Finite-Size Effects on First-Order Phase Transitions: fcc Binary Alloys

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Size effects in fcc binary alloys undergoing a bulk first-order phase transition are investigated in the limit of *very thin films*. The interplay between surface segregation and spatial ordering is studied by means of a discrete model in the Bragg-Williams approximation. Concentration and long-range-order-parameter profiles in the film are calculated for equilibrium and for metastable states. Results for the thickness dependence of the transition temperature and of the discontinuity of the order parameter are presented.

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Surface effects in systems undergoing a bulk first-order phase transition have been studied for continuous[1-3] and discrete models[4-6] by use of Landau free-energy expansions,[1-6] the mean-field approximation,[4,5] and the tetrahedron cluster approximation.[6] A significant result of these studies for semi-infinite systems is the fact that the surface may undergo a continuous transition and, furthermore, that the width of the surface region diverges logarithmically at the surface transition temperature. This behavior was initially predicted for systems in which the bulk phase is described by a single order parameter[1-4] (such as ferromagnetic systems, one-component fluids, and segregating alloys), and was later confirmed for the two-order-parameter case of ordering alloys with the fcc crystal structure.[5,6]

Finite size and geometry effects have recently been studied for the ferromagnetic Ising model with a field-driven first-order transition in the bulk,[7] and for very thick films by use of a continuous Landau free-energy expansion in a single long-range order parameter.[8,9] Concerning the surface behavior of finite systems, one expects that the disappearance of the logarithmic divergence of the surface region will result in a discontinuous surface transition. This particular surface behavior was recently confirmed within the continuous Landau theory in the limit of very thick films.[8,9] The main conclusions reported for a film of thickness L are that (i) the thin-film transition temperature T_0 is lowered relative to that of the infinite system, with the difference between these two transition temperatures behaving like L^{-1}; (ii) the value of the surface long-range order parameter at T_0 is finite and decreases with thickness like $L^{-1/2}$; and (iii) for L smaller than a critical value L_c, which depends on the boundary conditions, no transition occurs.[9]

Here, we study the case of an ordering A_3B fcc alloy with n layers. Our model has several advantages over the continuous Landau theories developed in the past. In particular, (i) the theory applies to specific alloy systems that can be measured experimentally; (ii) we may study thin films over the whole range of thickness; (iii) we may investigate metastable states, which are often realized in real systems; and (iv) we can investigate the competing effects of two order parameters (surface segregation and surface ordering).

The infinite A_3B alloy undergoes an order-disorder transition of first order which is well characterized both theoretically[10] and experimentally. Semi-infinite ordering alloys have also been studied in detail and they possess all the features discussed above.[5,6] The calculated results[6] are also in good agreement with measurements of the surface order parameter[11-13] and surface concentration[14] in thick Cu_3Au films.[6]

In this Letter we show how finite-size effects modify previous results in semi-infinite alloy systems. We also point out the main differences with previous Landau theories for finite systems. These differences arise primarily from the fact that our model allows for the coupling of surface segregation and ordering. We find that finite-size effects as well as the interplay between surface ordering and segregation are significant. Our main objective is thus to characterize such effects in order to provide the basis for the correct interpretation of experimental results in thin films. We have also investigated the temperature evolution of the concentration and spatial order in several planes in the film. The analysis provides a clear picture of the mechanism of first-order phase transitions in real systems. Moreover, the predictions of the model con-

cerning segregation and ordering on different layers in the film should be subject to direct experimental verification via low-energy electron-diffraction and low-energy ion-scattering techniques.

We study an fcc binary alloy thin film with (111) surfaces within the discrete Bragg-Williams approximation. The internal energy is written in terms of nearest-neighbor pair interactions U_{AA}, U_{BB}, and U_{AB} between A and B atoms. The thermodynamic properties of the film depend on two parameters: the effective pair interaction $W = U_{AA} + U_{BB} - 2U_{AB}$, which is positive for an ordering alloy, and the surface segregation parameter $\Delta = (U_{AA} - U_{BB})/W$. The order-disorder transition for A_3B alloys is described by subdividing the sites on each (111) lattice plane into two nonequivalent sublattices α and β with, respectively, $\frac{3}{4}$ and $\frac{1}{4}$ the total number of sites on the plane. The phase transition is then described by a set of long-range order parameters on each plane,

$$\eta_i = p_i^{\alpha} - p_i^{\beta} \quad (i = 0, 1, 2, \ldots, n), \tag{1}$$

where p_i^{μ} is the probability of finding an A atom on plane i in sublattice μ. The concentration of A atoms on each (111) layer, x_i, is given by

$$x_i = (3p_i^{\alpha} + p_i^{\beta})/4 \quad (i = 0, 1, 2, \ldots, n). \tag{2}$$

Equilibrium values of η_i and x_i were obtained by minimizing the usual Bragg-Williams free energy with respect to all these parameters, subject to the constraint of a constant average concentration x.

