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# Thermodynamics and Long-Range Order of Interstitials in a Hexagonal Close-Packed Lattice

BART J. KOOI, MARCEL A.J. SOMERS, and ERIC J. MITTEMEIJER

Statistical thermodynamics was applied to describe long-range order (LRO) of interstitial atoms in a hexagonal close-packed (hcp) host lattice. On the basis of the Gorsky–Bragg–Williams (GBW) approximation and a division of the interstitial sublattice into six interpenetrating sublattices, all the possible ordered configurations were derived for this assembly. Special attention was devoted to two of the possible ordered configurations of interstitial atoms, *viz.*, the two ground-state structures that have been indicated for  $\epsilon\text{-Fe}_2\text{N}_{1-z}$ . A description of the order-disorder transition was obtained, and the evolution of the occupancies of the different types of interstitial sites on changing the total interstitial content was given. Composition-temperature regions of stability for the two ordered configurations were given in phase diagrams for different combinations of pairwise interaction energies. The results are compatible with observations for  $\epsilon\text{-Fe}_2\text{N}_{1-z}$  as reported in the literature. The advantages of the present treatment were discussed relative to an earlier one, which *a priori* excluded nearest neighboring interstitial sites from simultaneous occupancy.

## I. INTRODUCTION

THE present article is concerned with the thermodynamics of a binary solid solution consisting of a hexagonal close-packed (hcp) sublattice of atoms containing, in its octahedral interstices, atoms that show long-range order (LRO). Expressions for the Gibbs free energy, the interstitial-site occupancies, and the order-disorder transition are derived. The treatment can equally well be applied to a binary substitutional solid solution with a (simple) hexagonal lattice.

The energy of a given configuration of atoms can in principle be assessed according to statistical thermodynamics applying the concept of (pairwise) near-neighbor interaction. Considering such existing descriptions, the generalized Ising model has the most general validity: the partition function is obtained by summation of the energy for a given configuration of atoms over all configurations possible for a certain alloy composition.<sup>[1,2]</sup> The Ising model naturally incorporates disorder and long-range as well as short-range order. So far, exact descriptions have only been obtained for two-dimensional systems.<sup>[1]</sup> To allow a description of three-dimensional systems, approximations to the (generalized) Ising model are necessary. Such approximations comprise the zeroth or Gorsky–Bragg–Williams (GBW)<sup>[3,4]</sup> and the first approximation<sup>[5]</sup> (to the long-range-ordered solutions) and Kikuchi's cluster variation method.<sup>[6]</sup> If long-range order vanishes, the GBW and the first approximation (to long-range-ordered solutions) become the zeroth<sup>[7]</sup> and first approximation<sup>[5]</sup> to the regular solutions, respectively.

Here, the effect of long-range order on the thermodynamics of a system is accounted for by the GBW approximation to the Ising model,<sup>[3,4]</sup> considering pairwise

interaction up to third nearest neighbors. Although it has been pointed out that the accuracy of the GBW approximation, if used, for example, to model the Cu–Au system, is rather poor,<sup>[1,8]</sup> it is expected to be better in the case of interstitial solid solutions, where in general pronounced strain-induced interactions occur.<sup>[9]</sup> Such interactions extend over several atomic distances and thus have a long-range character and, therefore, improve the accuracy of the GBW approximation.<sup>[9]</sup> The successful application of the present model to nitrogen absorption isotherms of  $\epsilon\text{-Fe}_2\text{N}_{1-z}$  (*i.e.*, equilibrium nitrogen content in  $\epsilon\text{-Fe}_2\text{N}_{1-z}$  as a function of imposed nitrogen activity) demonstrates its usefulness.<sup>[10]</sup>

Two essentially different routes are followed in the present work. The first route starts with a subdivision of the interstitial sublattice in six interpenetrating sublattices, each occupied with a certain, variable concentration of interstitial atoms. Then, equilibrium requires that the chemical potentials of the interstitial atoms on these six sublattices are equal, thus providing equilibrium conditions necessary for describing the thermodynamic properties of the system. As a result, all the possible ground-state structures for the considered assembly are derived (Section III–A). The second route begins with two of the ground-state structures found *via* route 1 and which have been proposed for  $\epsilon\text{-Fe}_2\text{N}_{1-z}$ .<sup>[11,12]</sup> The adoption of a ground-state structure allows definition of the degree(s) of order. Then, equilibrium requires that the stable values for the degree(s) of order correspond with a minimum value for the Gibbs free energy (Section III–B).

Earlier work on interstitial ordering in an hcp lattice has been presented as a "Regular Solution Model" (RS model) in Reference 13 and presupposed a complete order of interstitials along rows of interstitial sites parallel to the *c*-axis of the hexagonal lattice, *viz.*, an alternation of permitted and excluded sites for occupancy by interstitial atoms. The present LRO model allows a variable degree of order along rows of interstitial atoms parallel to the *c*-axis, because in principle, every site is

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permitted for occupancy by interstitial atoms. The results obtained with the present model are compared to those of the regular solution model given in Reference 13 (Section IV-B).

## II. BASIC CONSIDERATIONS

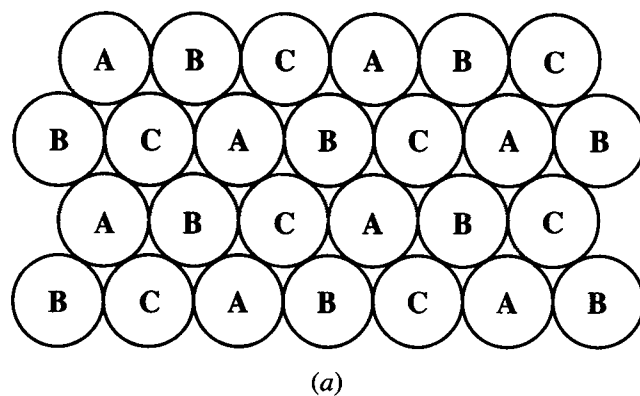
The binary solid solution M-I is considered, in which the I atoms are situated in the interstices of the crystal lattice set up by the M atoms. This assembly can be conceived as constructed from two interpenetrating sublattices: one for atoms M and one for atoms I. Both M and I atoms can only be located at sites of their own sublattices. In an hcp M sublattice, the octahedral interstices are the largest interstitial holes and the ones considered for occupation by I atoms; it is assumed that the fraction of I atoms residing at tetrahedral interstices is negligible. Hence, the sites for I atoms compose a (simple) hexagonal sublattice.

The model to be presented provides a thermodynamic description for an M-I alloy, with sublattices for M and I as given in the preceding paragraph, as a function of interstitial content. A change of the composition is realized by changing the occupancy of the I sublattice only; the M sublattice is and remains completely occupied. The I sublattice is composed of variable amounts of atoms I and empty sites V (vacancies for I atoms). The (possible) occurrence of ordering of I and V on their hexagonal sublattice is dealt with here. To arrive at a thermodynamic description for the M-I alloy, the thermodynamics of the M and the I sublattices, separately, as well as the interaction of these sublattices will be considered.

It is convenient to conceive the hexagonal I sublattice as an alternation of two types of basal planes (1 and 2), each containing three different kinds of sites (for plane 1: A1, B1, and C1; for plane 2: A2, B2, and C2; Figure 1; Reference 13). Thus, for each type of plane (denoted as (001) planes hereafter), a particular site is surrounded within the plane by sites of the other kinds (Figure 1(a)). In the direction perpendicular to the planes (denoted as the *c*-direction hereafter), sites A1, B1, and C1 are adjacent to sites A2, B2, and C2, respectively (Figure 1(b)). Apart from the present choice of six sublattices composing the hexagonal I lattice, other possibilities for division of the I lattice into sublattices can be considered too. If interactions up to third nearest neighbors on the I lattice are considered a subdivision of the (simple) hexagonal I lattice into 6, 8, 10, 12, and 14 sublattices (kinds of sites), analogous to the division of the hcp lattice as described in Reference 14, is appropriate. The subdivision in six kinds of sites (six sublattices) is preferred here, for it reflects the crystallography of the ground-state structures as given for  $\epsilon\text{-Fe}_2\text{N}_{1-2}$  and the anti-CdI<sub>2</sub> structure type(s).<sup>[15]\*</sup>

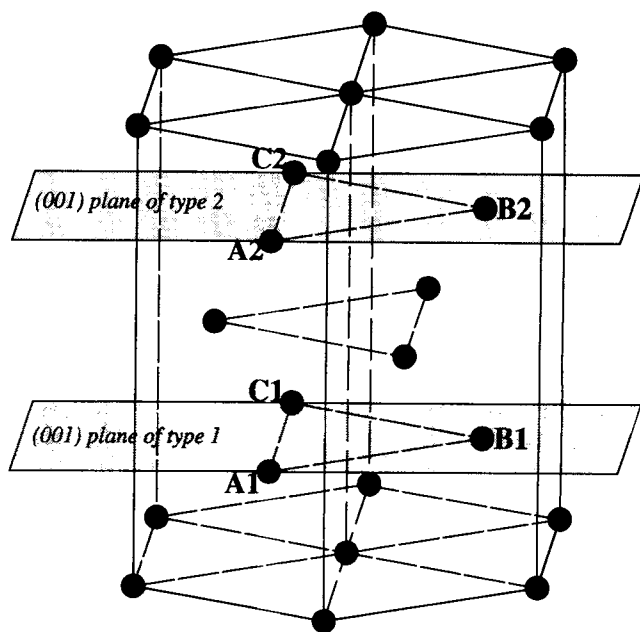
\*A division into eight sublattices is appropriate for describing (dis)ordering in accordance with the  $\zeta\text{-Fe}_2\text{N}$ , the Co<sub>2</sub>C (or anti-CaCl<sub>2</sub>), and the anti-CdI<sub>2</sub> structure types. The thermodynamic models for the subdivision into 8, 10, 12, and 14 sublattices can be obtained and dealt with in exactly the same way as the model that will be presented here for the subdivision into six sublattices.

For the case of a random distribution of I atoms over the



(a)

- M sites
- I sites



(b)

Fig. 1—(a) Each (001) plane of the hexagonal (interstitial) sublattice of I atoms contains three different kinds of sites: A, B, and C. (b) The hexagonal sublattice of I atoms, constituted by the octahedral interstices of the hcp sublattice of M atoms, is composed of planes of types 1 and 2, together having six kinds of sites (denoted by A1, B1, C1, A2, B2, and C2) that constitute a trigonal prism.

sites of the I sublattice, the six sites constituting a trigonal prism (Figure 1(b)) have the same probability to be occupied by an I atom. This probability equals the fraction of occupied sites of the I sublattice.

Ordering can occur, if it is energetically more favorable to form I-V nearest neighbors than I-I and V-V nearest neighbors, implying repulsion among I atoms. If ordering among atoms on the I sublattice occurs, in principle, each of the sites A1, . . . , C2 has its own probability to be occupied by an I atom. For a hexagonal sublattice, the interaction of I atoms on neighboring sites of an (001)-plane is not equal to that of I atoms on neighboring sites in the *c*-direction. For an ideal hcp sublattice of M atoms, the shortest possible separation occurs for two nearest neighbors in the *c*-direction of the hexagonal I sublattice: it is only  $\sqrt{2/3}$  of the separation between

two nearest neighbors within the (001)-plane. This suggests a larger tendency for nonoccupancy of neighboring sites in the *c*-direction than within the (001)-plane. If, in the *c*-direction, the nearest-neighbor sites to an occupied site remain vacant, then the maximum I content corresponds with the composition M<sub>2</sub>I. This reduction of the number of sites available for occupation by I atoms is denoted by site exclusion in the present article and was presupposed for the derivation of the regular solution model in Reference 13. If all sites of the I sublattice are available for occupation by I atoms, the maximum I content corresponds with the composition MI.

### III. LRO MODEL FOR INTERSTITIALS IN AN HCP LATTICE

The zeroth approximation to the Ising model due to GBW is adopted to describe LRO. This approach comprises the following:<sup>[4]</sup>

The configurational entropy is given by the number of permutations of I (and thus V) over the types of sites. The molar vibrational entropy for each component (M, I, and V) is assumed constant, and

The enthalpy is given by the sum of the products of each of the probabilities of I-I, V-V, I-V, M-M, M-I, and M-V pairwise interactions and their corresponding interaction energies. Interactions on the I sublattice of first nearest neighbors (A1-A2, B1-B2, C1-C2), second nearest neighbors (A1-B1, A1-C1, *etc.*) and (optionally) third nearest neighbors (A1-B2, A1-C2, *etc.*) are taken into account here.

The LRO model can be obtained *via* two essentially different routes, having different (dis)advantages. Route 1 begins with a description for the occupancy of each of the six sites A1, . . . , C2 on the trigonal prism introduced and the associated six chemical potentials. Equilibrium requires that these chemical potentials are equal. Route 2 adopts a ground-state structure (*i.e.*, a completely ordered structure that generally can only be defined for a (simple) stoichiometric composition) as the starting point for distinguishing between order and disorder sites and for defining the degree(s) of order. Equilibrium requires that values for the degree(s) of order correspond to a minimum value for the Gibbs free energy. Both routes are pursued here. Obviously, route 1 needs less *a priori* information than route 2 and offers (the possibility of) a more general solution. However, if the ground-state structure of interest is known *a priori*, route 2 is useful, because it provides directly values for the order parameters, which can be related to physical properties of the assembly under consideration.

#### A. Route 1

The interpenetrating hcp M and (simple) hexagonal I sublattices are considered, the latter having six kinds of I sites: A1, B1, . . . , C2. The M sublattice is completely occupied by M atoms. Each kind of site K of the I sublattice can be occupied by a fraction of I atoms,  $x_K$ . The total number of M sites considered is  $6N$ , and thus, there are  $N$  sites for each kind of I site.

