

Theory of surface effects in binary alloys. I. Ordering alloys

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A theory of the (110) surface concentration and short- and long-range orders for an AB body-centered-cubic alloy is presented. It is based on a model consisting of pairwise interactions between nearest-neighbor atoms only. The entropy is calculated in the pair approximation following Kikuchi's method. It is found that depending on the values of the interaction parameters (a) the surface concentration decreases monotonically as a function of temperature from 100% of one component at $T = 0$ to a random mixture as $T \rightarrow \infty$, or (b) it increases from a perfectly ordered AB layer of equal concentration of either component to a maximum concentration of one component at the order-disorder transition temperature T_c and then decreases again to the disordered $A_{0.5}B_{0.5}$ alloy as $T \rightarrow \infty$. Long-range and short-range order parameters as functions of temperature are also discussed.

I. INTRODUCTION

Order-disorder transformations as well as constitutional short-range and long-range orders in binary alloys are some of the classical problems in materials science. But, although copious data for the bulk are available, the amount of information on the phenomena as they apply to the surface is considerably smaller. In fact only a few special cases have been investigated.¹

It is well established that, in general, the chemical composition at the surface differs appreciably from that in the bulk.²⁻⁶ But the effect of the order-disorder transformation on the surface concentration and properties has not been investigated experimentally. In particular the variation in composition and short-range order at the surface should be paramount in understanding the catalytic behavior of alloys^{7,8} as well as other chemical properties. It is the purpose of this paper to examine theoretically such problems.

With this in mind we choose the simplest possible model: we describe a binary A_xB_{1-x} alloy by a superposition of short-range (nearest-neighbor-only) pairwise interactions. These are defined by three parameters U_{AA} , U_{BB} , and U_{AB} which give the various pair energies. We then minimize the total free energy of the system after the internal energy and the entropy are calculated in some approximation.

If the heat of mixing

$$W \equiv U_{AA} + U_{BB} - 2U_{AB}$$

is positive, there is a net attraction between unlike atoms and the alloy tends to develop long-range order. If $W < 0$, then A and B atoms tend to repel one another and the system tends to segregate into two separate phases. In this paper, we discuss in detail the surface properties of the ordering alloys ($W > 0$) and the following paper⁹ is

concerned with the segregating alloys.

The surface behavior of the alloy is of course intimately connected to the behavior in the bulk. The theories of the order-disorder transformations in bulk are almost exclusively concerned, within the simple nearest-neighbor only pairwise interaction model, with the calculation of the entropy of the system. The simplest approximation, the so-called single-site or Bragg-Williams approximation, gives already qualitatively correct results in most body-centered-cubic (bcc) and face-centered-cubic (fcc) A_xB_{1-x} alloys,¹⁰ except that it predicts a second-order transition for a fcc $A_{0.5}B_{0.5}$ alloy and a first-order transition is observed experimentally.¹¹

The first improvement on the Bragg-Williams approximation is the pair approximation, also called the Bethe or quasichemical approximation. It improves considerably the quantitative results, but it still fails in predicting a first-order transition for the fcc $A_{0.5}B_{0.5}$ system.¹²

Kikuchi¹³ has developed a method to analyze systematically and by successive approximation the entropy required in the study of order-disorder transformations. In particular, in the first two orders of approximation Kikuchi's method reproduces the Bragg-Williams and the Bethe results, respectively.

To study surface properties, the Bragg-Williams theory has been successfully applied to describe long-range order transformations in $A_{0.75}B_{0.25}$ -type alloys.¹⁴ Short-range order theories and segregation studies at high temperatures have also been presented.^{15,16} On the whole, however, there has been no theoretical study of surfaces which include short-range and long-range orders as well as concentration changes over the whole range of temperatures. We present here such a theory as applied to the $A_{0.5}B_{0.5}$ bcc lattice, with a (110) surface and by means of Kikuchi's method. The

theory and calculations for ordering alloys are described in Sec. II and the results are discussed in Sec. III. Details of the method are presented in Appendixes A and B. The following paper⁹ studies in a similar way a (111) surface of an fcc crystal for a segregating alloy.

II. CALCULATION AND RESULTS

A. Bulk properties

In order to describe long-range order, the bcc lattice is subdivided into two equivalent sublattices, α and β . The α sublattice consists of all corner sites and the β sublattice of all the body-center sites. All α sites have β sites as nearest neighbors and vice versa. In the perfectly ordered case of the $A_{0.5}B_{0.5}$ alloy, all α sites are occupied by A atoms and the β sites are occupied by B atoms. In the completely disordered case, the probabilities to find an A atom in the α and β sites are the same.