In Fig. 1, we show the temperature dependence of the long-range order parameters at planes 0, 1, 2, 3, 4, and 19 for a film of 39 layers with $x = 0.75$ and $\Delta = 0$. The order-disorder transition temperature T_0 (see Fig. 1) is defined by the equality of the free energies of ordered and disordered films with the *same* average composition x. This condition corresponds to a first-order transition in a strictly closed system and it differs from the equilibrium condition in the thermodynamic limit (equality of chemical potentials). In particular, the latter condition allows for different average concentrations in the two coexisting phases, a situation that is precluded in finite systems. As the number of layers in the film increases, T_0 approaches either the surface transition temperature T_s^{∞} or the bulk transition temperature T_b^{∞}, depending on the behavior of the semi-infinite system. When the surface of the semi-infinite system undergoes an extraordinary transition ($T_s^{\infty} > T_b^{\infty}$), T_0 approaches T_s^{∞}. In this case, the limiting value of T_0 falls either above or inside the two-phase region (if present) of the equilibrium phase diagram for the infinite system. If, on the other hand, the surface of the semi-infinite system undergoes an ordinary transition ($T_s^{\infty} \leq T_b^{\infty}$), T_0 will approach the temperature of the lower two-phase boundary of the equilibrium phase diagram. The parameters and surface geometry used in all our calculations are such that the semi-infinite system undergoes an ordinary transition with $T_s^{\infty} = T_b^{\infty}$. This can be also inferred from Fig. 1 which shows the ordering at the surface strongly reduced relative to the "bulk."

The long-range order-parameter profile is shown in Fig. 2 for temperatures near T_0. The surface phase transition is a *weak* first-order transition, i.e., the order parameter η_0^* at T_0 is small but finite. It is also worth noticing that at T_0, a disordered region of approximately eight layers (up to the inflection point) is formed near the surfaces of the film.

The concentration profile in the thin film just above (T_0^+) and below (T_0^-) the transition temperature is shown in Fig. 3. In a surface region approximately four layers thick, typical oscillations dominate the concentration profile which is almost independent of the spatial order. Further away from the surface, however, the layer concentrations depend strongly on the

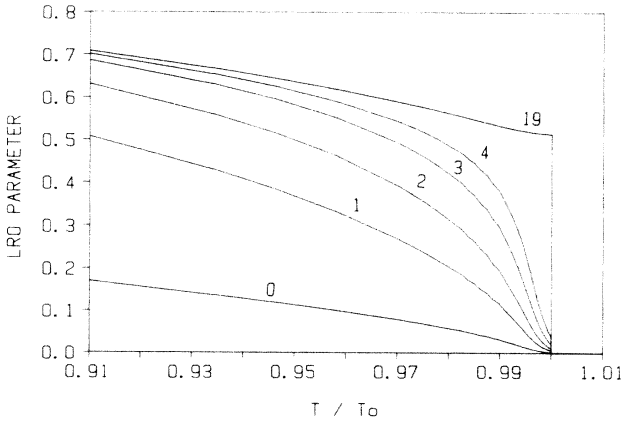

FIG. 1. Temperature dependence of the long-range order parameters for layers 0, 1, 2, 3, 4, and 19 in a 39-layer film with average concentration $x = 0.75$ and $\Delta = 0$.

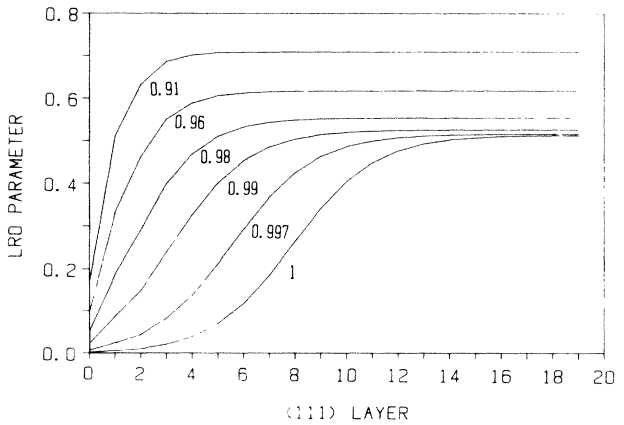

FIG. 2. Long-range order-parameter profile across the film for the various normalized temperatures (T/T_0) indicated on the curves.

