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ABSTRACT

Four models (Smeared-Displacement, Simple-Displacement, Modified Vacancy-Energy and Vacancy-Energy Models) for estimating the effects of long-range ordering on the equilibrium concentration of vacancies in binary alloys 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 differ on the different types of lattice sites when the alloy is ordered.

I. INTRODUCTION

This is a companion paper to "Vacancy Models for Concentrated Alloys. I. Short-Range Ordered and Clustered Alloys". Here we shall discuss 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 erected 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 differ, 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 models which follow we will consider alloys having various degrees of long-range order. The crystal 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.

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

$$n_A = n_{A\alpha} + n_{A\beta} \tag{1a}$$

$$n_B = n_{B\alpha} + n_{B\beta} \tag{1b}$$

$$n_\alpha/n_\beta = \frac{N_\alpha}{N_\beta} = \frac{n_{A\alpha} + n_{B\alpha} + n_{v\alpha}}{n_{A\beta} + n_{B\beta} + n_{v\beta}} \tag{1c}$$

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

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

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

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

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

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

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

Furthermore

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

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

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

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

where

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

When the concentration of vacancies is negligibly small relative to n_A and to n_B Eqs. (3) reduce to

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

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

$$p_{B\alpha} = \frac{n_{B\alpha}}{n_\alpha} \simeq N_\beta + \delta - N_\beta \eta \qquad (5c)$$

$$p_{B\beta} = \frac{n_{B\beta}}{n_\beta} \simeq N_\beta + \delta + N_\alpha \eta \qquad (5d)$$

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

$$S = k\ell n\Omega = k\ell n \frac{n_\alpha!}{n_{A\alpha}!\,n_{B\alpha}!\,n_{V\alpha}!} \cdot \frac{n_\beta!}{n_{A\beta}!\,n_{B\beta}!\,n_{V\beta}!} \qquad (6)$$

for all types of lattices. In contrast, however, the configurational energies differ dependent on the lattice type. We propose to study both the $L2_0$ and the $L1_2'$ lattices here. Whereas the former undertakes a second order phase transformation on ordering, the latter undergoes a first order phase transformation.

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). Each α (or β) site is coordinated with 8 β (or 8 α) sites. Furthermore $N_\alpha = N_\beta = 1/2$. Therefore in terms of the simple bond energy model the total energy of the crystal of the $L2_0$ lattice is given by

$$E = z\{n_{A\alpha} \frac{n_{A\beta}}{n_\beta} \varepsilon_{AA} + n_{A\alpha} \frac{n_{B\beta}}{n_\beta} \varepsilon_{AB}$$

$$+ n_{B\alpha} \frac{n_{A\beta}}{n_\beta} \varepsilon_{AB} + n_{B\alpha} \frac{n_{B\beta}}{n_\beta} \varepsilon_{BB}\}$$

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

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

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). Consequently $z = 12$ and $N_\alpha = 3/4$, $N_\beta = 1/4$ for this lattice. 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 model the energy of the $L1_2$ lattice is given by

$$E = z\{n_{A\beta}\frac{n_{A\alpha}}{n_\alpha}\varepsilon_{AA} + n_{A\beta}\frac{n_{B\alpha}}{n_\alpha}\varepsilon_{AB} + n_{B\beta}\frac{n_{A\alpha}}{n_\alpha}\varepsilon_{AB}$$

$$+ n_{B\beta}\frac{n_{B\alpha}}{n_\alpha}\varepsilon_{BB}\} + \frac{8}{2}\{n_{A\alpha}\frac{n_{A\alpha}}{n_\alpha}\varepsilon_{AA} + n_{A\alpha}\frac{n_{B\alpha}}{n_\alpha}\varepsilon_{AB}$$

$$+ n_{B\alpha}\frac{n_{A\alpha}}{n_\alpha}\varepsilon_{AB} + n_{B\alpha}\frac{n_{B\alpha}}{n_\alpha}\varepsilon_{BB}\}$$

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 $L1_2$ lattice reduces to

$$E = \frac{16}{n_\alpha + n_\beta}\{[n_{A\beta}n_{A\alpha} + \frac{1}{3}n_{A\alpha}n_{A\alpha}]\varepsilon_{AA}$$

$$+ [n_{A\beta}n_{B\alpha} + n_{B\beta}n_{A\alpha} + \frac{2}{3}n_{A\alpha}n_{B\alpha}]\varepsilon_{AB}$$

$$+ [n_{B\beta}n_{B\alpha} + \frac{1}{3}n_{B\alpha}n_{B\alpha}]\varepsilon_{BB}\} \qquad (8)$$

