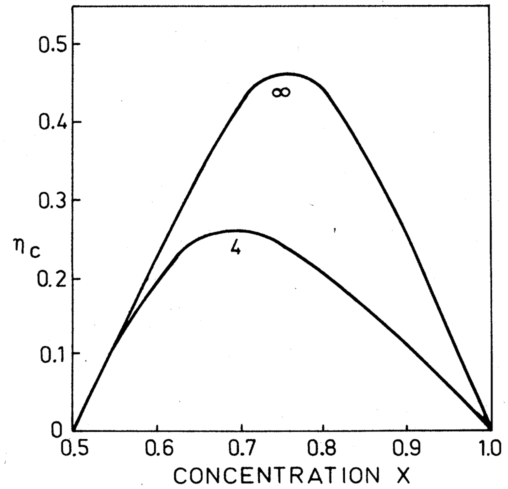

FIG. 2. Long-range-order parameter at T_o as a function of x. Lower curve corresponds to the Landau expansion of the free energy to the fourth order and the upper curve is obtained by taking the full expression for the free energy, Eq. (2.2).

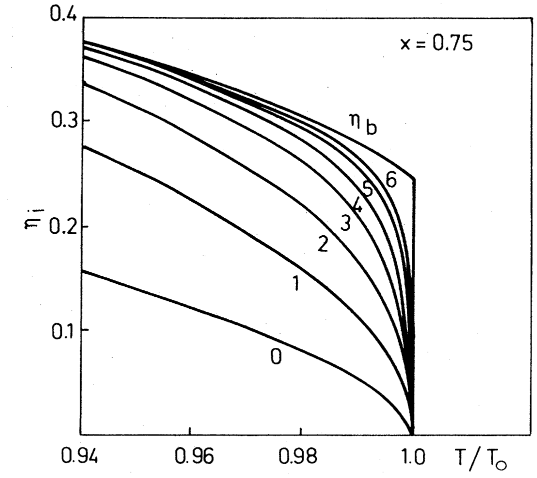

FIG. 3. Temperature dependence of the long-range-order parameters η_i ($i=0$, 1, 2, 3, 4, 5, and 6) at the (111) surface of $A_{0.75}B_{0.25}$ alloy. The long-range-order parameter of the bulk is also shown for comparison.

$T=0.999T_o$, $0.9999T_o$, $0.99999T_o$, and $0.999999T_o$ for an alloy with $x=0.65$. In the lower part of the same figure one observes that $\Delta\eta_i=\eta_{i+1}-\eta_i$ has a maximum at λ that diverge as

$$\lambda=r\ln(T_o-T)\ . \tag{3.1}$$

The maxima in $\Delta\eta_i$ were obtained by fitting the discrete data to a fifth-order polynomial. One can observe in Fig. 5, where we plotted λ as a function of $\ln(T_o-T)$ for several concentrations, that the coefficient in Eq. (3.1) depends on the concentration x. Furthermore, we find that λ diverges as one gets to the second-order point $x=0.5$ (see Fig. 6).

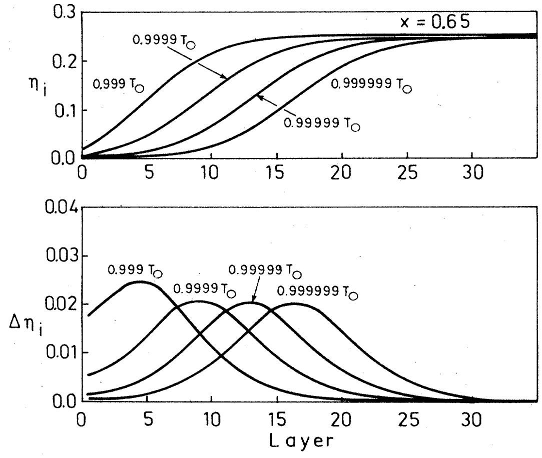

FIG. 4. Long-range-order parameters at the surface (upper figure) and the difference $\Delta\eta_i=\eta_{i+1}-\eta_i$ (lower figure) for several temperatures and for an alloy with $x=0.65$.

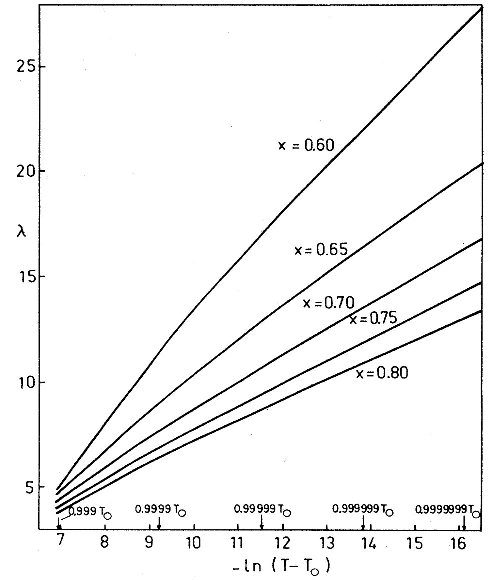

FIG. 5. The distance λ as a function of $-\ln(T-T_o)$ for several concentrations.

