Theoretical Study of Antiphase Boundaries in fcc Alloys

A. Finel, V. Mazauric, and F. Ducastelle
Office National d'Etudes et de Recherches Aérospatiales (ONERA), BP 72, 92322 Châtillon CEDEX, France
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We have investigated the behavior of nonconservative (100) antiphase boundaries in $L1_2$-ordered alloys, close to the congruent first-order order-disorder transition. Very accurate inhomogeneous cluster-variation-method calculations in the tetrahedron approximation show that wetting does occur through an infinite series of layering transitions with average logarithmic divergences for the width of the wetting layer and for the excess entropy.

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From a very general point of view, an order-disorder transition is associated with a broken symmetry: The ordered phase has less symmetry than the disordered one. When the ordering process starts at different places of the disordered lattice, different variants (or domains) of the same ordered phase can therefore appear and coexist. An antiphase boundary (APB) forms wherever two such domains contact.

Whether the ordering transition is first or second order is a very important factor for the qualitative behavior of the APB. At the critical temperature of a second-order transition, the ordered phase becomes identical with the disordered one and, consequently, the APB disappears.

On the other hand, for a first-order transition, the ordered domains always retain a certain degree of long-range order and APB exist up to the transition temperature T_c. In that case, the APB free energy (i.e., the excess free energy with respect to a situation with no APB) does not vanish at T_c. It may happen, however, that, precisely at T_c and in order to minimize the excess free energy, the APB takes a particular configuration and that a layer of disordered phase develops between the two ordered domains. In other words, the APB may split into two order-disorder interfaces: This is called complete wetting of the APB by the disordered phase. In fact, within a *continuous* theory and if the ordered phase can be described with a *one-dimensional* order parameter, it is easy to show that wetting must occur, and that the width of the wetting layer as well as the APB entropy diverge logarithmically as the temperature T increases up to T_c.[1]

Many experimental and theoretical studies have been devoted to wetting phenomena.[2] We will consider here the case of a binary alloy on the fcc lattice which orders according to the Cu_3Au-type $L1_2$ structure. Wetting in that case has recently been observed in a $Co_{30}Pt_{70}$ alloy,[3] and had in fact been predicted before by Kikuchi and Cahn using inhomogeneous cluster-variation-method (CVM) calculations.[4] The accuracy of their calculation, however, was not sufficient for studying in detail what happens close to T_c.

In this Letter, we present a detailed and very precise study of a nonconservative APB in $L1_2$ as a function of temperature. The numerical method used is the CVM in the tetrahedron approximation. A particular feature of this study is that the ordered phase is described by a *three*-dimensional order parameter. In such a case, wetting as mentioned above may not occur or may be modified because of lattice effects neglected in the continuous approximation. In particular, layering transitions, corresponding to discontinuous variations of the concentration profiles as a function of temperature, may well occur. This is precisely what has been found in this work, as we show below.

Note that since the present order-disorder transition is in the universality class of the four-state Potts model,[5] our study has some parentage with those dealing with interfacial wetting in the Potts model.[2]

To describe ordering effects, we use the Ising model with positive first-neighbor interactions:

$$H = J \sum_{(n,m)}{}' \sigma_n \sigma_m - h \sum_n \sigma_n , \qquad (1)$$

where the prime means that the sum is over first-neighbor pairs. The spinlike variables σ_n take values ± 1 depending on the type A or B of the atom at site n. The corresponding phase diagram presents three ordered phases at stoichiometries AB, A_3B, and AB_3 (Fig. 1). Its precise shape close to the AB-A_3B (or AB_3) boundary is still controversial,[6] but this is not the case near the congruent point of the A_3B structure.

This is the region we shall consider in the following.