#### 1. Gibbs free energy, chemical potential, and equilibrium condition

A full derivation of the expression for the Gibbs free energy of the M-I alloy is given in Appendix A for the example of a specific subdivision in types of interstitial sites (Section B-1). Therefore, only a brief description is given here for the case of six different sublattices composing the I lattice.

The configurational entropy corresponding to  $N$  sites of one kind, *e.g.*, A1, is given by

$$-Nk[x_{A1} \ln x_{A1} + (1 - x_{A1}) \ln (1 - x_{A1})]$$

where  $k$  is Boltzmann's constant and  $x_{A1}$  is the fraction occupied sites of kind A1. The summation of such entropy terms for all six kinds of sites yields the configurational entropy of the whole M-I alloy.

The probability for simultaneous occupancy of two adjacent sites in the *c*-direction (first nearest neighbors on the I sublattice), *e.g.*, A1 and A2, by I is  $x_{A1}x_{A2}$ , by V is  $(1 - x_{A1})(1 - x_{A2})$  and by I and V is  $x_{A1}(1 - x_{A2}) + x_{A2}(1 - x_{A1})$ . The enthalpy (energy) associated with these interactions between sites A1 and A2 is proportional to the sum of the products of these probabilities and their corresponding interaction energies  $e_{c,II}$ ,  $e_{c,VV}$ , and  $e_{c,IV}$ :

$$\{x_{A1}x_{A2}e_{c,II} + (1 - x_{A1})(1 - x_{A2})e_{c,VV} + [x_{A1}(1 - x_{A2}) + x_{A2}(1 - x_{A1})]e_{c,IV}\} 2N \frac{Z_c}{2}$$

with  $Z_c/2$  being the number of bonds in the *c*-direction per atom ( $Z_c/2 = 1$ ). This term can be rewritten as

$$(x_{A1} + x_{A2})H_{I,A1A2}^0 + [(1 - x_{A1}) + (1 - x_{A2})]H_{V,A1A2}^0 + NW_c[x_{A1}(1 - x_{A2}) + x_{A2}(1 - x_{A1})]$$

where  $H_{I,A1A2}^0 = N Z_c/2 e_{c,II}$  and  $H_{V,A1A2}^0 = N Z_c/2 e_{c,VV}$ ;  $W_c$  is the "exchange energy" in the *c*-direction, defined as

$$W_c = \frac{Z_c}{2} (2e_{c,IV} - e_{c,II} - e_{c,VV}).$$

The term  $H_{I,A1A2}^0$  is a fraction of  $H_I^0$ , the enthalpy of  $N$  atoms of the pure component I (with exactly the same lattice as the I sublattice). Accordingly,  $H_{V,A1A2}^0$  is a fraction of  $H_V^0$ , the enthalpy of  $N$  atoms of the pure component V (with exactly the same lattice as the I sublattice; for the present case, where V represents vacant I sites,  $H_V^0$  of course is zero). Summation of the enthalpies associated with the interactions between atoms at sites A1 and A2, atoms at sites B1 and B2, and atoms at sites C1 and C2 yields the enthalpy corresponding to all possible pairwise interactions (between first nearest neighbors) in the *c*-direction. The enthalpies corresponding with pairwise interactions between second (A1-B1, A1-C1, . . . , B2-C2) and third (A1-B2, A1-C2, . . . , C1-B2) nearest neighbors are obtained analogously, using exchange energies  $W_p$  and  $W_{pc}$ , respectively.

To obtain the enthalpy of the whole M-I alloy, the enthalpies of  $N$  atoms of the pure component M,  $H_M^0$ , and of the interactions of M and the  $N$  atoms of I,  $H_{MI}^0$ , have to be added ( $H_{MV}^0$  of course is zero). The

Gibbs free energy  $G_{M-I}$  of the M-I alloy can thus be given as follows:

$$\begin{aligned}
 G_{M-I} = & 6(H_M^0 - TS_{\text{vib},M}^0) \\
 & + \sum_{K=A1}^{C2} [x_K] [H_I^0 - TS_{\text{vib},I}^0 + H_{MI}^0 + NW_c \\
 & \quad + NW_p + NW_{pc}] \\
 & - 2NW_c[x_{A1}x_{A2} + x_{B1}x_{B2} + x_{C1}x_{C2}] \\
 & - NW_p[x_{A1}x_{B1} + x_{A1}x_{C1} + x_{B1}x_{C1} + x_{A2}x_{B2} \\
 & \quad + x_{A2}x_{C2} + x_{B2}x_{C2}] \\
 & - NW_{pc}[x_{A1}x_{B2} + x_{A1}x_{C2} + x_{B1}x_{A2} + x_{B1}x_{C2} \\
 & \quad + x_{C1}x_{A2} + x_{C1}x_{B2}] \\
 & + NkT \sum_{K=A1}^{C2} [x_K \ln x_K + (1 - x_K) \ln (1 - x_K)]
 \end{aligned} \quad [1]$$

where  $T$  is the temperature,  $H_Q^0$  is the enthalpy of  $N$  atoms of the pure component  $Q$  (summation of all enthalpies associated with the pairwise near-neighbor interactions considered), and  $S_{\text{vib},Q}^0$  is the vibrational entropy of  $N$  atoms of the pure component  $Q$ , which is assumed to be independent of composition and ordering. The first two terms on the right-hand side of Eq. [1] represent the standard state of the M-I alloy. It is noted that the contribution of the M sublattice and its interaction with the I sublattice only changes the standard state and consequently, does not affect ordering on the I sublattice. For brevity of notation,

$$\mu_I^0 = (H_I^0 - TS_{\text{vib},I}^0 + H_{MI}^0 + NW_c + NW_p + NW_{pc})$$

Considering the sublattice formed by sites of kind  $K$  as an open system ( $V$  has to represent vacancies), the chemical potential for  $N$  atoms I at sites of kind  $K$ ,  $\mu_I^K$ , is by definition given by

$$\mu_I^K = \frac{\partial G_{M-I}}{\partial x_K} \quad [2]$$

Using Eq. [1], one obtains

$$\begin{aligned}
 \mu_I^{A1} = & \mu_I^0 - 2NW_c[x_{A2}] - NW_p[x_{B1} + x_{C1}] \\
 & - NW_{pc}[x_{B2} + x_{C2}] + NkT \ln \left[ \frac{x_{A1}}{1 - x_{A1}} \right]
 \end{aligned} \quad [3]$$

The expressions for  $\mu_I^K$  of I atoms on the other kinds of sites are similar.

Thermodynamic equilibrium for this M-I alloy involves that the chemical potentials  $\mu_I^K$  of the interstitial element I are equal for all six kinds of I sites; *i.e.*,

$$\mu_I^{A1} = \mu_I^{B1} = \mu_I^{C1} = \mu_I^{A2} = \mu_I^{B2} = \mu_I^{C2} \equiv \mu_I \quad [4]$$

Thus, a set of five relations nonlinear in  $x_{A1}, \dots, x_{C2}$  is obtained from Eqs. [3] and [4]. Equal occupancy of the six kinds of sites fulfills the equilibrium condition

Eq. [4], and thus, the disordered state is always a solution of the set of relations. However, it does not necessarily yield the lowest possible Gibbs free energy.

The Gibbs free energy  $G_{M-I}$  of the M-I alloy in general can be related to chemical potentials of the atoms I,  $\mu_I$ , and of the atoms M,  $\mu_M$ :

$$G_{M-I} = 6\mu_M + \mu_I \sum_{K=A1}^{C2} x_K \quad [5]$$

## 2. Order-disorder transition and the evolving types of ordering

An ordered configuration of I atoms on their sublattice is only more stable than the random configuration if (a) the content of the I atoms is above some minimum value and (b) the temperature of the system is below some maximum value. The values for the I content and the temperature associated with the order-disorder transition depend on the values of the exchange energies,  $W_c$  and  $W_p$  and  $W_{pc}$ . The ordered configuration develops if, with respect to the disordered state, (one or some of) the fractions of I atoms on the different kinds of I sites are differently perturbed. To arrive at the ordered state solution(s) of the five nonlinear equations, an iterative numerical method has to be used. Root finding requires a good initial guess.<sup>[16]</sup> For a good initial guess, knowledge on the order-disorder transition is indispensable.

The equations of type Eq. [3] can each be written as  $f(\underline{x}) = f(x_{A1}, x_{B1}, \dots, x_{C2})$ . If  $\underline{x} + d\underline{x}$  and  $\underline{x}$  are sufficiently close and if  $f(\underline{x})$  is continuous for  $\underline{x}$ , it holds that any difference in the occupancy of the six kinds of sites tends to nil on approaching the order-disorder transition from the ordered configuration;

the six equations that make up Eq. [3] can be replaced by their total differentials:

$$df(\underline{x}) = \frac{\partial f}{\partial x_{A1}} dx_{A1} + \frac{\partial f}{\partial x_{B1}} dx_{B1} + \dots + \frac{\partial f}{\partial x_{C2}} dx_{C2};$$

within the range  $\underline{x}$  to  $\underline{x} + d\underline{x}$ , the infinitesimal changes  $dx_{A1}, dx_{B1}, \dots, dx_{C2}$  can be taken proportional to each other.

Using  $f = dx_{B1}/dx_{A1}$ ,  $g = dx_{C1}/dx_{A1}$ ,  $h = dx_{A2}/dx_{A1}$ ,  $i = dx_{B2}/dx_{A1}$ , and  $j = dx_{C2}/dx_{A1}$  ( $dx_{A1} \neq 0$ ), one thus obtains for changes of the chemical potentials at the order-disorder transition defined by  $T_i$  and  $x_i$ :

$$\begin{aligned}
 \frac{d\mu_I^{A1}}{Ndx_{A1}} = & -2W_c[h] - W_p[f + g] \\
 & - W_{pc}[i + j] + kT_i \left[ \frac{1}{x_i(1 - x_i)} \right]
 \end{aligned} \quad [6a]$$

$$\begin{aligned}
 \frac{d\mu_I^{B1}}{Ndx_{A1}} = & -2W_c[i] - W_p[1 + g] \\
 & - W_{pc}[h + j] + fkT_i \left[ \frac{1}{x_i(1 - x_i)} \right]
 \end{aligned} \quad [6b]$$

$$\begin{aligned}
 \frac{d\mu_I^{C1}}{Ndx_{A1}} = & -2W_c[j] - W_p[1 + f] \\
 & - W_{pc}[h + i] + gkT_i \left[ \frac{1}{x_i(1 - x_i)} \right]
 \end{aligned} \quad [6c]$$

$$\frac{d\mu_1^{A2}}{Ndx_{A1}} = -2W_c[1] - W_p[i + j] - W_{pc}[f + g] + hkT_i \left[ \frac{1}{x_i(1 - x_i)} \right] \quad [6d]$$

$$\frac{d\mu_1^{B2}}{Ndx_{A1}} = -2W_c[f] - W_p[h + j] - W_{pc}[1 + g] + ikT_i \left[ \frac{1}{x_i(1 - x_i)} \right] \quad [6e]$$

$$\frac{d\mu_1^{C2}}{Ndx_{A1}} = -2W_c[g] - W_p[h + i] - W_{pc}[1 + f] + jkT_i \left[ \frac{1}{x_i(1 - x_i)} \right] \quad [6f]$$

Because  $f(x)$  has to be continuous for  $x$  and because  $f(x)$  represents first derivatives of the Gibbs free energy with respect to  $x_{A1}, x_{B1}, \dots, x_{C2}$ , the order-disorder transition (in this analysis) cannot be a first-order phase transition. For equilibrium at the order-disorder transition, the six equations of Eq. [6] (linear in  $f, \dots, j$ ) have to give identical values for  $d\mu_1/dx_{A1}$  (cf. Eq. [4]). The problem can be solved exactly and provides four sets of solutions.

For  $d\mu_1/dx_{A1} \neq 0$ , only one solution holds:

(1)  $f = g = h = i = j = 1$ ; no ordering occurs.

For  $d\mu_1/dx_{A1} = 0$  and the constraint  $1 + f + g + h + i + j = 0$  (because the order-disorder transition holds for one particular total interstitial content), three solutions hold:

(2)  $h = -1, f = -i, g = -j$ , and  $i + j = 1$ ; an increase of the occupancy of sites A1 is associated with a decrease of the occupancies of sites A2 and B1 + C1, and an increase of the occupancies of sites B2 + C2, *i.e.*, a tendency for not forming first and second nearest neighbors but for forming third nearest neighbors.

(3)  $f = g = 1$  and  $h = i = j = -1$ ; an increase of the occupancy of sites A1 is associated with a decrease of the occupancies of sites A2, B2, and C2 and an increase of the occupancies of sites B1 and C1, *i.e.*, a tendency for not forming first and third nearest neighbors but for forming second nearest neighbors.

(4)  $h = 1, f = i, g = j$ , and  $i + j = -1$ ; an increase of the occupancy of sites A1 is associated with an increase of the occupancies of sites A2 and a decrease of the occupancies of sites B1 + C1 and B2 + C2, *i.e.*, a tendency for not forming second and third nearest neighbors but for forming first nearest neighbors.

The values of the above parameters  $f, g, h, i$ , and  $j$  can thus physically be interpreted as a prescription for the evolution of (the differences in) the occupancies of the different kinds of I sites at the onset of ordering.

From the condition  $d\mu_1/dx_{A1} = 0$ , necessary at the onset of ordering (to obtain the sets (2) through (4)), it immediately follows from Eq. [6] for the order-disorder transition:

$$x_i = \frac{1}{2} \left( 1 \pm \sqrt{1 + \frac{4kT_i}{W_{\text{eff}}}} \right) \quad [7]$$

where  $W_{\text{eff}}$  is an effective exchange energy according to

$$W_{\text{eff}} = -2W_c[h] - W_p[f + g] - W_{pc}[i + j] \quad [8]$$

According to Eq. [7], the critical temperature for the order-disorder transition is  $T_c = -W_{\text{eff}}/4k$  and occurs at  $x = 1/2$ .

