Landau Theory of Surface Segregation and Phase Transitions in Binary Alloys with fcc Crystal Structure

J. L. Morán-López[a]
Laboratoire de Magnétisme et Structure Electronique des Solides,
Université Louis Pasteur, F-67070 Strasbourg Cedex, France

and

F. Mejía-Lira
Instituto de Física, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí,
San Luis Potosí, Mexico

and

K. H. Bennemann
Institut für Theoretische Physik, Freie Universität Berlin,
1 Berlin 33, Germany

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The order-disorder transition at the surface of binary alloys with fcc structure is studied within the Landau theory. The interplay of spatial order and segregation leads to results that provide a different mechanism for the bulk first-order phase transition characteristic of these systems. The surface transition may be of first or second order. A new instability temperature towards phase separation, regulated by the surface, is obtained.

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Semi-infinite systems which undergo a first-order phase transition in the bulk have been the subject of recent research.[1,2] Novel results for the order-parameter profile near the surface have been obtained.[1] In particular, in the continuous Landau theory of phase transitions, it has been found that under given circumstances the surfaces may undergo a second-order phase transition. In that case it was also found that near the bulk transition temperature T_o, a disordered surface region of macroscopic dimensions is formed.

Here we present a more general theory where, in addition to the minimization of the free energy with respect to the order parameters, constraints on the semi-infinite system variables are used. That is the case for order-disorder transformations in fcc binary alloys A_xB_y $(y=1-x)$, where, in addition to the surface order parameters, the equilibrium surface concentrations have to be determined. We find that the interplay of spatial order and segregation produces new effects not obtained before. In particular, by change of the composition in the surface-disordered phase, the system *does not allow the disordered region to diverge* as one gets near the order-disorder temperature T_o.

We investigate the general features of the surface phase transition by performing a Landau expansion of the free energy calculated in the Bragg-Williams (BW) approximation.[3] It is known that to obtain the correct phase diagram for fcc alloys the entropy has to be calculated at least in the tetrahedron approximation.[4,5] However, it is expected that our main results hold also in more accurate theories, where the coefficients of the Landau expansion might adopt a different form.

The order-disorder phase transition in the bulk is described by subdivision of 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. Thus, there are four different single-site probabilities, p_I^ν $(\nu=\alpha,\beta;\ I=A,B)$ and the phase transition is described by the order parameter

$$\eta \equiv p_A^\alpha - p_A^\beta. \tag{1}$$

Given the assumption that the contributions to the internal energy are only the nearest-neighbor pair energies U_{AA}, U_{BB}, and U_{AB}, the free energy per atom can be written[6]

$$f=F/N=f(0)+\tfrac{1}{2}a\eta^2-\tfrac{1}{3}b\eta^3+\tfrac{1}{4}c\eta^4, \tag{2}$$

where

$$a=\frac{3}{4}\left[\frac{kT}{4xy}-W\right],\quad b=\frac{3}{64}\left[\frac{x^2-y^2}{x^2y^2}\right]kT,$$
$$c=\frac{7}{256}\left[\frac{x^3+y^3}{x^3y^3}\right]kT, \tag{3}$$

with

$$W=U_{AA}+U_{BB}-2U_{AB}. \tag{4}$$

The temperature T_o and the order parameter at that temperature are

$$\left[\frac{3}{2}-\frac{1}{7}\frac{(x^2-y^2)^2}{x^3+y^3}\right]\frac{kT_o}{xy}=6W \tag{5}$$

and

$$\eta_o=\tfrac{8}{7}xy(x^2-y^2)/(x^3+y^3). \tag{6}$$

From Eq. (6) we see that the transition is of first order $(\eta\neq 0)$ in the whole range of concentrations except for $x=y=0.5$, a characteristic of the BW approximation.[3]