In bulk, there are four site probabilities p_A^α , p_B^α , p_A^β , and p_B^β and four pair probabilities $p_{AA}^{\alpha\beta}$, $p_{AB}^{\alpha\beta}$, $p_{BA}^{\alpha\beta}$, and $p_{BB}^{\alpha\beta}$. The symbol p_I^ν denotes the probability of finding an I atom in the ν sublattice and $p_{IJ}^{\alpha\beta}$ is the probability of finding an IJ bond with the I atom in the α sublattice and the J atom in the β sublattice. The pair probabilities are normalized by

$$p_{AA}^{\alpha\beta} + p_{AB}^{\alpha\beta} + p_{BA}^{\alpha\beta} + p_{BB}^{\alpha\beta} = 1, \quad (2.1)$$

and the average concentration x of species A is given by

$$x = \frac{1}{2}(2p_{AA}^{\alpha\beta} + p_{AB}^{\alpha\beta} + p_{BA}^{\alpha\beta}). \quad (2.2)$$

We define the long-range order parameter η and the short-range order parameter σ by

$$p_{AA}^{\alpha\beta} + p_{AB}^{\alpha\beta} = x + \frac{1}{2}\eta \quad (2.3)$$

and

$$\sigma = 1 - [(p_{AB}^{\alpha\beta} + p_{BA}^{\alpha\beta})/2x(1-x)]. \quad (2.4)$$

By means of Eq. (2.1)–(2.4) it is possible to write the pair and site probabilities as functions of the alloy concentration x , the long-range order parameter η and the short-range order parameter σ . This is done in Appendix A. The equilibrium values of η and σ , for a given concentration x , are obtained by minimizing the free energy $F = U - TS$ with respect to σ and η .

$$\frac{\partial F}{\partial \sigma} = 0 \quad \frac{\partial F}{\partial \eta} = 0. \quad (2.5)$$

$$U = \text{const} + \mathcal{N}W \sum_{n=0}^{\infty} \left\{ \frac{1}{2} Z_0 [x_n^2 + x_n(\Delta - 1) - \frac{1}{2}\Delta + x_n(1 - x_n)\sigma_{nn}] + Z_1 [x_n x_{n+1} + \frac{1}{2}(x_n + x_{n+1})(\Delta - 1) - \frac{1}{2}\Delta + x_n(1 - x_{n+1})\sigma_{n(n+1)}] \right\} \quad (2.11)$$

The internal energy U is given by

$$U = \frac{1}{2} Z (N_{AA}U_{AA} + N_{AB}U_{AB} + N_{BB}U_{BB}), \quad (2.6)$$

where Z is the number of nearest neighbors and N_{IJ} is the total number of I - J bonds. With the probabilities given in Appendix A, we can write

$$U(\sigma) = U(0) + \frac{1}{2} Z N x(1-x)\sigma W. \quad (2.7)$$

Here N is the total number of atoms. For the entropy we use Kikuchi's expression¹³ for the pair approximation (see Appendix B). With the use of (2.7) and (B1), the minimization (2.5) is straightforward. It should be noted that, since U as given by (2.7) is independent of η , the second equation (2.5) gives a unique (parameter independent) relationship which yields η as a function of x and σ .

For the $A_{0.5}B_{0.5}$ alloy, we obtain a second-order transition, with a temperature T_c given by

$$kT_c = W \{2 \ln [Z/(Z-2)]\}^{-1}. \quad (2.8)$$

At $T = T_c$, the short-range-order parameter is

$$\sigma(T_c) = 1 - Z/(Z-1). \quad (2.9)$$

These results are, of course, those obtained in the quasichemical or Bethe approximation.¹⁰

B. Surface properties

We classify the atoms in the crystal according to the (110) planes n they belong to in order to study the surface properties. Plane $n=0$ corresponds to the surface layer. We introduce four site probabilities per plane n :

$$p_I^\nu(n), \quad \nu = \alpha, \beta, \quad I = A, B.$$

We also define four intralayer pair probabilities

$$p_{IJ}^{\alpha\beta}(n, n), \quad I, J = A, B$$

and eight interlayer pair probabilities

$$p_{IJ}^{\alpha\beta}(n, m), \quad p_{IJ}^{\beta\alpha}(n, m) \quad \text{for } I, J = A, B$$

(n, m are adjacent planes). They can be defined in terms of a layer concentration x_n , a layer long-range order parameter η_n , and intralayer short-range order parameter σ_{nn} , and two interlayer short-range-order parameters σ_{nm}^α and σ_{nm}^β . This is done in Appendix A.