The three possible starting points for ordering (solutions (2) through (4)) lead to five distinct cases of ordering. This is caused by a nonexplicit prescription for the values of  $f, g, i$ , and  $j$ , according to the solutions (2) and (4). Depending on the actual values for  $f, g, i$ , and  $j$  and the values for the exchange energies, two cases of ordering are found to be possible for each of the solutions (2) and (4). The two cases of ordering evolving from solution (2) will be considered in detail in Section B as configurations A and B and were reported to have been observed.<sup>[11,12,17]</sup> The case of ordering evolving from the order-disorder transition according to solution (3) can be regarded as a tendency for forming an alternation of fully occupied and completely empty (001)-planes of the I sublattice for the composition  $M_2I$ . This has been observed for many cases.<sup>[15,17]</sup>

The occurrence of disordering and of ordering according to the three discussed possibilities (2) through (4) can be presented as a function of the various exchange energies in a "phase diagram" (Figure 2). The diagrams shown represent only the type of ordering most likely to occur in the regions concerned; the actual occurrence of an ordered state requires that the total fraction of interstitial sites occupied is in between the fractions, as prescribed by Eqs. [7] and [8]. The ground-state structures of the distinct cases of ordering have also been indicated in Figure 2.

The method applied for the numerical evaluation of the cases of ordering evolving from the six nonlinear equations that make up Eq. [3] is given in Appendix B.

## B. Route 2

The derivation of the LRO model according to route 2 starts with the two ground-state structures obtained by route 1 as solution (2), which have first been indicated for  $\epsilon\text{-Fe}_2\text{N}_{1-z}$ .<sup>[11,12]</sup> The other possible ground-state structure types as given by route 1 will not be dealt with. For a ground-state structure, different types of sites can be discerned:

- order sites for occupation by I (denoted by  $i$ );
- order sites for occupation by V (denoted by  $v$ );
- disorder sites (denoted by  $d$ ), *i.e.*, sites that are indifferently with respect to occupation by I or V.

Assuming that the repulsion among I atoms becomes stronger on decreasing their separation is in accordance with solution (2) obtained by route 1 (see its discussion in Section A-2). This leads to the following subdivision of the sites of the trigonal prism. If A1 is an order site ( $i$ ) for I, then A2 is an order site for V ( $v$ ). Further, either site B1 or site C1 has to be indicated as an order site for V. Here, B1 is taken as an order site for V ( $v$ ), and

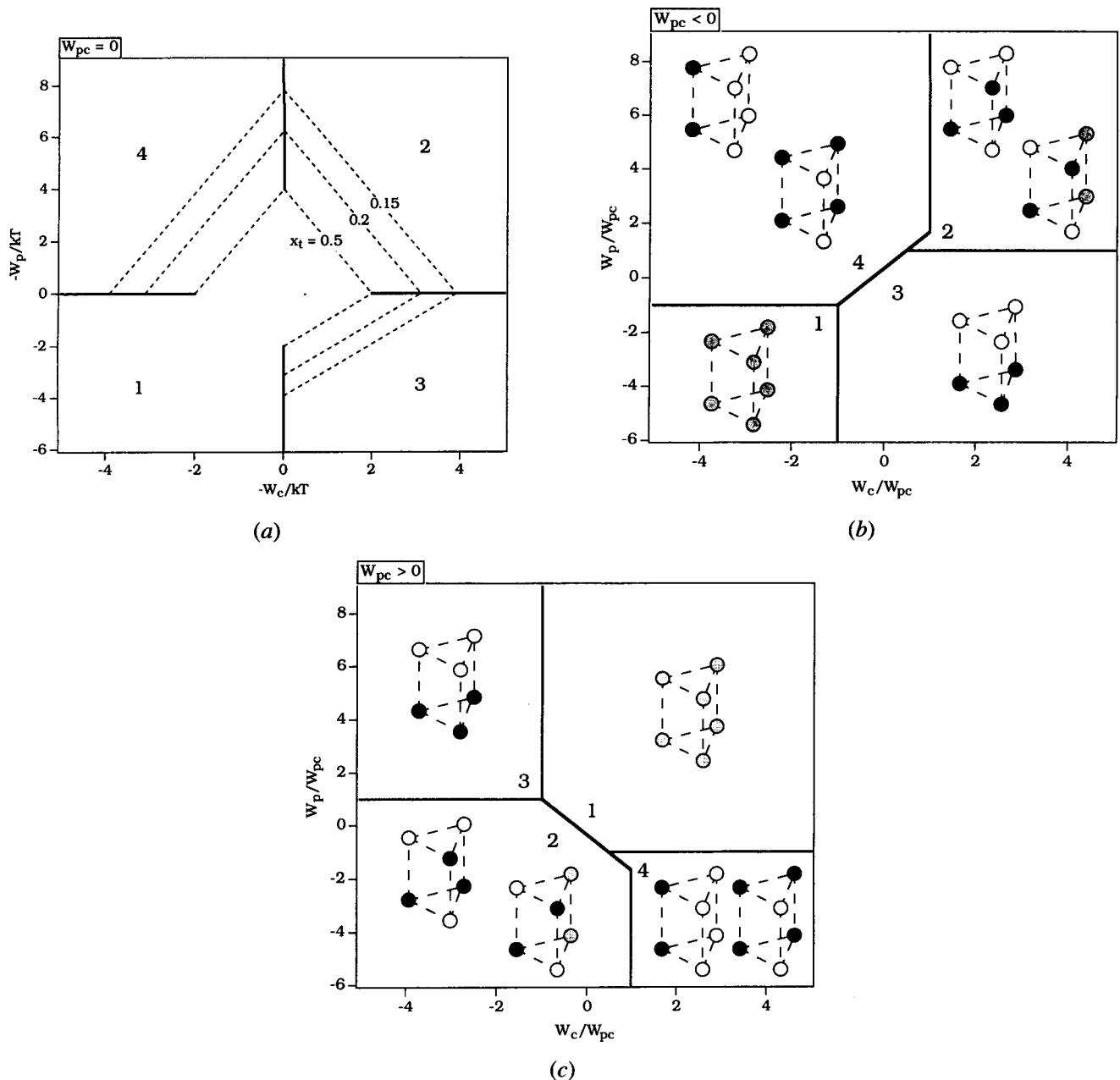


Fig. 2—Phase-stability diagram showing the region of stability for each of the four cases of interstitial configuration, cases (1) through (4) (see text), with respect to the values of  $W_c/kT$ ,  $W_p/kT$ , and  $W_{pc}/kT$ : (a)  $W_{pc} = 0$ ; (b)  $W_{pc} < 0$ ; and (c)  $W_{pc} > 0$ . The corresponding ground-state structures on the basis of the trigonal prism of interstitial sites have also been indicated; the black, white, and shaded dots represent sites of type  $i$  (order sites for I atoms),  $v$  (order sites for V), and  $d$  (disorder sites), respectively. The diagrams shown represent only the type of ordering most likely to occur in the regions indicated. The actual occurrence of an ordered state requires that the total fraction of interstitial sites occupied is in between the fractions,  $x_i$ , as prescribed by Eqs. [7] and [8]. As an illustration, the dashed lines in (a) separate the ordered regions from the disordered region for various values of  $x_i$ .

consequently, B2 is an order site for I ( $i$ ). Finally, for sites C1 and C2, two possibilities remain:

- (A) one of the two sites is an order site for I ( $i$ ), and the other is an order site for V ( $v$ ); or
- (B) both sites have the same tendency to become occupied by I or V and are disorder ( $d$ ) sites.

Now, the possibilities for complete ordering (the ground-state structures) at the composition corresponding with  $M_2I$  are considered. Situation (A) leads to an

alternation of (001) planes with unequal compositions, viz.,  $i_2v$  and  $v_2i$ . This is the so-called  $\epsilon\text{-Fe}_2\text{N}$  ground-state structure (Figure 3(a)).\* Possibility (B) leads to an alternation of (001) planes with equal compositions, viz.,  $ivd$  and  $vid$  (Figure 3(b))\*\* and is, because of the

\*This structure was proposed for the first time for the distribution of nitrogen atoms over the octahedral interstices of an hcp lattice of iron atoms in  $\epsilon\text{-Fe}_2\text{N}^{(11)}$  and was assessed by X-ray diffraction results.<sup>[12]</sup>

\*\*This structure (with  $i$  sites completely occupied and  $v$  and  $d$  sites

completely empty) was proposed for the distribution of nitrogen atoms over the octahedral interstices in  $\epsilon\text{-Fe}_2\text{N}_{1-z}$  ( $z = 1/3$ )<sup>111</sup> and was assessed by X-ray diffraction results.<sup>112</sup>

$d$  sites, not a ground-state structure in the true sense. The specification of these two ground-state structures and the three types of sites is only meant to define the reference (ideal) structures for the LRO. In reality, the total amount of I atoms on the hexagonal sublattice and the degree of order deviate from that for the ground-state structures, which apply to absolute zero temperature.

For route 2, the degree of LRO has to be described, and to this end, the LRO parameter  $r$  is introduced. This parameter is defined with respect to the ground-state structure(s), such that  $0 \leq r \leq 1$ :

if the fraction of the I atoms occupying  $v$  sites is equal to the fraction of the  $v$  sites relative to the total number of sites ( $i + v + d$ ), the distribution of I atoms on its sublattice is random:  $r = 0$ ;

if no I atoms occupy  $v$  sites, the distribution of I atoms on its sublattice is ordered:  $r = 1$ .

For the case of ordering conforming to ground-state structure (A) with unequal compositions for the two types of (001)-planes, two LRO parameters are defined, one for each type of plane. The results of applying the LRO model to this ground-state structure are denoted by configuration A hereafter. For the case of ordering conforming to the ground-state structure (B) with equal compositions for the two types of (001)-planes, only one LRO parameter is defined. The results of applying the LRO model to this ground-state structure are denoted by configuration B hereafter.

### 1. Configuration A

#### Site occupancy

Configuration A is based on the ground-state structure with alternating (001) planes of type  $i_2v$  and  $v_2i$ . The (001) planes of composition  $i_2v$  will be denoted as planes of type 1 with order parameter  $r_1$ ; the (001) planes of composition  $v_2i$  will be denoted as planes of type 2 with order parameter  $r_2$  (Figure 3(a)). The order parameters can then be defined as follows.

For an (001) plane of composition  $i_2v$  (plane of type 1), having a total number of  $N$  sites, the numbers of I atoms on  $i$  sites ( $N_{i,i1}$ ) and on  $v$  sites ( $N_{i,v1}$ ) are given as follows:

$$N_{i,i1} = (2 + r_1) x_1 \frac{N}{3} \quad [9a]$$

$$N_{i,v1} = x_1 N - N_{i,i1} = (1 - r_1) x_1 \frac{N}{3} \quad [9b]$$

where  $x_1$  is the fraction of the occupied  $N$  sites in a plane of type 1. Then the numbers of vacancies on  $i$  sites  $N_{v,i1}$  and on  $v$  sites  $N_{v,v1}$  are

$$N_{v,i1} = \frac{2}{3} N - N_{i,i1} = [2 - (2 + r_1) x_1] \frac{N}{3} \quad [9c]$$

$$N_{v,v1} = \frac{1}{3} N - N_{i,v1} = [1 - (1 - r_1) x_1] \frac{N}{3} \quad [9d]$$

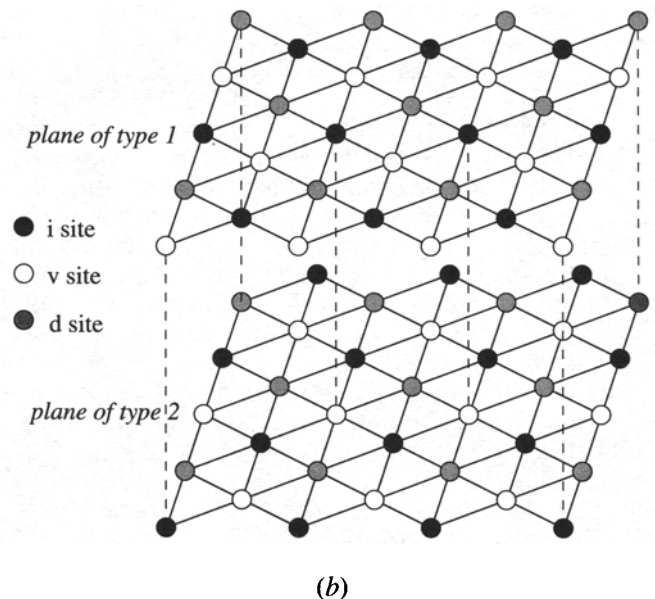
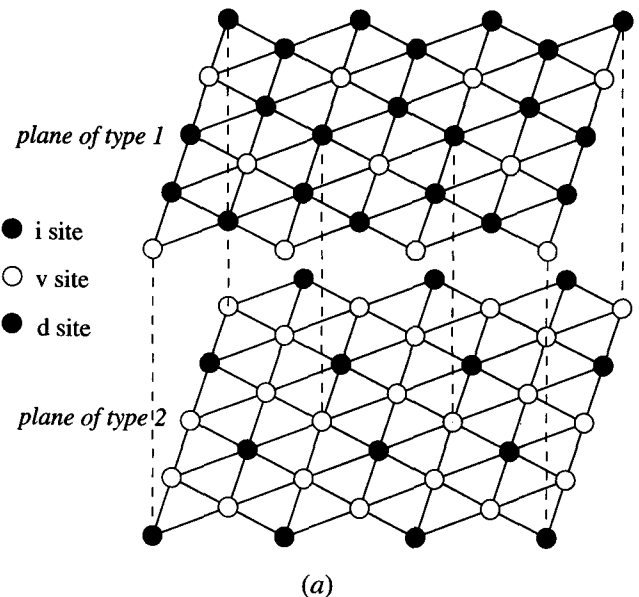


Fig. 3—(a) The ground-state structure consisting of an alternation of (001) planes of types 1 and 2 with compositions  $i_2v$  and  $v_2i$ , respectively, and denoted as configuration A in the text. ( $i$  = order site for interstitial atoms I;  $v$  = order site for vacancies V). (b) The ground-state structure consisting of an alternation of (001) planes of types 1 and 2 with compositions  $ivd$  and  $vid$ , denoted as configuration B in the text ( $i$  = order site for interstitial atoms I;  $v$  = order site for vacancies V;  $d$  = disorder site).