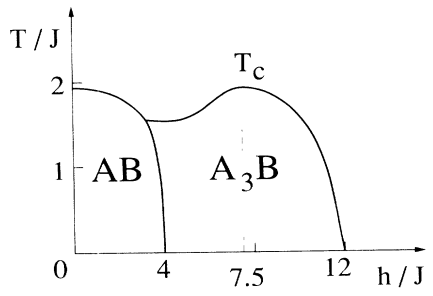

FIG. 1. Schematic phase diagram obtained within the tetrahedron CVM (see Ref. 6).

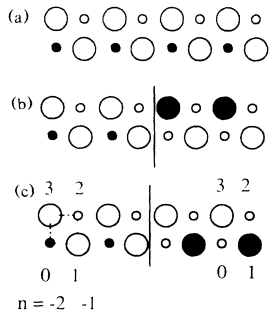

FIG. 2. Solid (open) circles represent B (A) atoms. Large (small) circles are the sites on ($00n$) planes with n integer (half integer). The index $i=0$, 1, 2, and 3 labels the four simple cubic sublattices, and n the tetrahedra along [001] (one of them is represented by dotted lines).

More precisely, we shall work at field $h=7.5J$. The corresponding critical temperature is $T_c/J=1.942\,637\,506\,1$, which is very close to the congruent point. At zero temperature, the A_3B equilibrium state is infinitely degenerate but, at finite temperature, this degeneracy is lifted and the stablest structure is the simplest A_3B one, namely, the $L1_2$ phase.

In $L1_2$, one simple-cubic sublattice of the fcc structure is predominantly occupied by B atoms, and the three others by A atoms. Since there is a choice for the sublattice occupied by B atoms, $L1_2$-type ordering leads to four different variants or domains. The $L1_2$ phase can also be analyzed as an infinite sequence of alternating pure A and mixed AB (001) planes [Fig. 2(a)]. The contact between two different ordered domains leads either to a conservative APB [Fig. 2(b)] or to a nonconservative one [Fig. 2(c)]. With first-neighbor interactions only, the energy of a conservative APB vanishes at zero temperature, and in fact at any temperature within the CVM tetrahedron approximation. We therefore consider the nonconservative situation, as in Ref. 4.

Our aim is to calculate the equilibrium state of an inhomogeneous system with definite boundary conditions. We use the CVM which is known to be a very precise method and is in principle fairly easy to implement. The free-energy minimization is performed on a finite system containing typically one or two hundred tetrahedra along [001], and therefore involves a few thousand variational parameters. The APB free energy per site is of the order of $0.1J$ close to T_c, to be compared with a total energy of about a few hundred J. On the other hand, the splitting of the APB involves energies less than $10^{-3}J$. Different numerical minimization procedures can be used. We have found that a very efficient method is the brute-force global Newton-Raphson procedure, provided advantage is taken of the nearly block-diagonal structure of the Hessian matrix. This method ensures an accuracy on free energies better than $10^{-10}J$.

The index n will now label the nth tetrahedron along direction [001] and the index $i=0$, 1, 2, or 3 the four simple-cubic sublattices [see Fig. 2(c)]. Each tetrahedron shares one site with each sublattice. Let $c_n^i=(1-\sigma_n^i)/2$ be the concentration in minority atoms at