In order to calculate the internal energy, it is useful to define the dimensionless parameter Δ :

$$\Delta \equiv (U_{AA} - U_{BB}) / (U_{AA} + U_{BB} - 2U_{AB}). \quad (2.10)$$

If in addition we take all pair energies to be independent of the layer location, i.e., no major surface rearrangement, we can write

In (2.11), \mathfrak{N} is the number of atoms per layer, Z_0 is the number of nearest neighbors to each atom within the same layer, and Z_1 is the number of nearest neighbors to one atom which are in one of the adjacent layers. When Kikuchi's entropy expression, as applied to layered structures is included [see Appendix B, Eq. (B2)], we may once again determine the equilibrium values of the concentrations x_n and the order parameters, η_n , σ_{nn} , σ_{nm}^α and σ_{nm}^β by minimizing the resulting free-energy expression with respect to all these. The condition of chemical equilibrium imposes the constraints¹⁷

$$\frac{\partial F}{\partial x_n} \text{ (all other } x_n \text{ constant)} = \frac{\partial F}{\partial x} \text{ (bulk)} \quad (2.12)$$

which yields the values of x_n .

C. Results at $T=0$

At zero temperature, through long calculations it is possible to prove in a rather straightforward way that only the surface layer can be, at equilibrium, different from the bulk. If the bulk parameters are x , η , and σ , only x_0 may be different from x , only η_0 may be different from η , and only σ_{00} , σ_{01}^α and σ_{01}^β may be different from σ . In particular, the values which minimize the free energy are

$$\sigma_{00} = \begin{cases} -x_0/(1-x_0), & x_0 \leq \frac{1}{2}, \\ -(1-x_0)/x_0, & x_0 \geq \frac{1}{2}, \end{cases} \quad (2.13)$$

and

$$\sigma_{01} \equiv \frac{1}{2}(\sigma_{01}^\alpha + \sigma_{01}^\beta) = \begin{cases} -1, & x_0 \leq \frac{1}{2}, \\ -(1-x_0)/x_0, & x_0 \geq \frac{1}{2}. \end{cases} \quad (2.14)$$

The values of x_0 are determined from (2.12). The results are shown in Fig. 1. For values of Δ such that $-\Delta_0 \leq \Delta \leq \Delta_0$, where

$$\Delta_0 \equiv (Z - Z_1)/Z_1, \quad (2.15)$$

there is no difference between surface and bulk, i.e.,

$$x_0 = \frac{1}{2}, \quad \sigma_{00} = \sigma_{01} = -1, \quad \eta_0 = 1.$$

For $\Delta > \Delta_0$, x_0 takes the value +1, and for $\Delta < -\Delta_0$, $x_0 = 0$. In other words, the surface layer is made of atoms of only one species, either pure A if $U_{AA} > U_{BB} + \Delta_0 W$ or pure B if $U_{AA} < U_{BB} - \Delta_0 W$. In either case $\sigma_{00} = \eta_0 = 0$.

D. Results at finite T

The details of the minimization of the free energy at finite temperature are given in Appendix B. The resulting transcendental equations are solved numerically. For simplicity, and based on the re-

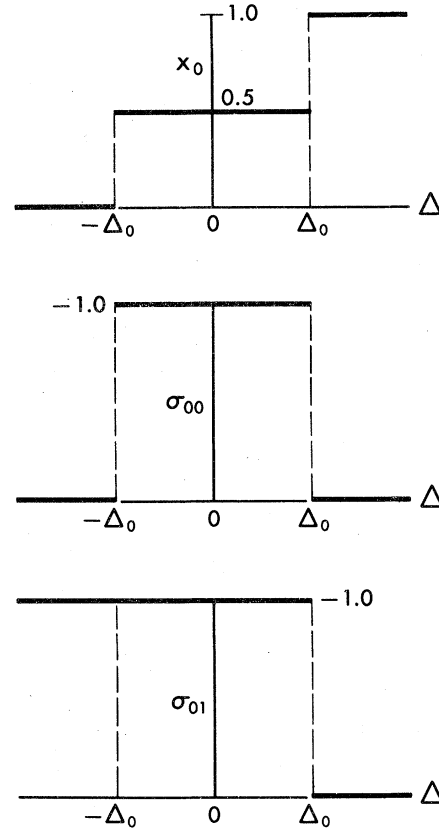


FIG. 1. Surface concentration x_0 , the internal surface short-range order parameter σ_{00} , and the interplane short-range order parameter σ_{01} as a function of $\Delta \equiv (U_{AA} - U_{BB})/(U_{AA} + U_{BB} - 2U_{AB})$. The discontinuities take place at $\pm \Delta_0$, where $\Delta_0 \equiv (Z - Z_1)/Z_1$, Z is the number of nearest neighbors in the bulk, and Z_1 the number of nearest neighbors to an atom in a plane adjacent to it. For the bcc materials and the (110) surface $\Delta_0 = 3$.