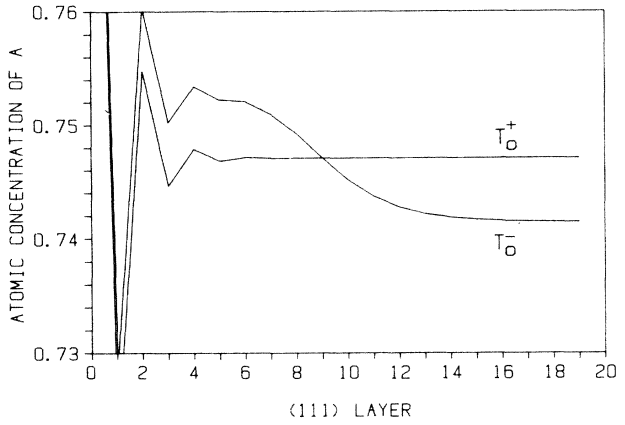

FIG. 3. Concentration profile across the film for temperatures just below (T_0^-) and above (T_0^+) the transition temperature.

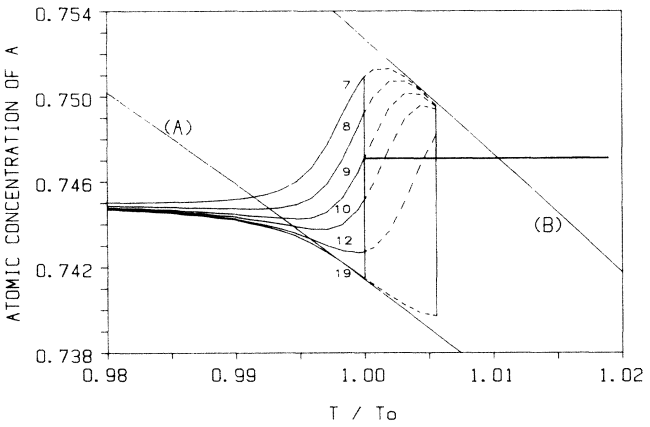

FIG. 4. Temperature dependence of the concentration for layers 7, 8, 9, 10, 12, and 19. The lines marked (A) and (B) correspond to the lower and upper boundaries of the two-phase region of the infinite system. The dashed lines indicate the layer concentrations for metastable states above T_0.

spatial order. For temperatures lower than T_0, a disordered region richer in element A is followed by an ordered central core richer in element B (note that in the calculations the total numbers of A and B atoms are kept constant). The mechanism of the first-order phase transition may be visualized as the growth of this disordered surface region that begins to develop below T_0 and becomes approximately eight layers thick, on each surface, for the 39-layer film. In semi-infinite systems, the thickness of this disordered layer diverges at T_0 which in this limit approaches T_s^∞. Just above the transition temperature T_0 (see Fig. 3), the atoms in the inner region rearrange into a homogeneous disordered phase.

Results for the temperature dependence of the concentration at layers 7, 8, 9, 10, 12, and 19, are shown in Fig. 4. Also shown in Fig. 4 are lines labeled (A) and (B) which correspond, respectively, to the lower and upper two-phase boundaries predicted by the Bragg-Williams approximation for the infinite system[15]: below line (A), the equilibrium state is the ordered A_3B phase; above line (B) the equilibrium state is the disordered phase; and in between lines (A) and (B) the ordered and disordered phases coexist. From Fig. 4 it is evident that two regions of distinct average concentration develop near T_0: one near the surface that is richer in A atoms and one at the center of the film that is richer in B atoms. As the temperature increases, the concentrations in these two regions approach the two phase boundaries of the equilibrium phase diagram for the infinite system. We have also included in Fig. 4 the layer concentrations for metastable states at temperatures higher than T_0 (dashed lines). These metastable states correspond to states located well inside the two-phase region. Once again, the evolution of the concentration near the surface and in the inner regions of the film closely follow, respectively, the upper and lower boundaries of the equilibrium phase diagram.