Two other transition temperatures might be considered,[7] i.e., (i) the temperature T_{md} at which, in addition to the absolute minimum at $\eta \neq 0$, a relative minimum at $\eta = 0$ appears (the state with $\eta = 0$ is metastable for temperatures $T_o > T > T_{md}$; T_{md} is called instability temperature of the disorder phase),

$$kT_{md} = 4Wxy, \tag{7}$$

and (ii) the temperature T_{mo} at which a relative minimum at $\eta \neq 0$ develops in addition to the absolute minimum at $\eta = 0$ (for $T_o < T < T_{mo}$ the state with $\eta \neq 0$ is metastable),

$$kT_{mo} = \frac{112xy(x^3+y^3)W}{25x^2 - 22xy + 25y^2}. \tag{8}$$

We consider now the (111) surface of the fcc lattice and subdivide the crystal into planes parallel to the surface. Each plane contains $3N_{\parallel}/4$ and $N_{\parallel}/4$ sites of type α and β, respectively. In a way similar to the bulk order parameter η we define at the ith plane the order parameter

$$\eta_i \equiv p^{\alpha}_{A,i} - p^{\beta}_{A,i}, \quad i = 0, 1, 2, \ldots . \tag{9}$$

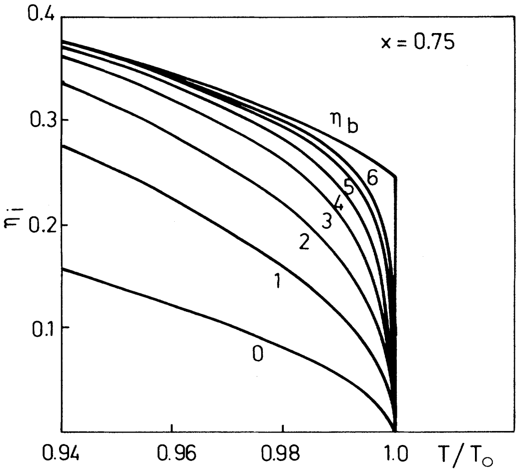

FIG. 1. Temperature dependence of the long-range order parameters at the surface, η_i ($i = 0, 1, \ldots, 6$), and the bulk, η_b, for the case $x_0 = x_1 = \ldots = x = 0.75$.

In terms of these parameters the free energy can be written

$$f = f(0,0,\ldots) + \sum_{i=0}^{\infty} \left(\tfrac{1}{2}a_{ii}\eta_i^2 - \tfrac{3}{16}W\eta_i\eta_{i+1} - \tfrac{1}{3}b_{ii}\eta_i^3 + \tfrac{1}{4}c_{ii}\eta_i^4\right), \tag{10}$$

where

$$a_{ii} = \tfrac{3}{8}(kT/2x_iy_i - W), \quad b_{ii} = \tfrac{3}{64}[(x_i^2 - y_i^2)/x_i^2y_i^2]kT, \quad c_{ii} = \tfrac{7}{256}[(x_i^3 + y_i^3)/x_i^3y_i^3]kT, \tag{11}$$

and

$$f(0,0,0,\ldots) = 3W\sum_{i=0}^{\infty}[x_i^2 + x_ix_{i+1} + \tfrac{1}{2}(\Delta - 1)(3x_i + x_{i+1}) + kT(x_i\ln x_i + y_i\ln y_i)], \tag{12}$$

with $\Delta \equiv (U_{AA} - U_{BB})/W$. Here we have assumed that the concentrations at the different planes x_i may differ from the bulk value x.

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

$$\partial f/\partial\eta_i = 0, \quad i = 0, 1, 2, \ldots, \tag{13}$$

$$\partial f/\partial x_i = \partial f/\partial x = \mu, \quad i = 0, 1, 2, \ldots . \tag{14}$$

First, we ignore Eq. (14) and study the case of no segregation,[1] i.e., $x_0 = x_1 = \ldots = x$. The results for the temperature dependence of the order parameters η_i for the different layers and for $x = 0.75$ are shown in Fig. 1. The order parameter in the bulk η_b is also shown. The surface undergoes a second-order phase transition. This is more evident in Fig. 2 where the long-range-order profile near the surface is shown for temperatures near T_o. In the lower part of the same figure one observes that the difference $\Delta\eta = \eta_{i+1} - \eta_i$ has a maximum at a distance λ that diverges as

$$\lambda \sim \ln|T - T_o|. \tag{15}$$

The inset shows the concentration dependence of λ at $0.9999999T_o$. We see that the disordered region diverges also as one gets to the second-order phase transition point, $x = 0.5$.