sults at $T=0$, we have taken only the surface layer to have concentration and order parameters which differ from the bulk values. The results for different temperatures and values of Δ are exhibited in Figs. 2-5. Figure 2 gives values of x_0 as a function of Δ for various temperatures, while Fig. 3 gives x_0 as a function of T for various Δ values. A similar pair of graphs for σ_{00} and η_0 are given in Figs. 4 and 5; in the last case we also plot the bulk values $\eta(T)$ and $\sigma(T)$.

III. DISCUSSION

By means of Kikuchi's method and the pair approximation, we have developed a theory for the surface effects on the order-disorder transformation and applied it to a bcc ($A_{0.5}B_{0.5}$) alloy. This type of superlattice is very common. Typical examples¹⁸ are CuZn, AuCd, AlNi, NiZn, LiTi, FeCo, etc.

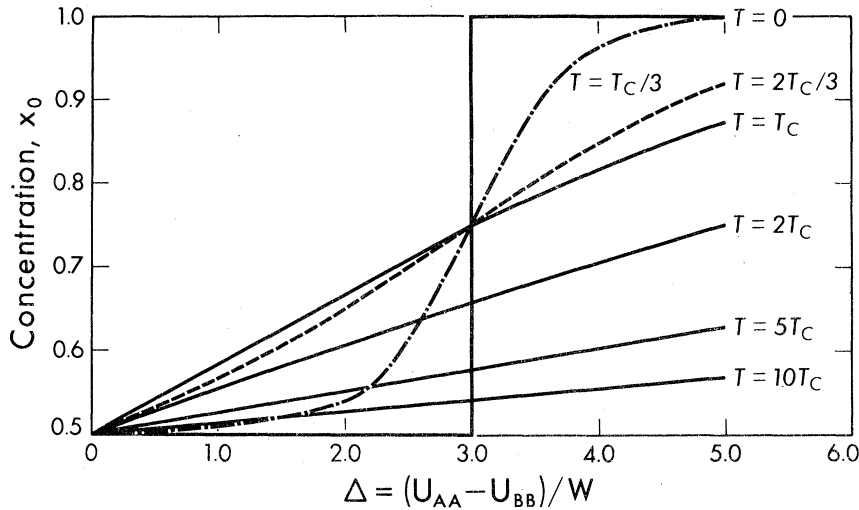


FIG. 2. Surface concentration x_0 as a function of Δ for the (110) face of a bcc material and for various temperatures; T_c in the order-disorder transition temperature.

The main effect, i.e., the segregation at the surfaces, is caused in this model by the reduction in nearest-neighbor coordination of the atoms at the surface. The system is therefore stabilized, in general, by placing at the outer atomic plane those atoms for which the broken bonds contribute least to the total energy. The driving parameter at the surface is thus the difference in the bond energies ($U_{AA} - U_{BB}$) or, more accurately its ratio Δ to the heat of mixing W . As shown in Fig. 1, at $T=0$ we find that the surface layer might have different concentration and order than the bulk. This occurs at $\Delta > \Delta_0$, where Δ_0 , as given by (2.15), depends only on coordination parameters. For $0 < \Delta < \Delta_0$ the surface concentration increases with temperature up to the maximum value

$$x_{\max} = \frac{1}{2} + \frac{1}{12}\Delta \quad (3.1)$$

at the transition temperature T_c , and then it de-

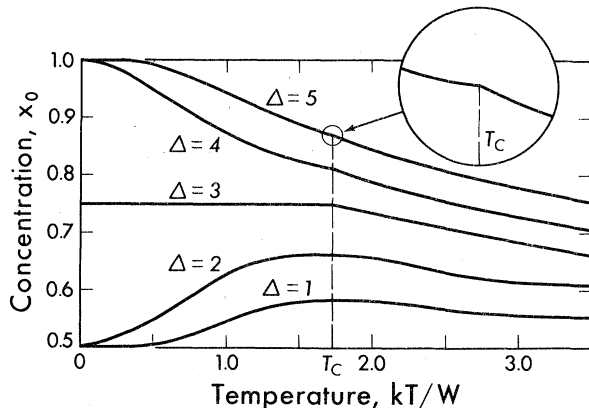


FIG. 3. Surface concentration x_0 as a function of temperature for the (110) face of a bcc material and for various values of Δ .

