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1967-05-01

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Research and Development

UCRL-17462

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

VACANCY MODELS FOR CONCENTRATED BINARY ALLOYS

Ching-Yao Cheng

Ph.D. Thesis

April, 1967

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VACANCY MODELS FOR CONCENTRATED BINARY ALLOYS

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March, 1967

PREFACE

Theoretical studies have been made on the effect of ordering or clustering on the equilibrium concentration of vacancies in binary alloys. Four models for estimating this effect are developed in terms of statistical thermodynamics. Part A presents the effect of short-range ordering or clustering on the equilibrium vacancy concentrations. Part B discusses the effect of long-range ordering on the equilibrium number of vacancies in binary alloys with $L2_0$ (b.c.c.) or $L1_2$ (f.c.c.) lattice.

PART A

SHORT-RANGE ORDERED AND CLUSTERED ALLOYS

ABSTRACT

Four models (Smeared-Displacement, Simple-Displacement, Modified Vacancy-Energy and Vacancy-Energy Models) for estimating the effect of short-range ordering (or clustering) on the equilibrium concentration of vacancies in binary alloys are developed in terms of statistical thermodynamics. The Smeared-Displacement, Simple-Displacement and Modified Vacancy-Energy Models assume that the energy to produce a vacancy can be estimated from the change in bond energy when an atom is displaced from the bulk of the crystal to the surface. Each model differs, however, relative to the details of the environment about vacancies that are taken into consideration. All such models suggest that the vacancy concentration decreases as a result of ordering. The Vacancy-Energy Model is physically more realistic and more detailed but somewhat less tractable than the other models. It assumes that the free energy to produce a vacancy depends primarily on the immediate environment of the vacancy.

I. INTRODUCTION

Vacancies (vacant lattice sites) are crystalline irregularities of atomic dimensions. These simple imperfections are expected to play the same important role during diffusion, creep, sintering and other kinetic phenomena in concentrated alloys that undertake ordering or clustering as they do in pure metals and dilute alloys. Before such processes can be described in detail for ordered alloys, however, it is necessary to gain some understanding of the equilibrium number and distribution of vacancies as a function of the ordered state. In fact, until a satisfactory theory for equilibrium distribution of vacancies in such alloys is formulated, it may not be readily possible to design appropriate experiments for determination of the factors that might affect the equilibrium concentration of vacancies. Stimulated by this need, several models have recently been described for vacancy concentration in long-range ordered alloys.¹⁻³ As far as the present author is aware, however, there has been no announcement of vacancy models for short-range ordered or clustered alloys.

An accurate procedure for accounting for the number of statistical states in three dimensional alloys has yet to be developed. The same difficulties intrude, with perhaps even greater import, in any sophisticated attempt to describe the statistical thermodynamics of vacancies in real binary alloys. Until such difficulties in accounting are surmounted, it will be necessary to employ less rigorous techniques which hopefully will not do too much violence to the physical facts. In this more modest vein we shall consider, here, four models which emphasize various factors that are indigenous to an understanding of equilibrium concentration

of vacancies in concentrated alloys. The usual but somewhat naive nearest-neighbor atom bond-energy assumption will be adopted for all models. In the Smeared-Displacement, Simple-Displacement and Modified Vacancy-Energy Models the energy to produce vacancies will be determined in terms of the energies of the broken bonds. A more detailed and physically more acceptable designation will be made for the energies to produce vacancies in the Vacancy-Energy Model. These models will be compared with one another and their deficiencies and virtues will be discussed.

II. TERMINOLOGY AND PRELIMINARY CONSIDERATION

The alloys will contain A and B atoms plus various distinguishable types of vacancies, V, where

n_k = number of species where $k = A$ or B (atoms) or V (vacancies)

n_S = total number of lattice sites

z = coordination number

N_k = atomic fraction of k^{th} atomic species

p_{kj} = probability that the k^{th} species is coordinated about the j^{th} species where $k = A, B, V$ and $j = A, B, V$

$\epsilon_{AA}, \epsilon_{AB}, \epsilon_{BB}$ = bond energies.

The bond energies will be taken as zero when the atoms are an infinite distance apart and therefore they have negative values for the stable crystal. The change in energy for the bond reaction $1/2 A - A + 1/2 B - B \rightarrow A - B$ is

$$\epsilon = \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \quad (1)$$

where ϵ is the ordering energy and has a negative value when the alloy orders and a positive value when it clusters.

Another convenient way of characterizing short-range ordering or clustering is expressed in terms of Cowley's⁴ short-range order parameter, α , which is defined as

$$\alpha = 1 - \frac{p_{AB}}{N_A} = 1 - \frac{p_{BA}}{N_B} \quad (2a)$$

When the distribution of A and B atoms in a solid solution is completely

random, the probability p_{AB} that a given neighbor of a B atom is an A atom is just the atomic fraction N_A of A atoms in the alloy. That is, $p_{AB}/N_A = 1$. The amount α by which this ratio differs from unity in a given case is a useful measure of the departure of a solid solution from randomness. There are two possible departures from $\alpha = 0$, the value for a random solution. If B atoms group themselves preferentially around other B atoms, then p_{AB} is less than N_A and α is positive. This behavior is called clustering in the solid solution. On the other hand, if a given B atom is preferentially surrounded by A atoms, α is negative and the solid solution is said to show short-range ordering.

Either Cowley's⁴ or Bethe's⁵ short-range order theory could be employed here. In order to provide a common basis for comparison, however, all four models will be described exclusively in terms of Cowley's theory, subject to the limitation of considering only nearest-neighbor interactions. Accordingly there are nine probabilities, p_{kj} , and such probabilities are interrelated by the three equations:

$$p_{AA} + p_{BA} + p_{VA} = 1 \quad (3a)$$

$$p_{AB} + p_{BB} + p_{VB} = 1 \quad (3b)$$

$$p_{AV} + p_{BV} + p_{VV} = 1 \quad (3c)$$

The conservation of the number of each type of bonds further requires that

$$z_n p_{AB} = z_n p_{BA} \quad (4a)$$

$$zn_A p_{VA} = zn_V p_{AV} \quad (4b)$$

$$zn_B p_{VB} = zn_V p_{BV} \quad (4c)$$

Cowley's degree of short-range order will be redefined to take vacancies into consideration as

$$\alpha = 1 - \frac{p_{AB}}{\frac{n_A}{n_A + n_B + n_V}} = 1 - \frac{p_{BA}}{\frac{n_B}{n_A + n_B + n_V}} \quad (2b)$$

But inasmuch as n_V will always be very small relative to $n_A + n_B$, the change in Cowley's degree of order due exclusively to vacancies will also be negligibly small. Thus

$$p_{AB} \approx N_A (1 - \alpha) \quad (5a)$$

$$p_{BA} \approx N_B (1 - \alpha) \quad (5b)$$

$$p_{AA} \approx 1 - p_{BA} = N_A + \alpha N_B \quad (5c)$$

$$p_{BB} \approx 1 - p_{AB} = N_B + \alpha N_A \quad (5d)$$

III. SMEARED-DISPLACEMENT MODEL

This model is essentially the short-range order analogue of the model proposed by Krivoglaz and Smirnov² for vacancies in long-range ordered alloys. It is based on the approximation that only nearest neighbors interact and that the energy to produce a vacancy can be equated to the energy change required to break z bonds and remake $z/2$ bonds when an atom is displaced from the interior of the crystal and placed on the surface thus leaving a vacancy on its original sites. Since the number of divacancies will always be small relative to the total number of vacancies, $p_{VV} \approx 0$ and Eqs. (3) and (4) reduce to

$$p_{AA} + p_{BA} + p_{VA} = 1 \quad (6a)$$

$$\frac{n_A}{n_B} p_{BA} + p_{BB} + p_{VB} = 1 \quad (6b)$$

$$n_A p_{VA} + n_B p_{VB} = n_V \quad (6c)$$

Because there are five variables in the three Eqs. (6), the analysis can be based on two independent variables. It will prove analytically more convenient, however, to replace n_V by its equivalent value given in Eq. (6c) and employ the method of undetermined Lagrangian multipliers to introduce the restrictions of Eqs. (6a) and (6b).

The configurational bond energy of the alloy is simply

$$E_c = \frac{z}{2} (n_A p_{AA} \epsilon_{AA} + 2n_A p_{BA} \epsilon_{AB} + n_B p_{BB} \epsilon_{BB}) \quad (7)$$

since the free bond extending toward a vacant site always has zero energy in this kind of a model. Using the approximation of Cowley's first coordination sphere and including the coordinated vacancies suggests that the ways of mixing atoms is proportional to $\Omega_A \Omega_B \Omega_V$ where

$$\Omega_A = \left[\frac{z!}{(z p_{AA})! (z p_{BA})! (z p_{VA})!} \right]^{\frac{n_A}{z}} \quad (2a)$$

$$\Omega_B = \left[\frac{z!}{(z p_{AB})! (z p_{BB})! (z p_{VB})!} \right]^{\frac{n_B}{z}} = \left[\frac{z!}{\left(\frac{z n_A}{n_B} p_{BA}\right)! (z p_{BB})! (z p_{VB})!} \right]^{\frac{n_B}{z}} \quad (8b)$$

$$\Omega_V = \left[\frac{z!}{(z p_{AV})! (z p_{BV})! (z p_{VV})!} \right]^{\frac{n_V}{z}} = \left[\frac{z!}{\left(\frac{z n_A p_{VA}}{n_A p_{VA} + n_B p_{VB}}\right)! \left(\frac{z n_B p_{VB}}{n_A p_{VA} + n_B p_{VB}}\right)! 0!} \right]^{\frac{n_A p_{VA} + n_B p_{VB}}{z}} \quad (8c)$$

and where the second equalities follow from Eqs. (4) and (6). The powers n_A/z etc. appear in these expressions because each atom is introduced z times in the contemplated mixing. Since, however, the n_A A atoms with their surroundings cannot be mixed independently of the n_B B atoms with their surroundings, the total ways of mixing is approximately proportional to but does not equal $\Omega_A \Omega_B \Omega_V$. For example, in a vacancy free alloy, the ways with which A and B atoms can be mixed at random is

$$[\Omega_{AB}]_R = \frac{(n_A + n_B)!}{n_A! n_B!} \quad (9a)$$

whereas the ways suggested above are

$$[\Omega_A \Omega_B]_R = \left[\frac{z!}{(zN_A)!(zN_B)!} \right]^{\frac{n_A}{z}} \left[\frac{z!}{(zN_A)!(zN_B)!} \right]^{\frac{n_B}{z}} \quad (9b)$$

The entropy for mixing atoms and vacancies in a short-range ordered binary alloy is given by

$$S = k \ln \Omega \quad (10a)$$

where from Eqs. (8) and (9) Ω is closely approximated by

$$\Omega = \Omega_A \cdot \Omega_B \cdot \Omega_V \frac{[\Omega_{AB}]_R}{[\Omega_A \cdot \Omega_B]_R} \quad (10b)$$

Since the changes in thermal entropy are small they will be neglected here. The configurational Helmholtz free energy is

$$F_c = E_c - TS_c \quad (11)$$

which is now expressed in terms of the five variables p_{AA} , p_{BA} , p_{VA} , p_{BB} and p_{VB} , that are related by the Eqs. (6a) and (6b). Using $kT \ln \lambda_A$ and $kT \ln \lambda_B$ as Lagrangian multipliers where λ_A and λ_B are the activities of the A and B atoms respectively, the two zeros deduced from Eqs. (6a) and (6b), namely

$$-kT \ln \lambda_A (p_{AA} + p_{BA} + p_{VA} - 1) = 0 \quad (12a)$$

and

$$-kT \ln \lambda_B \left(\frac{n_A}{n_B} p_{BA} + p_{BB} + p_{VB} - 1 \right) = 0 \quad (12b)$$

can be added directly to Eq. (11). Minimizing the resulting expression with respect to each of the now independently variable quantities, gives the results,

$$p_{AA} = \frac{1}{e} \lambda_A \frac{1}{n_A} e^{-\frac{z\epsilon_{AA}}{2kT}} \quad (13a)$$

$$p_{BB} = \frac{1}{e} \lambda_B \frac{1}{n_B} e^{-\frac{z\epsilon_{BB}}{2kT}} \quad (13b)$$

$$p_{BA} = \frac{1}{e} \left(\frac{n_B}{n_A}\right)^{\frac{1}{2}} \lambda_A \frac{1}{2n_A} \lambda_B \frac{1}{2n_B} e^{-\frac{z\epsilon_{AB}}{2kT}} \quad (13c)$$

$$p_{VA} = \frac{1}{e} \lambda_A \frac{1}{n_A} + \frac{1}{e} \left(\frac{n_B}{n_A}\right)^{\frac{1}{2}} \lambda_A \frac{1}{2n_A} \lambda_B \frac{1}{2n_B} \quad (13d)$$

$$p_{VB} = \frac{1}{e} \lambda_B \frac{1}{n_B} + \frac{1}{e} \left(\frac{n_A}{n_B}\right)^{\frac{1}{2}} \lambda_A \frac{1}{2n_A} \lambda_B \frac{1}{2n_B} \quad (13e)$$

Consequently, from Eqs. (13a), (13b) and (13c)

$$\frac{p_{BA}^2}{p_{AA}p_{BB}} = \frac{n_B}{n_A} e^{\frac{z(\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB})}{2kT}} \quad (14)$$

Since the vacancy concentrations are small, the probabilities can be expressed very accurately in terms of Eqs. (5). Therefore

$$\frac{(1 - \alpha)^2}{\left(\frac{N_A}{N_B} + \alpha\right) \left(\frac{N_B}{N_A} + \alpha\right)} = e^{-\frac{z\epsilon}{kT}} \quad (15)$$

which is the equilibrium equation for the Cowley theory in the absence of vacancies. Obviously vacancies do not significantly alter the all-over degree of order.

Introducing Eqs. (13a), (13b), (13d) and (13e) into Eq. (6c) in such a way as to eliminate the activities, gives the vacancy concentration as

$$\begin{aligned} \frac{n_v}{n_A + n_B} = & N_A^2 e^{-\frac{z\epsilon_{AA}}{2kT}} + 2N_A N_B e^{-\frac{z\epsilon_{AB}}{2kT}} + N_B^2 e^{-\frac{z\epsilon_{BB}}{2kT}} \\ & + \alpha N_A N_B \left(e^{-\frac{z\epsilon_{AA}}{2kT}} + e^{-\frac{z\epsilon_{BB}}{2kT}} - 2 e^{-\frac{z\epsilon_{AB}}{2kT}} \right) \end{aligned} \quad (16)$$

IV. SIMPLE-DISPLACEMENT MODEL

This vacancy model is an internally consistent short-range ordering analogue of that proposed by Girifalco³ for long-range ordered alloys. It also assumes that only nearest neighbors interact and that the energy to produce a vacancy might be equated to the energy required to break z bonds when an atom is displaced from the lattice and to remake $z/2$ bonds when this atom is placed at a point on the surface consistent with the existing degree of order. Two identifiable types of vacancies, however, exist in this case, namely $n_V^{(A)}$ and $n_V^{(B)}$ which result from the replacement of either an A atom or a B atom by the vacancy. Thus the configurational energy change upon introduction of $n_V^{(A)}$ and $n_V^{(B)}$ vacancies is

$$\Delta E_c = -\frac{z}{2} (p_{AA}\epsilon_{AA} + p_{BA}\epsilon_{AB}) n_V^{(A)} - \frac{z}{2} (p_{AB}\epsilon_{AB} + p_{BB}\epsilon_{BB}) n_V^{(B)} \quad (17)$$

since the $n_V^{(A)}$ and $n_V^{(B)}$ vacancies are taken to be distributed at random over sites formerly occupied only by n_A A atoms and n_B B atoms respectively. The configurational entropy change is

$$\Delta S_c = k \ln \frac{(n_A + n_V^{(A)})!}{n_A! n_V^{(A)}!} \cdot \frac{(n_B + n_V^{(B)})!}{n_B! n_V^{(B)}!} \quad (18)$$

Neglecting, in this model, the small change in thermal entropy, the Helmholtz free energy is

$$F(\alpha, n_V^{(A)}, n_V^{(B)}) = F(\alpha, 0, 0) + \Delta E_c - T\Delta S_c \quad (19)$$

where α here refers to Cowley's degree of order in the absence of vacancies.

Therefore, the equilibrium numbers of vacancies are directly determined by minimizing $F(\alpha, n_V^{(A)}, n_V^{(B)})$ with respect to $n_V^{(A)}$ and also $n_V^{(B)}$, giving

$$\begin{aligned} \frac{n_V^{(A)}}{n_A + n_B} &= N_A e^{\frac{z}{2kT} (p_{AA}\epsilon_{AA} + p_{BA}\epsilon_{AB})} \\ &= N_A e^{\frac{z}{2kT} [N_A\epsilon_{AA} + N_B\epsilon_{AB} + \alpha N_B(\epsilon_{AA} - \epsilon_{AB})]} \end{aligned} \quad (20a)$$

and the symmetrical expression

$$\begin{aligned} \frac{n_V^{(B)}}{n_A + n_B} &= N_B e^{\frac{z}{2kT} (p_{AB}\epsilon_{AB} + p_{BB}\epsilon_{BB})} \\ &= N_B e^{\frac{z}{2kT} [N_B\epsilon_{BB} + N_A\epsilon_{AB} + \alpha N_A(\epsilon_{BB} - \epsilon_{AB})]} \end{aligned} \quad (20b)$$

The total vacancy concentration is given by the sum of Eqs. (20a) and (20b), namely:

$$\begin{aligned} \frac{n_V}{n_A + n_B} &= \frac{n_V^{(A)} + n_V^{(B)}}{n_A + n_B} = N_A e^{\frac{z}{2kT} [N_A\epsilon_{AA} + N_B\epsilon_{AB} + \alpha N_B(\epsilon_{AA} - \epsilon_{AB})]} \\ &\quad + N_B e^{\frac{z}{2kT} [N_B\epsilon_{BB} + N_A\epsilon_{AB} + \alpha N_A(\epsilon_{BB} - \epsilon_{AB})]} \end{aligned} \quad (20c)$$

V. VACANCY-ENERGY MODEL

This model is based on the concepts originally introduced by Lomer⁶ for vacancies in extremely dilute solutions and extended more recently by Dorn and Mitchell⁷ to include vacancies over wide ranges of composition in regular solutions of binary alloys.

Undoubtedly the energy of a vacancy depends principally on its immediate environment in the alloy lattice. In the following we assume that the free energy of formation of a vacancy depends only on the kind and arrangement of the atoms coordinated directly with that vacancy. Thus g_{ic} is defined as the free energy of formation of a vacancy which is coordinated with i B atoms and $(z - i)$ A atoms. The subscript c refers to each unique configuration of the A and B atoms about the vacancy. For example, in the b.c.c. lattice for $i = 2$ the three types of arrangements (a, b, c) of A and B atoms about a vacancy shown in Fig. 1 are possible. As indicated, each arrangement has a unique energy of formation of a vacancy. In general the number of g_{ic} s is extremely high. Although the complete details can be incorporated into the analysis it appears desirable here to let g_i be a mean weighted-average value over all configurations c for vacancies of the i^{th} kind. Even then there yet remain $z + 1$ individual values of g_i to be considered. It appears unlikely that these $z + 1$ values of g_i , excepting of course g_0 and g_z , might be calculated in the near future from first principles. Consequently the individual values of g_i will have to be evaluated by comparison of appropriate experimental results on vacancy concentrations with deductions based on the proposed thermodynamic theory.