II. Vacancy Models for the $L2_0$ 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

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

where E is given by Eq. (7) 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

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

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

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

where the λs are Lagrangian multipliers and where the condition appropriate to the $L2_0$ 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

$$\begin{aligned}
\frac{\partial E}{\partial n_{A\alpha}} &= kT \frac{\partial \ell n\Omega}{\partial n_{A\alpha}} - \lambda_{\alpha\beta} - \lambda_A, &\quad \frac{\partial E}{\partial n_{A\beta}} &= kT \frac{\partial \ell n\Omega}{\partial n_{A\beta}} + \lambda_{\alpha\beta} - \lambda_A \\
\frac{\partial E}{\partial n_{B\alpha}} &= kT \frac{\partial \ell n\Omega}{\partial n_{B\alpha}} - \lambda_{\alpha\beta} - \lambda_B, &\quad \frac{\partial E}{\partial n_{B\beta}} &= kT \frac{\partial \ell n\Omega}{\partial n_{B\beta}} + \lambda_{\alpha\beta} - \lambda_B \\
\frac{\partial E}{\partial n_{V\alpha}} &= kT \frac{\partial \ell n\Omega}{\partial n_{V\alpha}} - \lambda_{\alpha\beta}, &\quad \frac{\partial E}{\partial n_{V\beta}} &= kT \frac{\partial \ell n\Omega}{\partial n_{V\beta}} + \lambda_{\alpha\beta}
\end{aligned} \tag{11}$$

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

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

$$\ell n \frac{n_{V\alpha}}{n_\alpha} = \frac{16}{kT(n_\alpha+n_\beta)^2} \{n_{A\alpha}n_{A\beta}\varepsilon_{AA}+(n_{A\alpha}n_{B\beta}+n_{B\alpha}n_{A\beta})\varepsilon_{AB}+n_{B\alpha}n_{B\beta}\varepsilon_{BB}\} + \frac{1}{4}\,\ell n \frac{n_{A\alpha}n_{B\alpha}}{n_{A\beta}n_{B\beta}}$$

$$- \frac{4}{kT(n_\alpha+n_\beta)} \{(n_{A\alpha}-n_{A\beta})(\varepsilon_{AA}+\varepsilon_{AB}) + (n_{B\alpha}-n_{B\beta})(\varepsilon_{AB}+\varepsilon_{BB})\} \quad (13)$$

and

$$\ell n \frac{n_{V\beta}}{n_\beta} = \frac{16}{kT(n_\alpha+n_\beta)^2} \{n_{A\alpha}n_{A\beta}\varepsilon_{AA}+(n_{A\alpha}n_{B\beta}+n_{B\alpha}n_{A\beta})\varepsilon_{AB}+n_{B\alpha}n_{B\beta}\varepsilon_{BB}\} - \frac{1}{4}\,\ell n \frac{n_{A\alpha}n_{B\alpha}}{n_{A\beta}n_{B\beta}}$$

$$+ \frac{4}{kT(n_\alpha+n_\beta)} \{(n_{A\alpha}-n_{A\beta})(\varepsilon_{AA}+\varepsilon_{AB}) + (n_{B\alpha}-n_{B\beta})(\varepsilon_{AB}+\varepsilon_{BB})\} \quad (14)$$

Eq. (12) is identical with the original Bragg-Williams relationship.[1] Introducing Eqs. (5) gives

$$\ell n \frac{(1+\eta+2\delta)(1+\eta-2\delta)}{(1-\eta-2\delta)(1-\eta+2\delta)} = -\frac{8\eta}{kT}\{2\,\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}\} \quad (15)$$

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

$$\frac{4}{1-4\delta^2} = -\frac{8}{kT_c}\{2\,\varepsilon_{AB}-\varepsilon_{AA}-\varepsilon_{BB}\} = -\frac{16}{kT_c}\,\varepsilon \qquad (16)$$