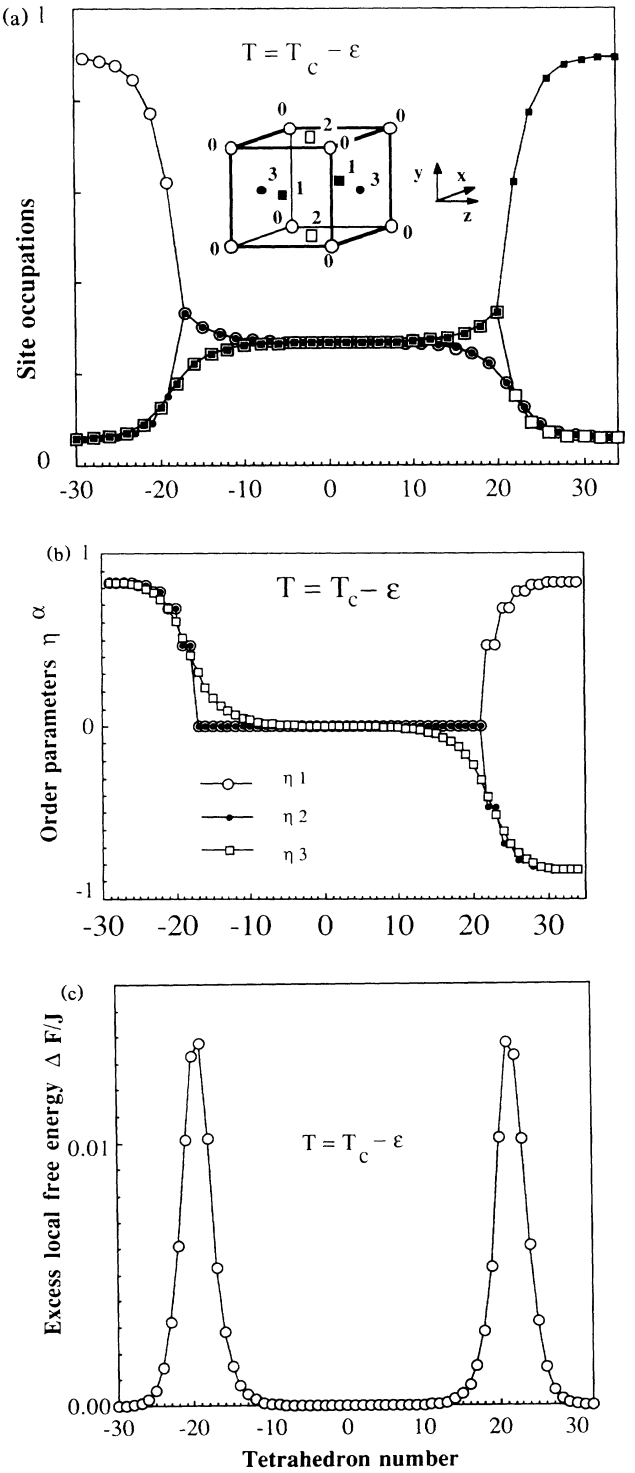

FIG. 3. Calculated profiles for the APB at $T=T_c-0.778\times10^{-6}J$ ($h=7.5J$): (a) sublattice concentrations c^0, c^1, c^2, and c^3, (b) order parameters η^1, η^2, and η^3 (note the region where η^1 and η^2 strictly vanish), and (c) excess local free energy.

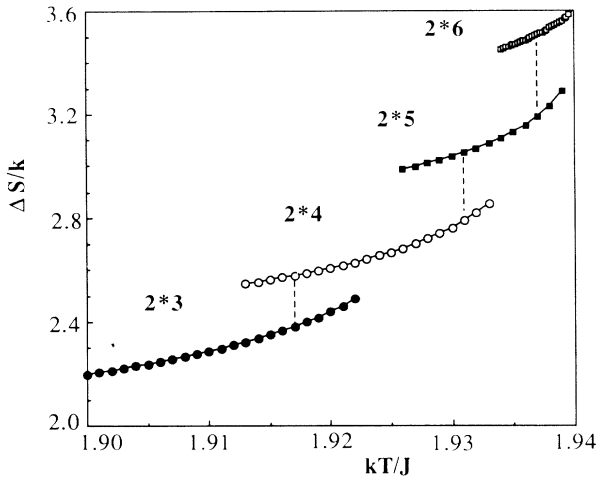

FIG. 4. Excess entropy ΔS as a function of temperature T. The dotted lines mark the first-order layering transitions.