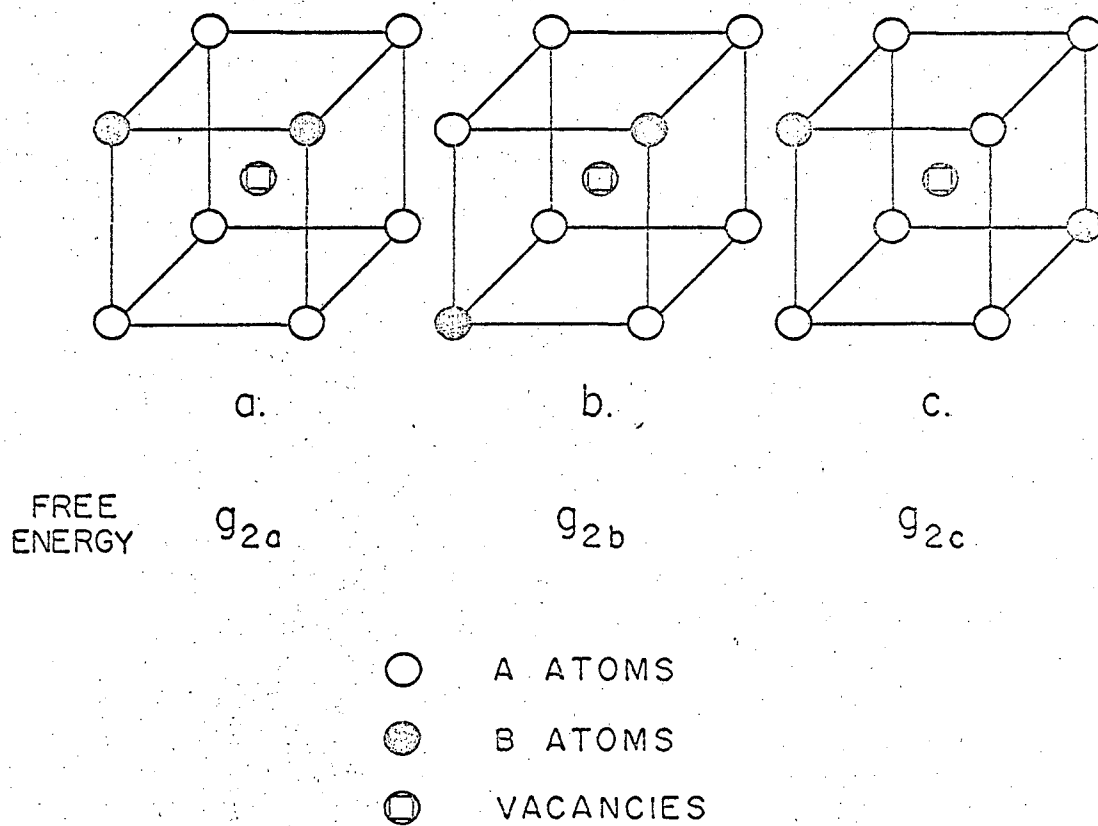


FIG. 1. ARRANGEMENTS OF SIX A ATOMS
 AND TWO B ATOMS ABOUT VACANCIES
 IN THE b.c.c. LATTICE.

Admittedly the neglect of the effect of second nearest neighbors etc. of a vacancy on the value of g_i is made solely for the sake of simplicity. More sophisticated assumptions interpose insurmountable handicaps to any analysis at this time. Furthermore, this assumption is probably no more at odds with the physical facts than the very useful and equivalent assumption of nearest-neighbor bond energies that is so helpful in rationalizing, at least qualitatively, many phenomena on ordering in alloys.

In order to illustrate the method of analysis we propose to derive again the relationship given by Dorn and Mitchell⁷ for random alloys employing, in this example, a new and simpler approach than they originally used. For this purpose we consider first a regular solution without vacancies. Each term of the binomial expansions

$$(N_A + N_B)^z = \sum_{i=0}^z \frac{z!}{(z-i)!i!} N_A^{z-i} N_B^i = 1 \quad (21)$$

gives the probability that any given sites is coordinated with i B atoms and $(z - i)$ A atoms. Therefore, there are

$$n_{Li} = (n_A + n_B) \frac{z!}{(z-i)!i!} N_A^{z-i} N_B^i \quad (22)$$

lattice sites of the i^{th} kind surrounding which there are i B atoms and $(z - i)$ A atoms. At random on n_i of these sites we introduce vacancies of the i^{th} type each of which has a free energy of formation of g_i . We do this without otherwise disturbing the random arrangement of atoms by placing the atoms that have been removed from the new vacant sites on

appropriate equivalent sites on the surface. Thus the free energy change is closely given by

$$\Delta F = \sum_{i=0}^z n_i g_i - kT \ln \pi \frac{n_{Li}!}{n_i! (n_{Li} - n_i)!} \quad (23)$$

Minimizing the free energy relative to n_i , and noting that $n_i \ll n_{Li}$, gives the Dorn-Mitchell relationship

$$\frac{n_i}{n_s} \approx \frac{z!}{(z-i)! i!} N_A^{z-i} N_B^i e^{-\frac{g_i}{kT}} \quad (24)$$

The same technique is readily applied to short-range ordered or clustered alloys. Each term of the expansions

$$(p_{AA} + p_{BA})^z = \sum_{i=0}^z \frac{z!}{(z-i)! i!} p_{AA}^{z-i} p_{BA}^i = 1 \quad (25a)$$

$$(p_{AB} + p_{BB})^z = \sum_{i=0}^z \frac{z!}{(z-i)! i!} p_{AB}^{z-i} p_{BB}^i = 1 \quad (25b)$$

gives the probability of having i B atoms and $(z - i)$ A atoms about any A atom, Eq. (25a), and about any B atom, Eq. (25b), respectively. Thus the total number of lattice sites of the i^{th} kind surrounded by i B atoms and $(z - i)$ A atoms is

$$n_{Li} = (n_A p_{AA}^{z-i} p_{BA}^i + n_B p_{AB}^{z-i} p_{BB}^i) \frac{z!}{(z-i)! i!} \quad (26)$$

Whereas the configurational entropy of mixing n_i vacancies on these

sites, where $n_i \ll n_{Li}$, follows as given above for regular solutions, the free energy of formation of vacancies in the ordered alloy requires further consideration. This arises as a result of changes in lattice parameters, moduli of elasticity, average bond energies etc. that occur as a result of ordering. We therefore acknowledge that the free energy of formation of a vacancy of the i^{th} kind might change somewhat as the alloy orders from the value of g_i for the random case. To a first approximation we suspect that these changes are related to the changes in the average bond energy as a result of ordering. The average bond energy $\bar{\epsilon}$ is given by

$$\bar{\epsilon} = N_A p_{AA} \epsilon_{AA} + N_A p_{BA} \epsilon_{AB} + N_B p_{AB} \epsilon_{AB} + N_B p_{BB} \epsilon_{BB} \quad (27a)$$

Introducing Eqs. (5) reveals that

$$\bar{\epsilon} = N_A^2 \epsilon_{AA} + 2N_A N_B \epsilon_{AB} + N_B^2 \epsilon_{BB} - 2\alpha N_A N_B \epsilon \quad (27b)$$

where ϵ is the ordering energy. Thus, we suggest, in analogy to a Taylor's series, where only the first two terms are retained, that the free energy of formation of a vacancy of the i^{th} kind when the degree of order is α , might be approximated by $g_i + \alpha N_A N_B g'_i$ where g'_i is a constant free energy term and the second term represents a small correction for the changes induced as a result of ordering. This approximation gives the vacancy concentration in a short-range ordered or clustered alloy of

$$\frac{n_i}{n_S} = \frac{z!}{(z-i)!i!} (N_A p_{AA}^{z-i} p_{BA}^i + N_B p_{AB}^{z-i} p_{BB}^i) e^{-\frac{g_i + \alpha N_A N_B g'_i}{kT}} \quad (28a)$$

For the disordered case this relationship reduces to Eq. (24). When p_{AA} etc. are replaced by the degree of order, Eq. (28a) becomes

$$\frac{n_i}{n_S} = \frac{z!}{(z-i)!i!} \{N_A(N_A + \alpha N_B)^{z-i} [N_B(1-\alpha)]^i + N_B[N_A(1-\alpha)]^{z-i} (N_B + \alpha N_A)^i\} e^{-\frac{\epsilon_i + \alpha N_A N_B \epsilon_i}{kT}} \quad (28b)$$

VI. MODIFIED VACANCY-ENERGY MODEL

The Vacancy-Energy Model for equilibrium concentration of vacancies in binary alloys is based on rather good assumptions and should therefore rather accurately correspond with the experimental facts. On the other hand, its utility is seriously limited due to the numerous details that have been incorporated into analysis. For example, it appears unlikely that any experimental attempt will be made to deduce all of the $2(z + 1)$ terms of g_i and g'_i that are indigenous to the model. Furthermore, it is doubtful whether, if such an attempt were made, the set of $2(z + 1)$ numbers so obtained from simultaneous solution of the total vacancy concentration as a function of composition and temperature might reliably represent the physical quantities in question. These issues suggest that the energies to produce vacancies be represented by somewhat simpler and therefore more tractable terms. As a preliminary step in this direction we shall introduce a modified bond-energy concept for the formation energy of a vacancy where, for the present, we neglect the thermal entropy of formation of a vacancy.

As suggested by Eqs. (25a) and (25b) vacancies of the i^{th} kind might be visualized as produced by displacement of either A or B atoms from the lattice to the surface. For each A or B atom so displaced, the bond energy changes are $-[(z - i) \epsilon_{AA} + i \epsilon_{AB}]/2$ or $-[(z - i) \epsilon_{AB} + i \epsilon_{BB}]/2$ respectively. Accordingly, the equilibrium number of vacancies, created by displacing those A atoms (and B atoms) coordinated with i B atoms and $(z - i)$ A atoms, to the surface is given by

$$\frac{n_i^{(A)}}{n_A} = \frac{z!}{(z-i)!i!} p_{AA}^{z-i} p_{BA}^i e^{\frac{(z-i)\epsilon_{AA} + i\epsilon_{BA}}{2kT}} \quad (29a)$$

and by

$$\frac{n_i^{(B)}}{n_B} = \frac{z!}{(z-i)!i!} p_{AB}^{z-i} p_{BB}^i e^{\frac{(z-i)\epsilon_{AB} + i\epsilon_{BB}}{2kT}} \quad (29b)$$

respectively.

The total equilibrium number of vacancies of the i^{th} kind is simply

$$\begin{aligned} \frac{n_i}{n_S} = \frac{n_i^{(A)} + n_i^{(B)}}{n_S} &= \frac{z!}{(z-i)!i!} \left\{ N_A p_{AA}^{z-i} p_{BA}^i e^{\frac{(z-i)\epsilon_{AA} + i\epsilon_{BA}}{2kT}} \right. \\ &\quad \left. + N_B p_{AB}^{z-i} p_{BB}^i e^{\frac{(z-i)\epsilon_{AB} + i\epsilon_{BB}}{2kT}} \right\} \quad (30) \end{aligned}$$

Thus the total number of vacancies is given by

$$\begin{aligned} \frac{n_V}{n_S} &= \sum_{i=0}^z \frac{n_i}{n_S} = N_A \left\{ p_{AA} e^{\frac{\epsilon_{AA}}{2kT}} + p_{BA} e^{\frac{\epsilon_{BA}}{2kT}} \right\}^z \\ &\quad + N_B \left\{ p_{AB} e^{\frac{\epsilon_{AB}}{2kT}} + p_{BB} e^{\frac{\epsilon_{BB}}{2kT}} \right\}^z \\ &= N_A \left\{ (N_A + \alpha N_B) e^{\frac{\epsilon_{AA}}{2kT}} + N_B (1-\alpha) e^{\frac{\epsilon_{BA}}{2kT}} \right\}^z \\ &\quad + N_B \left\{ N_A (1-\alpha) e^{\frac{\epsilon_{AB}}{2kT}} + (N_B + \alpha N_A) e^{\frac{\epsilon_{BB}}{2kT}} \right\}^z \quad (31) \end{aligned}$$

VII. DISCUSSION

The vacancy models for short-range ordered or clustered alloys that were presented in the preceding sections were based on a number of common simplifying assumptions: (1) The energy was taken to depend only on nearest-neighbor atomic interactions and the longer range potentials were neglected, (2) Since exact accounting methods have not yet been developed for alloys on three-dimensional lattices, the configurational entropy, even for the vacancy free lattice was calculated by standard approximate methods.

The major problem encountered in the formulation of the various models concerned whether the presence of vacancies might not, at least locally, change the degree of order. The results on the Smeared-Displacement Model reveal that vacancies did not materially affect the all-over degree of order; but in the Simple-Displacement and the Vacancy-Energy Models the assumption was tacitly made that the local as well as the all-over degree of order was not affected by vacancies. Detailed accounting of bond energies showed that if the local order near vacancies were changed, the energy of formation of vacancies would also have to be charged with such local reordering energy. For alloys that normally order or cluster, such changes in local order so greatly increases the energy to produce a vacancy that it appears highly improbable that vacancies cause even local reordering. Consequently the assumption that local reordering does not take place in the vicinity of vacancies appears to be quite good.

Undoubtedly the energy of formation of a vacancy depends principally on its immediate surroundings. Using the technique that was adopted in

the Smeared-Displacement Model, however, such unique designation is not possible. Not only does this model give an energy of formation of smeared vacancies but also a somewhat questionable configurational entropy of mixing vacancies on the lattice sites.

In the Simple-Displacement Model, a somewhat more detailed inspection was made of the problem. Each A atom was assumed to be coordinated, on the average, with $z p_{AA}$ and $z p_{BA}$ atoms of type A and B respectively, with similar accountings for atoms surrounding each B atom. Thus a more appropriate, less drastically smeared energy of formation of individual vacancies could be calculated. Furthermore, a much more realistic, less drastically smeared configurational entropy of mixing vacancies on somewhat more uniquely defined lattice sites could be estimated.

Although Eqs. (16) and (20c) for the Smeared-Displacement Model and the Simple-Displacement Model respectively appear to be significantly different they nevertheless lead to almost identical results. For example, at high temperatures where the arguments of the exponential are much less than one, it can be readily shown that both Eqs. (16) and (20c) reduce to

$$\frac{n_V}{n_S} \approx e^{\frac{z}{2kT} (N_A^2 \epsilon_{AA} + 2N_A N_B \epsilon_{AB} + N_B^2 \epsilon_{BB} - 2\alpha N_A N_B \epsilon)} = e^{\frac{z\bar{\epsilon}}{2kT}} \quad (32)$$

The similarity of deductions based on these two models is illustrated in Fig. 2 for the conditions $z = 8$, $N_A = N_B = 1/2$ and $\epsilon_{AA} = \epsilon_{BB}$. Such agreement confirms at least the nominal validity of the assumption that the local distribution of atoms about an atom remains unchanged when that atom is replaced by a vacancy. This assumption was inherent to the Simple-

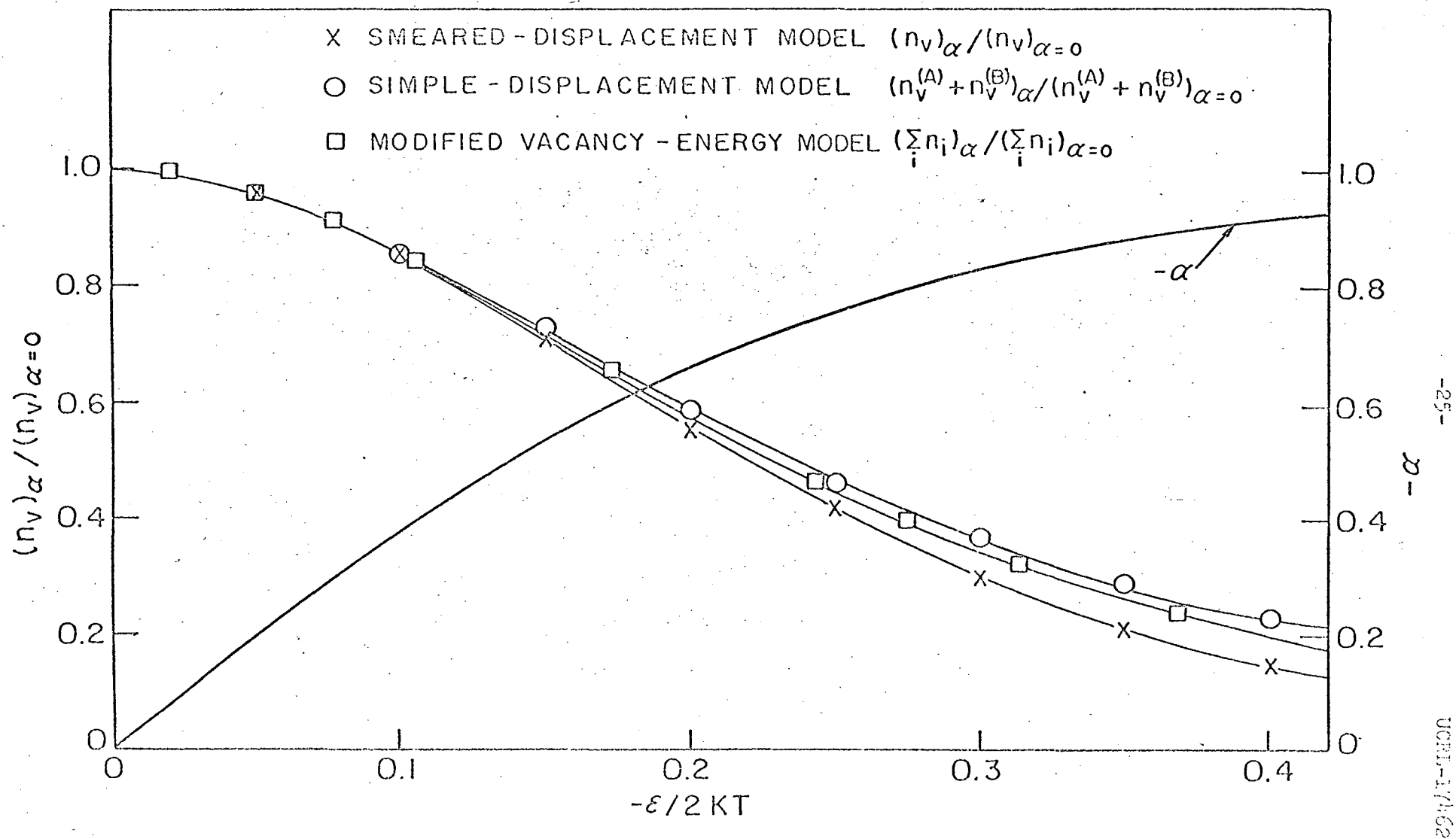


FIG. 2. TEMPERATURE EFFECT ON THE EQUILIBRIUM VACANCY CONCENTRATIONS AND THE SHORT-RANGE ORDER PARAMETER FOR THE CASE $N_A = N_B = \frac{1}{2}$, $\epsilon_{AA} = \epsilon_{BB}$ AND $Z=8$.