Results for the dependence of the transition temperature T_0 and of the surface long-range order parameter at T_0, η_0^*, on the number of layers n in the film are presented in Fig. 5. We see from the inset in Fig. 5 that in the calculated range of 1 to 39 layers T_0 and η_0^* do not follow, respectively, the n^{-1} and $n^{-1/2}$ behavior predicted by the Landau expansions on a single long-range order parameter.[8,9] We attribute this to the fact that in the alloy film the surface concentration is strongly coupled to the surface long-range order. Thus, the change in concentration near the surface of the film tends to stabilize the low-temperature ordered phase. In Fig. 5, we also see that η_0^* becomes very small for films with a relatively small number of layers (≈ 30). This behavior reflects the delocalization of the disordered surface region at T_s^∞ in the semi-

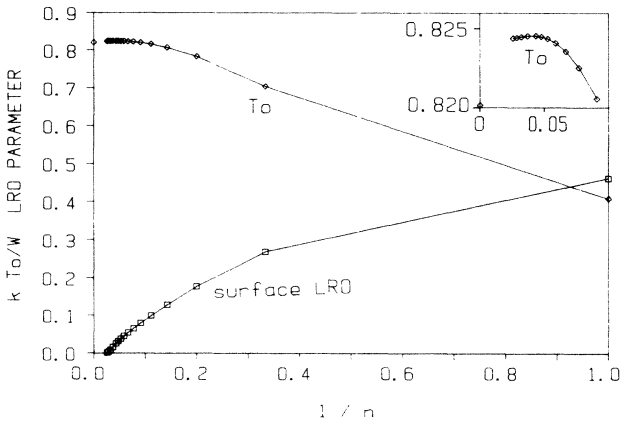

FIG. 5. Thickness dependence of the transition temperature T_0, and of surface long-range order parameter T_0, η_0^*. All cases are calculated for $x = 0.75$ and $\Delta = 0$.

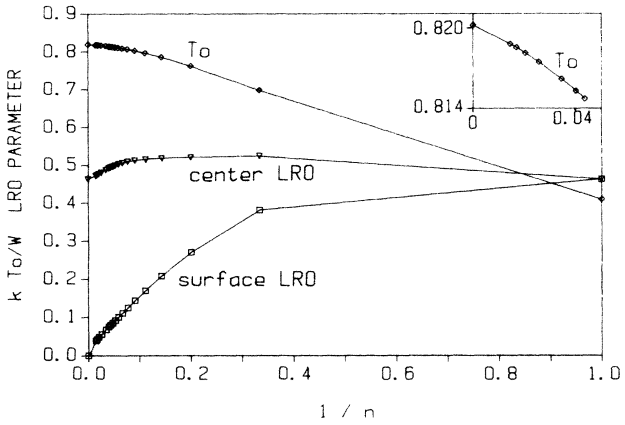

FIG. 6. Thickness dependence of the transition temperature T_0 and of the surface long-range order parameter at T_0, η_0^*. The concentration in each layer was kept fixed at 0.75 (no segregation).

infinite limit.

In order to compare with previous results,[8,9] we show in Fig. 6 the thickness dependence of T_0 and η_0^* under the constraint of no surface segregation; i.e., $x_0 = x_1 = \ldots = x_n = x$. In this case, one sees that for films thicker than 30 layers, T_0 and η_0^* follow, respectively, the n^{-1} and $n^{-1/2}$ behaviors predicted by the Landau expansions. This regime for T_0 is shown in the inset of Fig. 6. Also shown in Fig. 6 is the long-range order parameter at the center of the film, which is larger than that of the infinite system.

Within the continuous Landau theory, it has been predicted that for a strong surface perturbation no transformation takes place below a critical film width L_c.[9] In the model we investigated here, an equivalent situation develops for very thin films when the values of Δ are such that the outer layers saturate to $x \approx 1$ (or $x \approx 0$). For example, for a film of three layers with an average concentration of $\frac{2}{3}$ (or $\frac{1}{3}$), the transition will be suppressed if segregation is sufficiently strong (large Δ) so that the two outer layers are saturated to $x \approx 1$ (or $x \approx 0$) and the central layer is almost completely depleted with $x \approx 0$ ($x \approx 1$).

In conclusion, we have presented a theory of size effects on the first-order phase transition in fcc binary alloys. We have worked out in detail all the consequences of the finite character of the system. We expect that all the predictions obtained in this theory can be measured experimentally by means of the surface-sensitive techniques developed recently.[11-14] As a particular case, we obtained the results predicted by one-parameter theories for very thick films.

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