This is the familiar Bragg-Williams relationship giving the ordering energy 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

$$\ln p_{V\alpha} = \frac{1}{kT}\{[(1-2\delta)^2-\eta^2]\varepsilon_{AA} + 2[1+\eta^2-4\delta^2]\varepsilon_{AB} + [(1+2\delta)^2-\eta^2]\varepsilon_{BB}\}$$

$$+\frac{1}{4}\ln\frac{1-(\eta-2\delta)^2}{1-(\eta+2\delta)^2} + \frac{2\eta}{kT}\{\varepsilon_{BB}-\varepsilon_{AA}\} \qquad (17)$$

$$\ln p_{V\beta} = \frac{1}{kT}\{[(1-2\delta)^2-\eta^2]\varepsilon_{AA} + 2[1+\eta^2-4\delta^2]\varepsilon_{AB} + [(1+2\delta)^2-\eta^2]\varepsilon_{BB}\}$$

$$-\frac{1}{4}\ln\frac{1-(\eta-2\delta)^2}{1-(\eta+2\delta)^2} - \frac{2\eta}{kT}\{\varepsilon_{BB}-\varepsilon_{AA}\} \qquad (18)$$

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 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

$$\Delta E_V = -\frac{8}{2}\left[n_{VA\alpha}(p_{A\beta}\varepsilon_{AA} + p_{B\beta}\varepsilon_{AB}) + n_{VB\alpha}(p_{A\beta}\varepsilon_{AB} + p_{B\beta}\varepsilon_{BB})\right.$$

$$\left. + n_{VA\beta}(p_{A\alpha}\varepsilon_{AA} + p_{B\alpha}\varepsilon_{AB}) + n_{VB\beta}(p_{A\alpha}\varepsilon_{AB} + p_{B\alpha}\varepsilon_{BB})\right] \tag{19}$$

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

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

and the free energy of this system is

$$F(\eta,n_V) = F(\eta,0) + \Delta F_V(n_V)$$

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

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

At equilibrium therefore

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

The equilibrium condition yields the four equations

$$\begin{aligned}
p_{VA\alpha} &= \frac{n_{VA\alpha}}{n_\alpha} = \frac{e^{\frac{4}{kT}(p_{A\beta}\varepsilon_{AA}+p_{B\beta}\varepsilon_{AB})}}{1 - e^{\frac{4}{kT}(p_{A\beta}\varepsilon_{AA}+p_{B\beta}\varepsilon_{AB})}}\, p_{A\alpha} \\
p_{VB\alpha} &= \frac{n_{VB\alpha}}{n_\alpha} = \frac{e^{\frac{4}{kT}(p_{A\beta}\varepsilon_{AB}+p_{B\beta}\varepsilon_{BB})}}{1 - e^{\frac{4}{kT}(p_{A\beta}\varepsilon_{AB}+p_{B\beta}\varepsilon_{BB})}}\, p_{B\alpha} \\
p_{VA\beta} &= \frac{n_{VA\beta}}{n_\beta} = \frac{e^{\frac{4}{kT}(p_{A\alpha}\varepsilon_{AA}+p_{B\alpha}\varepsilon_{AB})}}{1 - e^{\frac{4}{kT}(p_{A\alpha}\varepsilon_{AA}+p_{B\alpha}\varepsilon_{AB})}}\, p_{A\beta} \\
p_{VA\beta} &= \frac{n_{VB\beta}}{n_\beta} = \frac{e^{\frac{4}{kT}(p_{A\alpha}\varepsilon_{AB}+p_{B\alpha}\varepsilon_{BB})}}{1 - e^{\frac{4}{kT}(p_{A\alpha}\varepsilon_{AB}+p_{B\alpha}\varepsilon_{BB})}}\, p_{B\beta}
\end{aligned} \tag{21}$$

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

$$p_{V\alpha} = \frac{n_{V\alpha}}{n_\alpha} = \frac{n_{VA\alpha}}{n_\alpha} + \frac{n_{VB\alpha}}{n_\alpha} = p_{VA\alpha} + p_{VB\alpha} \tag{22a}$$

$$p_{V\beta} = \frac{n_{V\beta}}{n_\beta} = \frac{n_{VA\beta}}{n_\beta} + \frac{n_{VB\beta}}{n_\beta} = p_{VA\beta} + p_{VB\beta} \tag{22b}$$