creases slowly to $x = \frac{1}{2}$ as $T \rightarrow \infty$. For $\Delta = \Delta_0$, the concentration is constant and equal to 0.75 for $0 < T < T_c$. It decreases at higher temperatures. For $\Delta > \Delta_0$, the concentration decreases monotonically between 1 and 0.5. As expected, the surface concentration x_0 has a discontinuous slope at the transition temperature as shown in the inset figure of Fig. 3. Our theory predicts that concentration differences $\Delta x = x_{\text{surf}} - x_{\text{bulk}}$ of the order of 1% would be present near the transition temperature T_c even for very small values of Δ ($\Delta \geq 0.12$). All these effects should be experimentally observable.

The surface short- and long-range orders (σ_{00}, η_0) at $T=0$ are -1 and 1 , respectively, for $-\Delta_0 \leq \Delta \leq \Delta_0$ and 0 for $\Delta > \Delta_0$ and $\Delta < -\Delta_0$ (Fig. 1). At higher temperatures, the order decreases monotonically as a function of Δ , as seen in Fig. 4. As a function of temperature, the surface short- and the long-range orders decrease for $0 \leq \Delta \leq \Delta_0$. For $\Delta > 3$ all orders increase from zero at $T=0$ up to a maximum and then decrease again. The long-range order vanishes at the common transition

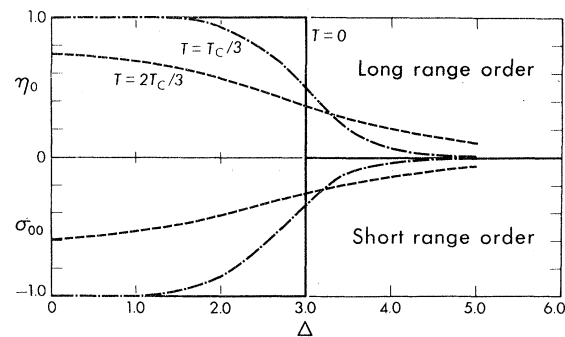


FIG. 4. Surface long-range order parameter η_0 and the internal surface short-range order parameter for a (110) surface of a bcc material as a function of Δ and for various temperatures.

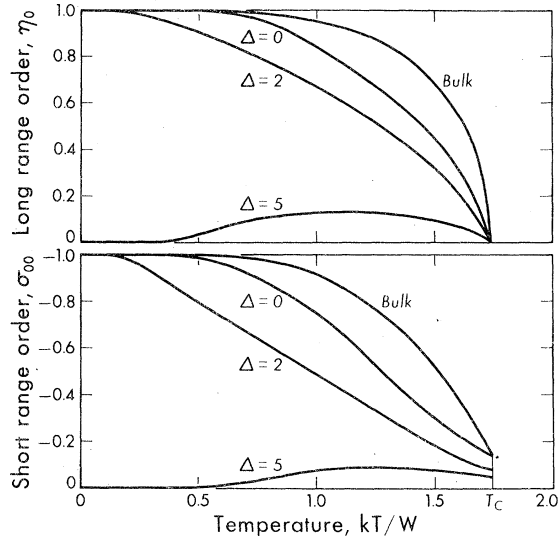


FIG. 5. Bulk (η) and surface long-range order parameters η_0 and the bulk (σ) and internal short-range order parameter σ_{00} for a (110) surface of a bcc material as a function of T and for various values of Δ .

temperature T_c given by (2.13). The short-range order at the transition temperature is finite and decreases as a function of Δ as shown in Fig. 5. For comparison we show also in Fig. 5 the temperature dependence of the bulk short- and long-range orders. In bulk as well as at the surface the derivative of the short-range-order parameter with respect to temperature has a discontinuity at the transition temperature T_c .

Results for segregation parameters obtained from regular solution theory^{19,20} are valid only at high temperatures where the system can be assumed to be completely disordered. At low temperatures, these theories yield wrong results. Recently²¹ the surface properties of FeCo systems were investigated experimentally at temperatures below the order-disorder transition temperature. It is found that the segregation values calculated from the regular solution theory do not agree with the experimental results.