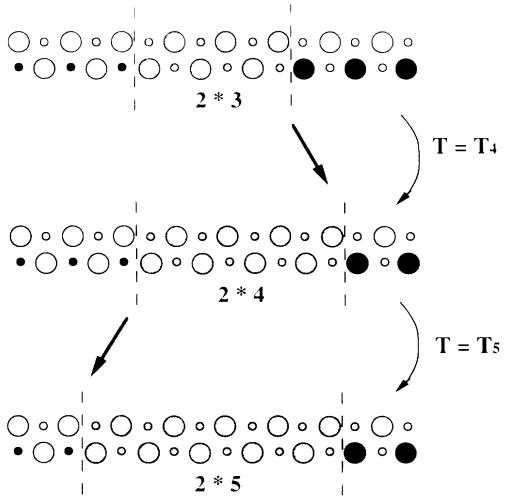

FIG. 5. Illustration of the wetting process: As the temperature increases up to T_c, the width of the wetting layer increases discontinuously (by jumps of two atomic planes) through an infinite series of first-order transitions (see Fig. 2 for the site representations).

site i in tetrahedron number n. In a perfectly ordered $L1_2$ phase, this concentration does not depend on the index n and one of them is equal to 1, the three others to 0 (say, $c^0=1$, $c^1=c^2=c^3=0$).

We consider here the case of a nonconservative APB along direction [001]; i.e., we assume that minority atoms principally occupy sublattice 0 (or 3) at $z=-\infty$ and 1 (or 2) at $z=+\infty$ [see Fig. 2(c)]. As this is an inhomogeneous situation, the concentrations c_n^i now depend explicitly on indices n and i. More precisely, for a given tetrahedron n, the four concentrations c_n^i, $i=0$, 1, 2, and 3, can be *all* different. Therefore, besides the mean concentration $(c_n^0+c_n^1+c_n^2+c_n^3)/4$, a *three*-dimensional order parameter η_n is needed to describe completely the degree of order. We therefore introduce $\eta_n=(\eta_n^1,\eta_n^2,\eta_n^3)$ with $\eta_n^1=c_n^0+c_n^1-c_n^2-c_n^3$, $\eta_n^2=c_n^0-c_n^1+c_n^2-c_n^3$, and $\eta_n^3=c_n^0-c_n^1-c_n^2+c_n^3$. These quantities measure the local amplitudes of the concentration waves of q vectors (100), (010), and (001), respectively.

We first discuss the equilibrium state of the APB at a temperature very close to the transition temperature: $T=T_c-0.778\times10^{-6}J$. In Fig. 3(a) are shown the concentration profiles c_n^i, $i=0$, 1, 2, or 3, which clearly display a large (but finite) wet region (the profiles at lower temperature are similar to those presented by Kikuchi and Cahn[4]). A remarkable feature of these profiles is that the (001) planes in the central layer are strictly disordered when they are considered as two-dimensional square lattices. This is still more striking when we draw the order-parameter profiles η_n^α, $\alpha=1,2,3$. The order parameters $\eta_n^{1,2}$ then strictly vanish in the wetting layer [Fig. 3(b)]. We also show in Fig. 3(c) the free-energy profile obtained by decomposing the total free energy into a sum of tetrahedron free energies.

We have then investigated in more detail the wetting process by computing the variation with temperature of the APB free energy and entropy. Typical results concerning the APB entropy are presented in Fig. 4. The remarkable point is that we have found an *infinite* series of first-order transitions associated with entropy jumps. We have verified that each jump corresponds to the disordering of a mixed plane in the central region. As a result, the APB is completely wet at T_c by the disordered phase. More precisely, as the temperature increases up to T_c, the width of the wetting layer increases discontinuously through an infinite series of jumps of *two* atomic planes (see Fig. 5 for an illustration of this layering process; completely similar results have been obtained using the Bragg-Williams approximation). Hence, the width of the APB, defined as the number of consecutive disordered atomic planes in the central layer is always an even number $2l$. Let T_l be the transition temperature between phases $2(l-1)$ and $2l$. We have computed the first twenty temperatures T_l; Fig. 6 clearly shows that l behaves asymptotically as $\ln(T_c-T_l)^{-1}$. This kind of logarithmic behavior is in fact common to numerous wetting effects in the presence of short-range interactions.[2] As a technical remark, it may also be noted that, due to the first-order character of these transitions, many metastable states can exist close to T_c: For example, all phases $2l$ with $l>6$ are metastable at $T=T_c$. As a consequence, the true equilibrium state cannot be obtained through a single minimization process: For a given temperature, one has to compare the free energies of all phases $2l$.