Displacement Model but was not made in the Smeared-Displacement Model. As shown in Fig. 2, over the range of $-\epsilon/2kT$ where $-\alpha$ increases, the ratio of the total vacancy concentration in the ordered alloy to that which would have been obtained for the same alloy in the disordered state decreases rather effectively. This expected trend is due to the greater energy of formation of vacancies, on the bond-energy model, with increasing degrees of order. The same results apply to clustering where both ϵ and α have positive values.

As shown in Fig. 2, the Modified Vacancy-Energy Model also follows the same trends and at high temperatures it predicts the same result because Eq. (31) reduces to Eq. (32). Here the additional assumption that $N_0 \epsilon_{AB} = -14.50$ kcal and $N_0 \epsilon_{AA} = N_0 \epsilon_{BB} = -14.15$ kcal, where N_0 is Avogadro's number, was made for the Modified Vacancy-Energy Model. This model, however, has the added virtue of providing the additional details on the types of vacancies that are present which are so important for consideration of diffusion mechanisms. As shown in Fig. 3, when the degree of order ($-\alpha$) increases, the ratio of the number of various specific types of vacancies in the ordered alloy to those in the alloy if it had not ordered changes. This ratio increases for $i = 0$ and 8 etc. and decreases for $i = 4$ etc. Furthermore, this model gives the additional information on the distribution of the various types of vacancies for a given temperature. For example, as shown in Fig. 4, at high temperatures the $i = 4$ type of vacancy is the most populous type of vacancy but at low temperatures its concentration becomes almost negligible. At low temperatures it is seen that $i = 0$ and 8 types of vacancies are predominant.

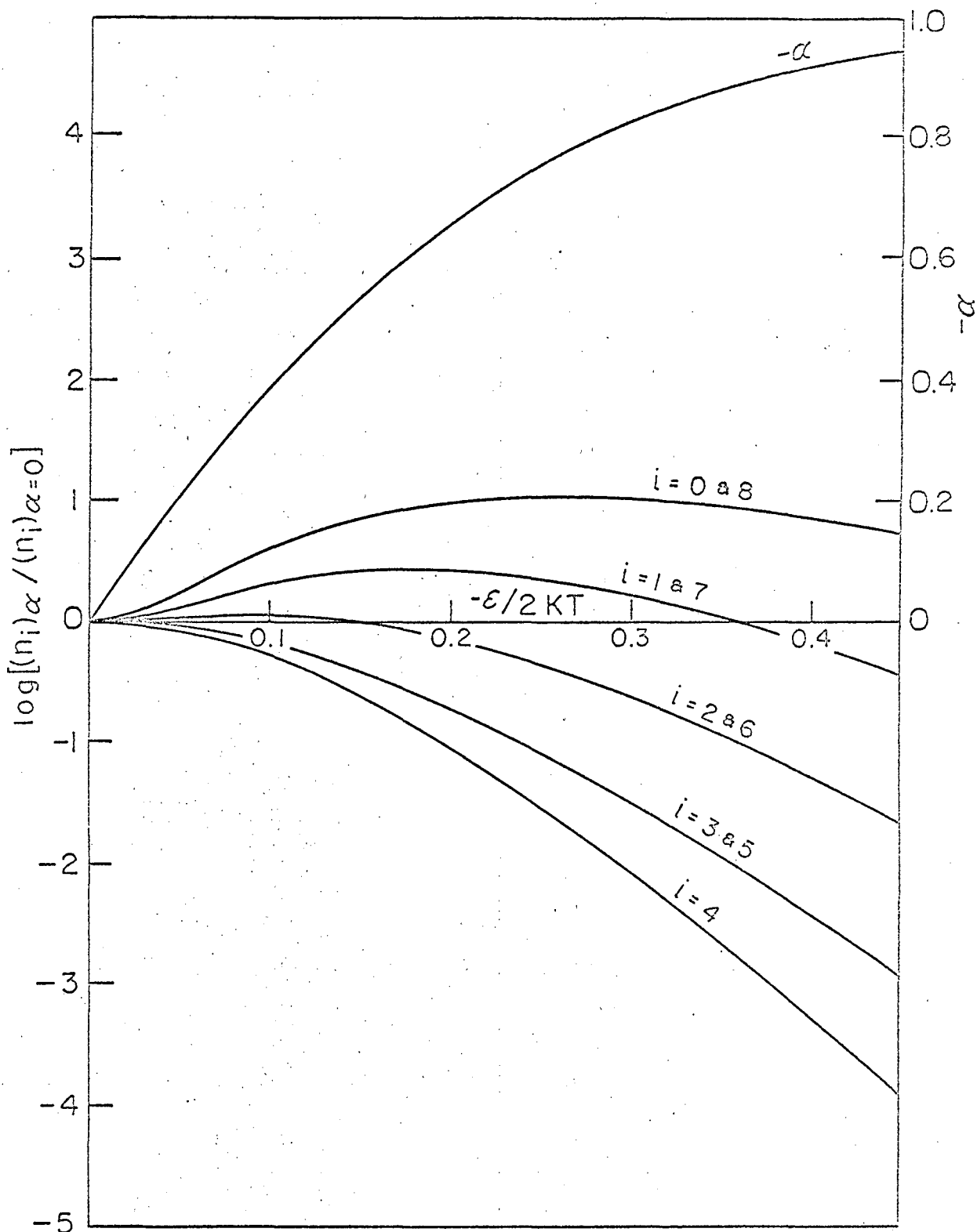


FIG. 3 EFFECT OF ORDERING ON THE DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ACCORDING TO THE MODIFIED VACANCY-ENERGY MODEL.

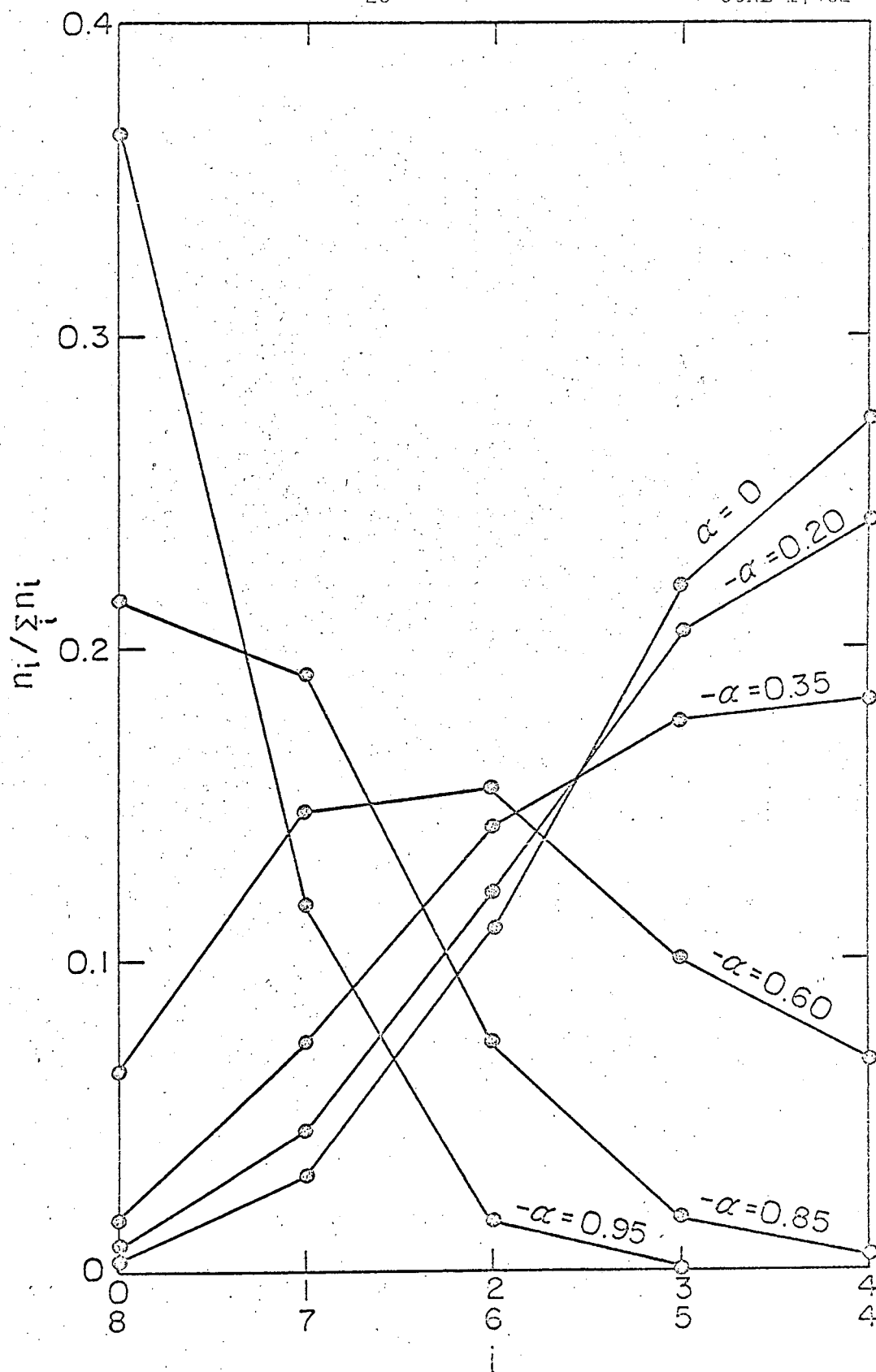


FIG. 4 DISTRIBUTIONS OF THE VARIOUS VACANCY CONCENTRATIONS FOR THE CASE $N_A = N_B = 1/2$, $N_0 \epsilon_{AA} = N_0 \epsilon_{BB} = -14.15$ KCAL, $N_0 \epsilon_{AB} = -14.50$ KCAL AND $Z = 8$.

However, this distribution is strongly affected by the values of bond energies used in the calculation. This can be readily shown from the following equation which is reduced from Eqs. (30) and (31) for the case $N_A = N_B = 1/2$ and $z = 8$.

$$\frac{n_i}{n_V} = \frac{n_i}{\sum_{i=0}^8 n_i}$$

$$= \frac{8!}{(8-i)!i!} \left\{ (1+\alpha)^{8-i} (1-\alpha)^i e^{\frac{(8-i)\epsilon_{AA} + i\epsilon_{BA}}{2kT}} + (1-\alpha)^{8-i} (1+\alpha)^i e^{\frac{(8-i)\epsilon_{AB} + i\epsilon_{BB}}{2kT}} \right\} \quad (33)$$

$$\left\{ (1+\alpha) e^{\frac{\epsilon_{AA}}{2kT}} + (1-\alpha) e^{\frac{\epsilon_{BA}}{2kT}} \right\}^8 + \left\{ (1-\alpha) e^{\frac{\epsilon_{AB}}{2kT}} + (1+\alpha) e^{\frac{\epsilon_{BB}}{2kT}} \right\}^8$$

If the bond energies $N_0 \epsilon_{AA} = -7.9$ kcal, $N_0 \epsilon_{BB} = -20.4$ kcal and $N_0 \epsilon_{AB} = -14.50$ kcal (where N_0 is Avogadro's number) are assumed, the second term inside each of the braces is negligible with respect to the first term and the exponentials become the predominant factor. Therefore, as shown in Fig. 5, at low temperatures the $i = 0$ type of vacancy is most populous.

The assumption, common to the Smeared-Displacement, Simple-Displacement and Modified Vacancy-Energy Models, that the energy to form a vacancy can be estimated from the energy of the broken bonds is notoriously inexact. In pure metals the actual energy to form a vacancy is often less than one-third of the value calculated by the naive bond-energy estimation. As suggested originally by Lomer, it appears that the thermodynamics of vacancies in alloys is more accurately formulated in terms of their local environment as was done in the Vacancy-Energy Model. Undoubtedly vacancies

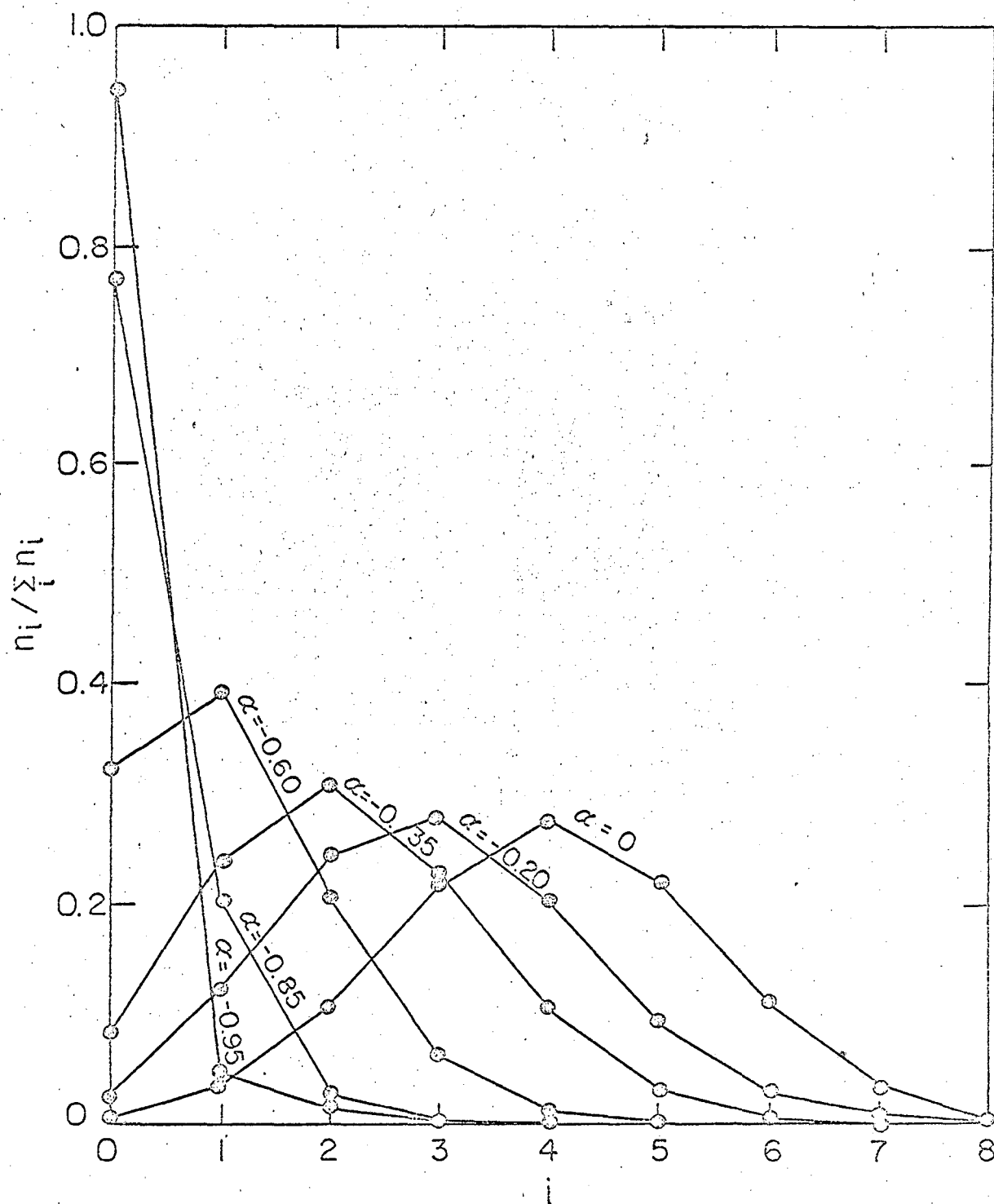


FIG. 5 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS FOR THE CASE $N_A = N_B = 1/2$, $N_0 \epsilon_{AA} = -7.9$ KCAL, $N_0 \epsilon_{BB} = -20.4$ KCAL, $N_0 \epsilon_{AB} = 14.50$ KCAL AND $Z = 8$.

having different configurations for the same numbers of coordinated A and B atoms have somewhat different formation energies and these energies also vary dependent on next etc. nearest-neighbor interactions. Such details, however, were not incorporated in the Vacancy-Energy Model primarily for the sake of simplicity. Thus the Vacancy-Energy Model, although somewhat more realistic than the previously described models, is nevertheless an approximation. It has the virtues of more accurate formulation of vacancy energies and mixing entropies.

A major handicap in applying the Vacancy-Energy Model concerns the fact that the $2(z + 1)$ values of g_i and the g'_i must at present be evaluated experimentally. It is not clear at present just how this might be done with facility. Obviously the bond energies account for part of the values of g_i and therefore the general trends given by the Modified Vacancy-Energy Model have some validity although the absolute values of the concentration of vacancies so deduced is inaccurate and other factors serve to modify further the trends. One of these factors concerns the irresolvable dichotomy of viewpoint between the Vacancy-Energy Model and the remaining three models based on the bond-energy approximation for the energy to produce a vacancy. For example, as illustrated by Eqs. (29a) and (29b) for the Modified Vacancy-Energy Model, the energy to produce a vacancy coordinated with i B atoms and $(z - i)$ A atoms is uniquely different depending on whether the newly produced vacancy is made by displacing an A atom or a B atom to the surface. In contrast, in the more realistic Vacancy-Energy Model, the energy to produce a vacancy coordinated with i B atoms and $(z - i)$ A atoms is assigned a single unique value.

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PART B

LONG-RANGE ORDERED ALLOYS

ABSTRACT

Four models for estimating the effects of long-range ordering on the equilibrium concentration of vacancies in binary alloys with $L2_0$ (b.c.c.) or $L1_2$ (f.c.c.) lattice are described. The models differ first with respect to the details with which vacancy environments are inspected and secondly with reference to methods of estimating vacancy energies. Whereas the Smeared-Displacement, Simple-Displacement and Modified Vacancy-Energy Models approximate the energy to form a vacancy with the change in bond energy when a vacancy is produced by displacing an atom from the bulk of the crystal to the surface, the more detailed and more accurate Vacancy-Energy Model assumes that the free energy to form a vacancy depends principally on the atoms with which it is coordinated. All four models suggest that, in general, the concentration of vacancies differs on the different types of lattice sites when the alloy is ordered.

I. INTRODUCTION

In Part A we have discussed the vacancy models for short-range ordered and clustered binary alloys. Here we shall present the statistical thermodynamics of the equilibrium concentration of vacancies in long-range ordered alloys employing, as a basis for discussion, four models that are similar to those previously used for short-range ordered alloys. To provide a common basis for comparison, each of these models will be established in terms of the Bragg-Williams theory of long-range ordering.¹ The naive nearest-neighbor bond-energy approach inherent to the Bragg-Williams and various other ordering theories will be assumed. In the Smeared-Displacement, Simple-Displacement and Modified Vacancy-Energy Models, vacancy energies will be approximated by the change in bond energy when a vacancy is produced by displacing an atom from the bulk to an equivalent site on the surface of a crystal. Each of the above mentioned models differs, however, with respect to the details of vacancy environment that are incorporated into the analysis. The Vacancy-Energy Model, in contrast, provides a detailed description of vacancy environments, and assumes the more physically realistic concept that the energy to form a vacancy depends principally on its immediate environment.

In the subsequent sections we propose to study the vacancy models in both the $L2_0$ and the $L1_2$ lattices. Whereas the former undertakes a second order phase transformation on ordering, the latter undergoes a first order phase transformation. The characteristics of these phase transformations will be discussed later. The models will be compared with one another and their virtues and deficiencies will be discussed.