A better description of the system is achieved by the Bragg-Williams theory applied to the surface,¹⁴ where long-range order is included. However, this approximation gives a relative high transition temperature ($kT_c/W=2$) as compared with the series-expansion transition temperature ($kT_c/W=1.587$), and the results for segregation at $T > T_c$ would be the same as those in the regular solution theory.

Theories for segregation taking into account only short-range order have been also presented.^{15,16} These theories for $T > T_c$ give a better description of the system than the regular solution theory and the Bragg-Williams theory, but are not valid for

$T < T_c$.

The theory presented here, including short- and long-range order is valid over the whole temperature range. The transition temperature in this approximation ($kT_c/W=1.738$) is better than in the Bragg-Williams approximation.

The extension of the theory to a higher approximation (the so-called tetrahedron approximation¹²) is straightforward. More accurate values for the surface concentration, short- and long-range orders at $T > 0$ should be obtained but no new features are expected. At $T=0$, the results are the same, since the internal energy depends only on the pair probabilities.

We have studied only the (110) surface. In general, for other surface orientations which have other coordination parameters Z_0 and Z_1 , the results could be very different. In particular, if either Z_0 or Z_1 is zero the theory should be reformulated.

Nonetheless we believe that with the present calculation, and within the validity of the pairwise interaction model (with nearest-neighbors only) we have obtained general qualitative results which are found experimentally. For instance Nakamura and Wise²¹ find that in FeCo, at $T \cong 600$ K, the surface (which is of unspecified orientation in their sample) has a Fe concentration of 0.75. Since $T_c = 1250$ K, this would place our parameter Δ at approximately 3 if the surface were of the {110} orientation. From thermodynamic values, Δ can be estimated to be 1.9, which would indicate either a different surface or the type of accuracy expected from our model.

Extensions of our theory are possible in many directions: (i) better approximations for the entropy¹²; (ii) change of the U_{AA} , U_{BB} , and U_{AB} parameters at the surface caused by the very existence of the surface and the atomic rearrangement in its vicinity; (iii) extension to neighbors other than the first; (iv) inclusion of other effects, such as conduction electron contributions and screening, which would make the two-body pairwise interaction inadequate.

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APPENDIX A

In the bulk the pair probabilities can be written

$$p_{AA}^{\alpha\beta} = x^2 + x(1-x)\sigma, \quad (\text{A1})$$

$$p_{AB}^{\alpha\beta} = x(1-x)(1-\sigma) + \frac{1}{2}\eta, \quad (\text{A2})$$

$$p_{BA}^{\alpha\beta} = x(1-x)(1-\sigma) - \frac{1}{2}\eta, \quad (\text{A3})$$

$$p_{BB}^{\alpha\beta} = (1-x)^2 + (1-x)\sigma. \quad (\text{A4})$$

The site probabilities are obtained from the pair probabilities

$$p_A^\alpha = p_{AA}^{\alpha\beta} + p_{AB}^{\alpha\beta} = x + \frac{1}{2}\eta, \quad (\text{A5})$$

$$p_A^\beta = p_{AA}^{\alpha\beta} + p_{BA}^{\alpha\beta} = x - \frac{1}{2}\eta, \quad (\text{A6})$$

$$p_B^\alpha = p_{BA}^{\alpha\beta} + p_{BB}^{\alpha\beta} = 1 - x - \frac{1}{2}\eta, \quad (\text{A7})$$

$$p_B^\beta = p_{AB}^{\alpha\beta} + p_{BB}^{\alpha\beta} = 1 - x + \frac{1}{2}\eta. \quad (\text{A8})$$

The range of possible values for σ and η are

$$\left. \begin{array}{l} -x/(1-x) \leq \sigma \leq 0 \\ 0 \leq \eta \leq 2x \end{array} \right\} x \leq \frac{1}{2}, \quad (\text{A9})$$

$$\left. \begin{array}{l} -(1-x)/x \leq \sigma \leq 0 \\ 0 \leq \eta \leq 2(1-x) \end{array} \right\} x \geq \frac{1}{2}. \quad (\text{A10})$$