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 the companion paper "I. Short-Range Ordered and Clustered Alloys", 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 considerations alone suggest 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, $\bar{\varepsilon}$, of a bond is given by

$$\bar{\varepsilon} = p_{A\alpha}p_{A\beta}\varepsilon_{AA} + p_{A\alpha}p_{B\beta}\varepsilon_{AB} + p_{B\alpha}p_{A\beta}\varepsilon_{AB} + p_{B\alpha}p_{B\beta}\varepsilon_{BB}$$

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

$$\bar{\varepsilon} = \frac{1}{4}\{(1-2\delta)^2\varepsilon_{AA} + 2(1+2\delta)(1-2\delta)\varepsilon_{AB} + (1+2\delta)^2\varepsilon_{BB}\} + \frac{\eta^2\varepsilon}{2} \quad (23)$$

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

$$g_{i\alpha} = g_i + g'_{i\alpha}\,\eta^2 \quad (24a)$$

$$g_{i\beta} = g_i + g'_{i\beta}\,\eta^2 \quad (24b)$$

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 η^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 the companion paper, "I. Short-Range Ordered and Clustered Alloys", 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

$$(p_{A\alpha} + p_{B\alpha})^z = \sum_{i=0}^{z} \frac{z!}{(z-i)!\,i!}\, p_{A\alpha}^{(z-i)}\, p_{B\alpha}^{\ i} = 1 \quad (25)$$

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

$$\frac{n_{i\beta}}{n_\beta} = \frac{z!}{(z-i)!i!} p_{A\alpha}^{(z-i)} p_{B\alpha}^{i} e^{-\frac{g_{i\beta}}{kT}} \tag{26a}$$

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{z!}{(z-i)!i!} p_{A\beta}^{(z-i)} p_{B\beta}^{i} e^{-\frac{g_{i\alpha}}{kT}} \tag{26b}$$

It is significant that these equations reduce to those previously suggested by Dorn and Mitchell[2] for a random alloy. When expressed in terms of the degree of order, Eqs. (26a) and (26b) become

$$\frac{n_{i\beta}}{n_\beta} = \frac{z!}{(z-i)!i!2^z} (1+\eta-2\delta)^{z-i}(1-\eta+2\delta)^{i} e^{-\frac{g_{i\beta}}{kT}} \tag{27a}$$

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{z!}{(z-i)!i!2^z} (1-\eta-2\delta)^{z-i}(1+\eta+2\delta)^{i} e^{-\frac{g_{i\alpha}}{kT}} \tag{27b}$$

where

$$p_{V\beta} = \frac{n_{V\beta}}{n_\beta} = \sum_i \frac{n_{i\beta}}{n_\beta} \text{ and } p_{V\alpha} = \frac{n_{V\alpha}}{n_\alpha} = \sum_i \frac{n_{i\alpha}}{n_\alpha} \tag{28}$$

D. Modified Vacancy-Energy Model

The Vacancy-Energy Model, as expressed in Eqs. (26a) and (26b), 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_is 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

$$-\{(z-i)\varepsilon_{AA} + i\varepsilon_{AB}\}/2$$

and

$$-\{(z-i)\varepsilon_{AB} + i\varepsilon_{BB}\}/2$$

respectively. Thus following Eq. (25), 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

$$\frac{n_{i\beta}}{n_\beta} = \frac{n_{i\beta}^{(A)} + n_{i\beta}^{(B)}}{n_\beta} = \frac{z!}{(z-i)!\,i!}\, p_{A\alpha}^{\,z-i}\, p_{B\alpha}^{\,i} \left\{ p_{A\beta}\, e^{\frac{(z-i)\varepsilon_{AA}+i\varepsilon_{AB}}{2kT}} + p_{B\beta}\, e^{\frac{(z-i)\varepsilon_{AB}+i\varepsilon_{BB}}{2kT}} \right\} \qquad (29a)$$

and similarly for the vacant α sites

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{n_{i\ \alpha}^{(A)}+n_{i\ \alpha}^{(B)}}{n_\alpha} = \frac{z!}{(z-i)!i!}\, p_{A\beta}^{\ z-i}\, p_{B\beta}^{\ i} \left\{ p_{A\alpha} e^{\frac{(z-i)\varepsilon_{AA}+i\varepsilon_{AB}}{2kT}} + p_{B\alpha}\, e^{\frac{(z-i)\varepsilon_{AB}+i\varepsilon_{BB}}{2kT}} \right\} \qquad (29b)$$