For an (001) plane of composition  $v_2i$  (plane of type 2), using analogously defined symbols, it is obtained that

$$N_{i,i2} = (1 + 2r_2) x_2 \frac{N}{3} \quad [10a]$$

$$N_{i,v2} = (2 - 2r_2) x_2 \frac{N}{3} \quad [10b]$$

$$N_{v,i2} = [1 - (1 + 2r_2) x_2] \frac{N}{3} \quad [10c]$$



$$N_{v,v_2} = [2 - (2 - 2r_2) x_2] \frac{N}{3} \quad [10d]$$

On this basis, the expression for the Gibbs free energy according to the GBW approximation can be derived straightforwardly; see Appendix A for the description of configuration A.

## 2. Configuration B

### Site occupancy

Configuration B is based on the ground-state structure with alternating (001) planes of type *ivd* and type *vid*. This ground-state structure can only be obtained if the tendency for a particular type of site to become occupied by I atoms is the same in both planes considered; *i.e.*, the degree of order is the same for both planes. This can be rationalized as follows. If the *i* site in (001)-plane 1 would have a stronger tendency to become occupied by I atoms than the *i* site in plane 2, then—because a stronger interaction occurs in the *c*-direction than within the (001) planes—also the *v* site in plane 1 would have a stronger tendency to become occupied by I atoms than the *v* site in plane 2. Thus, the planes of type 1 tend to contain more I atoms than the planes of type 2, implying that the third type of site is a *v* site in plane 1 and an *i* site in plane 2. Accordingly, the ground-state structure of configuration A results. Hence, if configuration B occurs, there is no difference in occupation of *i* sites (nor *v* or *d* sites) between planes 1 and 2. Then, for configuration B, only one LRO parameter *r* and the contents  $x_{iv}$  and  $x_d$ —representing the fractions of I on order sites (*i* and *v*) and on disorder sites (*d*), respectively—need to be considered. The LRO parameter *r* only applies to the order sites.

In contrast with configuration A, for configuration B the same description holds for all (001) planes of the I sublattice, each containing *N* sites. Thus, for a (001) plane of composition *ivd* (or *vid*), it holds for the total numbers of I atoms on *i*, *v*, and *d* sites denoted by  $N_{i,i}$ ,  $N_{i,v}$ , and  $N_{i,d}$ , respectively:

$$N_{i,i} = (1 + r) x_{iv} \frac{N}{3} \quad [11a]$$

$$N_{i,v} = (1 - r) x_{iv} \frac{N}{3} \quad [11b]$$

$$N_{i,d} = x_d \frac{N}{3} \quad [11c]$$

Then, the numbers of vacancies on *i*, *v*, and *d* sites denoted by  $N_{v,i}$ ,  $N_{v,v}$ , and  $N_{v,d}$ , respectively, are

$$N_{v,i} = \frac{1}{3} N - N_{i,i} = [1 - (1 + r) x_{iv}] \frac{N}{3} \quad [11d]$$

$$N_{v,v} = \frac{1}{3} N - N_{i,v} = [1 - (1 - r) x_{iv}] \frac{N}{3} \quad [11e]$$

$$N_{v,d} = \frac{1}{3} N - N_{i,d} = [1 - x_d] \frac{N}{3} \quad [11f]$$

On this basis, the expression for the Gibbs free energy

according to the GBW approximation can be derived straightforwardly; see Appendix A for the description of configuration B.

## IV. RESULTS AND DISCUSSION

### A. Results for Long-Range Order Configurations A and B

Neglecting the effect of third nearest-neighbor interactions (*i.e.*,  $W_{pc}/kT$  is nil), the order-disorder phase boundary is depicted in Figure 4 for various combinations of values for  $W_c/kT$  and  $W_p/kT$ . Evidently, increasing the value for  $W_c$  with respect to  $W_p$  broadens the stable composition region of an ordered configuration and enlarges the stability region of an ordered configuration up to a higher temperature (Figure 4).

In the sequel of this section site occupancies of the I sublattice and the Gibbs free energy of the M-I alloy are discussed for both configuration A and B for fixed values of  $W_i/kT$ :  $W_c/kT = -2$ ,  $W_p/kT = -3$ , and  $W_{pc} = 0$ ,\* except where stated otherwise. In Section B, the

\*These values of  $W_c$  and  $W_p$  imply that pairwise interaction in the *c*-direction is taken twice as strong as pairwise interaction within the (001)-planes (the coordination numbers for these interactions are 2 and 6, respectively). The values chosen for  $W_i/kT$  yield representative results; the degrees of order are not very large or small and the composition regions where order and disorder occur are both of significant size. Choosing values for  $W_{pc}$  different from  $W_{pc} = 0$  does not lead to major changes, and the conclusions to be drawn remain unaffected.

results of the present LRO approach will be discussed in relation to those of the Regular Solution (RS) model given in Reference 13.

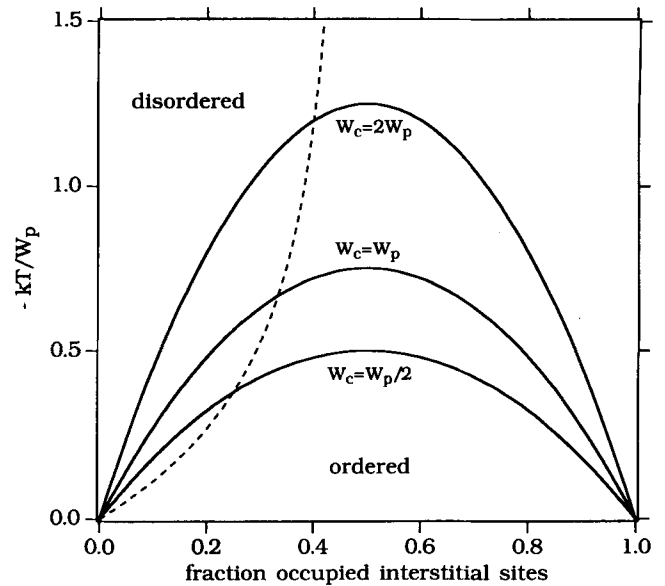
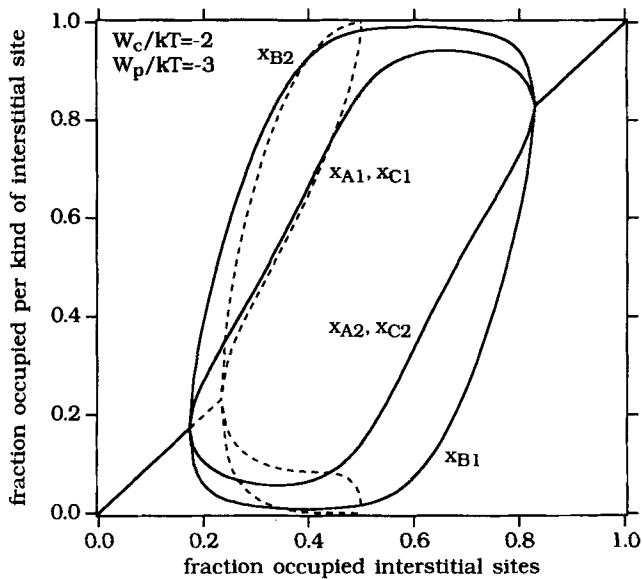
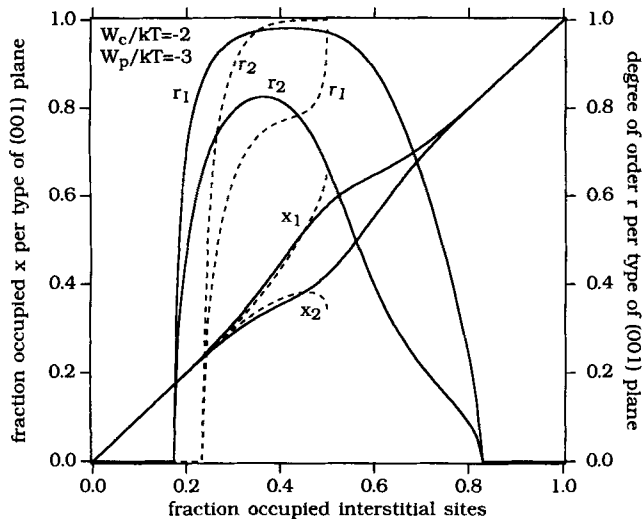


Fig. 4—Phase diagram showing order-disorder transitions according to the LRO model (solid line) and the RS model (dashed line). The composition ranges of the ordered and the disordered regions depend on the interaction energies and the temperature, *i.e.*, on the combination of  $W_c/kT$  and  $W_p/kT$  (here  $W_{pc} = 0$ ).



(a)



(b)

Fig. 5—(a) Occupied fraction for each of the six kinds of I sites A1, . . . , C2 (Fig. 1(b)) as a function of the total fraction occupied of the sites of the hexagonal sublattice that is occupied by I atoms for configuration A, according to the LRO model (solid lines) and the RS model (dashed lines) for the interaction energies indicated. (b) Site occupancies,  $x_1$  and  $x_2$ , and degrees of order,  $r_1$  and  $r_2$ , as a function of the total fraction of the sites of the hexagonal sublattice that is occupied by I atoms for configuration A, according to the LRO model (solid lines) and the RS model (dashed lines;  $r_1$  and  $r_2$  in italics) for the interaction energies indicated.

### 1. Site occupancies and degrees of order for the I sublattice

The occupied fraction for each of the six kinds of sites (A1, B1, . . . , C2; Figure 1(b)), as obtained by route 1, is given in Figures 5(a) and 6(a) as a function of the total occupied fraction of I sites,  $y$  ( $y = 1/6 \sum_{K=A1}^{C2} x_K$ ). In Figures 5(b) and 6(b), the (same) results are presented as obtained by route 2: the occupancies of the I sublattice and the degrees of order are presented as a function of the total occupied fraction of I sites,  $y$  ( $y = (x_1 + x_2)/2$

for A and  $y = (2x_{iv} + x_d)/3$  for B). Using Eqs. [9] and [10] for configuration A or Eq. [11] for configuration B, results obtained by route 1 can be expressed as results obtained by route 2 (and *vice versa*): it was found that, for the present case, routes 1 and 2 yield identical results.

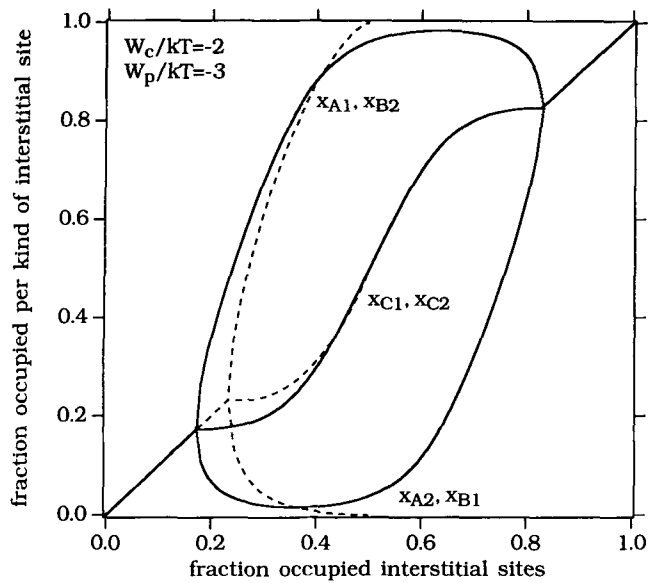
At the composition of the order-disorder transition, the degrees of order are continuous, but their derivatives, with respect to the total interstitial content, change discontinuously (Figures 5(b) and 6(b)). It is observed that the values of  $r$  are asymmetric with respect to  $y = 1/2$ . This can be understood from the definition of the degree of order, which is not affected in a symmetrical way by occupation by V of  $i$  sites and by I of  $v$  sites: if V "atoms" reside on  $i$  sites,  $r$  can still be equal to one, but if I atoms reside on  $v$  sites,  $r$  deviates from one (Eqs. [9] and [10]). For configuration A, the fractions  $x_1$  and  $x_2$  of occupied interstitial sites for the two types of (001)-planes diverge gradually at the onset of ordering and show a maximum difference at the composition  $M_2I$  (or IV on the I sublattice) (Figure 5(b)). This is accompanied with large differences in occupation of the various kinds of sites (Figure 5(a)). For configuration B, at the onset of ordering all I atoms prefer to occupy the sites involved in ordering. At the composition  $M_2I$ , the occupied fractions for the two types of sites ( $iv$  and  $d$  sites) are the same (Figure 6(b)). Of course, at the composition  $M_2I$ , a large difference occurs between the occupied fractions of the  $i$  (A1, B2) and  $v$  (A2, B1) sites (Figure 6(a)).