II. TERMINOLOGY AND PRELIMINARY CONSIDERATION

The arrangements of atoms in both the $L2_0$ and the $L1_2$ superlattices are shown in Fig. 1. For a random arrangement of atoms the $L2_0$ lattice exhibits b.c.c. symmetry. When the alloy becomes ordered, A atoms prefer to reside on α sites at $(0, 0, 0)$ and B atoms on equivalent β sites at $(1/2, 1/2, 1/2)$. On the other hand, when they are random, alloys crystallizing in the $L1_2$ superlattice have f.c.c. symmetry. Based on the f.c.c. unit cell they have three α sites at $(0, 1/2, 1/2)$, $(1/2, 0, 1/2)$ and $(1/2, 1/2, 0)$ plus one β site at $(0, 0, 0)$.

In the models which follow we will consider alloys having various degrees of long-range order. The crystal, as shown in Fig. 1, will be taken to have two types of lattice sites, α and β , occupied by two atomic species, A and B, plus vacancies, V. The following terminology will be adopted:

n_j = number of j^{th} sites where $j = \alpha$ or β .

n_k = number of species where $k = A$ or B (atoms) or V (vacancies).

n_{kj} = number of k^{th} species on j^{th} sites.

n_{Vkj} = number of vacancies produced on j^{th} sites by removal of k^{th} atomic species.

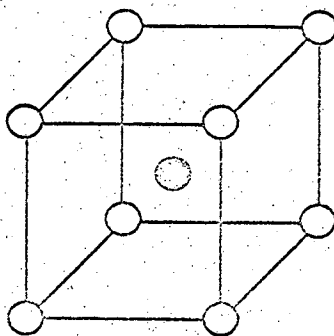
$p_{kj} = \frac{n_{kj}}{n_j}$ = probability that j^{th} type of site is occupied by k^{th} species.

N_k = atomic fraction of k^{th} atomic species.

N_j = fraction of sites that are of type j .

$\delta = N_B - N_\beta = N_\alpha - N_A$ = deviation from stoichiometry.

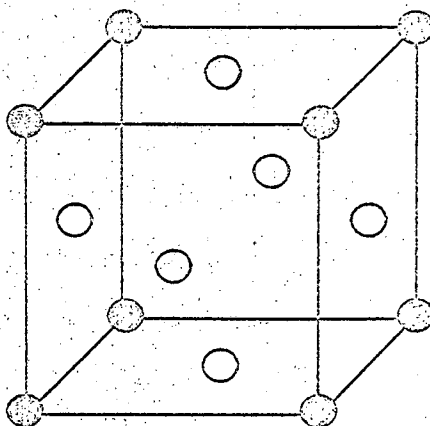
z = coordination number.



a. $L2_0$ (b.c.c.) SUPERLATTICE

○ A ATOMS ON α SITES

● B ATOMS ON β SITES



b. $L1_2$ (f.c.c.) SUPERLATTICE

FIG.1 ATOMIC ARRANGEMENTS IN THE
UNIT CELL OF COMPLETELY ORDERED
ALLOY WITH $L2_0$ OR $L1_2$ LATTICE.

$\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}$ = bond energies.

The following relations result from the conservation of atomic species and the conservation of lattice sites:

$$n_A = n_{A\alpha} + n_{A\beta} \quad (1a)$$

$$n_B = n_{B\alpha} + n_{B\beta} \quad (1b)$$

$$n_\alpha/n_\beta = \frac{N_\alpha}{N_\beta} = \frac{n_{A\alpha} + n_{B\alpha} + n_{V\alpha}}{n_{A\beta} + n_{B\beta} + n_{V\beta}} \quad (1c)$$

Furthermore, the degree of order, η , will be defined as

$$2\eta = \frac{n_{A\alpha} - n_{B\alpha}}{N_\alpha(n_A + n_B)} + \frac{n_{B\beta} - n_{A\beta}}{N_\beta(n_A + n_B)} \quad (1d)$$

which coincides with the usual Bragg-Williams definition of order. It has the virtue over other possible definitions of η insofar as the degree of order is defined only in terms of the relative occupancy of sites by the atoms independent of vacancy concentrations. Simultaneous solution of Eqs. (1) gives

$$n_{A\alpha} = N_\alpha n_A + \frac{N_\alpha n_{V\beta} - N_\beta n_{V\alpha}}{2} + N_\alpha N_\beta (n_A + n_B) \eta \quad (2a)$$

$$n_{A\beta} = N_\beta n_A - \frac{N_\alpha n_{V\beta} - N_\beta n_{V\alpha}}{2} - N_\alpha N_\beta (n_A + n_B) \eta \quad (2b)$$

$$n_{B\alpha} = N_{\alpha} n_B + \frac{N_{\alpha} n_{V\beta} - N_{\beta} n_{V\alpha}}{2} - N_{\alpha} N_{\beta} (n_A + n_B) \eta \quad (2c)$$

$$n_{B\beta} = N_{\beta} n_B - \frac{N_{\alpha} n_{V\beta} - N_{\beta} n_{V\alpha}}{2} + N_{\alpha} N_{\beta} (n_A + n_B) \eta \quad (2d)$$

Furthermore

$$p_{A\alpha} = \frac{n_{A\alpha}}{n_{\alpha}} = \frac{1}{(n_{\alpha} + n_{\beta})} \left\{ n_A + \frac{N_{\alpha} n_{V\beta} - N_{\beta} n_{V\alpha}}{2N_{\alpha}} + N_{\beta} (n_A + n_B) \eta \right\} \quad (3a)$$

$$p_{A\beta} = \frac{n_{A\beta}}{n_{\beta}} = \frac{1}{(n_{\alpha} + n_{\beta})} \left\{ n_A - \frac{N_{\alpha} n_{V\beta} - N_{\beta} n_{V\alpha}}{2N_{\beta}} - N_{\alpha} (n_A + n_B) \eta \right\} \quad (3b)$$

$$p_{B\alpha} = \frac{n_{B\alpha}}{n_{\alpha}} = \frac{1}{(n_{\alpha} + n_{\beta})} \left\{ n_B + \frac{N_{\alpha} n_{V\beta} - N_{\beta} n_{V\alpha}}{2N_{\alpha}} - N_{\beta} (n_A + n_B) \eta \right\} \quad (3c)$$

$$p_{B\beta} = \frac{n_{B\beta}}{n_{\beta}} = \frac{1}{(n_{\alpha} + n_{\beta})} \left\{ n_B - \frac{N_{\alpha} n_{V\beta} - N_{\beta} n_{V\alpha}}{2N_{\beta}} + N_{\alpha} (n_A + n_B) \eta \right\} \quad (3d)$$

where

$$n_{\alpha} + n_{\beta} = n_A + n_B + n_{V\alpha} + n_{V\beta} \quad (4)$$

When the concentration of vacancies is negligibly small relative to

n_A and to n_B , Eqs. (3) reduce to

$$p_{A\alpha} = \frac{n_{A\alpha}}{n_{\alpha}} \approx N_{\alpha} - \delta + N_{\beta} \eta \quad (5a)$$

$$p_{A\beta} = \frac{n_{A\beta}}{n_{\beta}} \approx N_{\alpha} - \delta - N_{\alpha} \eta \quad (5b)$$

$$p_{B\alpha} = \frac{n_{B\alpha}}{n_{\alpha}} = N_{\beta} + \delta - N_{\beta} n \quad (5c)$$

$$p_{B\beta} = \frac{n_{B\beta}}{n_{\beta}} = N_{\beta} + \delta + N_{\alpha} n \quad (5d)$$

Assuming that the various species are randomly mixed in Ω ways on two types of lattice sites gives the same configurational entropy of

$$S = k \ln \Omega = k \ln \frac{n_{\alpha}!}{n_{A\alpha}! n_{B\alpha}! n_{V\alpha}!} \cdot \frac{n_{\beta}!}{n_{A\beta}! n_{B\beta}! n_{V\beta}!} \quad (6)$$

for all types of lattices. In contrast, however, the configurational energies differ dependent on the lattice type. For the $L2_0$ superlattice each α (or β) site is coordinated with 8 β (or 8 α) sites. Therefore, in terms of the simple bond energy model the total energy of the crystal of the $L2_0$ lattice where $N_{\alpha} = N_{\beta} = 1/2$ is given by

$$E = z \left\{ n_{A\alpha} \frac{n_{A\beta}}{n_{\beta}} \epsilon_{AA} + n_{A\alpha} \frac{n_{B\beta}}{n_{\beta}} \epsilon_{AB} + n_{B\alpha} \frac{n_{A\beta}}{n_{\beta}} \epsilon_{AB} + n_{B\alpha} \frac{n_{B\beta}}{n_{\beta}} \epsilon_{BB} \right\} \quad (7a)$$

or, since for this lattice $n_{\alpha} = n_{\beta}$ and $z = 8$,

$$E = \frac{16}{n_{\alpha} + n_{\beta}} \{ n_{A\alpha} n_{A\beta} \epsilon_{AA} + n_{A\alpha} n_{B\beta} \epsilon_{AB} + n_{B\alpha} n_{A\beta} \epsilon_{AB} + n_{B\alpha} n_{B\beta} \epsilon_{BB} \} \quad (7b)$$

For the $L1_2$ superlattice, as shown in Fig. 1, $N_{\alpha} = 3/4$, $N_{\beta} = 1/4$

and $z = 12$. Furthermore, whereas each β site is coordinated with $z = 12$ neighboring α sites, each α site is coordinated with $z_\alpha = 8$ neighboring α sites and $z_\beta = 4$ neighboring β sites. Complete ordering is obtained for the stoichiometric composition corresponding to A_3B when all of the A atoms reside on α sites and all of the B atoms on β sites. In terms of the simple bond energy model the energy of the Ll_2 lattice is given by

$$\begin{aligned}
 E = z \{ & n_{A\beta} \frac{n_{A\alpha}}{n_\alpha} \epsilon_{AA} + n_{A\beta} \frac{n_{B\alpha}}{n_\alpha} \epsilon_{AB} + n_{B\beta} \frac{n_{A\alpha}}{n_\alpha} \epsilon_{AB} \\
 & + n_{B\beta} \frac{n_{B\alpha}}{n_\alpha} \epsilon_{BB} \} + \frac{8}{2} \{ n_{A\alpha} \frac{n_{A\alpha}}{n_\alpha} \epsilon_{AA} + n_{A\alpha} \frac{n_{B\alpha}}{n_\alpha} \epsilon_{AB} \\
 & + n_{B\alpha} \frac{n_{A\alpha}}{n_\alpha} \epsilon_{AB} + n_{B\alpha} \frac{n_{B\alpha}}{n_\alpha} \epsilon_{BB} \} \quad (8a)
 \end{aligned}$$

where the first bracketed term refers to all bonds between α and β sites and the second term refers to bonds between α and adjacent α sites.

Since $z = 12$ and $n_\alpha = N_\alpha (n_\alpha + n_\beta)$, E for the Ll_2 lattice reduces to

$$\begin{aligned}
 E = \frac{16}{n_\alpha + n_\beta} \{ & [n_{A\beta} n_{A\alpha} + \frac{1}{3} n_{A\alpha} n_{A\alpha}] \epsilon_{AA} \\
 & + [n_{A\beta} n_{B\alpha} + n_{B\beta} n_{A\alpha} + \frac{2}{3} n_{A\alpha} n_{B\alpha}] \epsilon_{AB} \\
 & + [n_{B\beta} n_{B\alpha} + \frac{1}{3} n_{B\alpha} n_{B\alpha}] \epsilon_{BB} \} \quad (8b)
 \end{aligned}$$

III. VACANCY MODELS FOR THE L2₀ LATTICE

A. Smeared-Displacement Model

In this model the vacancies are assumed to reside in a smeared environment averaged over the entire lattice. The free energy is given by

$$F = E - TS \quad (9)$$

where E is given by Eq. (7b) and S by Eq. (6), which in conjunction with Eq. (4) are expressed in terms of the six unknowns n_{kj} . The variance of the six values of n_{kj} , however, are constrained by the conditions expressed in Eqs. (1a), (1b) and (1c) and therefore, in terms of the Lagrangian multiplier technique they reduce to

$$\lambda_A (n_{A\alpha} + n_{A\beta} - n_A) = 0 \quad (10a)$$

$$\lambda_B (n_{B\alpha} + n_{B\beta} - n_B) = 0 \quad (10b)$$

$$\lambda_{\alpha\beta} (n_{A\alpha} + n_{B\alpha} + n_{V\alpha} - n_{A\beta} - n_{B\beta} - n_{V\beta}) = 0 \quad (10c)$$

where the λ s are Lagrangian multipliers and where the condition appropriate to the L2₀ lattice of $N_\alpha = N_\beta$ has been introduced into the last equation. Each of the six unknowns n_{kj} can now be taken as independently variable. The condition for equilibrium, obtained by minimizing the final free energy equation (Eq. (9) plus Eqs. (10)), gives

$$\begin{aligned}\frac{\partial E}{\partial n_{A\alpha}} &= kT \frac{\partial \ln \Omega}{\partial n_{A\alpha}} - \lambda_{\alpha\beta} - \lambda_A, & \frac{\partial E}{\partial n_{A\beta}} &= kT \frac{\partial \ln \Omega}{\partial n_{A\beta}} + \lambda_{\alpha\beta} - \lambda_A \\ \frac{\partial E}{\partial n_{B\alpha}} &= kT \frac{\partial \ln \Omega}{\partial n_{B\alpha}} - \lambda_{\alpha\beta} - \lambda_B, & \frac{\partial E}{\partial n_{B\beta}} &= kT \frac{\partial \ln \Omega}{\partial n_{B\beta}} + \lambda_{\alpha\beta} - \lambda_B\end{aligned}\quad (11)$$

$$\frac{\partial E}{\partial n_{V\alpha}} = kT \frac{\partial \ln \Omega}{\partial n_{V\alpha}} - \lambda_{\alpha\beta}, \quad \frac{\partial E}{\partial n_{V\beta}} = kT \frac{\partial \ln \Omega}{\partial n_{V\beta}} + \lambda_{\alpha\beta}$$

Introducing the values for E and Ω and eliminating the λ s we arrive at the three important relationships:

$$\ln \frac{n_{A\alpha} n_{B\beta}}{n_{A\beta} n_{B\alpha}} = \frac{16}{kT(n_\alpha + n_\beta)} \{ (n_{A\alpha} - n_{A\beta}) \epsilon_{AA} - (n_{A\alpha} + n_{B\beta} - n_{A\beta} - n_{B\alpha}) \epsilon_{AB} + (n_{B\beta} - n_{B\alpha}) \epsilon_{BB} \} \quad (12)$$

$$\begin{aligned}\ln \frac{n_{V\alpha}}{n_\alpha} &= \frac{16}{kT(n_\alpha + n_\beta)^2} \{ n_{A\alpha} n_{A\beta} \epsilon_{AA} + (n_{A\alpha} n_{B\beta} + n_{B\alpha} n_{A\beta}) \epsilon_{AB} + n_{B\alpha} n_{B\beta} \epsilon_{BB} \} + \frac{1}{4} \ln \frac{n_{A\alpha} n_{B\alpha}}{n_{A\beta} n_{B\beta}} \\ &\quad - \frac{4}{kT(n_\alpha + n_\beta)} \{ (n_{A\alpha} - n_{A\beta}) (\epsilon_{AA} + \epsilon_{AB}) + (n_{B\alpha} - n_{B\beta}) (\epsilon_{AB} + \epsilon_{BB}) \}\end{aligned}\quad (13)$$

and

$$\begin{aligned}\ln \frac{n_{V\beta}}{n_\beta} &= \frac{16}{kT(n_\alpha + n_\beta)^2} \{ n_{A\alpha} n_{A\beta} \epsilon_{AA} + (n_{A\alpha} n_{B\beta} + n_{B\alpha} n_{A\beta}) \epsilon_{AB} + n_{B\alpha} n_{B\beta} \epsilon_{BB} \} - \frac{1}{4} \ln \frac{n_{A\alpha} n_{B\alpha}}{n_{A\beta} n_{B\beta}} \\ &\quad + \frac{4}{kT(n_\alpha + n_\beta)} \{ (n_{A\alpha} - n_{A\beta}) (\epsilon_{AA} + \epsilon_{AB}) + (n_{B\alpha} - n_{B\beta}) (\epsilon_{AB} + \epsilon_{BB}) \}\end{aligned}\quad (14)$$

Eq. (12) is identical with the original Bragg-Williams relationship.¹

Introducing Eqs. (5) gives

$$\ln \frac{(1+\eta+2\delta)(1+\eta-2\delta)}{(1-\eta-2\delta)(1-\eta+2\delta)} = -\frac{8\eta}{kT} \{2 \epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}\} \quad (15)$$

We can examine Eq. (15) in the limit $\eta \rightarrow 0$ by expanding the left hand side as a power series in η . The limit as $\eta \rightarrow 0$ corresponds to $T \rightarrow T_c$, where T_c is the critical temperature for long-range ordering, whence we find that

$$\frac{4}{1-4\delta^2} = -\frac{8}{kT_c} \{2 \epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}\} = -\frac{16}{kT_c} \epsilon \quad (16)$$

This is the familiar Bragg-Williams relationship giving the ordering energy, ϵ (which is defined in Eq. (1) in Part A), in terms of the critical temperature.

Eqs. (13) and (14) give the concentrations of vacancies on the two sublattices. Introducing the approximation of Eqs. (5) we have

$$\begin{aligned} \ln p_{Va} = & \frac{1}{kT} \{[(1-2\delta)^2 - \eta^2] \epsilon_{AA} + 2[1+\eta^2-4\delta^2] \epsilon_{AB} + [(1+2\delta)^2 - \eta^2] \epsilon_{BB}\} \\ & + \frac{1}{4} \ln \frac{1-(\eta-2\delta)^2}{1-(\eta+2\delta)^2} + \frac{2\eta}{kT} \{\epsilon_{BB} - \epsilon_{AA}\} \end{aligned} \quad (17)$$

$$\begin{aligned} \ln p_{Vb} = & \frac{1}{kT} \{[(1-2\delta)^2 - \eta^2] \epsilon_{AA} + 2[1+\eta^2-4\delta^2] \epsilon_{AB} + [(1+2\delta)^2 - \eta^2] \epsilon_{BB}\} \\ & - \frac{1}{4} \ln \frac{1-(\eta-2\delta)^2}{1-(\eta+2\delta)^2} - \frac{2\eta}{kT} \{\epsilon_{BB} - \epsilon_{AA}\} \end{aligned} \quad (18)$$

B. Simple-Displacement Model

The alloy is assumed to have the equilibrium degree of order, η , in the absence of vacancies. Vacancies are formed by removing particular kinds of atoms (A or B) from particular types of sites (α or β) inside the crystal and replacing them on the surface at the same type of site from which they were removed. The change in internal energy on producing each vacancy is defined in terms of the bond-energy approximation as the difference in energy between the z bonds broken by removing that atom from the bulk of the crystal and the $z/2$ bonds reformed on the average when the atom is placed on the surface. It is assumed that the number and configuration of A and B atoms about the vacancy remains the same as it was before the atom was removed. Therefore the energy required to form a vacancy on an α -site depends on whether that site was previously occupied by an A atom or a B atom. Since these kinds of vacancies are energetically distinguishable, they must be treated as independent species both in the energy and entropy terms.