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

$$p_{V\beta} = \sum_{i=0}^{z} \frac{n_{i\beta}}{n_\beta} = p_{A\beta} \left\{ p_{A\alpha}\, e^{\frac{\varepsilon_{AA}}{2kT}} + p_{B\alpha}\, e^{\frac{\varepsilon_{AB}}{2kT}} \right\}^z + p_{B\beta} \left\{ p_{A\alpha}\, e^{\frac{\varepsilon_{AB}}{2kT}} + p_{B\alpha}\, e^{\frac{\varepsilon_{BB}}{2kT}} \right\}^z \qquad (30a)$$

and

$$p_{V\alpha} = \sum_{i=0}^{z} \frac{n_{i\alpha}}{n_\alpha} = p_{A\alpha} \left\{ p_{A\beta}\, e^{\frac{\varepsilon_{AA}}{2kT}} + p_{B\beta}\, e^{\frac{\varepsilon_{AB}}{2kT}} \right\}^z + p_{B\alpha} \left\{ p_{A\beta}\, e^{\frac{\varepsilon_{AB}}{2kT}} + p_{B\beta}\, e^{\frac{\varepsilon_{BB}}{2kT}} \right\}^z \qquad (30b)$$

When $\eta = 0$, as is required, Eqs. (30) reduce to $p_{V\alpha} = p_{V\beta}$

III. 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 occurance 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. (8) in lieu of Eq. (7) 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

$$\lambda_{\alpha\beta} \{\frac{1}{4} (n_{A\alpha}+n_{B\alpha}+n_{V\alpha}) - \frac{3}{4} (n_{A\beta}+n_{B\beta}+n_{V\beta})\} = 0 \qquad (10c)$$

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

$$\ln \frac{n_{A\alpha}n_{B\beta}}{n_{A\beta}n_{B\alpha}} = \frac{16}{kT(n_\alpha+n_\beta)} \{(\frac{1}{3} n_{A\alpha}-n_{A\beta})\varepsilon_{AA}-[\frac{1}{3} (n_{A\alpha}-n_{B\alpha})-(n_{A\beta}-n_{B\beta})]\varepsilon_{AB}$$

$$-(\frac{1}{3}\, n_{B\alpha}-n_{B\beta})\varepsilon_{BB}\} \qquad (31)$$

$$\ell n\, \frac{n_{V\alpha}}{n_\alpha} = \frac{16}{kT(n_\alpha+n_\beta)^2}\, \{(n_{A\alpha}n_{A\beta}+\frac{1}{3}\, n_{A\alpha}n_{A\alpha})\varepsilon_{AA}+(n_{A\alpha}n_{B\beta}+n_{B\alpha}n_{A\beta}+\frac{2}{3}\, n_{A\alpha}n_{B\alpha})\varepsilon_{AB}$$

$$+\ (n_{B\alpha}n_{B\beta}+\frac{1}{3}\, n_{B\alpha}n_{B\alpha})\varepsilon_{BB}\} + \frac{1}{8}\, \ell n\, \frac{n_{A\alpha}n_{B\alpha}}{9n_{A\beta}n_{B\beta}}$$

$$-\ \frac{2}{kT(n_\alpha+n_\beta)}\, \{(\frac{1}{3}\, n_{A\alpha}-n_{A\beta})(\varepsilon_{AA}+\varepsilon_{AB})+(\frac{1}{3}\, n_{B\alpha}-n_{B\beta})(\varepsilon_{AB}+\varepsilon_{BB})\} \qquad (32)$$

and

$$\ell n\, \frac{n_{V\beta}}{n_\beta} = \frac{16}{kT(n_\alpha+n_\beta)^2}\, \{(n_{A\alpha}n_{A\beta}+\frac{1}{3}\, n_{A\alpha}n_{A\alpha})\varepsilon_{AA}+(n_{A\alpha}n_{B\beta}+n_{B\alpha}n_{A\beta}+\frac{2}{3}\, n_{A\alpha}n_{B\alpha})\varepsilon_{AB}$$

$$+\ (n_{B\alpha}n_{B\beta}+\frac{1}{3}\, n_{B\alpha}n_{B\alpha})\varepsilon_{BB}\} - \frac{3}{8}\, \ell n\, \frac{n_{A\alpha}n_{B\alpha}}{9n_{A\beta}n_{B\beta}}$$

$$+\ \frac{6}{kT(n_\alpha+n_\beta)}\, \{(\frac{1}{3}\, n_{A\alpha}-n_{A\beta})(\varepsilon_{AA}+\varepsilon_{AB})+(\frac{1}{3}\, n_{B\alpha}-n_{B\beta})(\varepsilon_{AB}+\varepsilon_{BB})\} \qquad (33)$$