### 2. Gibbs free energy of the M-I alloy

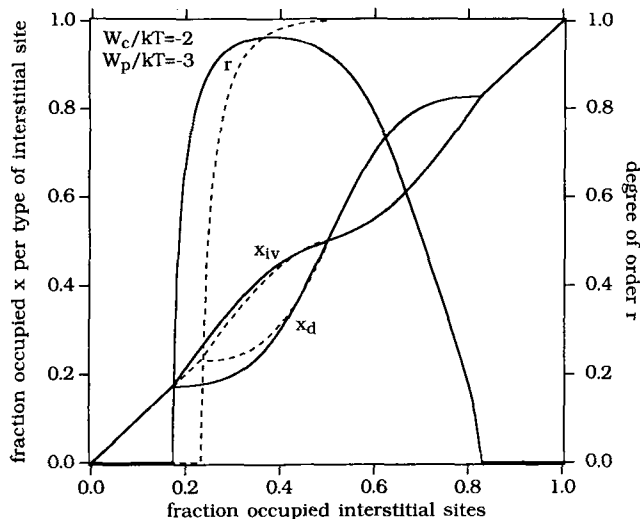
The equilibrium Gibbs free energy for the M-I alloy,  $G_{M-I}$ , is given as a function of the total occupied fraction of I sites,  $y$ , in Figure 7; these results were obtained by substituting the equilibrium values for  $x_{A1}, x_{B1}, \dots, x_{C2}$  in Eq. [1] (or  $x_1, x_2, r_1, r_2$  in Eq. [A14] and  $x_{iv}, x_d, r$  in Eq. [A22]). This thermodynamic property is taken relative to a standard state, *viz.*,  $G_{M-I}^0 = 6(\mu_M^0 + y\mu_I^0 + (1-y)\mu_V^0)$  (*cf.*, Eq. [1]). The bold square dots in Figure 7 indicate the order-disorder transitions; the drawn line in between these dots at less negative values for the Gibbs free energy, represents the Gibbs free energy for the disordered state.

The chemical potentials of I and M atoms on their respective sublattices can be readily obtained from  $G_{M-I}$ , applying Eqs. [2] and [5] for route 1 (or for route 2: Eqs. [A15] and [A16] for configuration A or Eqs. [A23] and [A24] for configuration B). The values for the Gibbs free energy are always finite. This is not the case for the chemical potentials of M and I: for  $y \rightarrow 0$ ,  $\mu_I \rightarrow -\infty$  and  $\mu_M \rightarrow 0$ ; for  $y \rightarrow 1$ ,  $\mu_I \rightarrow +\infty$  and  $\mu_M \rightarrow -\infty$ . It can be easily shown that there is no discontinuity for the first derivative of the Gibbs free energy with respect to  $y$ , but the derivatives of the chemical potentials with respect to  $y$  are discontinuous at the order-disorder transition. Hence, the order-disorder transition as described by the present model is classified as second order [1], consistent with the condition that it cannot be a first-order phase transition (see Section III-A).

Obviously, for values of  $y$  in between the compositions for the order-disorder transition, ordering according to either of the configurations (A or B) leads to a



(a)



(b)

Fig. 6—(a) Occupied fraction for each of the six kinds of I sites A1, . . . , C2 (Fig. 1(b)) as a function of the total fraction of the sites of the hexagonal sublattice that is occupied by I atoms for configuration B, according to the LRO model (solid lines) and the RS model (dashed lines) for the interaction energies indicated. (b) Site occupancies,  $x_{iv}$  and  $x_d$ , and degree of order,  $r$ , as a function of the total fraction of the sites of the hexagonal sublattice that is occupied by I atoms for configuration B, according to the LRO model (solid lines) and the RS model (dashed lines) for the interaction energies indicated.

lower Gibbs free energy than that for the disordered configuration (Figures 7(a) and (b)). In view of the scale of the ordinate in Figures 7(a) and (b), the relative stabilities of configurations A and B cannot be distinguished in these figures. Therefore, the difference in Gibbs free energy between configurations B and A,  $G_{M-1}^B - G_{M-1}^A$ , is given as a function of the total fraction of occupied I sites,  $y$ , in Figure 7(c). Configuration B yields the more stable configuration of I atoms if  $G_{M-1}^B - G_{M-1}^A < 0$  and

configuration A yields the more stable configuration of I atoms if  $G_{M-1}^B - G_{M-1}^A > 0$ .

Phase diagrams representing the stability ranges of configurations A and B were calculated by considering thermodynamic equilibrium between these configurations for different combinations of the interaction energies  $W_p$  and  $W_c$  (i.e., imposition of the conditions  ${}^A\mu_1 = {}^B\mu_1$  and  ${}^A\mu_M = {}^B\mu_M$ , where  ${}^J\mu_K$  is the chemical potential of atoms K in configuration J). The results are given in Figure 8 for two values of  $W_c/W_p$ . If  $|W_c/kT| \geq |W_p/kT|$ , configuration A is the more stable type for the entire range of compositions within the ordered region, provided the value for  $|W_p/kT|$  is not too large (i.e.,  $|W_p| \leq \sim 3kT$  in Figure 8(a)). This can be understood as follows: a strong interaction in the  $c$ -direction (i.e., a relatively large value of  $|W_c/kT|$ ) is incompatible with the occurrence of  $d$  sites. If  $|W_c/kT|$  becomes considerably smaller than  $|W_p/kT|$ , configuration A is only preferred in a narrow composition range around the composition  $M_2I$ . For example, for  $W_c = 1/2 W_p$ , the homogeneity range of configuration A is confined to approximately  $0.4 < y < 0.6$  (Figure 8(a)). It is noted that the transition from configuration A to configuration B is a first-order phase transition, whereas the disorder-order transition is a second-order phase transition.

The present theoretical results on the relative stabilities of configurations A and B can be compared with X-ray diffraction results for the  $\epsilon$ -Fe<sub>2</sub>N<sub>1-z</sub> phase. This iron nitride can be conceived as an hcp sublattice of Fe atoms containing N atoms at the sublattice formed by the octahedral interstices. The crystal structure proposed for the composition  $\epsilon$ -Fe<sub>2</sub>N<sub>2/3</sub> ( $z = 1/3$ ;  $y = 1/3$ )<sup>[11,12]</sup> is in accordance with ordering of the interstitial nitrogen atoms, according to configuration B. The crystal structure proposed for the composition  $\epsilon$ -Fe<sub>2</sub>N ( $z = 0$ ;  $y = 1/2$ )<sup>[11,12]</sup> is in accordance with ordering of the interstitial nitrogen atoms, according to configuration A. These experimental results are thus compatible with the theoretical predictions (Figure 8).

### B. Comparison of the Long-Range Order Model with the Regular Solution Model for Ordering of Interstitials in an hcp Lattice

Ordering on the basis of the two ground-state structures A and B (cf. Section III-B) was considered in Reference 13 by applying a "Regular Solution Model" (RS model). In the sequel, the present long range order approach will be indicated by LRO and the regular solution model of Reference 13 will be referred to as RS. The principal difference between the LRO and the RS models involves *a priori* exclusion of simultaneous occupation of nearest neighbor sites in the  $c$ -direction for the latter. This site-exclusion condition has a strong effect on the distribution possibilities of the I atoms on their sublattice and thus on the corresponding configurational entropy. Moreover, because of the site-exclusion condition, interactions in the  $c$ -direction do not occur, and hence, the corresponding exchange energy does not occur, and thus, the enthalpy is affected too. A further consequence of the site-exclusion condition is that the maximum occupation of the I sublattice

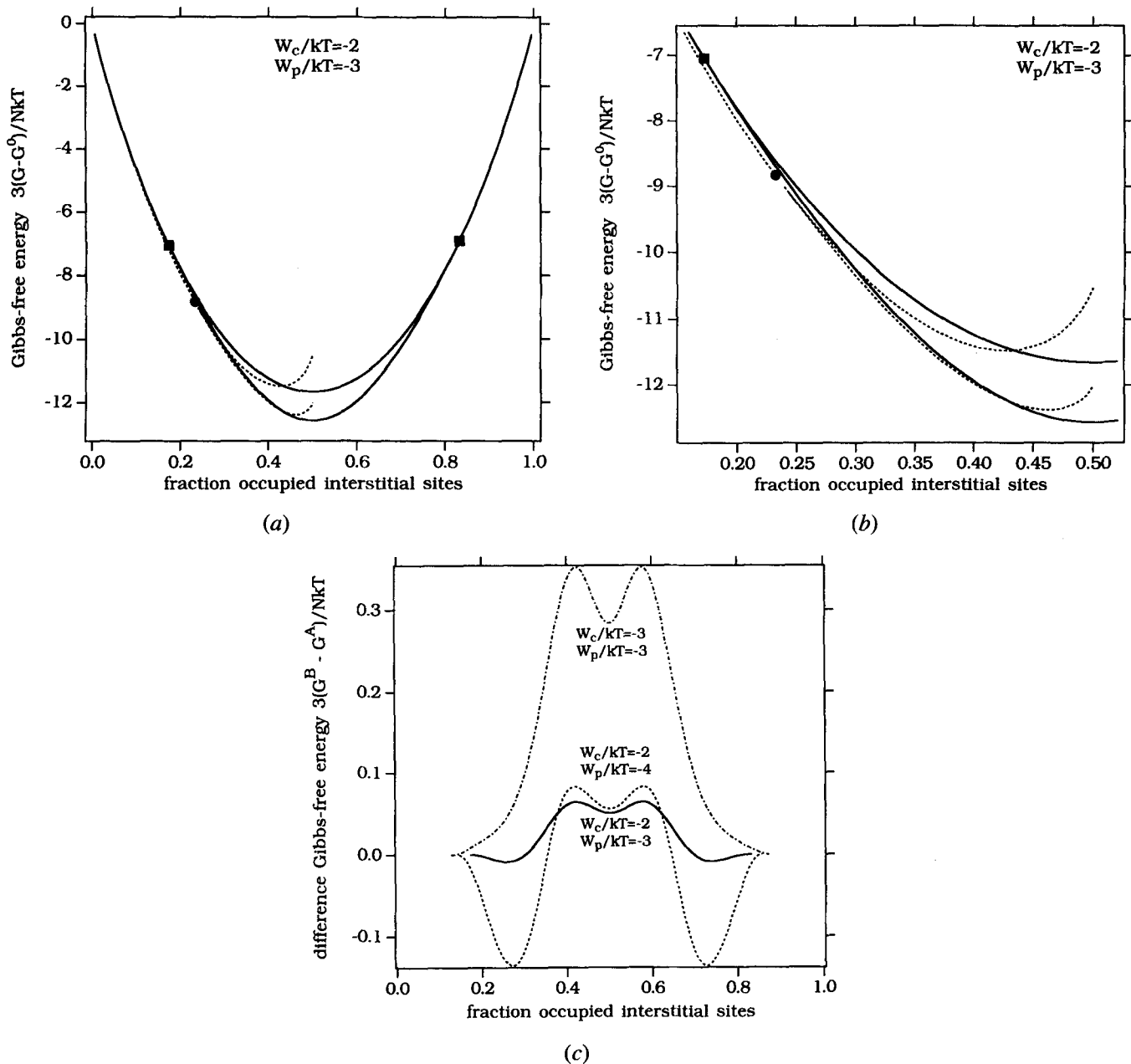


Fig. 7—(a) Gibbs free energy,  $(G_{M-1} - G_{M-1}^0)/(1/3)NkT$ , as a function of the total fraction of the sites of the hexagonal sublattice that is occupied by I atoms. The drawn lines outside and in between the square dots, at the less negative values, represent the Gibbs free energy for a disordered distribution of I atoms; the drawn line in between the square dots at the more negative values represents the Gibbs free energy for the LRO configurations A and B. The dashed lines hold for the RS model that predicts ordering within the (001)-planes for I contents above that indicated by the dot (less negative values: disordered; more negative values: ordered). (b) Enlargement of (a). (c) Difference in Gibbs free energy,  $G_{M-1}^B - G_{M-1}^A$ , between configurations B and A.  $(G_{M-1}^B - G_{M-1}^A)/(1/3)NkT$ , as a function of the total fraction of the sites of the hexagonal sublattice that is occupied by I atoms for different combinations of  $W_c/kT$  and  $W_p/kT$ .

is given by  $y = 1/2$ . Results of the RS model are presented in Figures 4 through 7(a) and (b) by use of dashed lines. These results were obtained using analogous procedures as employed in the LRO approach. Routes 1 and 2 (Section III) yielded identical results for the RS model.

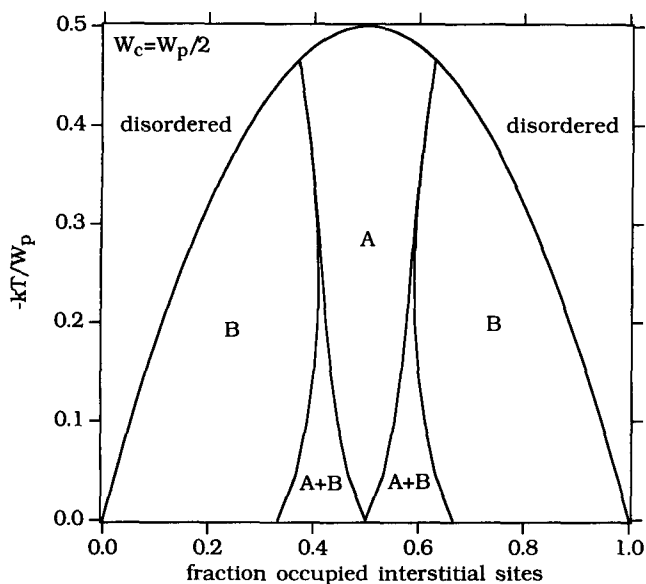
For the content of interstitials at the order-disorder transition,  $x_t$ , it holds according to the RS model<sup>[13]</sup> that

$$x_t = \frac{1}{2} \left( 1 - \frac{2kT_t}{W_p - W_{pc}} - \sqrt{1 + \left[ \frac{2kT_t}{W_p - W_{pc}} \right]^2} \right) \quad [12]$$

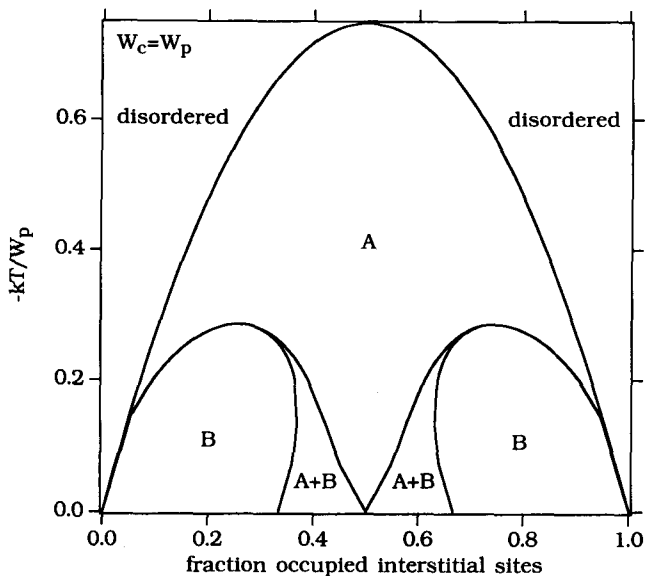
In Reference 13, Eq. [12] was obtained with  $W_p/k = -L/R$  ( $R$  is the gas constant) and without taking into account third nearest-neighbor interaction (represented here by  $W_{pc}$ ); this effect is included here to allow comparison with the results of the present LRO model (Eqs. [7] and [A21]). A large difference occurs between the order-disorder boundaries of the LRO model and the RS model (Figure 4). In this respect, it is noted that a fully disordered state cannot exist within the RS model, since the site-exclusion condition in the  $c$ -direction is assumed for all compositions. Therefore, the dashed line

in Figure 4 in fact indicates the order-disorder transition within the (001)-planes only. For the RS model, ordering is only possible if  $(W_p - W_{pc}) < 0$  (cf. Eq. [12]). A physically unrealistic situation arises for  $y = 1/2$ , because for all possible temperatures, full ordering and thus no order-disorder transition occurs (Figure 4). This result is another immediate consequence of the site-exclusion condition: for  $y = 1/2$  the configurational entropy equals zero, and thus, the Gibbs free energy relative to the standard state is independent of temperature, implying that the ground-state structure occurs at all temperatures.