C. Surface with $x_0\neq x$, $x_1=x_2=\cdots=x$

We ignore the chemical potential constraint, change arbitrarily the surface concentration x_0, and keep all other concentrations x_1, x_2, etc., equal to the bulk x. We now find that it is possible to get at the surface a first-order phase transition. The phase diagram in the x_0 versus x parameter space showing the second- and the first-order regions is shown on the left-hand side of Fig. 7. The situation discussed in Sec. III B corresponds to the dashed line. The surface undergoes a first-order phase transition mainly for high values of x. In that case, two situations might be distinguished: (i) $T_{os}=T_o$ and (ii) $T_{os}>T_o$, where T_{os} is the surface transition temperature. In the shaded area of the phase diagram the first situation takes place and the condition leading to multicritical transitions[22] is given by

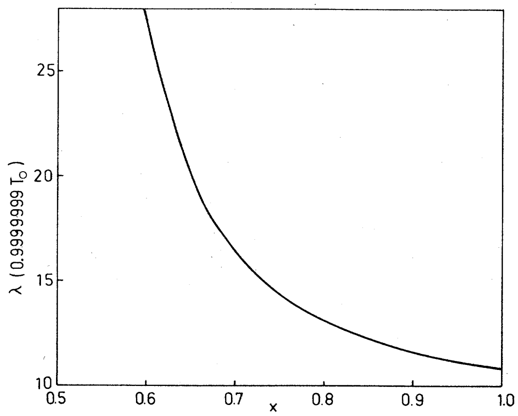

FIG. 6. Concentration dependence of λ at a temperature $T=0.9999999T_o$.

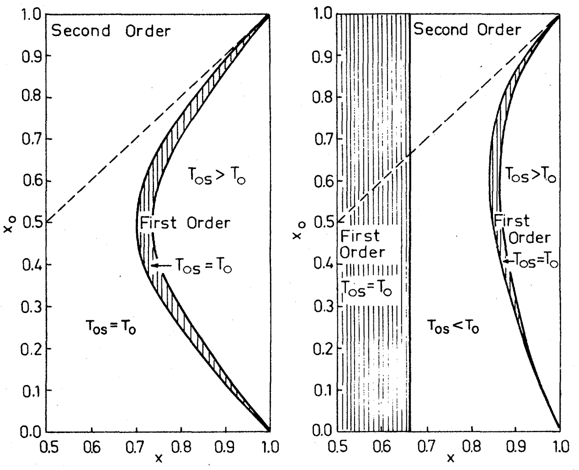

FIG. 7. Phase diagram in the parameter space x_0 vs x: (a) refers to the case where $x_1 = x_2 = \cdots = x$ and x_0 is changed arbitrarily, and (b) refers to the equilibrium values of all x_i. The dashed line marks the case where no segregation occurs.

$$x_0 y_0 \left[\frac{3}{4} + \frac{2b_{00}^2}{9c_{00}} \right] = xy(1 + 8b^2/27c) . \quad (3.2)$$

We show in Fig. 8 the temperature dependence of the long-range-order parameters at layers 0,1,2,3,4,5,6,10 and for the bulk of a system lying in the shaded area ($x_0 = 0.75$ and $x_1 = x_2 = \cdots = x = 0.8$). Figure 9 contains the profile of η_i and $\Delta\eta_i$ at T_o for $x = 0.8$ and various surface concentrations ($x_0 = 0.6$, 0.7, and 0.75). For $x_0 = 0.7$ and 0.75 the surface disorders at the same temperature as the bulk (ordinary transition), but for $x_0 = 0.6$ the surface disorders at $T_{os} > T_o$ (extraordinary transition).

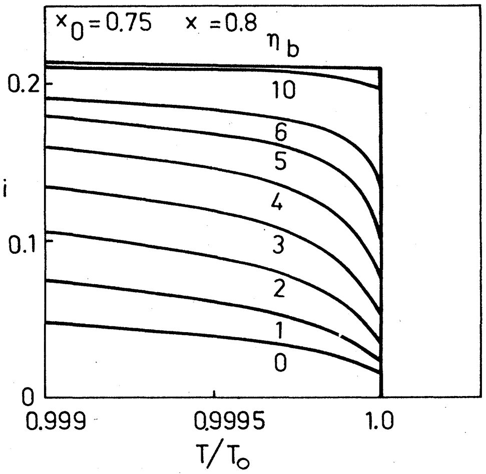

FIG. 8. Temperature dependence of the surface long-range-order parameters η_i ($i = 0,1,2,3,4,5,10$) and in the bulk η_b for a system with $x_0 = 0.75$ and $x_1 = x_2 = \cdots = x_b = 0.8$.