Introducing Eqs. (5) where $N_\alpha = \frac{3}{4}$ and $N_\beta = \frac{1}{4}$ into Eq. (30) gives

$$\ell n\, \frac{(3-4\delta+\eta)(1+4\delta+3\eta)}{(3-4\delta-3\eta)(1+4\delta-\eta)} = -\ \frac{4\eta}{kT}\, (2\varepsilon_{AB}-\varepsilon_{AA}-\varepsilon_{BB}) \qquad (34)$$

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

Upon introduction of Eqs. (5) and $N_\alpha = \frac{3}{4}$, $N_\beta = \frac{1}{4}$, the equilibrium vacancy concentrations on the two sublattices are respectively

$$\ln p_{V\alpha} = \frac{3}{8kT}\{[(3-4\delta)^2-\eta^2]\varepsilon_{AA}+2(3+8\delta-16\delta^2+\eta^2)\varepsilon_{AB}+[(1+4\delta)^2-\eta^2]\varepsilon_{BB}\}$$

$$+\frac{1}{8}\ln\frac{(3+8\delta-2\eta)-(\eta-4\delta)^2}{(3+8\delta+6\eta)-(3\eta+4\delta)^2}+\frac{\eta}{2kT}(\varepsilon_{BB}-\varepsilon_{AA}) \qquad (35)$$

and

$$\ln p_{V\beta} = \frac{3}{8kT}\{[(3-4\delta)^2-\eta^2]\varepsilon_{AA}+2(3+8\delta-16\delta^2+\eta^2)\varepsilon_{AB}+[(1+4\delta)^2-\eta^2]\varepsilon_{BB}\}$$

$$-\frac{3}{8}\ln\frac{(3+8\delta-2\eta)-(\eta-4\delta)^2}{(3+8\delta+6\eta)-(3\eta+4\delta)^2}-\frac{3\eta}{2kT}(\varepsilon_{BB}-\varepsilon_{AA}) \qquad (36)$$

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

$$\Delta E_V = -\frac{12}{2}\{n_{VA\alpha}\left[\left(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta}\right)\varepsilon_{AA}+\left(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta}\right)\varepsilon_{AB}\right]$$

$$+n_{VB\alpha}\left[\left(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta}\right)\varepsilon_{AB}+\left(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta}\right)\varepsilon_{BB}\right]$$

$$+n_{VA\beta}[p_{A\alpha}\varepsilon_{AA}+p_{B\alpha}\varepsilon_{AB}]+n_{VB\beta}[p_{A\alpha}\varepsilon_{AB}+p_{B\alpha}\varepsilon_{BB}]\} \qquad (37)$$

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

$$p_{VA\alpha} = \frac{n_{VA\alpha}}{n_\alpha} = \frac{e^{\frac{6}{kT}[(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta})\varepsilon_{AA}+(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta})\varepsilon_{AB}]}}{1-e^{\frac{6}{kT}[(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta})\varepsilon_{AA}+(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta})\varepsilon_{AB}]}}\, p_{A\alpha}$$

$$p_{VB\alpha} = \frac{n_{VB\alpha}}{n_\alpha} = \frac{e^{\frac{6}{kT}[(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta})\varepsilon_{AB}+(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta})\varepsilon_{BB}]}}{1-e^{\frac{6}{kT}[(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta})\varepsilon_{AB}+(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta})\varepsilon_{BB}]}}\, p_{B\alpha} \tag{38}$$

$$p_{VA\beta} = \frac{n_{VA\beta}}{n_\beta} = \frac{e^{\frac{6}{kT}[p_{A\alpha}\varepsilon_{AA}+p_{B\alpha}\varepsilon_{AB}]}}{1-e^{\frac{6}{kT}[p_{A\alpha}\varepsilon_{AA}+p_{B\alpha}\varepsilon_{AB}]}}\, p_{A\beta}$$

$$p_{VB\beta} = \frac{n_{VB\beta}}{n_\beta} = \frac{e^{\frac{6}{kT}[p_{A\alpha}\varepsilon_{AB}+p_{B\alpha}\varepsilon_{BB}]}}{1-e^{\frac{6}{kT}[p_{A\alpha}\varepsilon_{AB}+p_{B\alpha}\varepsilon_{BB}]}}\, p_{B\beta}$$