If  $|W_c|$  is not very small (for site exclusion the virtual  $|W_c| = \infty$ ), the content  $x_i$  for the order-disorder transition as obtained from the LRO model is smaller than that



(a)



(b)

Fig. 8—Phase diagram showing single- and dual-phase regions for the ordered configurations (phases) A and B: (a)  $W_c = W_p/2$  and (b)  $W_c = W_p$ .

predicted by the RS model; *i.e.*, ordering according to the LRO model starts at smaller interstitial contents than according to the RS model. The partial order imposed by the site-exclusion condition in the RS model postpones ordering to a higher total occupied fraction.

### 1. Site occupancy

In order to allow a direct comparison of the results obtained with the LRO model and the RS model, the values for  $W_p$  were taken equal. The case of ordering under the constraint of the site-exclusion condition in the RS model demands the degrees of order to be equal to 1 at the composition  $M_2I$ . Equivalently, for this composition, the occupied fractions per type of (001)-plane or per type of interstitial site are strictly prescribed. This is not the case for the present LRO model. So, in principle, at least near the composition  $M_2I$ , the site occupancies according to the LRO and the RS model are different.

In contrast with the RS model, the LRO model does not prescribe a zero probability for simultaneous occupation by I atoms of neighboring sites in the *c*-direction of configurations A and B (cf. Eq. [A4a]). This probability is shown in Figure 9 for the values of the exchange energies indicated. As compared to the disordered situation, on ordering the probability that neighboring sites in the *c*-direction are both occupied by I atoms decreases and remains low for interstitial contents smaller than 1/2 (the composition  $M_2I$ ). Obviously, the amount of nearest neighbors in the *c*-direction increases rapidly on approaching the interstitial content 1/2 and beyond. From Figure 9, it can be seen that in the LRO approach, simultaneous occupation of nearest neighboring sites in the *c*-direction tends to be excluded.

### 2. Gibbs free energy

Comparing the Gibbs free energies for configurations A and B as obtained by the RS model, it was concluded

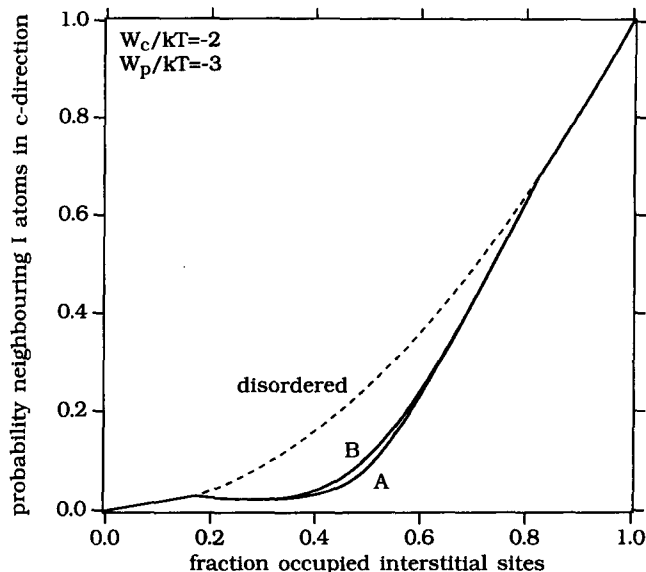


Fig. 9—Probability according to the LRO model for the occurrence of simultaneous occupancy by I atoms of neighboring sites in the *c*-direction as a function of the total fraction occupied of the sites of the I sublattice.

in Reference 13 that configuration B yields a more negative value for the Gibbs free energy than configuration A for all compositions within the ordered region according to the RS model. This finding is opposite to the results obtained with the LRO approach, where configuration A (1) is always stable near the stoichiometric composition  $M_2I$  and (2) for  $|W_c/kT| \gg |W_p/kT|$  it becomes stable in the entire ordered region (Figures 7(c) and 8 and the discussion in Section A-2).

The stabilities of a configuration (A or B) according to the LRO model and the RS model can be compared on the basis of the corresponding Gibbs free energies. Such a comparison of the LRO and the RS model is only justified (1) if equal values for the exchange energies are used and (2) if the reference states, *i.e.*,  $G_{M-1}^0 = 6(\mu_M^0 + y\mu_I^0 + (1-y)\mu_V^0)$ , are identical. Adopting the treatment of section III and taking into account interactions among I atoms up to the third nearest neighbors, it holds

$$\begin{aligned} \text{LRO model: } H_1^0 &= N(Z_c/2 e_{c,II} + Z_p/2 e_{p,II} + Z_{pc}/2 e_{pc,II}); \\ \text{RS model: } H_1^0 &= N(Z_p/2 e_{p,II} + Z_{pc}/2 e_{pc,II});^* \end{aligned}$$

\*The reference state as described in Reference 13 was not explicitly defined, but expressed in the present terminology, it holds that  $\mu_I^0 = H_1^0 - TS_{vb,1}^0 + H_{M-1}^0 + W_p$ , with  $H_1^0$  of the RS model given above. The regular solution parameter  $L$  of Reference 13 is identical to  $-NW_p$  in this article.

where  $Z_{pc}/2$  is the number of bonds among third nearest neighbors. Thus, the reference states for the LRO and the RS model are not identical because of omittance of interstitial interactions in the  $c$ -direction by the RS model. Then, if the interaction energies  $e_{c,IV}$  and  $e_{c,VV}$  are small as compared to  $e_{c,II}$ , which is likely to be the case if V represents vacancies, the exchange energy  $W_c$ , as given by Eq. [A7], reads  $-Z_c/2 e_{c,II}$ . Then, the reference state for the RS model can be made compatible with that for the LRO model by subtracting the value of  $NW_c$  from the value of  $H_1^0$  for the RS model, as indicated in this section. The Gibbs free energies for the RS model adapted in this way, *i.e.*, to all values for the Gibbs free energy the value of  $NW_c$  is added, are presented in Figures 7(a) and (b).

For small fractions of occupied interstitial sites, the RS model yields more negative values for the Gibbs free energy than the LRO model, but the differences are relatively small (Figure 7(b)). However, if the interstitial content approaches the composition  $M_2I$ , a substantial difference of opposite sign occurs: ordering as considered in the LRO model corresponds to the most stable state. The less stable interstitial configuration predicted by the RS model near the composition  $M_2I$  is caused by the rigid demand of the site-exclusion condition. Apparently, even if the repulsion between I atoms in the  $c$ -direction is strong, the presence of a small fraction of I atoms on nearest neighboring sites in the  $c$ -direction is favorable. Then, the small negative effect on the enthalpy is compensated by the strong positive effect on the configurational entropy.

## V. CONCLUSIONS

1. Long-range ordering of atoms I and vacancies V on the sublattice constituted by the octahedral interstices

of an hcp sublattice of atoms M can be described by applying the Gorsky–Bragg–Williams (GBW) approximation (or zeroth approximation to the Ising model) to a trigonal prism constituted by six kinds of sites for atoms I and vacancies V, considering pairwise interaction up to third nearest neighbors. Two routes can be followed:

- Route 1 starts with a description for the occupancy of each of the six sites on the trigonal prism and the associated chemical potentials.
  - Route 2 starts with a ground-state structure for distinguishing between order and disorder sites. Relative to the ground-state structure, LRO parameters can be defined.
2. The possible ground-state structures on sites of the trigonal prism have been derived as a function of the pairwise interaction energies following route 1. Two of these ground-state structures form the basis for two configurations, denoted as configurations A and B, to which the GBW approximation is applied following route 2. The ground-state structure forming the basis for configuration A is characterized by an alternation of (001)-planes having average compositions  $I_2V$  and  $IV_2$ ; the ground-state structure forming the basis for configuration B is characterized by (001)-planes having equal compositions.
  3. The stabilities of the ordered configurations A and B with respect to one another and with respect to the disordered configuration as a function of the overall occupancy of the interstitial sublattice can be represented by phase diagrams showing monophasic (A and B and disorder) and dual-phase (A + B) regions. Configuration B is the more stable configuration for interstitial contents lower than the one for the stoichiometric composition  $M_3I$  and higher than the one for the stoichiometric composition  $M_3I_2$ ; configuration A is generally preferred near the stoichiometric composition  $M_2I$ . This agrees with reported data for  $\epsilon\text{-Fe}_2\text{N}_{1-z}$ . It was found that the stronger the repulsive interaction in the  $c$ -direction, relative to the repulsive interaction within the (001)-planes, the broader is the homogeneity range of configuration A. Further, the results showed that ordering itself is a second-order phase transition, while the transition from one ordered configuration to the other is a first-order phase transition.
  4. The results were compared to those of a regular solution model for interstitials in an hcp lattice that excludes simultaneous occupancy of neighboring sites in the  $c$ -direction for all compositions. The present LRO model provides a physically more realistic description and leads to thermodynamically more stable configurations in the ordered region.

## APPENDIX A

The thermodynamic description of configuration A, based on the prescription of the site occupancies according to Eqs. [9] and [10], and the thermodynamic description of configuration B, based on the prescription of the site occupancies according to Eq. [11], will be given here.

## Configuration A

### Configurational entropy

For the (001) planes of type 1, the number of distribution possibilities  $D_{i1}$  of I and V on the  $i1$  sites follows from the total number of  $i1$  sites ( $2/3N$ ), the number of I atoms on  $i1$  sites ( $N_{I,i1}$ , Eq. [9a]), and the number of V on  $i1$  sites ( $N_{V,i1}$ , Eq. [9c]):

$$D_{i1} = \frac{\frac{2}{3}N!}{N_{I,i1}! N_{V,i1}!} = \frac{\frac{2}{3}N!}{\left[(2+r_1)x_1 \frac{N}{3}\right]! \left[2 - (2+r_1)x_1 \frac{N}{3}\right]!} \quad [A1]$$

The numbers of distribution possibilities  $D_{v1}$ ,  $D_{i2}$ , and  $D_{v2}$  of I and V on the  $v1$ ,  $i2$ , and  $v2$  sites, respectively, are obtained in a similar way (using Eqs. [9] and [10]).

The total configurational entropy  $S$  of the pseudo-binary alloy I-V (entropy of mixing I and V) for one (001) plane of type I and one (001) plane of type 2 (each plane containing a total of  $N$  sites) is given by

$$S = k [\ln(D_{i1}) + \ln(D_{v1}) + \ln(D_{i2}) + \ln(D_{v2})] \quad [A2]$$

where  $k$  is Boltzmann's constant. Substituting the numbers of distribution possibilities (cf. Eq. [A1]) in Eq. [A2] and using Stirling's approximation ( $\ln(n!) = n \ln(n) - n$  for large  $n$ ) the total configurational entropy  $S_{\text{conf}}$  is readily obtained as

$$S_{\text{conf}} = \frac{1}{3} Nk \{ 4 \ln(2) - [(2+r_1)x_1] \ln[(2+r_1)x_1] - [2 - (2+r_1)x_1] \ln[2 - (2+r_1)x_1] - [(1-r_1)x_1] \ln[(1-r_1)x_1] - [1 - (1-r_1)x_1] \ln[1 - (1-r_1)x_1] - [(1+2r_2)x_2] \ln[(1+2r_2)x_2] - [1 - (1+2r_2)x_2] \ln[1 - (1+2r_2)x_2] - [(2-2r_2)x_2] \ln[(2-2r_2)x_2] - [2 - (2-2r_2)x_2] \ln[2 - (2-2r_2)x_2] \} \quad [A3]$$

Since the occupation of the M sublattice is complete and M and I atoms do not reside on each other's sublattices, M does not contribute to the configurational entropy and Eq. [A3] pertains to the whole M-I alloy as well.