On this basis, the change in internal energy of the crystal due to the formation of vacancies for the $L2_0$ lattice is

$$\begin{aligned} \Delta E_V = -\frac{8}{2} [& n_{VA\alpha} (p_{A\beta} \epsilon_{AA} + p_{B\beta} \epsilon_{AB}) + n_{VB\alpha} (p_{A\beta} \epsilon_{AB} + p_{B\beta} \epsilon_{BB}) \\ & + n_{VA\beta} (p_{A\alpha} \epsilon_{AA} + p_{B\alpha} \epsilon_{AB}) + n_{VB\beta} (p_{A\alpha} \epsilon_{AB} + p_{B\alpha} \epsilon_{BB})] \end{aligned} \quad (19)$$

The configurational entropy change for the crystal due to random mixing of the vacancies on the sites is

$$\Delta S_V = k \ln \frac{(n_{A\alpha} + n_{VA\alpha})! (n_{B\alpha} + n_{VB\alpha})! (n_{A\beta} + n_{VA\beta})! (n_{B\beta} + n_{VB\beta})!}{n_{A\alpha}! n_{VA\alpha}! n_{B\alpha}! n_{VB\alpha}! n_{A\beta}! n_{VA\beta}! n_{B\beta}! n_{VB\beta}!} \quad (20)$$

and the free energy of this system is

$$F(n, n_V) = F(n, 0) + \Delta F_V(n_V) \quad (21)$$

where $F(n, 0)$ is the free energy of the system for the given degree of order, n , and no vacancies, and where

$$\Delta F_V(n_V) = \Delta E_V - T \Delta S_V \quad (22)$$

At equilibrium therefore

$$\frac{\partial F(n, n_V)}{\partial n_{Vkj}} = \frac{\partial \Delta F_V(n_V)}{\partial n_{Vkj}} = 0 \quad (23)$$

The equilibrium condition yields the four equations:

$$p_{VA\alpha} = \frac{n_{VA\alpha}}{n_\alpha} = \frac{e^{\frac{4}{kT} (p_{A\beta} \epsilon_{AA} + p_{B\beta} \epsilon_{AB})}}{1 - e^{\frac{4}{kT} (p_{A\beta} \epsilon_{AA} + p_{B\beta} \epsilon_{AB})}} p_{A\alpha} \quad (24a)$$

$$p_{VB\alpha} = \frac{n_{VB\alpha}}{n_\alpha} = \frac{e^{\frac{4}{kT} (p_{A\beta} \epsilon_{AB} + p_{B\beta} \epsilon_{BB})}}{1 - e^{\frac{4}{kT} (p_{A\beta} \epsilon_{AB} + p_{B\beta} \epsilon_{BB})}} p_{B\alpha} \quad (24b)$$

$$p_{VA\beta} = \frac{n_{VA\beta}}{n_\beta} = \frac{e^{\frac{4}{kT} (p_{A\alpha} \epsilon_{AA} + p_{B\alpha} \epsilon_{AB})}}{1 - e^{\frac{4}{kT} (p_{A\alpha} \epsilon_{AA} + p_{B\alpha} \epsilon_{AB})}} p_{A\beta} \quad (24c)$$

$$p_{VB\beta} = \frac{n_{VB\beta}}{n_{\beta}} = \frac{e^{\frac{h}{kT} (p_{A\alpha} \epsilon_{AB} + p_{B\alpha} \epsilon_{BB})}}{1 - e^{\frac{h}{kT} (p_{A\alpha} \epsilon_{AB} + p_{B\alpha} \epsilon_{BB})}} p_{B\beta} \quad (24d)$$

The probabilities of finding vacancies on α and β sites respectively are given by

$$p_{V\alpha} = \frac{n_{V\alpha}}{n_{\alpha}} = \frac{n_{VA\alpha}}{n_{\alpha}} + \frac{n_{VB\alpha}}{n_{\alpha}} = p_{VA\alpha} + p_{VB\alpha} \quad (25a)$$

$$p_{V\beta} = \frac{n_{V\beta}}{n_{\beta}} = \frac{n_{VA\beta}}{n_{\beta}} + \frac{n_{VB\beta}}{n_{\beta}} = p_{VA\beta} + p_{VB\beta} \quad (25b)$$

where the values of the p_{kj} are given by Eqs. (5) for the case where $N_{\alpha} = N_{\beta} = 1/2$ appropriate to the $L2_0$ lattice.

C. Vacancy-Energy Model

For this model we assume that the free energy of formation of a vacancy depends principally on its immediate environment. As discussed more thoroughly in Part A, we let g_i be the free energy of formation of a vacancy coordinated with i atoms of type B and $(z - i)$ atoms of type A in the disordered alloy. Undoubtedly the free energy of formation of each type of vacancy changes somewhat during ordering. Geometric consideration alone suggests that such changes can be different for vacancies on each of the two different types of sites. It seems not too unreasonable to believe, however, that such changes in the energy of formation of vacancies might be related to the change in the average bond energy during ordering.

The average energy, $\bar{\epsilon}$, of a bond is given by

$$\bar{\epsilon} = p_{A\alpha}p_{A\beta}\epsilon_{AA} + p_{A\alpha}p_{B\beta}\epsilon_{AB} + p_{B\alpha}p_{A\beta}\epsilon_{AB} + p_{B\alpha}p_{B\beta}\epsilon_{BB} \quad (26a)$$

for the $L2_0$ type of lattice. Upon introduction of Eqs. (5) and the ordering energy, ϵ ,

$$\bar{\epsilon} = \frac{1}{4} \{ (1-2\delta)^2 \epsilon_{AA} + 2(1+2\delta)(1-2\delta) \epsilon_{AB} + (1+2\delta)^2 \epsilon_{BB} \} + \frac{n^2 \epsilon}{2} \quad (26b)$$

Thus we suggest, in analogy to a Taylor's series where only the first two terms are retained, that the free energies of formation of vacancies of the i^{th} type can be represented by

$$g_{i\alpha} = g_i + g'_{i\alpha} n^2 \quad (27a)$$

$$g_{i\beta} = g_i + g'_{i\beta} n^2 \quad (27b)$$

respectively for α and β sites. Consequently $g_{i\alpha} = g_{i\beta} = g_i$ for the random case and the values of $g'_{i\alpha}$ and $g'_{i\beta}$ account for possible changes in free energies of formation of vacancies per unit change in n^2 during ordering.

As deduced from the Smeared-Displacement Model we assume here that the all-over degree of long-range order is not materially modified as a result of the introduction of a small fraction of vacancies. Furthermore, as previously described in Part A, we acknowledge that the probability vacancies might change the local ordering configuration is also negligible.

The probability that a β site is coordinated with i B atoms and $(z - i)$ A atoms in the $L2_0$ lattice where $z = 8$ is given by the general term in the binomial expansion

$$(p_{A\alpha} + p_{B\alpha})^z = \sum_{i=0}^z \frac{z!}{(z-i)!i!} p_{A\alpha}^{(z-i)} p_{B\alpha}^i = 1 \quad (28)$$

Thus, employing the same technique as that described in Part A, we obtain the following equilibrium vacancy concentration on the two types of sites:

$$\frac{n_{i\beta}}{n_\beta} = \frac{z!}{(z-i)!i!} p_{A\alpha}^{(z-i)} p_{B\alpha}^i e^{-\frac{g_{i\beta}}{kT}} \quad (29a)$$

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{z!}{(z-i)!i!} p_{A\beta}^{(z-i)} p_{B\beta}^i e^{-\frac{g_{i\alpha}}{kT}} \quad (29b)$$

It is significant that these equations reduce to those previously suggested by Dorn and Mitchell² for a random alloy. When expressed in terms of the degree of order, Eqs. (29a) and (29b) become

$$\frac{n_{i\beta}}{n_{\beta}} = \frac{z!}{(z-i)!i!2^z} (1+\eta-2\delta)^{z-i} (1-\eta+2\delta)^i e^{-\frac{\epsilon_{i\beta}}{kT}} \quad (30a)$$

$$\frac{n_{i\alpha}}{n_{\alpha}} = \frac{z!}{(z-i)!i!2^z} (1-\eta-2\delta)^{z-i} (1+\eta+2\delta)^i e^{-\frac{\epsilon_{i\alpha}}{kT}} \quad (30b)$$

where

$$p_{V\beta} = \frac{n_{V\beta}}{n_{\beta}} = \sum_i \frac{n_{i\beta}}{n_{\beta}} \text{ and } p_{V\alpha} = \frac{n_{V\alpha}}{n_{\alpha}} = \sum_i \frac{n_{i\alpha}}{n_{\alpha}} \quad (31)$$

D. Modified Vacancy-Energy Model

The Vacancy-Energy Model, as expressed in Eqs. (29a) and (29b), cannot be compared directly with the previously developed Smeared-Displacement and Simple-Displacement Models inasmuch as the values of $g_{i\alpha}$ and $g_{i\beta}$ are not known. To provide a basis for comparison, the values of the g_i s will be estimated by a crude bond-energy approximation. For each A or B atom displaced to the surface to make a vacancy, the bond energy changes are $-\{(z-i)\epsilon_{AA} + i\epsilon_{AB}\}/2$ and $-\{(z-i)\epsilon_{AB} + i\epsilon_{BB}\}/2$ respectively. Thus following Eq. (28), the total number of vacant β sites which are coordinated with i B atoms and $(z-i)$ A atoms can be visualized as the result of displacing an A atom (or a B atom) to the surface from the β lattice sites and is simply given by

$$\frac{n_{i\beta}}{n_\beta} = \frac{n_{i\beta}^{(A)} + n_{i\beta}^{(B)}}{n_\beta} = \frac{z!}{(z-i)!i!} p_{A\alpha}^{z-i} p_{B\alpha}^i \left[p_{A\beta} e^{\frac{(z-i)\epsilon_{AA} + i\epsilon_{AB}}{2kT}} + p_{B\beta} e^{\frac{(z-i)\epsilon_{AB} + i\epsilon_{BB}}{2kT}} \right] \quad (32a)$$

and similarly for the vacant α sites

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{n_{i\alpha}^{(A)} + n_{i\alpha}^{(B)}}{n_\alpha} = \frac{z!}{(z-i)!i!} p_{A\beta}^{z-i} p_{B\beta}^i \left[p_{A\alpha} e^{\frac{(z-i)\epsilon_{AA} + i\epsilon_{AB}}{2kT}} + p_{B\alpha} e^{\frac{(z-i)\epsilon_{AB} + i\epsilon_{BB}}{2kT}} \right] \quad (32b)$$

Thus the probabilities of vacancies on α and β sites are given by

$$p_{V\alpha} = \sum_{i=0}^z \frac{n_{i\alpha}}{n_{\alpha}} = p_{A\alpha} \left[p_{A\beta} e^{\frac{\epsilon_{AA}}{2kT}} + p_{B\beta} e^{\frac{\epsilon_{AB}}{2kT}} \right]^z + p_{B\alpha} \left[p_{A\beta} e^{\frac{\epsilon_{AB}}{2kT}} + p_{B\beta} e^{\frac{\epsilon_{BB}}{2kT}} \right]^z \quad (33a)$$

and

$$p_{V\beta} = \sum_{i=0}^z \frac{n_{i\beta}}{n_{\beta}} = p_{A\beta} \left[p_{A\alpha} e^{\frac{\epsilon_{AA}}{2kT}} + p_{B\alpha} e^{\frac{\epsilon_{AB}}{2kT}} \right]^z + p_{B\beta} \left[p_{A\alpha} e^{\frac{\epsilon_{AB}}{2kT}} + p_{B\alpha} e^{\frac{\epsilon_{BB}}{2kT}} \right]^z \quad (33b)$$

When $\eta = 0$, as is required, Eqs. (33) reduce to $p_{V\alpha} = p_{V\beta}$.

IV. VACANCY MODELS FOR THE $L1_2$ LATTICE

A. Smeared-Displacement Model

The basic assumptions for this model coincide exactly with those that were previously used when the same model was applied to the $L2_0$ lattice. However, because of the difference in lattice type and the occurrence of a first order transformation in the $L1_2$ lattice in lieu of the second order transformation obtained in the $L2_0$ lattice, the final results on vacancy distributions are interestingly different. The entropy to be introduced in the free energy expression of Eq. (9) is the same, namely that given by Eq. (6), for both types of lattices. In contrast, the energy that must be used in the free energy expression for the $L1_2$ lattice is given by Eq. (8b) in lieu of Eq. (7b) which is appropriate only for the $L2_0$ lattice. Furthermore, the conditions given by Eqs. (10a) and (10b) apply also to the $L1_2$ lattice but the condition for the conservation of lattice sites, Eq. (1c) where $N_\alpha = 3/4$ and $N_\beta = 1/4$ becomes

$$\lambda_{\alpha\beta} \left\{ \frac{1}{4} (n_{A\alpha} + n_{B\alpha} + n_{V\alpha}) - \frac{3}{4} (n_{A\beta} + n_{B\beta} + n_{V\beta}) \right\} = 0 \quad (10d)$$

where $\lambda_{\alpha\beta}$ is the Lagrangian multiplier. Employing the same technique as that used previously in Section III A for minimizing the free energy we obtain three important relationships:

$$\ln \frac{n_{A\alpha} n_{B\beta}}{n_{A\beta} n_{B\alpha}} = \frac{16}{kT(n_\alpha + n_\beta)} \left\{ \left(\frac{1}{3} (n_{A\alpha} - n_{A\beta}) \right) \epsilon_{AA} - \left[\frac{1}{3} (n_{A\alpha} - n_{B\alpha}) - (n_{A\beta} - n_{B\beta}) \right] \epsilon_{AB} \right. \\ \left. - \left(\frac{1}{3} (n_{B\alpha} - n_{B\beta}) \right) \epsilon_{BB} \right\} \quad (34)$$

$$\begin{aligned} \ln \frac{n_{V\alpha}}{n_\alpha} = & \frac{16}{kT(n_\alpha + n_\beta)^2} \{ (n_{A\alpha} n_{A\beta} + \frac{1}{3} n_{A\alpha} n_{A\alpha}) \epsilon_{AA} + (n_{A\alpha} n_{B\beta} + n_{B\alpha} n_{A\beta} + \frac{2}{3} n_{A\alpha} n_{B\alpha}) \epsilon_{AB} \\ & + (n_{B\alpha} n_{B\beta} + \frac{1}{3} n_{B\alpha} n_{B\alpha}) \epsilon_{BB} \} + \frac{1}{8} \ln \frac{n_{A\alpha} n_{B\alpha}}{9 n_{A\beta} n_{B\beta}} \\ & - \frac{2}{kT(n_\alpha + n_\beta)} \{ (\frac{1}{3} n_{A\alpha} - n_{A\beta}) (\epsilon_{AA} + \epsilon_{AB}) + (\frac{1}{3} n_{B\alpha} - n_{B\beta}) (\epsilon_{AB} + \epsilon_{BB}) \} \end{aligned} \quad (35)$$

and

$$\begin{aligned} \ln \frac{n_{V\beta}}{n_\beta} = & \frac{16}{kT(n_\alpha + n_\beta)^2} \{ (n_{A\alpha} n_{A\beta} + \frac{1}{3} n_{A\alpha} n_{A\alpha}) \epsilon_{AA} + (n_{A\alpha} n_{B\beta} + n_{B\alpha} n_{A\beta} + \frac{2}{3} n_{A\alpha} n_{B\alpha}) \epsilon_{AB} \\ & + (n_{B\alpha} n_{B\beta} + \frac{1}{3} n_{B\alpha} n_{B\alpha}) \epsilon_{BB} \} - \frac{3}{8} \ln \frac{n_{A\alpha} n_{B\alpha}}{9 n_{A\beta} n_{B\beta}} \\ & + \frac{6}{kT(n_\alpha + n_\beta)} \{ (\frac{1}{3} n_{A\alpha} - n_{A\beta}) (\epsilon_{AA} + \epsilon_{AB}) + (\frac{1}{3} n_{B\alpha} - n_{B\beta}) (\epsilon_{AB} + \epsilon_{BB}) \} \end{aligned} \quad (36)$$

Introducing Eqs. (5) where $N_\alpha = 3/4$ and $N_\beta = 1/4$ into Eq. (34) gives

$$\ln \frac{(3-4\delta+\eta)(1+4\delta+3\eta)}{(3-4\delta-3\eta)(1+4\delta-\eta)} = - \frac{4\eta}{kT} (2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}) \quad (37)$$

which is identical with the usual Bragg-Williams results in the absence of vacancies.

Similarly, upon introduction of Eqs. (5) and $N_\alpha = 3/4$, $N_\beta = 1/4$, the equilibrium vacancy concentrations on the two sublattices are respectively

$$\begin{aligned} \ln p_{V\alpha} = & \frac{3}{8kT} \{ [(3-4\delta)^2 - \eta^2] \epsilon_{AA} + 2(3+8\delta-16\delta^2 + \eta^2) \epsilon_{AB} + (1+4\delta)^2 - \eta^2 \} \epsilon_{BB} \\ & + \frac{1}{8} \ln \frac{(3+8\delta-2\eta) - (\eta-4\delta)^2}{(3+8\delta+6\eta) - (3\eta+4\delta)^2} + \frac{\eta}{2kT} (\epsilon_{BB} - \epsilon_{AA}) \end{aligned} \quad (38)$$

and

$$\begin{aligned} \ln p_{V\beta} = & \frac{3}{8kT} \{ [(3-4\delta)^2 - \eta^2] \epsilon_{AA} + 2(3+8\delta-16\delta^2 + \eta^2) \epsilon_{AB} + [(1+4\delta)^2 - \eta^2] \epsilon_{BB} \} \\ & - \frac{3}{8} \ln \frac{(3+8\delta-2\eta) - (\eta-4\delta)^2}{(3+8\delta+6\eta) - (3\eta+4\delta)^2} - \frac{3\eta}{2kT} (\epsilon_{BB} - \epsilon_{AA}) \end{aligned} \quad (39)$$

B. Simple-Displacement Model

The alloy is assumed to have the equilibrium degree of order and then vacancies are formed by removing atoms A or B from α or β sites in the bulk of the crystal and replacing such atoms on the surface. On this basis the change in the energy of the crystal for the $L1_2$ lattice is

$$\begin{aligned} \Delta E_V = & -\frac{12}{2} \{ n_{VA\alpha} \left[\left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right) \epsilon_{AA} + \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right) \epsilon_{AB} \right] \right. \\ & + n_{VB\alpha} \left[\left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right) \epsilon_{AB} + \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right) \epsilon_{BB} \right] \\ & \left. + n_{VA\beta} [p_{A\alpha} \epsilon_{AA} + p_{B\alpha} \epsilon_{AB}] + n_{VB\beta} [p_{A\alpha} \epsilon_{AB} + p_{B\alpha} \epsilon_{BB}] \right\} \end{aligned} \quad (40)$$

Correspondingly the change in configurational entropy due to random mixing of vacancies on appropriate sites is identical with that given by Eq. (20). Thus upon minimizing the free energy we obtain

$$p_{VA\alpha} = \frac{n_{VA\alpha}}{n_\alpha} = \frac{e^{\frac{6}{kT} \left[\left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right) \epsilon_{AA} + \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right) \epsilon_{AB} \right]}}{1 - e^{\frac{6}{kT} \left[\left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right) \epsilon_{AA} + \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right) \epsilon_{AB} \right]}} p_{A\alpha} \quad (41a)$$

$$p_{VB\alpha} = \frac{n_{VB\alpha}}{n_\alpha} = \frac{e^{\frac{6}{kT} \left[\left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right) \epsilon_{AB} + \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right) \epsilon_{BB} \right]}}{1 - e^{\frac{6}{kT} \left[\left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right) \epsilon_{AB} + \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right) \epsilon_{BB} \right]}} p_{B\alpha} \quad (41b)$$

$$p_{VA\beta} = \frac{n_{VA\beta}}{n_\beta} = \frac{e^{\frac{6}{kT} [p_{A\alpha} \epsilon_{AA} + p_{B\alpha} \epsilon_{AB}]}}{1 - e^{\frac{6}{kT} [p_{A\alpha} \epsilon_{AA} + p_{B\alpha} \epsilon_{AB}]}} p_{A\beta} \quad (41c)$$

$$p_{VB\beta} = \frac{n_{VB\beta}}{n_{\beta}} = \frac{e^{\frac{6}{kT}[p_{A\alpha}\epsilon_{AB} + p_{B\alpha}\epsilon_{BB}]}}{1 - e^{\frac{6}{kT}[p_{A\alpha}\epsilon_{AB} + p_{B\alpha}\epsilon_{BB}]}} p_{B\beta} \quad (41d)$$

The values of $p_{V\alpha}$ and $p_{V\beta}$ can then be deduced from the above by utilizing Eqs. (25).