The values of $p_{V\alpha}$ and $p_{V\beta}$ can then be deduced from the above by utilizing Eqs. (22).

C. Vacancy-Energy Model

For the $L1_2$ 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

$$(p_{A\alpha}+p_{B\alpha})^z = \sum \frac{z!}{(z-i)!i!}\, p_{A\alpha}{}^{z-i}\, p_{B\alpha}{}^{i} = 1 \qquad (25)$$

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

$$\frac{n_{i\beta}}{n_\beta} = \frac{z!}{(z-i)!i!}\, p_{A\alpha}{}^{z-i}\, p_{B\alpha}{}^{i}\, e^{-\frac{g_{i\beta}}{kT}} \qquad (26a)$$

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

$$[\frac{8}{12}(p_{A\alpha}+p_{B\alpha}) + \frac{4}{12}(p_{A\beta}+p_{B\beta})]^z$$

$$= [\frac{2}{3}(p_{A\alpha}+p_{B\alpha}) + \frac{1}{3}(p_{A\beta}+p_{B\beta})]^z$$

$$= \sum \frac{z!}{(z-i)!i!}\left(\frac{2}{3}p_{A\alpha} + \frac{1}{3}p_{A\beta}\right)^{z-i}\left(\frac{2}{3}p_{B\alpha} + \frac{1}{3}p_{B\beta}\right)^{i} = 1 \qquad (39)$$

Formulating and minimizing the free energy of formation of vacancies, as done before, gives

$$\frac{n_{i\alpha}}{n_\alpha} = \frac{z!}{(z-i)!i!}\left(\frac{2}{3}p_{A\alpha} + \frac{1}{3}p_{A\beta}\right)^{z-i}\left(\frac{2}{3}p_{B\alpha} + \frac{1}{3}p_{B\beta}\right)^{i} e^{-\frac{g_{i\alpha}}{kT}} \qquad (40)$$

Significantly Eqs. (26a) and (40) 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. (28).

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

$$\bar{\varepsilon} = (p_{A\alpha}p_{A\alpha}+p_{A\alpha}p_{A\beta})\varepsilon_{AA}+(2p_{A\alpha}p_{B\alpha}+p_{A\alpha}p_{B\beta}+p_{A\beta}p_{B\alpha})\varepsilon_{AB}$$

$$+ (p_{B\alpha}p_{B\alpha}+p_{B\alpha}p_{B\beta})\varepsilon_{BB} \qquad (41)$$

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

$$\bar{\varepsilon} = \frac{1}{8}\{(3-4\delta)^2\varepsilon_{AA}+2(3-4\delta)(1+4\delta)\varepsilon_{AB}+(1+4\delta)^2\varepsilon_{BB}\} + \frac{\eta^2\varepsilon}{4} \qquad (42)$$

Thus, the free energies of formation of the i^{th} kind of vacancies can be represented by Eqs. (24a) and (24b) respectively for α and β sites.

D. Modified Vacancy-Energy Model

Whereas the total number of vacant β sites is identical with Eq. (29a) where z is now equal to 12, that of vacant α sites can be evaluated from Eq. (40). Following the same reasoning given previously for the $L2_0$ lattice,

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

$$\left(p_{A\alpha}\, e^{\frac{(z-i)\varepsilon_{AA}+i\varepsilon_{AB}}{2kT}} + p_{B\alpha}\, e^{\frac{(z-i)\varepsilon_{AB}+i\varepsilon_{BB}}{2kT}}\right) \qquad (43)$$

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

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

$$+\ p_{B\alpha}\ \left\{\left(\frac{2}{3}p_{A\alpha}+\frac{1}{3}p_{A\beta}\right) e^{\frac{\varepsilon_{AB}}{2kT}} + \left(\frac{2}{3}p_{B\alpha}+\frac{1}{3}p_{B\beta}\right) e^{\frac{\varepsilon_{BB}}{2kT}}\right\}^{z} \qquad (44)$$

and the probability of vacancies on β sites is given by Eq. (30a).