### Pairwise nearest neighbor interaction in the $c$ -direction of the I sublattice

The probability  $P_{ii}$  that two neighboring sites in the  $c$ -direction are both occupied by I atoms is given by the chance for simultaneous occupancy of  $i1$  and  $v2$  and of  $v1$  and  $i2$  sites. Hence, recognizing that the probability

of occupancy of, e.g., an  $i1$  site by an I atom is  $N_{I,i1}/(2/3N)$ , it follows that

$${}^cP_{ii} = \frac{2}{3} \frac{N_{I,i1}}{2} \frac{N_{I,v2}}{2} + \frac{1}{3} \frac{N_{I,v1}}{1} \frac{N_{I,i2}}{1} \quad [A4a]$$

The number of  $i1$ - $v2$  neighbors is twice as high as the number of  $v1$ - $i2$  neighbors due to the respective composition of the type 1 ( $i_2v$ ) and type 2 ( $v_2i$ ) planes. Further,  ${}^cP_{ii}$  can maximally equal 1. Both constraints are expressed in Eq. [A4a] by the factors  $2/3$  and  $1/3$ . The probabilities  ${}^cP_{VV}$  and  ${}^cP_{IV}$  for V-V and I-V nearest neighbors, respectively (in the  $c$ -direction), are obtained likewise:

$${}^cP_{VV} = \frac{2}{3} \frac{N_{V,v1}}{2} \frac{N_{V,v2}}{2} + \frac{1}{3} \frac{N_{V,v1}}{1} \frac{N_{V,i2}}{1} \quad [A4b]$$

$${}^cP_{IV} = \frac{2}{3} \left[ \frac{N_{I,i1}}{2} \frac{N_{V,v2}}{2} + \frac{N_{V,v1}}{2} \frac{N_{I,i2}}{2} \right] + \frac{1}{3} \left[ \frac{N_{V,v1}}{1} \frac{N_{V,i2}}{1} + \frac{N_{V,v1}}{1} \frac{N_{I,i2}}{1} \right] \quad [A4c]$$

The sum  ${}^cP_{ii} + {}^cP_{VV} + {}^cP_{IV}$  of course, equals 1.

The energy  $E_c$  resulting from the pairwise nearest neighbor interactions in the  $c$ -direction is proportional to the sum of the products of the probabilities  ${}^cP_{ii}$ ,  ${}^cP_{VV}$ , and  ${}^cP_{IV}$  and their corresponding interaction energies  $e_{c,ii}$ ,  $e_{c,vv}$ , and  $e_{c,iv}$ . Neglecting pressure and volume ( $pV$ ) effects of mixing I and V, the enthalpy  $H_c$  is equal to the energy  $E_c$ . Hence, recognizing that the total number of  $c$  interactions for a pair of type 1 and type 2 planes is  $2N$ , it follows for such a pair

$$H_c = [{}^cP_{ii} e_{c,ii} + {}^cP_{VV} e_{c,vv} + {}^cP_{IV} e_{c,iv}] 2N \quad [A5]$$

Using Eqs. [9] and [10], substitution of the probabilities given by Eq. [A4] in Eq. [A5] yields

$$H_c = [x_1 + x_2] H_{I,c}^0 + [(1-x_1) + (1-x_2)] H_{V,c}^0 + NW_c [x_1(1-x_2) + x_2(1-x_1)] + 2NW_c r_1 r_2 x_1 x_2 \quad [A6]$$

where  $H_{I,c}^0 = N Z_c/2 e_{c,ii}$  and  $H_{V,c}^0 = N Z_c/2 e_{c,vv}$  with  $Z_c/2$  being the number of bonds in the  $c$ -direction per atom ( $Z_c/2 = 1$ ).  $W_c$  is the "exchange energy" in the  $c$ -direction:

$$W_c = \frac{Z_c}{2} [2e_{c,iv} - e_{c,ii} - e_{c,vv}] \quad [A7]$$

The term  $H_{I,c}^0$  is a fraction of  $H_I^0$ , the enthalpy of  $N$  atoms of the pure component I (with exactly the same lattice as the I sublattice). Accordingly,  $H_{V,c}^0$  is a fraction of  $H_V^0$ , the enthalpy of  $N$  atoms of the pure component V (with exactly the same lattice as the I sublattice; for the

present case, where V of the hypothetical IV alloy represents vacant I sites,  $H_V^0$  of course is zero). The first two terms on the right-hand side of Eq. [A6] represent the "ideal mixing" enthalpy of the hypothetical I-V alloy. The third term on the right-hand side of Eq. [A6] represents the change in enthalpy due to random mixing, but taking into account the difference in interaction energy of I-I, V-V, and I-V, nearest neighbors. This is the same enthalpy change as emerging in the "zeroth approximation to the regular solutions" for an I-V alloy. The last term on the right-hand side of Eq. [A6] represents the change in enthalpy due to ordering.

*Pairwise nearest neighbor interaction within the (001) planes of the I sublattice*

The probability  ${}^1P_{II}$  that two neighboring sites within a plane of type 1 ( $i_2v$ ) are both occupied by I atoms is given by the chance for simultaneous occupancy by I atoms of two  $i1$  sites and of  $i1$  and  $v1$  sites:

$${}^1P_{II} = \frac{1}{3} \frac{N_{I,i1}}{N} \frac{N_{I,i1}}{N} + \frac{2}{3} \frac{N_{I,i1}}{N} \frac{N_{I,v1}}{N} \quad [A8a]$$

In a plane of type 1, the number of  $i1$ - $i1$  interactions is half of the number of  $i1$ - $v1$  interactions (Figure 3(a)), which is expressed in Eq. [A8a] by the factors 1/3 and 2/3, respectively. The other probabilities in a plane of type 1,  ${}^1P_{VV}$  and  ${}^1P_{IV}$ , are obtained analogously:

$${}^1P_{VV} = \frac{1}{3} \frac{N_{V,i1}}{N} \frac{N_{V,i1}}{N} + \frac{2}{3} \frac{N_{V,i1}}{N} \frac{N_{V,v1}}{N} \quad [A8b]$$

$${}^1P_{IV} = \frac{1}{3} \left[ \frac{N_{I,i1}}{N} \frac{N_{V,i1}}{N} + \frac{N_{V,i1}}{N} \frac{N_{I,i1}}{N} \right] + \frac{2}{3} \left[ \frac{N_{I,i1}}{N} \frac{N_{V,v1}}{N} + \frac{N_{V,i1}}{N} \frac{N_{I,v1}}{N} \right] \quad [A8c]$$

The probabilities  ${}^2P_{II}$ ,  ${}^2P_{VV}$ , and  ${}^2P_{IV}$  for a plane of type 2 ( $v_2i$ ) can be obtained directly from Eq. [A8], by replacing  $i1$  by  $v2$  and  $v1$  by  $i2$ .

The enthalpy  $H_p$  for a pair of planes of types 1 and 2 due to nearest neighbor interaction within the planes is

$$H_p = [({}^1P_{II} + {}^2P_{II}) e_{p,II} + ({}^1P_{VV} + {}^2P_{VV}) e_{p,VV} + ({}^1P_{IV} + {}^2P_{IV}) e_{p,IV}] 3N \quad [A9]$$

where  $e_{p,II}$ ,  $e_{p,VV}$ , and  $e_{p,IV}$  are the interaction energies between I-I, V-V, and I-V nearest neighbors within the (001) planes, respectively, and the factor  $3N$  accounts for the total number of nearest neighbor interactions within one plane. Using Eqs. [9] and [10], substitution of the probabilities given by Eq. [A8] in Eq. [A9] yields

$$H_p = [x_1 + x_2] H_{I,p}^0 + [(1 - x_1) + (1 - x_2)] H_{V,p}^0 + NW_p [x_1(1 - x_1) + x_2(1 - x_2)] + NW_p \left[ \frac{1}{4} (x_1 r_1)^2 + (x_2 r_2)^2 \right] \quad [A10]$$

where  $H_{I,p}^0 = N Z_p/2 e_{p,II}$  and  $H_{V,p}^0 = N Z_p/2 e_{p,VV}$  with  $Z_p/2$  being the number of bonds within one (001) plane per atom ( $Z_p/2 = 3$ ). The term  $W_p$  is the "exchange energy" for the (001) planes:

$$W_p = \frac{Z_p}{2} [2e_{p,IV} - e_{p,II} - e_{p,VV}] \quad [A11]$$

Interpretation of the terms on the right-hand side of Eq. [A10] corresponds to that given for Eq. [A6].

*Interaction of the M and I sublattices*

Since the occupation of the M sublattice is complete and every site of the I sublattice is surrounded by atoms M in a similar way, the probability  $P_{MI}$  of finding a pair M-I for a pair of planes of type 1 and type 2 is determined only by the occupancy of the I sublattice by I atoms:

$$P_{MI} = \frac{1}{2} \left\{ \frac{2}{3} \left( \frac{N_{I,i1}}{N} + \frac{N_{I,v2}}{N} \right) + \frac{1}{3} \left( \frac{N_{I,v1}}{N} + \frac{N_{I,i2}}{N} \right) \right\} = \frac{1}{2} (x_1 + x_2) \quad [A12a]$$

The probability  $P_{MV}$  of finding V adjacent to M is obtained likewise:

$$P_{MV} = 1 - P_{MI} = \frac{1}{2} (1 - x_1 + 1 - x_2) \quad [A12b]$$

The enthalpy  $H_{MI}$  due to interaction of I atoms and their surrounding M atoms, per pair of type 1 and type 2 planes, can thus be described by

$$H_{MI} = (x_1 + x_2) H_{MI}^0 \quad [A13a]$$

where  $H_{MI}^0$  represents the interaction of  $N$  atoms I with their surrounding M atoms (Note that there are  $2N$  sites for I atoms per pair of type 1 and type 2 planes). For the enthalpy  $H_{MV}$  associated with interaction of M and V, it is obtained

$$H_{MV} = (1 - x_1 + 1 - x_2) H_{MV}^0 \quad [A13b]$$

where  $H_{MV}^0$  represents the interaction energy of  $N$  atoms V with their surrounding M atoms. If V represents vacant I sites with no interaction of M and V,  $H_{M-V}^0$  is zero.

*Gibbs free energy, chemical potential, and equilibrium condition*

Using Eqs. [A3], [A6], [A10], and [A13] and superimposing the Gibbs free energy of the M sublattice (*i.e.*, the Gibbs free energy of the pure component M, which is given by  $H_M^0 - TS_{\text{vib},M}^0$  for  $N$  atoms M) the total Gibbs free energy  $G_{M-1}$  of the M-I(-V) alloy, for the considered pair of type 1 and type 2 planes of the I sublattice and the associated pair of planes of the M sublattice (each containing  $N$  atoms M), becomes



$$\begin{aligned}
G_{M-I} = & 2(H_M^0 - TS_{\text{vib},M}^0) \\
& + [x_1 + x_2] (H_I^0 - TS_{\text{vib},I}^0 + H_{MI}^0) \\
& + [(1 - x_1) + (1 - x_2)] (H_V^0 - TS_{\text{vib},V}^0 + H_{MV}^0) \\
& + NW_c [x_1(1 - x_2) + x_2(1 - x_1)] + NW_c [2r_1 r_2 x_1 x_2] \\
& + NW_p [x_1(1 - x_1) + x_2(1 - x_2)] \\
& + NW_p \left[ \frac{1}{4} (x_1 r_1)^2 + (x_2 r_2)^2 \right] - TS_{\text{conf}}
\end{aligned} \tag{A14}$$

where  $S_{\text{conf}}$  is given by Eq. [A3] and  $H_Q^0$  is the enthalpy of  $N$  atoms of the pure component  $Q$  ( $Q = M, I, V$ ;  $H_I^0 = H_{I,p}^0 + H_{I,c}^0$ ,  $H_V^0 = H_{V,p}^0 + H_{V,c}^0$ ) and  $S_{\text{vib},Q}^0$  denotes the vibrational entropy of  $N$  atoms of the pure component  $Q$ , which is assumed to be independent of composition and ordering. The first three terms on the right-hand side of Eq. [A14] represent the standard state of the M-I alloy. It is noted that the contribution of the M sublattice and its interaction with the I sublattice only change the standard state and, consequently, do not affect ordering on the I sublattice. Recognizing that V represents empty sites on the I sublattice:  $e_{V,V} = 0$  and  $H_V^0 = 0$ .

In  $G_{M-I}$ , as given by Eq. [A14], pairwise interactions on the I sublattice up to second nearest neighbors (*i.e.*, first nearest neighbors within the (001) planes: interactions A1-B1, A1-C1, *etc.*) are taken into account. Accounting for the effect of at least second nearest neighbors is necessary to attain a useful thermodynamic description. In general, the exchange energies associated with the interactions are unknown and should, therefore, be considered as parameters to be fitted to experimental data. Adding more nearest-neighbor-interaction terms to the thermodynamic description increases the number of such fit parameters. This number should be kept as small as possible.

The Gibbs free energy  $G_{M-I}$  of the M-I alloy in general can be related to chemical potentials  ${}^1\mu_I$  and  ${}^1\mu_V$  of I and V, respectively, in (001) planes of type 1 and to chemical potentials  ${}^2\mu_I$  and  ${}^2\mu_V$  of I and V, respectively, in (001) planes of type 2 and to the chemical potential  $\mu_M$  of M:

$$\begin{aligned}
G_{M-I} \equiv & 2\mu_M + x_1 {}^1\mu_I + (1 - x_1) {}^1\mu_V \\
& + x_2 {}^2\mu_I + (1 - x_2) {}^2\mu_V
\end{aligned} \tag{A15}$$

where the chemical potentials pertain to  $N$  atoms (M, I, V), while the Gibbs free energy pertains to  $2N$  atoms of M and  $(x_1 + x_2)N$  atoms of I. If V represents vacant I sites, it holds that  ${}^1\mu_V = {}^2\mu_V \equiv 0$ . Then, the chemical potentials  ${}^1\mu_I$  and  ${}^2\mu_I$  each for  $N$  atoms I in the corresponding planes are defined as for an open system (*cf.* Eq. [2]):

$${}^1\mu_I = \frac{\partial G_{M-I}}{\partial x_1}, \quad {}^2\mu_I = \frac{\partial G_{M-I}}{\partial x_2} \tag{A16}$$

For equilibrium between I atoms in the two types of planes, it holds that

$${}^1\mu_I = {}^2\mu_I \equiv \mu_I \Rightarrow \frac{\partial G_{M-I}}{\partial x_1} - \frac{\partial G_{M-I}}{\partial x_2} = 0 \tag{A17}$$

The occurrence of ordering originates from a Gibbs free energy for an ordered configuration of the I atoms lower than that for the disordered configuration. The degrees of order in the planes of type 1 and type 2,  $r_1$  and  $r_2$ , respectively, will take values corresponding with a minimum value for the Gibbs free energy, according to Eq. [A14]. Hence, for equilibrium,

$$\frac{\partial G_{M-I}}{\partial r_1} = 0 \quad \text{and} \quad \frac{\partial G_{M-I}}{\partial r_2} = 0 \tag{A18}$$

Thermodynamical equilibrium of the M-I alloy is described by the Gibbs free energy given by Eq. [A14] subject to the equilibrium conditions, according to Eqs. [A17] and [A18]. The equations for the equilibrium conditions obtained in this way are nonlinear with respect to the variables  $x_1$ ,  $x_2$ ,  $r_1$ , and  $r_2$ . The numerical evaluation method for solving these equations is given in Appendix B.