Secondly, if we ignore (14) and vary x_0 but keep $x_1 = x_2 = \ldots = x$, it is possible to obtain for the surface also a first-order transition. The phase diagram is shown in Fig. 3(a). 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 case (i) occurs. The condition leading to $T_{os} \geqslant T_o$ is given by

$$x_0y_0\left[\frac{3}{4} + \frac{2}{9}\frac{b_{00}^2}{c_{00}}\right] \geqslant xy\left[1 + \frac{8}{27}\frac{b^2}{c}\right]. \tag{16}$$

The dashed line marks the values where no segregation occurs.

The system is in equilibrium only when Eq. (14) is fulfilled. Under those conditions, the phase diagram gets modified, as shown in Fig. 3(b). There we see that the first-order phase transition region present in the previous case gets considerably reduced. We observe that now the curves marking the regions $T_{os} = T_o$ and $T_{os} > T_o$ join at a point $x \neq 1.0$. This is because for

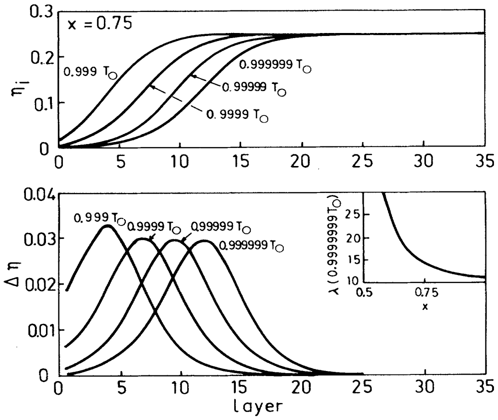

FIG. 2. The long-range order parameters at the surface (upper figure) and the difference $\Delta\eta=\eta_{i+1}-\eta_i$ (lower figure) for several temperatures and for the same parameters as those used in Fig. 1. The inset figure contains the concentration dependence of $\lambda(0.999\,9999\,T_o)$.

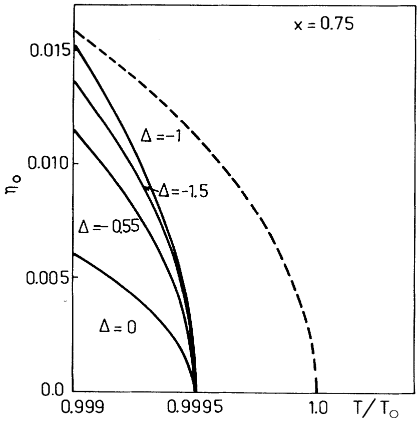

FIG. 4. Temperature dependence of the surface long-range order parameter η_0 for $\Delta=-1.5$, -1.0, -0.55, and 0 when surface segregation is included. The temperature dependence of η_0 without the chemical-potential constraint is also plotted (dashed line).

those parameters the equilibrium value for the concentration in the second layer saturates to 1.0, thereby decoupling the surface layer from the rest of the solid and thus behaving as a two-dimensional system. An additional region of first-order transitions is also obtained. This region does not depend on x_0 and is regulated by the bulk chemical potential.