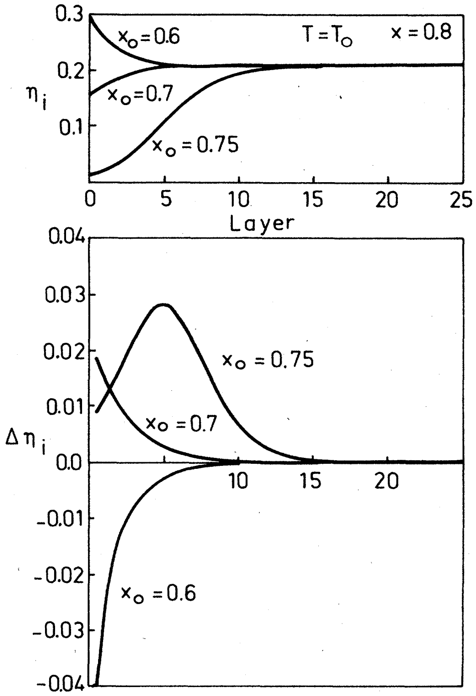

FIG. 9. Long-range-order parameters at the surface (upper figure) and the difference $\Delta\eta_i = \eta_{i+1} - \eta_i$ at $T = T_o$ and several values of x_0 (0.6, 0.7, 0.75). All other concentrations are equal to 0.8.

D. Surface with equilibrium concentrations

The situations discussed in Secs. III B and III C do not correspond to equilibrium states. The system is in equilibrium only when Eqs. (2.21) are also fulfilled. Under those conditions, the phase diagram gets modified as shown on the right-hand side of Fig. 7. To compare the results with those obtained in Sec. III C we choose the same parameter space; however, in this case $x_1 \neq x_2 \neq \cdots \neq x$. We see that the first-order phase-transition region present in the preceding case becomes considerably reduced. We observe that now the curves marking the regions $T_{os} = T_o$ and $T_{os} > T_o$ join in a point $x < 1$. This is because for those parameters the equilibrium value for the concentration in the second layer saturates to 1 and the surface layer decouples now from the rest of the solid. Then it behaves like a two-dimensional system with transition temperature

$$\left[\tfrac{3}{2} - (x_0^2 - y_0^2)^2/(x_0^3 + y_0^3)\right] k_B T_{os} = 3W x_0 y_0 . \quad (3.3)$$

The key parameter for surface segregation is Δ. In the complete disordered state ($\eta_0 = \eta_1 = \cdots = 0$) the element A gets segregated to the surface for values of $\Delta > \Delta_c = (1 - 2x)$, otherwise the surface gets enriched in element B. We show in Fig. 10 the temperature dependence of η_0 for $\Delta = -1.5$, -1.0, -0.55, and 0 for $x = 0.75$. Two important features can be noticed: (i) the transition temperature at the surface T_{os} is smaller than the one dictated by the bulk, and (ii) T_{os} for this value of

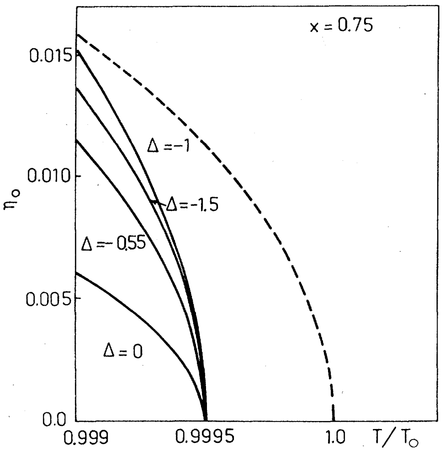

FIG. 10. Temperature dependence of the surface long-range-order parameter η_0 for $\Delta = -1.5$, -1.0, -0.55, and 0 when surface segregation is included. The temperature dependence of η_0 without the chemical potential constraint is also plotted (dashed line).

x is independent of surface segregation.