#### Order-disorder transition

The three equilibrium conditions (Eqs. [A17] and [A18]) can each be written as  $f(\underline{x}) = f(r_1, r_2, x_1, x_2) = 0$ . If  $\underline{x} + d\underline{x}$  and  $\underline{x}$  are sufficiently close, it holds for all  $\underline{x}$  that

$$f(\underline{x} + d\underline{x}) = f(\underline{x}) + \frac{\partial f}{\partial r_1} dr_1 + \frac{\partial f}{\partial r_2} dr_2 + \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2$$

provided that  $f(\underline{x})$  is continuous for  $\underline{x}$ . If equilibrium holds for both  $\underline{x}$  and  $\underline{x} + d\underline{x}$  it thus follows that

$$\frac{\partial f}{\partial r_1} dr_1 + \frac{\partial f}{\partial r_2} dr_2 + \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 = 0$$

Moreover, the infinitesimal changes  $dr_1$ ,  $dr_2$ ,  $dx_1$ , and  $dx_2$  within the range  $\underline{x}$  to  $\underline{x} + d\underline{x}$  can be taken proportional to one another. The ratios of  $dr_1$ ,  $dr_2$ ,  $dx_1$ , and  $dx_2$  are defined as follows:  $dr_2 = g \cdot dr_1$ ,  $dx_1 = h \cdot dr_1$ , and  $dx_2 = i \cdot dr_1$  ( $g$ ,  $h$ , and  $i$  are yet unknown real values), provided that  $dr_1 \neq 0$  (this holds within the ordered region at least at the order-disorder transition). Explicit substitution of  $f(\underline{x})$  by the three equilibrium conditions (Eqs. [A17] and [A18] and dropping the subscript M-I) thus yields

$$\begin{aligned}
\frac{\partial}{\partial r_1} \left( \frac{\partial G}{\partial r_1} \right) + g \frac{\partial}{\partial r_2} \left( \frac{\partial G}{\partial r_1} \right) + h \frac{\partial}{\partial x_1} \left( \frac{\partial G}{\partial r_1} \right) \\
+ i \frac{\partial}{\partial x_2} \left( \frac{\partial G}{\partial r_1} \right) = 0
\end{aligned} \tag{A19a}$$

$$\begin{aligned}
\frac{\partial}{\partial r_1} \left( \frac{\partial G}{\partial r_2} \right) + g \frac{\partial}{\partial r_2} \left( \frac{\partial G}{\partial r_2} \right) + h \frac{\partial}{\partial x_1} \left( \frac{\partial G}{\partial r_2} \right) \\
+ i \frac{\partial}{\partial x_2} \left( \frac{\partial G}{\partial r_2} \right) = 0
\end{aligned} \tag{A19b}$$

$$\begin{aligned}
\frac{\partial}{\partial r_1} \left( \frac{\partial G}{\partial x_1} - \frac{\partial G}{\partial x_2} \right) + g \frac{\partial}{\partial r_2} \left( \frac{\partial G}{\partial x_1} - \frac{\partial G}{\partial x_2} \right) \\
+ h \frac{\partial}{\partial x_1} \left( \frac{\partial G}{\partial x_1} - \frac{\partial G}{\partial x_2} \right) + i \frac{\partial}{\partial x_2} \left( \frac{\partial G}{\partial x_1} - \frac{\partial G}{\partial x_2} \right) = 0
\end{aligned} \tag{A19c}$$

Since  $f(x)$  has to be continuous for  $x$ , and since  $f(x)$  represents first derivatives of the Gibbs free energy with respect to  $r_1, r_2, x_1$ , and  $x_2$ , the order-disorder transition cannot be a first-order phase transition. At the order-disorder transition, equilibrium requires that

$$r_1 = r_2 = 0, \quad x_1 = x_2 \quad [\text{A20}]$$

Substitution of  $G$  according to Eq. [A14] and of Eq. [A20] in Eqs. [A19] yields a description of the order-disorder transition. It is obtained that

$$g = 0.5, \quad h = i,$$

$$x_{1,i} = x_{2,i} = \frac{1}{2} \left( 1 \pm \sqrt{1 + \frac{4kT}{2W_c + W_p - W_{pc}}} \right) \quad [\text{A21}]$$

where  $x_{1,i}$  and  $x_{2,i}$  are  $x_1$  and  $x_2$  respectively, at the order-disorder transition. Hence, ordering occurs for  $(1 - \alpha) < x_1 + x_2 < (1 + \alpha)$  with  $\alpha = \sqrt{1 + 4kT/(2W_c + W_p - W_{pc})}$ . In Eq. [A21] (and in  $\alpha$ ), the influence of the third nearest-neighbor exchange energy  $W_{pc}$  (due to interactions A1-B2, A1-C2, etc.) on the order-disorder transition is also taken into account (Section III-A). At the onset of ordering, the evolution of the  $r_1$  and  $r_2$  are coupled through  $g$ , and the evolution of the interstitial contents  $x_1$  and  $x_2$  are coupled through  $h$  and  $i$ . The results of Eq. [A21] are identical to the results of Eq. [7] for case (2) as expected.

### Configuration B

#### Gibbs free energy, chemical potential, and equilibrium condition

Proceeding analogously, as for configuration A, expressions are obtained for the configurational entropy of the I atoms on their sublattice and for the enthalpies associated with pairwise interactions of I atoms in the  $c$ -direction as well as within the (001) planes of the I sublattice. Then, including the interaction between the M and I sublattices, the Gibbs free energy  $G_{M-I}$  for a pair of (001) planes and the associated pair of planes of M atoms is obtained as (cf. Eq. [A14])

$$\begin{aligned} \frac{1}{2} G_{M-I} = & (H_M^0 - TS_{\text{vib},M}^0) + \left[ \frac{2}{3} x_{iv} + \frac{1}{3} x_d \right] (H_I^0 - TS_{\text{vib},I}^0 + H_{M_I}^0) \\ & + \left[ \left( \frac{2}{3} - \frac{2}{3} x_{iv} \right) + \left( \frac{1}{3} - \frac{1}{3} x_d \right) \right] (H_V^0 - TS_{\text{vib},V}^0 + H_{M_V}^0) \\ & + NW_c \left[ \frac{2}{3} x_{iv}(1 - x_{iv}) + \frac{1}{3} x_d(1 - x_d) \right] + NW_c \frac{2}{3} (x_{iv}r)^2 \\ & + NW_p \left[ \frac{1}{3} x_{iv}(1 - x_{iv}) + \frac{1}{3} x_{iv}(1 - x_d) + \frac{1}{3} x_d(1 - x_{iv}) \right] \\ & + NW_p \frac{1}{3} (x_{iv}r)^2 + \frac{1}{3} NkT \{ [(1+r)x_{iv}] \ln [(1+r)x_{iv}] \\ & + [1 - (1+r)x_{iv}] \ln [1 - (1+r)x_{iv}] \\ & + [(1-r)x_{iv}] \ln [(1-r)x_{iv}] \\ & + [1 - (1-r)x_{iv}] \ln [1 - (1-r)x_{iv}] \\ & + [x_d] \ln [x_d] + [1 - x_d] \ln [1 - x_d] \} \quad [\text{A22}] \end{aligned}$$

The Gibbs free energy  $G_{M-I}$  of the M-I alloy in general can be related to chemical potentials  $\mu_M, \mu_I^i, \mu_V^i, \mu_I^d$ , and  $\mu_V^d$  of M and I and V for  $iv$  and  $d$  sites, respectively:

$$\begin{aligned} G_{M-I} = & 2 \left\{ \mu_M + \frac{2}{3} x_{iv} \mu_I^i + \left( \frac{2}{3} - \frac{2}{3} x_{iv} \right) \mu_V^i \right. \\ & \left. + \frac{1}{3} x_d \mu_I^d + \left( \frac{1}{3} - \frac{1}{3} x_d \right) \mu_V^d \right\} \quad [\text{A23}] \end{aligned}$$

where the chemical potentials pertain to  $N$  atoms (M, I, V), while the Gibbs free energy pertains to  $2N$  atoms of M and  $[(4/3)x_{iv} + (2/3)x_d]N$  atoms of I. If V represents vacant I sites, it holds that  $\mu_V^i = \mu_V^d \equiv 0$ . For equilibrium, the chemical potentials of I on the order ( $i$  and  $v$ ) and disorder ( $d$ ) sites, where the two contents  $x_{iv}$  and  $x_d$  refer to, have to be identical. It thus holds that (cf. Eqs. [A16] and [A17])

$$\mu_I^i = \mu_I^d \equiv \mu_I \Rightarrow \frac{\partial G_{M-I}}{2 \partial x_{iv}} - \frac{\partial G_{M-I}}{1 \partial x_d} = 0 \quad [\text{A24}]$$

The degree of order  $r$  will take a value corresponding with the minimum value (stable state) for the Gibbs free energy according to Eq. [A22]. Hence,

$$\frac{\partial G_{M-I}}{\partial r} = 0 \quad [\text{A25}]$$

Thermodynamical equilibrium of the M-I alloy is described by the Gibbs free energy given by Eq. [A22] subject to the equilibrium conditions according to Eqs. [A24] and [A25]. The equations for the equilibrium conditions obtained in this way are nonlinear with respect to the variables  $x_{iv}, x_d$ , and  $r$ . The numerical evaluation method for solving these equations is given in Appendix B.

#### Order-disorder transition

A description of the order-disorder transition for configuration B can be obtained in a similar way as for configuration A. Now, instead of three equilibrium conditions with four parameters, there are only two conditions with three parameters. Of course, the same order-disorder transition is found, as expressed by Eq. [7] for case (2) (Section III-A) and by Eq. [A21]. No fixed interdependence exists for the evolutions of  $x_{iv}, x_d$ , and  $r$  at the onset of ordering in contrast with the evolutions of  $x_1, x_2, r_1$ , and  $r_2$  at the onset of ordering, according to Eq. [A21] for configuration A.

## APPENDIX B

### Numerical evaluation method for route 1

For the numerical evaluation of the cases of ordering evolving from the six nonlinear equations that make up Eq. [3], the following route can be conveniently followed. For a particular combination of the values for  $W_c/kT, W_p/kT$ , and  $W_{pc}/kT$ , Figure 2 indicates the most stable configuration and the values for  $f \dots j$  to be considered. From Eqs. [7] and [8],  $x_i$  is obtained. Using

one of the six equations of Eq. [3], the value for  $(\mu_1 - \mu_1^0)/kT$  for the order disorder transition can now be calculated. By a small variation of this value for  $(\mu_1 - \mu_1^0)/kT$ , the region where ordering occurs is entered. Next, a guess is made for the corresponding change of one of the  $x_k$ 's with respect to  $x_i$ . The values for  $f \dots j$  now provide (estimates for) the change of the occupancies of the other kinds of I sites with respect to  $x_i$ . Then, at equilibrium and for the chosen value of  $(\mu_1 - \mu_1^0)/kT$ , the real values for  $x_{A1}, \dots, x_{C2}$  can be obtained from the six equations that make up Eq. [3] by an iterative numerical method (e.g., Newton-Raphson<sup>[16]</sup>). Subsequent stepwise variation of the value for  $(\mu_1 - \mu_1^0)/kT$  allows investigation over the whole composition range of the M-I alloy, where the values of  $x_{A1}, \dots, x_{C2}$  obtained in the preceding step are used as initial guesses for the step considered.

#### Numerical evaluation method for route 2

For a particular combination of values for  $W_c/kT$ ,  $W_p/kT$  and  $W_{pc}/kT$ , the minimum content for ordering  $x_i$  is obtained from Eq. [A21]. Then, one of the interstitial content variables,  $x_1$  for configuration A and  $x_{iv}$  for configuration B, is raised to a value just above  $x_i$ . Next, for configuration A, the three nonlinear equilibrium conditions (Eqs. [A17] and [A18]) are used to calculate the values of  $x_2, r_1$ , and  $r_2$  pertaining to the chosen value of  $x_1$  in an iterative manner applying the Newton-Raphson method, where initial guesses for  $x_2, r_1$ , and  $r_2$  were taken such that  $x_2 = x_1$  and  $r_1 = 2r_2$  (cf. Eq. [A21]). For configuration B, the two nonlinear equilibrium conditions (Eqs. [A24] and [A25]) are used to calculate the values of  $x_d$  and  $r$  pertaining to the chosen value of  $x_{iv}$  in a similar manner. Investigation of the entire composition range of the M-I(V) alloy is realized by a stepwise increase (by a small amount) of the value of  $x_1$  for configuration A and the value of  $x_{iv}$  for configuration B; for a particular step, the values of  $x_2, r_1$ , and  $r_2$  for configuration A and of  $x_d$  and  $r$  for configuration B obtained in the preceding step are used as initial guesses for application of the Newton-Raphson procedure.

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