For the surface studies the four site probabilities corresponding to the plane n are

$$p_A^\alpha(n) = x_n + \frac{1}{2}\eta_n, \quad (\text{A11})$$

$$p_A^\beta(n) = x_n - \frac{1}{2}\eta_n. \quad (\text{A12})$$

$$p_B^\alpha(n) = 1 - x_n - \frac{1}{2}\eta_n, \quad (\text{A13})$$

$$p_B^\beta(n) = 1 - x_n + \frac{1}{2}\eta_n. \quad (\text{A14})$$

The four intralayer pair probabilities are

$$p_{AA}^{\alpha\beta}(n, n) = x_n^2 + x_n(1-x_n)\sigma_{nn}, \quad (\text{A15})$$

$$p_{AB}^{\alpha\beta}(n, n) = x_n(1-x_n)(1-\sigma_{nn}) + \frac{1}{2}\eta_n, \quad (\text{A16})$$

$$p_{BA}^{\alpha\beta}(n, n) = x_n(1-x_n)(1-\sigma_{nn}) - \frac{1}{2}\eta_n, \quad (\text{A17})$$

$$p_{BB}^{\alpha\beta}(n, n) = (1-x_n)^2 + x_n(1-x_n)\sigma_{nn}, \quad (\text{A18})$$

The eight interlayer pair probabilities are

$$\begin{aligned} S = k\mathfrak{N} & \left[\sum_{I,\nu} \left[\frac{1}{2}(Z_0 - 1)L_I^\nu(0) + \frac{1}{2}Z_1L_I^\nu(1) \right] - \sum_{I,J} \left[\frac{1}{2}Z_0L_{IJ}^{\alpha\beta}(0,0) + \frac{1}{2}Z_1[L_{IJ}^{\alpha\beta}(0,1) + L_{IJ}^{\beta\alpha}(0,1)] \right] \right. \\ & \left. + \sum_{n=1}^{\infty} \left(\sum_{I,\nu} \left[\frac{1}{2}(Z_0 - 1)L_I^\nu(n) + \frac{1}{2}Z_1L_I^\nu(n+1) + \frac{1}{2}Z_1L_I^\nu(n-1) \right] \right. \right. \\ & \left. \left. - \sum_{I,J} \left[\frac{1}{2}Z_0L_{IJ}^{\alpha\beta}(n,n) + \frac{1}{2}Z_1L_{IJ}^{\alpha\beta}(n,n+1) + \frac{1}{2}Z_1L_{IJ}^{\beta\alpha}(n,n+1) \right] \right) \right]. \quad (\text{B2}) \end{aligned}$$

In all these equations n labels the layer,

$$\nu = \alpha, \beta, \quad I, J = A, B;$$

\mathfrak{N} is the number of sites per layer and

$$p_{AA}^{\alpha\beta}(n, m) = x_n x_m + x_n(1-x_m)\sigma_{nm}^{\alpha} + \frac{1}{2}\eta_n, \quad (\text{A19})$$

$$p_{AB}^{\alpha\beta}(n, m) = x_n(1-x_m)(1-\sigma_{nm}^{\alpha}), \quad (\text{A20})$$

$$p_{BA}^{\alpha\beta}(n, m) = (1-x_n)x_m - x_n(1-x_m)\sigma_{nm}^{\alpha} - \frac{1}{2}(\eta_n + \eta_m), \quad (\text{A21})$$

$$p_{BB}^{\alpha\beta}(n, m) = (1-x_n)(1-x_m) + x_n(1-x_m)\sigma_{nm}^{\alpha} + \frac{1}{2}\eta_m, \quad (\text{A22})$$

$$p_{AA}^{\beta\alpha}(n, m) = x_n x_m + x_n(1-x_m)\sigma_{nm}^{\beta} - \frac{1}{2}\eta_n, \quad (\text{A23})$$

$$p_{AB}^{\beta\alpha}(n, m) = x_n(1-x_m)(1-\sigma_{nm}^{\beta}), \quad (\text{A24})$$

$$p_{BA}^{\beta\alpha}(n, m) = (1-x_n)x_m - x_n(1-x_m)\sigma_{nm}^{\beta} + \frac{1}{2}(\eta_n + \eta_m), \quad (\text{A25})$$

$$p_{BB}^{\beta\alpha}(n, m) = (1-x_n)(1-x_m) + x_n(1-x_m)\sigma_{nm}^{\beta} - \frac{1}{2}\eta_m. \quad (\text{A26})$$

The short-range-order parameters σ_{nm}^{α} and α_{nm}^{β} are defined by

$$\sigma_{nm}^{\alpha} \equiv 1 - [p_{AB}^{\alpha\beta}(n, m)/x_n(1-x_m)] \quad (\text{A27})$$

and

$$\alpha_{nm}^{\beta} \equiv 1 - [p_{BA}^{\alpha\beta}(n, m)/x_n(1-x_m)]. \quad (\text{A28})$$