C. Vacancy-Energy Model

For the Ll_2 lattice the probability that an atom on a β site is coordinated with i B atoms and $(z-i)$ A atoms is simply given by the general term of the binomial expansion

$$(p_{A\alpha} + p_{B\alpha})^z = \sum_{i=0}^z \frac{z!}{(z-i)!i!} p_{A\alpha}^{z-i} p_{B\alpha}^i = 1 \quad (28)$$

where the atoms on the α sites are randomly distributed and where $z = 12$. Applying the previously described methods of analysis for evaluating the equilibrium numbers of vacancies of the i^{th} kind on the β sites gives

$$\frac{n_{i\beta}}{n_{\beta}} = \frac{z!}{(z-i)!i!} p_{A\alpha}^{z-i} p_{B\alpha}^i e^{-\frac{\epsilon_{i\beta}}{kT}} \quad (29a)$$

On the other hand the probability that an atom on an α site is coordinated with i B atoms and $(z-i)$ A atoms is given by the general term of the binomial expansion

$$\begin{aligned} & \left[\frac{8}{12} (p_{A\alpha} + p_{B\alpha}) + \frac{4}{12} (p_{A\beta} + p_{B\beta}) \right]^z \\ &= \left[\frac{2}{3} (p_{A\alpha} + p_{B\alpha}) + \frac{1}{3} (p_{A\beta} + p_{B\beta}) \right]^z \\ &= \sum \frac{z!}{(z-i)!i!} \left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta} \right)^{z-i} \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta} \right)^i = 1 \quad (42) \end{aligned}$$

Formulating and minimizing the free energy of formation of vacancies, as

done before, gives

$$\frac{n_{i\alpha}}{n_{\alpha}} = \frac{z!}{(z-i)!i!} \left(\frac{2}{3} p_{A\alpha} + \frac{1}{3} p_{A\beta}\right)^{z-i} \left(\frac{2}{3} p_{B\alpha} + \frac{1}{3} p_{B\beta}\right)^i e^{-\frac{\epsilon_{i\alpha}}{kT}} \quad (43)$$

Significantly Eqs. (29a) and (43) reduce to the Dorn-Mitchell relationship when the alloy is disordered. The values of $p_{V\alpha}$ and $p_{V\beta}$ can be obtained by applying the summations of Eqs. (31).

For the $L1_2$ lattice the average energy, $\bar{\epsilon}$, of a bond is given by

$$\begin{aligned} \bar{\epsilon} = & (p_{A\alpha}p_{A\alpha} + p_{A\alpha}p_{A\beta})\epsilon_{AA} + (2p_{A\alpha}p_{B\alpha} + p_{A\alpha}p_{B\beta} + p_{A\beta}p_{B\alpha})\epsilon_{AB} \\ & + (p_{B\alpha}p_{B\alpha} + p_{B\alpha}p_{B\beta})\epsilon_{BB} \end{aligned} \quad (44a)$$

Introducing Eqs. (5), where $N_{\alpha} = 3/4$ and $N_{\beta} = 1/4$, and the ordering energy, ϵ , we obtain

$$\bar{\epsilon} = \frac{1}{8} \{ (3-4\delta)^2 \epsilon_{AA} + 2(3-4\delta)(1+4\delta) \epsilon_{AB} + (1+4\delta)^2 \epsilon_{BB} \} + \frac{n^2 \epsilon}{4} \quad (44b)$$

Thus, the free energies of formation of the i^{th} kind of vacancies can be represented by Eqs. (27a) and (27b) respectively for α and β sites.

D. Modified Vacancy-Energy Model

Whereas the total number of vacant β sites is identical with Eq. (32a) where z is now equal to 12, that of vacant α sites can be evaluated from Eq. (43). Following the same reasoning given previously for the $L2_0$ lattice,

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{n_{i\alpha}^{(A)} + n_{i\alpha}^{(B)}}{n_\alpha} = \frac{z!}{(z-i)!i!} \left(\frac{2}{3}p_{A\alpha} + \frac{1}{3}p_{A\beta}\right)^{z-i} \left(\frac{2}{3}p_{B\alpha} + \frac{1}{3}p_{B\beta}\right)^i$$

$$\left(p_{A\alpha} e^{\frac{(z-i)\epsilon_{AA} + i\epsilon_{AB}}{2kT}} + p_{B\alpha} e^{\frac{(z-i)\epsilon_{AB} + i\epsilon_{BB}}{2kT}} \right) \quad (45)$$

Thus the probability of vacancies on α sites is simply given by

$$p_{V\alpha} = \sum_{i=0}^z \frac{n_{i\alpha}}{n_\alpha} = p_{A\alpha} \left\{ \left(\frac{2}{3}p_{A\alpha} + \frac{1}{3}p_{A\beta}\right) e^{\frac{\epsilon_{AA}}{2kT}} + \left(\frac{2}{3}p_{B\alpha} + \frac{1}{3}p_{B\beta}\right) e^{\frac{\epsilon_{AB}}{2kT}} \right\}^z$$

$$+ p_{B\alpha} \left\{ \left(\frac{2}{3}p_{A\alpha} + \frac{1}{3}p_{A\beta}\right) e^{\frac{\epsilon_{AB}}{2kT}} + \left(\frac{2}{3}p_{B\alpha} + \frac{1}{3}p_{B\beta}\right) e^{\frac{\epsilon_{BB}}{2kT}} \right\}^z \quad (46)$$

and the probability of vacancies on β sites is given by Eq. (33b).

V. DISCUSSION

The Smeared-Displacement Models for the $L2_0$ and $L1_2$ lattices are based on the same general assumptions as those made by Krivoglaz and Smirnov.³ In these models no detailed inspection is made of vacancy environments. Rather, vacancies are assumed to exist in a smeared average environment dictated by the degree of order. Thus each vacancy on an α (or β) site is assumed to have the same average energy of formation regardless of the numbers and kinds of atoms with which it is coordinated. In the same sense, the configurational entropy is also some smeared value.

A more rigorous and direct analytical approach was adopted here than that used by Krivoglaz and Smirnov, introducing a less ambiguous definition of order in the presence of vacancies and greater clarity in the introduction of approximations. Nevertheless, despite differences in analytical approaches, the present results agree with those previously given by Krivoglaz and Smirnov. The degree of order is essentially unmodified by the vacancy concentration. In the disordered state $p_{V\alpha}/p_{V\beta} = 1$, as it should be, but when the alloy is ordered $p_{V\alpha}/p_{V\beta}$ deviates from unity.

The Simple-Displacement Model is, at least conceptually, somewhat similar to that suggested by Girifalco⁴ who, however, limited his discussion only to the $L2_0$ lattice type. It assumes that the degree of order is established in the absence of vacancies and the vacancies are then produced by displacing atoms (either A or B) from sites (either α or β) in the bulk of the crystal to ones on the surface. It is further assumed (a) that neither the average all-over occupancy of the various α and β sites by A and B atoms nor (b) the local arrangements of A and B atoms now

coordinated with a vacancy change as a result of atom displacement to the surface. Assumption (a) follows since the number of vacancies is very small relative to the number of atoms present and was further confirmed by the analysis for the Smeared-Displacement Model. The possible validity of assumption (b) was discussed previously in Part A. It is significant that the Smeared-Displacement Model is free from the taint of this assumption. Thus, the good agreement between predictions based on the Smeared-Displacement Model and the Simple-Displacement Model uphold at least the nominal validity of assumption (b).

As a consequence of the greater detail that was introduced a more accurate configurational entropy could be established for the Simple-Displacement Model than that which was used in the Smeared-Displacement Model. Furthermore, all vacancies on α (or β) sites were not ascribed, as in the Smeared-Displacement Model, the same average energy but were assigned values which depended on whether the vacancy was produced by displacement of an A or a B atom. Thus the Simple-Displacement Model is perhaps slightly more accurate and provides somewhat greater detail than the Smeared-Displacement Model.

The Simple-Displacement Model also gives $p_{V\alpha}/p_{V\beta} = 1$ for the disordered case. According to the analysis presented here, such equality of vacancy concentration on the two sublattices in the ordered, $L2_0$ alloy occurs only at the stoichiometric composition ($\delta = 0$) for the cases where $\epsilon_{AA} = \epsilon_{BB}$. This deduction which is also valid for the Smeared-Displacement and Modified Vacancy-Energy Models is in sharp contrast to that made by Girifalco who reached the conclusion that the concentration of vacancies on the two

types of sites in the $L2_0$ lattice was always the same in the stoichiometric alloy regardless of the degree of order. The discrepancy between the present results and those obtained by Girifalco stems from the more careful and detailed accounting employed in the present case. The fact that the Smeared-Displacement, Simple-Displacement and Modified Vacancy-Energy Models, each of which differs substantially relative to the details that can be extracted from them, give about the same average values for p_{V_a} and p_{V_b} , as will be shown later, is excellent confirmation that the Simple-Displacement Model presented here is reasonably reliable.

The Vacancy-Energy Model is the most detailed and physically acceptable of all of the four models established here. It is based on the previously discussed assumption that neither the average occupancy of sites nor the local configuration of atoms is significantly modified when vacancies are introduced. The naive bond-energy method of estimating the energy to form a vacancy is abandoned in favor of the more realistic concept that the energy of a vacancy depends primarily on its immediate environment. This physically attractive assumption on vacancy energies was coupled with an equally satisfactory estimate of the entropy for mixing the various types of vacancies on lattice sites. Consequently the formalism of the model appears to be good. Furthermore, for the disordered alloy, the relationships reduce to those previously established by Dorn and Mitchell for random binary alloys when based on a more detailed analysis.

Unfortunately it is not easy to compare deductions based on the Vacancy-Energy Model with those of the Smeared-Displacement and Simple-Displacement Models. This arises from the fact that the $3(z + 1)$ values of g_{1a} and

$g_{i\beta}$ must yet be deduced from appropriately designed experiments. Although other often very important factors intrude, at least in part, the values of the $g_{i\alpha}$ and $g_{i\beta}$ are expected to respond in somewhat the same ways as those deduced from the bond energy method of estimating the energy to produce a vacancy.

The Modified Vacancy-Energy Model is based on the same assumptions as those used in the Vacancy-Energy Model. It differs from the Vacancy-Energy Model only insofar as the values of $g_{i\alpha}$ and $g_{i\beta}$ are estimated in terms of the bond-energy approximation for the energy of formation of a vacancy. It can, therefore, be compared with the Smeared-Displacement and Simple-Displacement Models. Such comparisons are best made using specific examples.

The trends for the L2₀ lattice will be based on β -brass. The bond energies

$$\epsilon_{AA} = \epsilon_{ZnZn} = -7.9/N_0 \text{ kcal}$$

$$\epsilon_{BB} = \epsilon_{CuCu} = -20.4/N_0 \text{ kcal}$$

where N_0 is Avogadro's number, were estimated from the latent heats of sublimation of the pure metals. The value of

$$\epsilon_{AB} = \epsilon_{ZnCu} = -14.5/N_0 \text{ kcal}$$

was obtained from the known ordering temperature T_{co} for the stoichiometric alloy ($\delta = 0$) by means of Eq. (16). The calculated values of $\ln p_{V\alpha}$

and $\ln p_{V\beta}$ for the several models are given as a function of T_{co}/T in Figs. 2, 3 and 4. All models predict about the same general trends. Above the ordering temperature the sublattices are indistinguishable. Therefore, the concentrations of vacancies on α and β sites are the same. Below the critical temperature, however, a dichotomy occurs with more vacancies on β sites and less on α sites. This disparity of the concentrations of vacancies on the two sublattices is enhanced by an increase in the degree of order. Furthermore, the extent of disparity seems to become less when more detailed accounting of atomic arrangements about vacancies is taken into consideration.

Also shown in Figs. 2 and 3 are the effects of deviations from stoichiometry. It is seen that small deviations from the stoichiometric composition have a minor effect but do not significantly change the general trends.

Although the Modified Vacancy-Energy Model, as shown in Fig. 4, gives about the same trends for the vacancy concentrations, the detailed accounting procedure introduced into this model permits the extraction of more information regarding the types and distributions of vacancies present than is possible in either the Smeared-Displacement or Simple-Displacement Models. Figure 5 gives the distributions of the ratio of the equilibrium number of vacancies of the i^{th} type to that of the same alloy when it is in the disordered state as a function of T_{co}/T for the stoichiometric composition. The distribution of the various vacancy concentrations at a given temperature is shown in Fig. 6. It is seen that the most populous type of vacancies changes as the temperature or degree of order

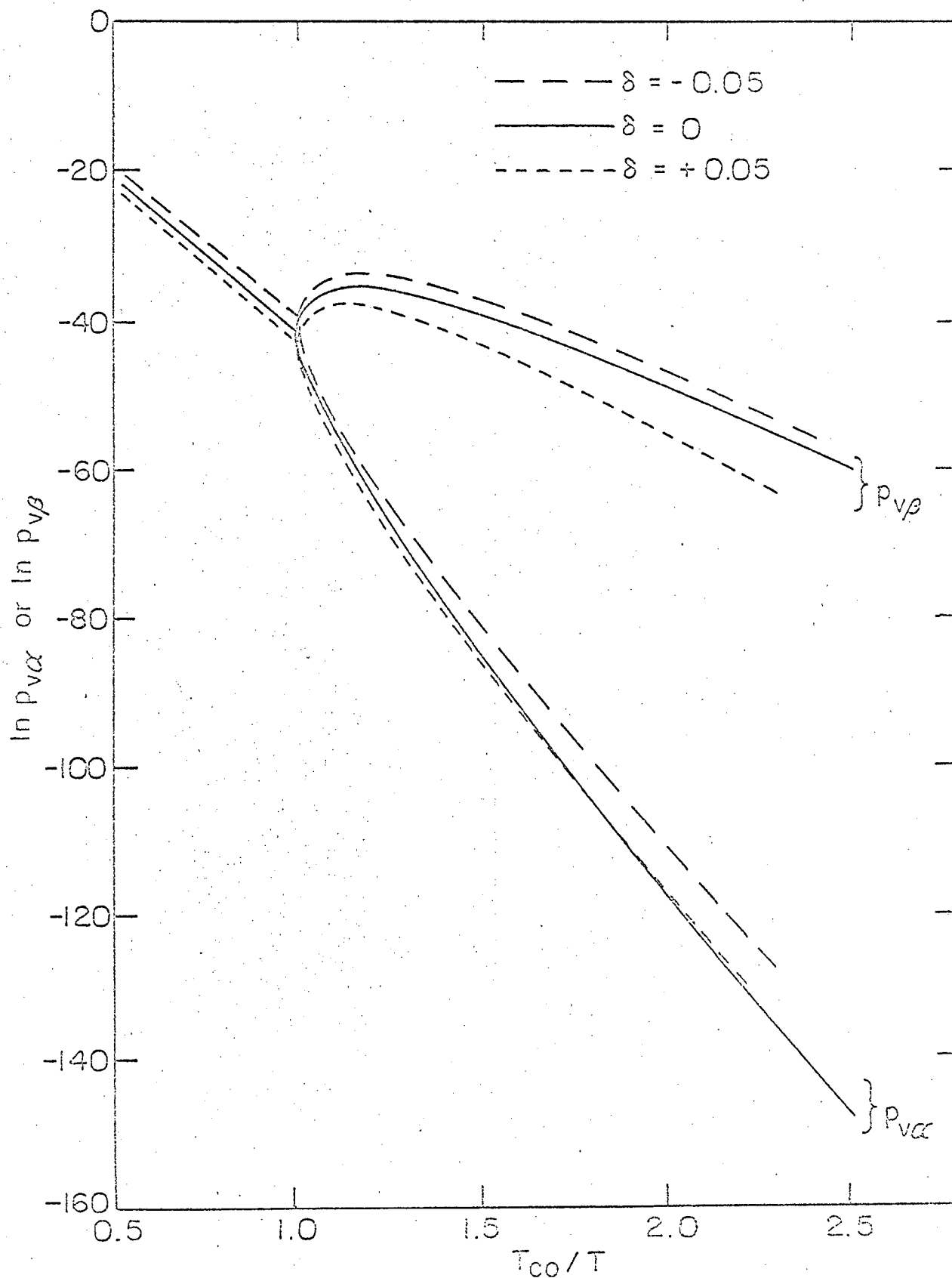


FIG. 2 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE L_{20} ALLOY ACCORDING TO THE SMEARED-DISPLACEMENT MODEL.