One can understand point (i) by looking to the concentration profile shown in Fig. 11. Near the surface (~ 5 layers), it exhibits the typical oscillatory behavior, but deeper inside, to achieve the chemical potential constraint, the system accumulates atoms of type A in the disordered region, compensating therefore the lack of spatial order. The reduction in the transition temperature is driven by this surface phase with concentration x_d larger than the bulk x. As one gets nearer T_{os}, λ increases (the surface-disordered region grows), and it diverges only in the case of an infinite system. One expects very different results in finite system, where the system cannot supply an infinite number of A atoms to the disordered region. In this case the ordered bulk phase will change the concentration to x_{or} smaller than x, and therefore behaving now like a system with higher bulk T_o. This mechanism is similar to that of clustering alloys at low temperature where two phases of different compositions coexist. It is worth noting that the temperature T_{os} is a temperature different from Eqs. (2.11) and (2.13). The fact that T_{os} does not depend on Δ for $x = 0.75$ is because this system stays in the second-order region independent of the value of x_0.

An additional region of first-order transitions is obtained for $0.5 < x \leq 0.66$. This region does not depend on x_0 and it is regulated by the bulk chemical potential. In this case the constraint produces a depletion of atoms A in the surface-disordered region and thereby behaving like a system with higher T_o.

Finally, we show in Fig. 12 the temperature dependence of x_0 for $x = 0.75$ and $\Delta = 0$. One can see clearly the effect of ordering on surface segregation. The dashed line is the surface concentration if the alloy would not order at T_o.

As we mentioned above, the BW approximation does not reproduce the correct phase diagram. However, we expect that the general features of this model should be present also in more refined theories.

We summarize our results in the following points.

(i) The surface may disorder through a first- or second-order transition.

(ii) The surface may disorder through an ordinary ($T_{os} = T_o$) or an extraordinary transition ($T_{os} > T_o$).

(iii) For values of $x \sim 1$ or 0 surface segregation may saturate the second layer to 1 or 0 (i.e., $\eta_1 \rightarrow 0$), thereby decoupling the surface layer. It behaves then as a two-dimensional system with a T_{os} that depends only on x_0 and that might be smaller or larger than T_o.

(iv) In a finite system, when the surface disorders in a continuous manner, the system does not allow the disordered region (λ) to diverge, by changing the composition in the bulk ordered and the surface disordered phases.

(v) The phase transformation in the solid states at the surface and evolves by a mechanism similar to the phase separation in clustering alloys.

(vi) The surface disorders at a temperature at which a surface-disordered phase of microscopic dimensions coexists with the ordered bulk.

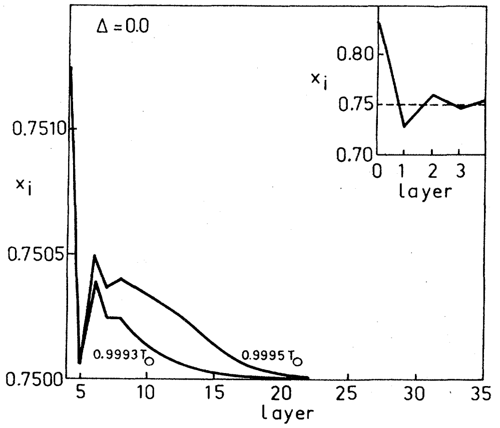

FIG. 11. Surface concentration profile of an $A_{0.75}B_{0.25}$ alloy for several temperatures and $\Delta = 0.0$. The inset figure shows the concentration in layers $i = 0$ to 4.

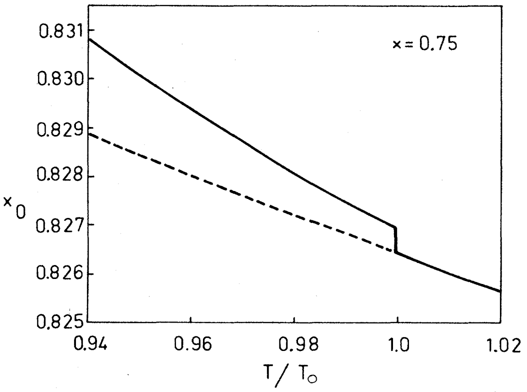

FIG. 12. Temperature dependence of the surface concentration x_0 for $\Delta = 0.0$ and $x = 0.75$. The dashed line corresponds to the case where a random alloy is assumed.

ACKNOWLEDGMENTS

We are grateful to Professor J. M. Sánchez for stimulating discussions. This work was supported in part by Dirección de Investigación Científica y Superación Académica de la Secretaria de Educación Publica, by Programa Regional de Desarrollo Científico y Tecnológico de la Organización de Estados Americanos, by Consejo Nacional de Ciencia y Tecnología through the México-Germany exchange program No. 140101 H22, and in the United States by the National Science Foundation through Grant No. INT-80-18688. One of us (J.L.M.-L.) also acknowledges support from the Guggenheim Foundation.

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