An average short-range-order parameter between the n th and the m th layer can be defined by

$$\sigma_{nm} = \frac{1}{2}(\sigma_{nm}^{\alpha} + \alpha_{nm}^{\beta}). \quad (\text{A29})$$

APPENDIX B

Kikuchi's expression¹³ for the entropy in the pair approximation is

$$S = kN \left(\frac{1}{2} (Z - 1) \sum_{I,\nu} p_I^\nu \ln p_I^\nu - \frac{1}{2} Z \sum_{IJ} p_{IJ}^{\alpha\beta} \ln p_{IJ}^{\alpha\beta} \right), \quad (\text{B1})$$

where N is the total number of sites in the crystal. The first term corrects the overcounting of configurations which appears in the second term. This formula, when extended to a layered structure, reduces to

$$L_I^\nu(n) \equiv p_I^\nu(n) \ln p_I^\nu(n), \quad (\text{B3})$$

$$L_{IJ}^{\alpha\beta}(n, m) \equiv p_{IJ}^{\alpha\beta}(n, m) \ln p_{IJ}^{\alpha\beta}(n, m) \quad (\text{B4})$$

When the free energy $F = U - TS$ is written with U

given by (2.11) and S is given by (B2), minimization with respect to the σ_{nn} parameters yields

$$\frac{W}{kT} = \ln \frac{p_{AB}^{\alpha\beta}(n, n) p_{BA}^{\alpha\beta}(n, n)}{p_{AA}^{\alpha\beta}(n, n) p_{BB}^{\alpha\beta}(n, n)}, \quad n=0, 1, 2 \dots \quad (\text{B5})$$

Minimization with respect to $\sigma_{n, n+1}^{\alpha}$ and $\sigma_{n, n+1}^{\beta}$ yields

$$\frac{W}{kT} = \ln \frac{p_{AB}^{\alpha\beta}(n, n+1) p_{BA}^{\alpha\beta}(n, n+1)}{p_{AA}^{\alpha\beta}(n, n+1) p_{BB}^{\alpha\beta}(n, n+1)}, \quad n=0, 1, 2 \dots \quad (\text{B6})$$

$$\frac{W}{kT} = \ln \frac{p_{AB}^{\beta\alpha}(n, n+1) p_{BA}^{\beta\alpha}(n, n+1)}{p_{AA}^{\beta\alpha}(n, n+1) p_{BB}^{\beta\alpha}(n, n+1)}, \quad n=0, 1, 2 \dots \quad (\text{B7})$$

and, with respect to η_n , it gives for $n=1, 2, 3 \dots$

$$\begin{aligned} \frac{1}{2}(Z-1) \ln \frac{p_A^{\alpha}(n) p_B^{\beta}(n)}{p_A^{\beta}(n) p_B^{\alpha}(n)} &= \frac{1}{2} Z_0 \ln \frac{p_{AB}^{\alpha\beta}(n, n)}{p_{BA}^{\alpha\beta}(n, n)} - \frac{1}{2} Z_1 \ln \frac{p_{AA}^{\alpha\beta}(n, n+1) p_{BA}^{\beta\alpha}(n, n+1)}{p_{BA}^{\alpha\beta}(n, n+1) p_{AA}^{\beta\alpha}(n, n+1)} \\ &- \frac{1}{2} Z_1 \ln \frac{p_{BB}^{\alpha\beta}(n-1, n) p_{BA}^{\beta\alpha}(n-1, n)}{p_{BA}^{\alpha\beta}(n-1, n) p_{BB}^{\beta\alpha}(n-1, n)} \end{aligned} \quad (\text{B8})$$

and for $n=0$

$$\frac{1}{2}(Z_0 + Z_1 - 1) \ln \frac{p_A^{\alpha}(0) p_B^{\beta}(0)}{p_A^{\beta}(0) p_B^{\alpha}(0)} = \frac{1}{2} Z_0 \ln \frac{p_{AB}^{\alpha\beta}(0, 0)}{p_{BA}^{\alpha\beta}(0, 0)} - \frac{1}{2} Z_1 \ln \frac{p_{AA}^{\alpha\beta}(0, 1) p_{BA}^{\beta\alpha}(0, 1)}{p_{BA}^{\alpha\beta}(0, 1) p_{BB}^{\beta\alpha}(0, 1)}. \quad (\text{B9})$$

Equations (B5)–(B9) give all σ 's and η 's in terms of the x_n ($n=0, 1, 2, \dots$) and T . The concentrations x_n are then obtained from the chemical equilibrium conditions (2.12).

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