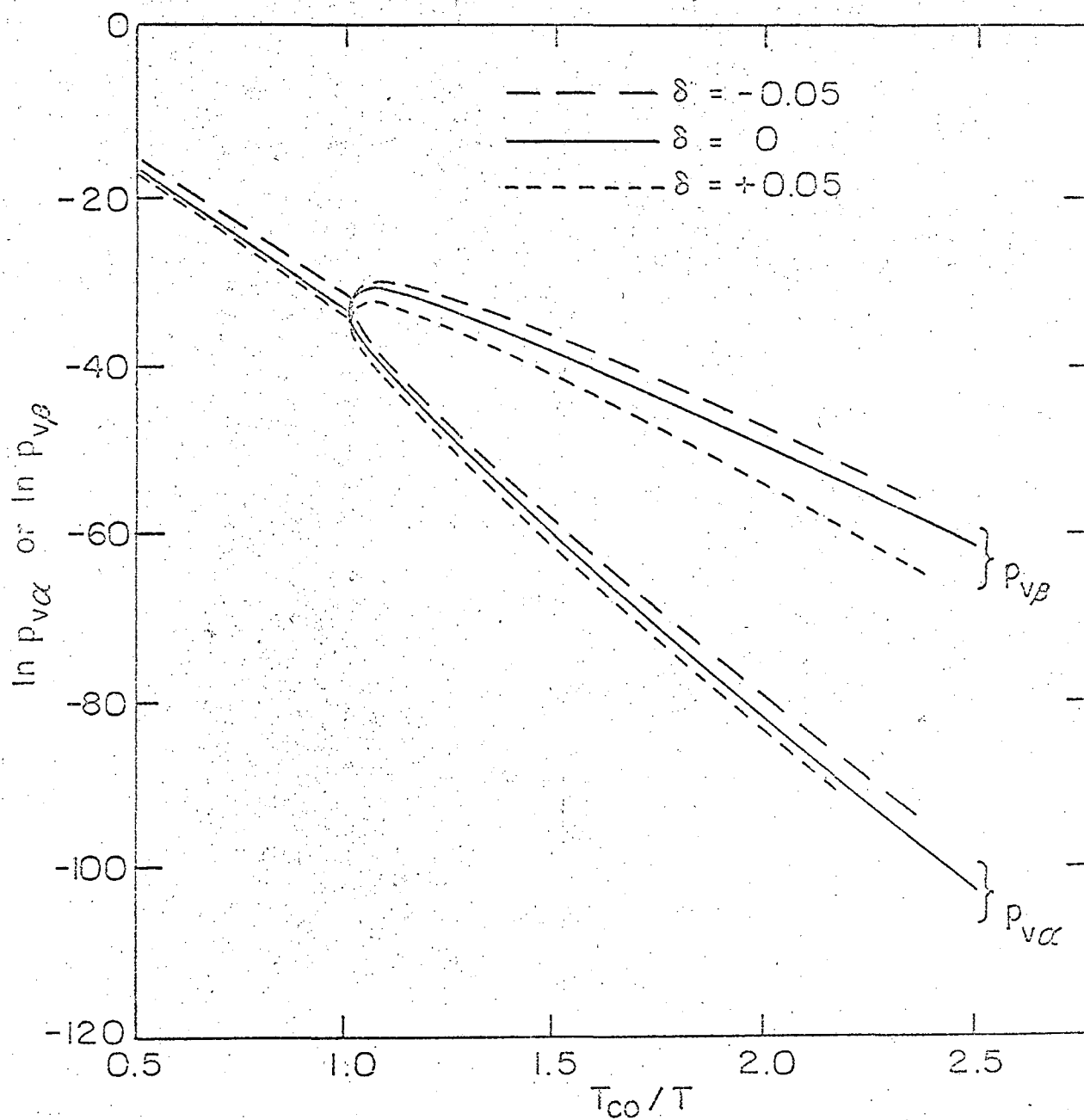


FIG. 3 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE $L2_0$ ALLOY ACCORDING TO THE SIMPLE-DISPLACEMENT MODEL.

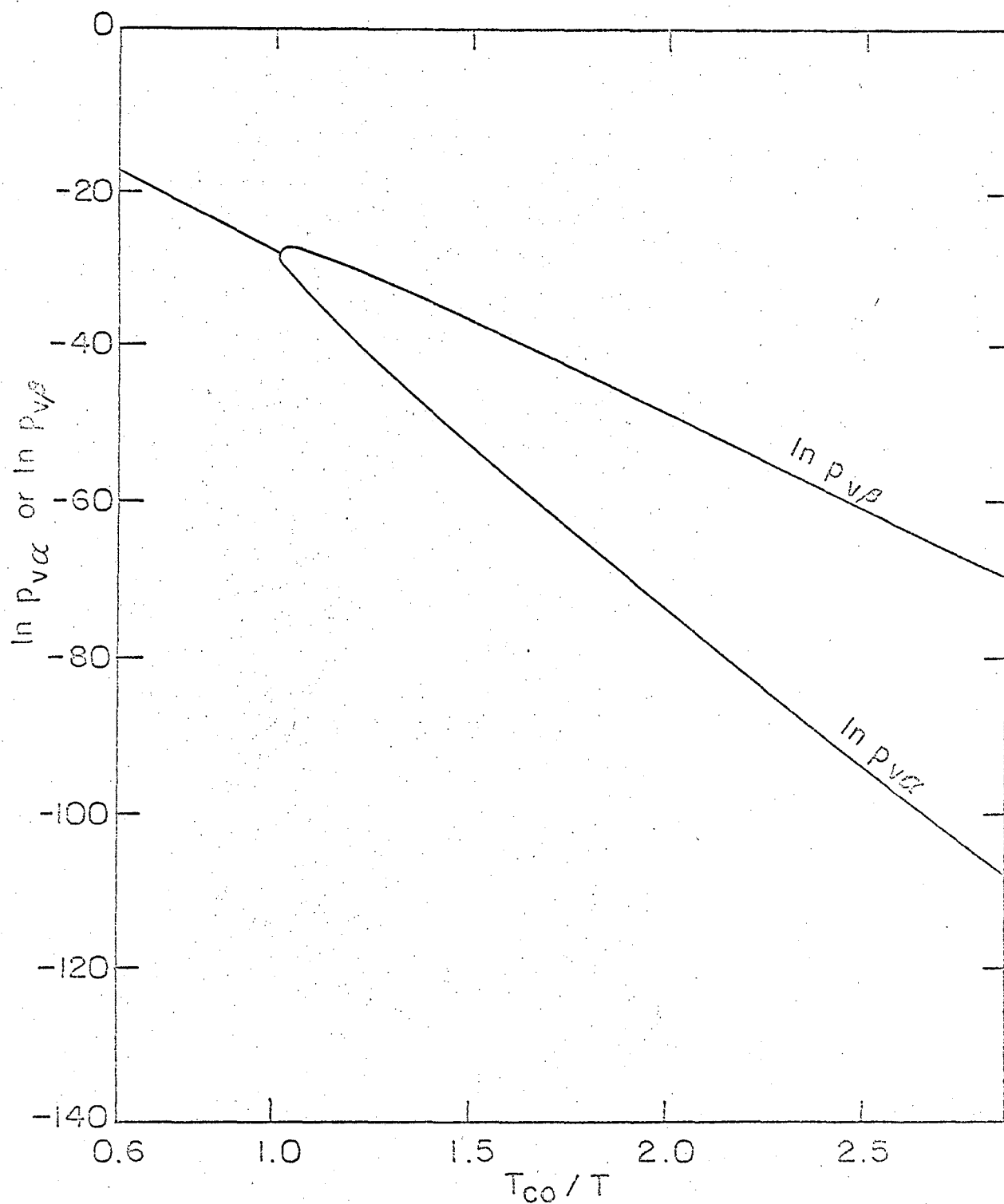


FIG. 4 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY ACCORDING TO THE MODIFIED VACANCY-ENERGY MODEL.

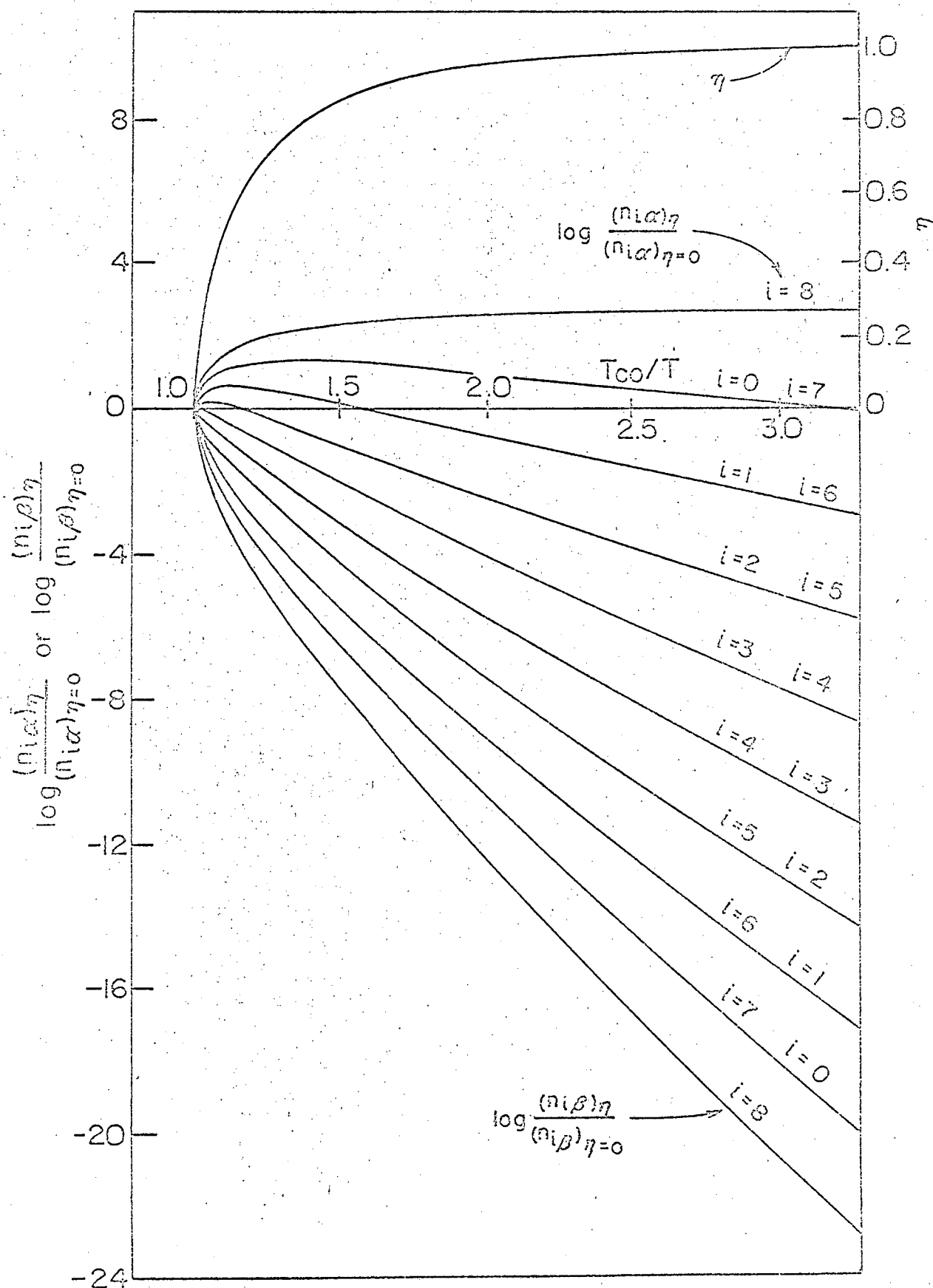


FIG. 5 EFFECT OF ORDERING ON THE DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY.

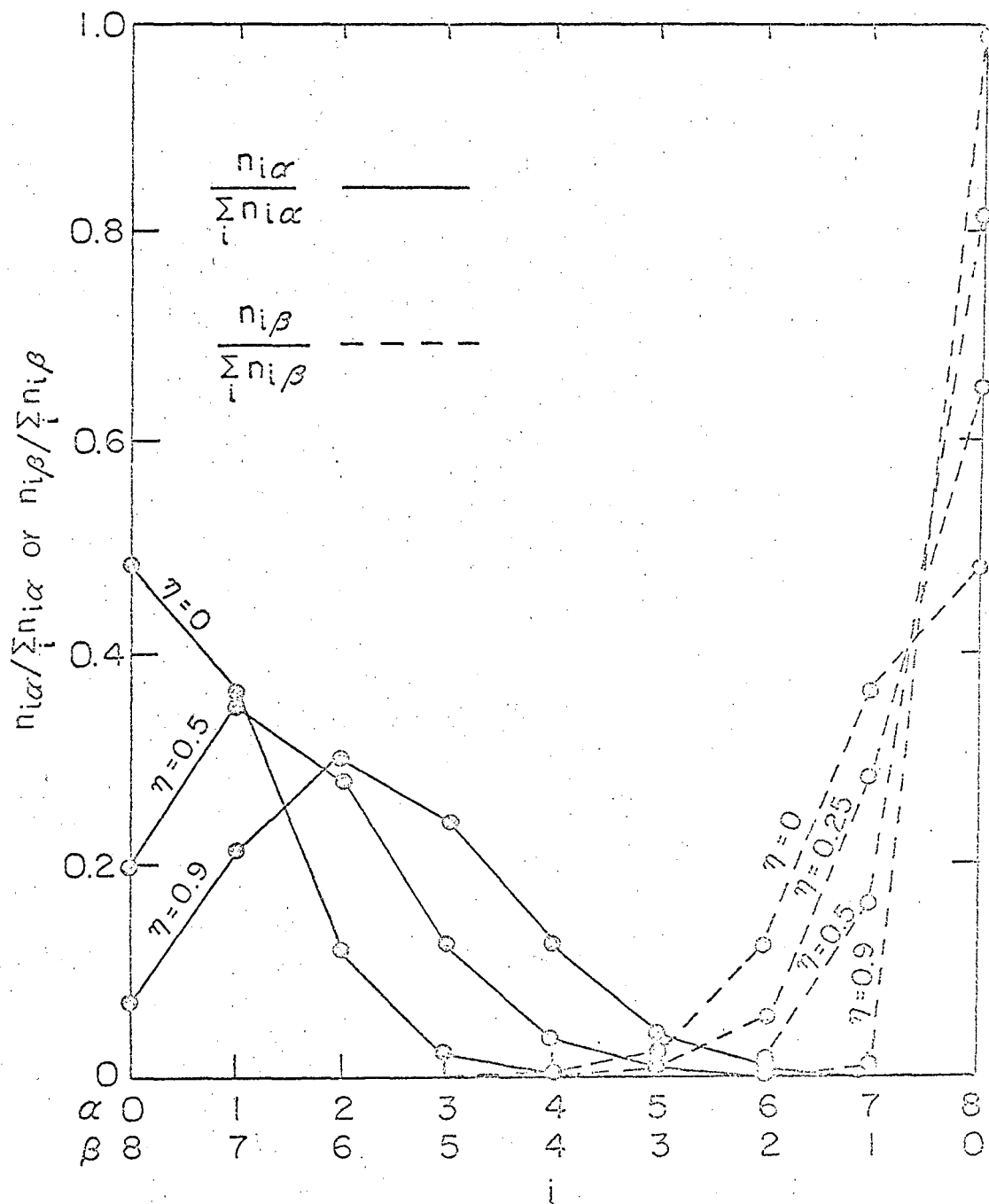


FIG. 6 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY WHERE $N_0\epsilon_{AA} = -7.9$ K CAL, $N_0\epsilon_{BB} = -20.4$ K CAL AND $N_0\epsilon_{AB} = -14.5$ K CAL.

varies. Furthermore, it is also strongly affected by the values of bond energies adopted in the calculation as shown in Fig. 7 for the case

$$\epsilon_{AA} = \epsilon_{BB}.$$

The comparisons of the results for the $L1_2$ lattice will be based on the Cu_3Au alloy. As mentioned previously, at the critical temperature the alloys with $L1_2$ type of lattice undergo a first order phase transformation in lieu of second order phase transition for the $L2_0$ lattice. The dependence of the configurational part of the free energy on the degree of long-range order for these two lattices⁵ is shown in Fig. 8. It should be noticed that the behavior of the free energy for A_3B alloys is characteristically different from that for AB alloys. At high temperatures in both cases the curves $F(\eta)$ have a single minimum at $\eta = 0$ indicating the stable state being that of complete disorder. As the temperature is decreased below some temperature T_{co} in the $L2_0$ alloys (Fig. 8a) the minimum of the curve $F(\eta)$ is shifted continuously to larger values of η , and the point $\eta = 0$ becomes a maximum point of F and corresponds to the unstable state of order. Such a pattern which corresponds to a continuous increase of η from zero with a decrease of temperature is the characteristics of a second order phase transition. Therefore a second order phase transformation is featured by a continuous change in entropy, no heat of transition and a finite jump in the specific heat at the transition point. On the other hand, in alloys with $L1_2$ lattice (Fig. 8b), as the temperature is lowered a minimum appears at a nonzero value of η and the point $\eta = 0$ as before is a minimum. Thus, in the case of equilibrium there may exist both an ordered and a disordered phase, but one of them (corresponding to a large

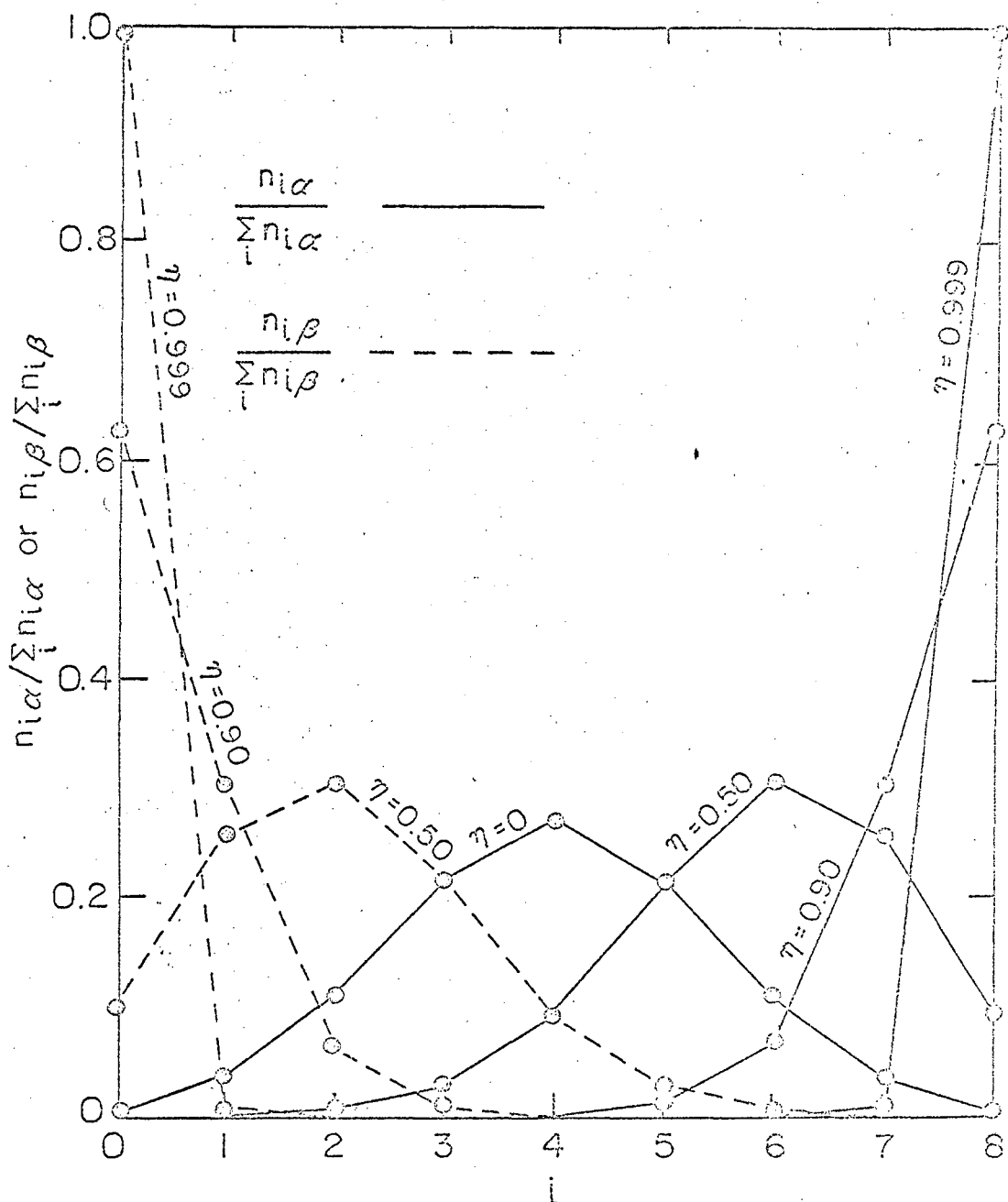
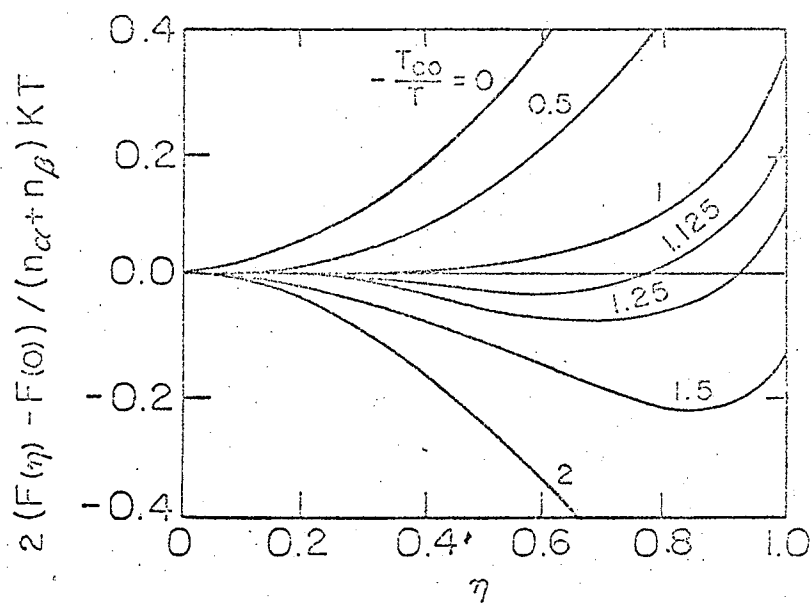
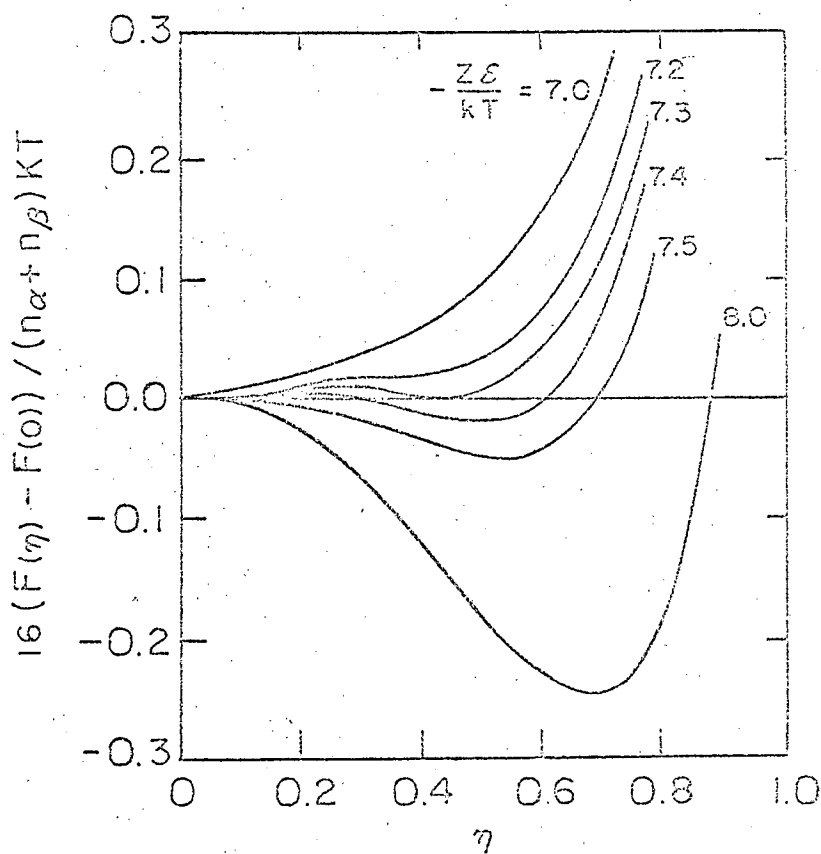