The wetting and layering mechanisms observed in this study can in fact be explained using fairly simple qualitative arguments. We just mention here two points. First, within a continuous theory, it is easy to show that the APB free-energy minimization, which depends on a

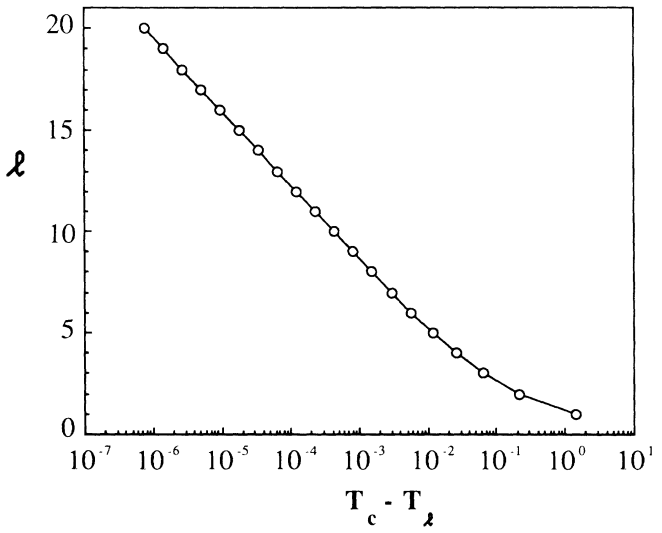

FIG. 6. Half-width of the wetting layer l vs $\log_{10}(T_c - T_l)$: Note that the logarithmic behavior is observed for more than four decades.

three-dimensional order parameter, reduces, in the presence of first-neighbor interactions *only*, to a one-dimensional problem and that, consequently, wetting should occur. Second, an analysis of the discrete mean-field (Bragg-Williams) equations can explain the layering mechanism.

To summarize, complete wetting of nonconservative (100) APB has been shown to occur as the temperature increases up to the transition temperature T_c, through an infinite series of first-order layering transitions. One may wonder whether layering is not forced by the mean-field theory that neglects fluctuations. Preliminary Monte Carlo simulations show that this is probably not the case and that the roughening temperature is above T_c.

On the other hand, other calculations in progress show that layering effects do not appear for (110) and (111) orientations and that the results are not qualitatively modified in the presence of second-neighbor interactions.

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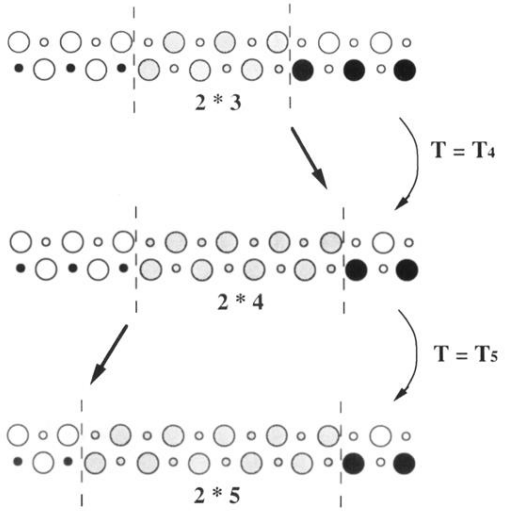

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