The key parameter for surface segregation is Δ. In the completely disordered state ($\eta_0=\eta_1=\ldots=\eta=0$) 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. 4 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 is smaller than the one given by the bulk and (ii) T_{os} for this value of x is independent of surface segregation. One can understand this behavior by looking to the concentration profile shown in Fig. 5. It exhibits the typical oscillatory behavior near the surface (see inset), but then, 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 greater than the bulk x. As one gets nearer T_o, λ starts to increase and the disordered region grows. However, λ *cannot diverge* since the system cannot

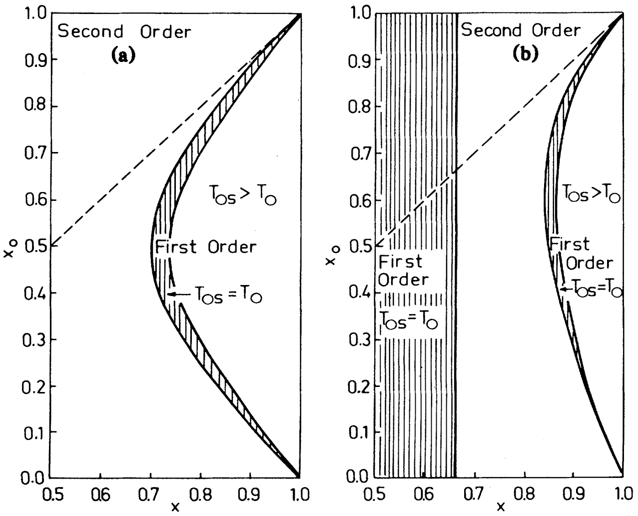

FIG. 3. The phase diagram in the parameter space x_0 vs x: (a) refers to the case where $x_1=x_2=\ldots=x$ and x_0 is changed arbitrarily, and (b) refers to the equilibrium values of all x_i. The dashed line marks the case where no segregation occurs.

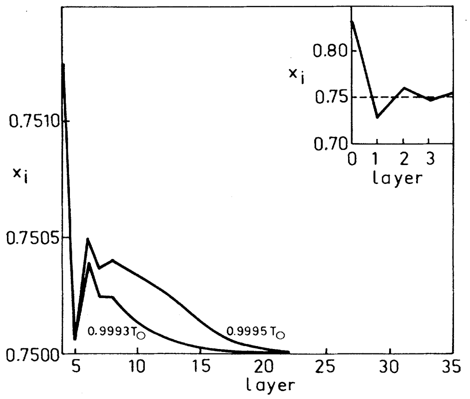

FIG. 5. The surface concentration profile of the A_3B alloy for several temperatures and $\Delta=0$. The inset figure shows the concentration profile in layers $i=0$ to 4.

supply an infinite number of type-A atoms. Instead, the ordered bulk phase will change its concentration to a value x_{or} smaller than x. This mechanism is similar to the one in clustering alloys, in which two phases with different concentrations coexist below a given transition temperature. In our case, the two phases with different concentrations are the bulk-ordered and the surface-disordered phases. It is worth noticing that the temperature T_{os} *is a new characteristic temperature at which the bulk transformation starts,* different from T_{md}, T_o, and T_{mo}.

The first-order region for $0.5 > x \geqslant 0.66$ in the phase diagram 3(b) is dictated by the bulk chemical potential, since in this case the constraint produces a depletion of type-A atoms in the surface-disordered region and thereby behaving like a system with higher T_o.

In conclusion, we have presented a Landau theory of surface effects on the phase transformation of alloys with a bulk first-order phase transition. This is an extension of previous work[1] where only the minimization of the free energy with respect to the order parameters was studied. The additional constraint on the chemical potential brought the following new results: (i) By change of the composition in the bulk-ordered and the surface-disordered phases, the system does not allow the disordered region (λ) to diverge. (ii) For values of $x = 1$ (or 0), surface segregation may saturate the second layer to 1 (or 0), i.e., $\eta_1 \rightarrow 0$, decoupling thereby 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. (iii) The phase transformation in the solid starts at the surface and evolves by a mechanism similar to the phase separation in clustering alloys. (iv) The surface gives rise to a new instability temperature towards phase separation.

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[a] On leave from Departamento de Física, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000 México, Distrito Federal, Mexico.

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