FIG.7 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY WHERE $N_0 \epsilon_{AA} = N_0 \epsilon_{BB} = -14.15$ KCAL AND $N_0 \epsilon_{AB} = -14.50$ KCAL.



a.



b.

FIG. 8 CONFIGURATIONAL FREE ENERGY $F(\eta)$ AS A FUNCTION OF η FOR AB ALLOYS (a) AND FOR A_2B ALLOYS (b) ACCORDING TO THE BRAGG-WILLIAMS APPROXIMATION FOR VARIOUS TEMPERATURE, T .

value of F at the minimum point) is found to be in a metastable state. A second minimum appears at once at an η which differs from zero by a finite magnitude. This behavior describes a first order phase transition. This phase transformation of the first order can be realized only when the two free energy minima are at the same level. Therefore, the degree of long-range order at the transition, η_{co} , and the relationship between the critical temperature, T_{co} , and the ordering energy, ϵ , can be found by solving simultaneously Eq. (37) and

$$F(0) = F(\eta_{co}) \quad (47)$$

A numerical solution of the above simultaneous equations gives

$$\eta_{co} = 0.46 \text{ and } kT_{co} = -1.64 \epsilon \quad (48)$$

These are identical with the results given by Krivoglaz and Smirnov.

For the convenience of comparisons among the described models the bond energies

$$\epsilon_{AA} = \epsilon_{CuCu} = - \frac{13.60}{N_o} \text{ kcal}$$

$$\epsilon_{BB} = \epsilon_{AuAu} = - \frac{15.10}{N_o} \text{ kcal}$$

where N_o is Avogadro's number, were estimated from the heats of sublimation of pure metals. By means of Eq. (48) and the known critical temperature for the alloy of stoichiometric composition ($\delta = 0$) the value of

$$\epsilon_{AB} = \epsilon_{CuAu} = - \frac{15.15}{N_o} \text{ kcal}$$

was also assumed. The calculated values of $\ln p_{V\alpha}$ and $\ln p_{V\beta}$ are shown in Fig. 9. Above the ordering temperature, again the two sublattices are indistinguishable, therefore the probabilities on α and β sites are the same. Below the critical temperature, the familiar dichotomy occurs in all three models but differs in extent. At the critical temperature, a step change occurs in the probabilities. This is the characteristics of the first order phase transformation.

Figure 10 shows the effect of ordering on the distribution of the various vacancy concentrations on α and β sites. Also plotted in this figure is the degree of long-range order as a function of T_{co}/T . The section ab of this curve gives the values of η which **correspond to the** maximum of F (Fig. 8b) and can not be realized. The values **η over the** **range** bc correspond to the metastable states, and the section **cd corresponds** **to the** equilibrium values of the degree of long-range order, η , which are **realized** only when $T < T_{co}$. The population distributions of the various types of vacancies are shown in Fig. 11.

Although the general trends given in the figures based on the Smearred-Displacement, Simple-Displacement and Modified Vacancy-Energy Models might be expected, the detailed results based on these models are not to be taken too literally. Obviously the methods of estimating vacancy formation energies from a bond energy model is extremely crude and inexact. Furthermore, on this basis the energy to produce a vacancy coordinated with $(z - i)$ A atoms and i B atoms differs depending on whether an A atom or a B atom was removed. In contrast the physically more acceptable vacancy-energy concept suggests that the energy, g_i , to produce a vacancy

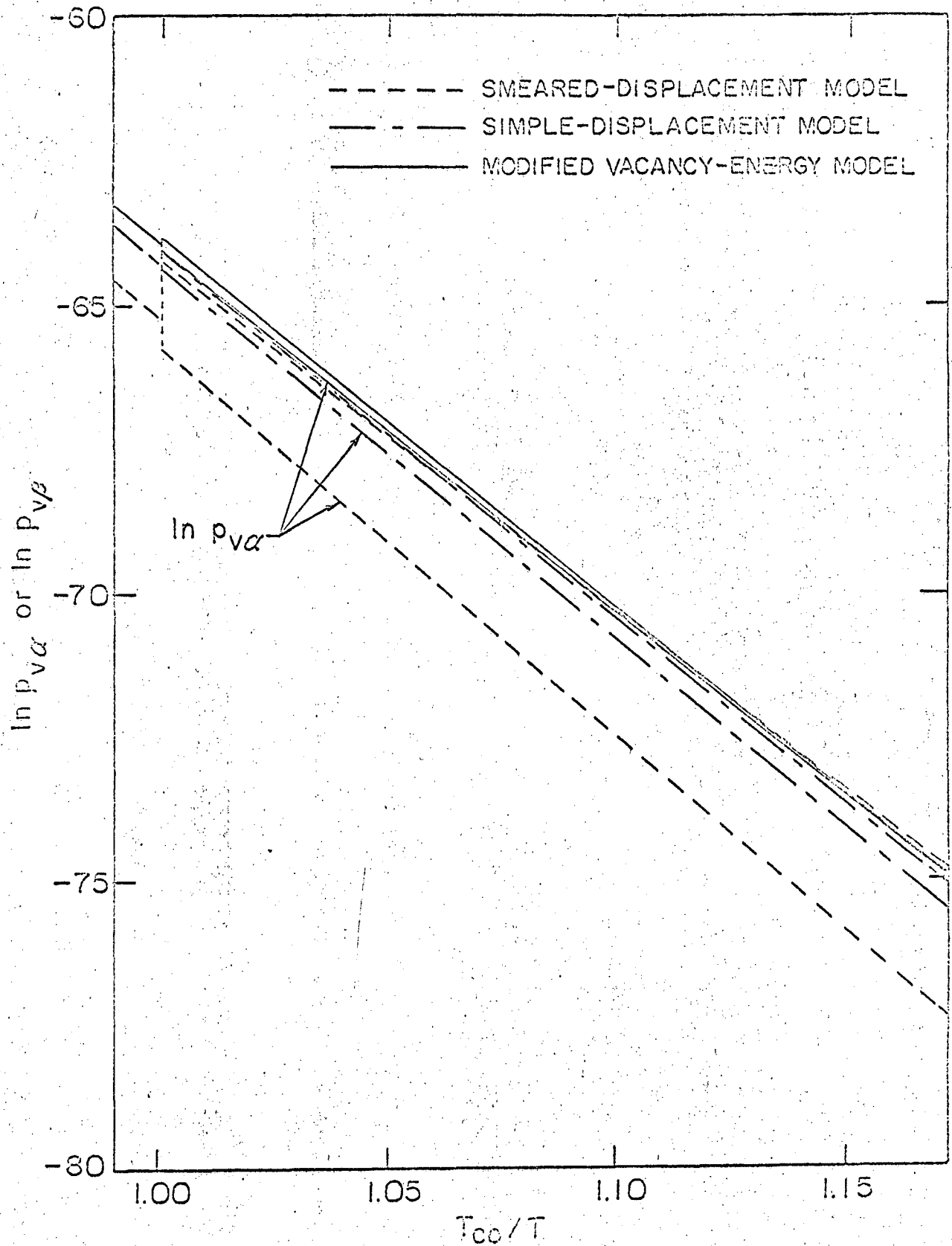


FIG. 9 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE STOICHIOMETRIC, $L1_2$ ALLOY.

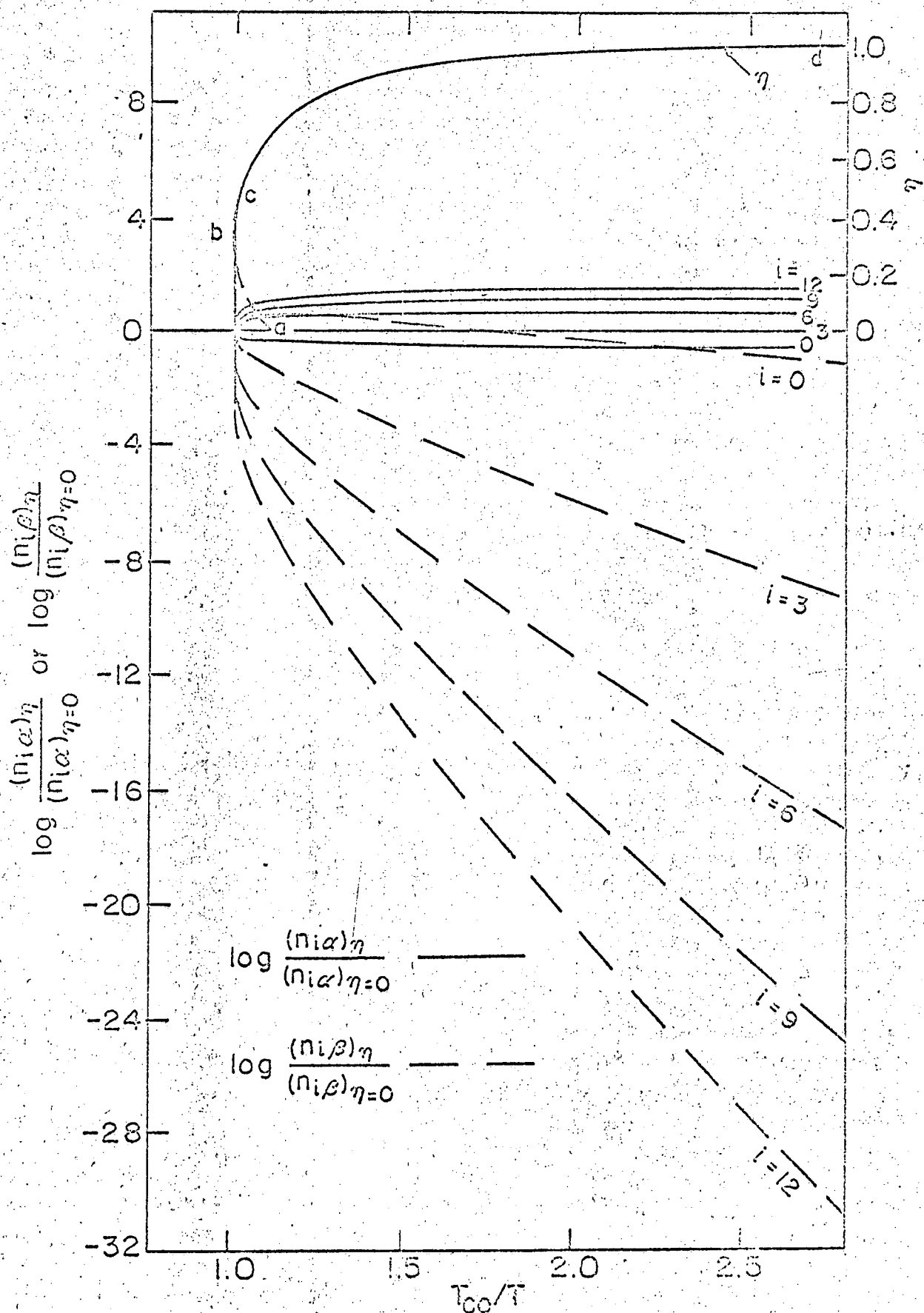


FIG. 10' EFFECT OF ORDERING ON THE DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L1_2$ ALLOY.

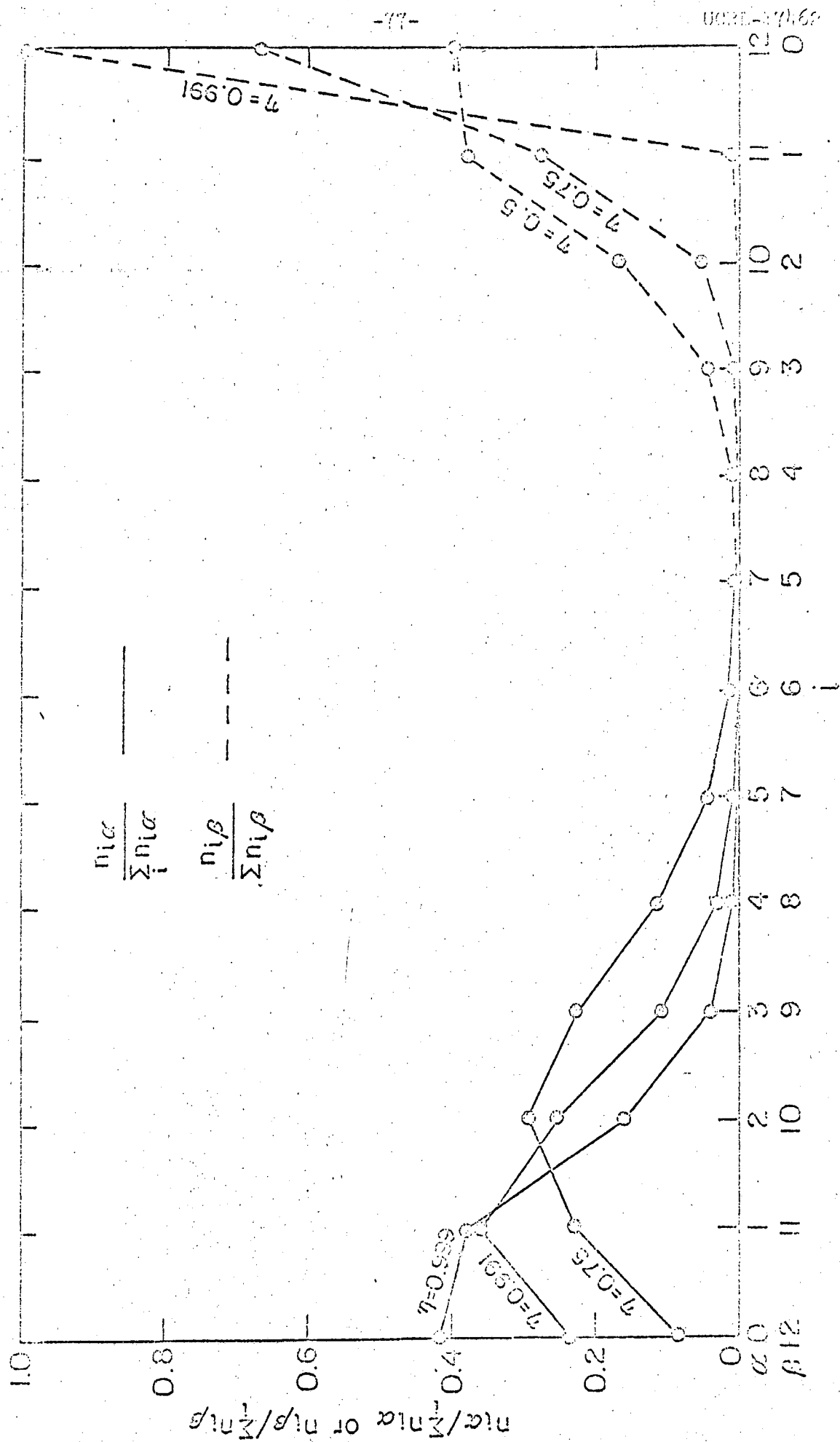


FIG. 11 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L1_2$ ALLOY.

should depend principally on its immediate environment. It is not clear whether this apparent dichotomy of concept is resolvable. Unfortunately no satisfactory theoretical method of estimating the values of the g_i is now available and therefore the nominal correctness of the Vacancy-Energy Model is dependent on future experimental verification.

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ACKNOWLEDGEMENT

The author is most grateful to Professor John E. Dorn for his guidance and help throughout the course of this research. The author would also like to express his thanks to Dr. P. Wynblatt for his kind assistance in carrying out portions of calculation of Part B and to Mr. D. M. Schwartz for assistance with part of computer programming. Thanks are also due to Gloria Pelatowski for drawing and to Lexie Anderson for typing.

This research was conducted as part of the activities of the Inorganic Materials Research Division of the Lawrence Radiation Laboratory of the University of California. The author wishes to express his appreciation to the United States Atomic Energy Commission for its support of this work.

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