IV. 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 Girifalco[4] 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 changes as a result of atom displacement to the surface. Assumption (a) follows since the number of vacancies are 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 in the companion paper "I. Short-Range Ordered and Clustered Alloys". 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 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 erected for the Simple-Displacement 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 concentration ($\delta = 0$) for the cases where $\varepsilon_{AA} = \varepsilon_{BB}$. 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 differ substantially relative to the details that can be extracted from them, give about the same average values for $p_{V\alpha}$ and $p_{V\beta}$, 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 erected here. It is based on the previously discussed assumption that neither the average occupancy of sites nor the local configuration of atoms are 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 $g_{i\alpha}$ 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 $L2_0$ lattice will be based on β-brass. The bond energies

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

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

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

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

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. 1, 2 and 3. 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. Futhermore, 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. 1 and 2 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. 3, 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. Fig. 4 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. 5. It is seen that the most populous type of vacancies changes as the temperature or degree of order varies. Furthermore, it is also strongly affected by the values of bond energies as shown in Fig. 6 for the case $\varepsilon_{AA} = \varepsilon_{BB}$.

The comparisons of the results for the $L1_2$ lattice will be based on the alloy Cu_3Au. 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 transition for the $L2_0$ lattice. The first order phase transition is featured by the existence of two minima in the curves of free energies, F, versus degree of order, η, plotting. The first minimum corresponds to a zero degree of order and the second minimum corresponds to a nonzero value of η. This phase transition 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. (34) and

$$F(0) = F(\eta_{Co}) \tag{45}$$

A numerical solution of the above simultaneous equations gives

$$\eta_{Co} = 0.46 \text{ and } kT_{Co} = -1.64\ \varepsilon \tag{46}$$

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

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

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

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

where N_o is Avogadro's number, were estimated from the heats of sublimation of the pure metals. By means of Eq. (46) and the known critical temperature for the alloy of stoichiometric composition ($\delta = 0$) the value of

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

is also assumed. The calculated values of $\ell n\ p_{V\alpha}$ and $\ell n\ p_{V\beta}$ are shown in Fig. 7. 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 8 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 cd of this curve corresponds to the equilibrium values of the degree of long-range order while sections bc and ab correspond to the metastable state and nonexisting state respectively. The population distributions of the various types of vacancies are shown in Fig. 9.

Although the general trends given in the figures based on the Smeared-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 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_is is now available and therefore the nominal correctness of the Vacancy-Energy Model is dependent on future experimental verification.

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FIGURE CAPTIONS

Figure 1. Probabilities of vacancies on α and β sites in the $L2_0$ alloy according to the Smeared-Displacement Model.

Figure 2. Probabilities of vacancies on α and β sites in the $L2_0$ alloy according to the Simple-Displacement Model.

Figure 3. Probabilities of vacancies on α and β sites in the stoichiometric, $L2_0$ alloy according to the Modified Vacancy-Energy Model.

Figure 4. Effect of ordering on the distribution of the various vacancy concentrations on α and β sites in the stoichiometric, $L2_0$ alloy.

Figure 5. Distribution of the various vacancy concentrations on α and β sites in the stoichiometric, $L2_0$ alloy where $N_o \epsilon_{AA} = -7.9$ kcal, $N_o \epsilon_{BB} = -20.4$ kcal, and $N_o \epsilon_{AB} = -14.50$ kcal.

Figure 6. Distribution of the various vacancy concentrations on α and β sites in the stoichiometric, $L2_0$ alloy where $N_o \epsilon_{AA} = = N_o \epsilon_{BB} = -14.15$ kcal, and $N_o \epsilon_{AB} = -14.50$ kcal.

Figure 7. Probabilities of vacancies on α and β sites in the stoichiometric, $L1_2$ alloy.

Figure 8. Effect of ordering on the distribution of the various vacancy concentrations on α and β sites in the stoichiometric, $L1_2$ alloy.

Figure 9. Distribution of the various vacancy concentrations on α and β sites in the stoichiometric, $L1_2$ alloy.

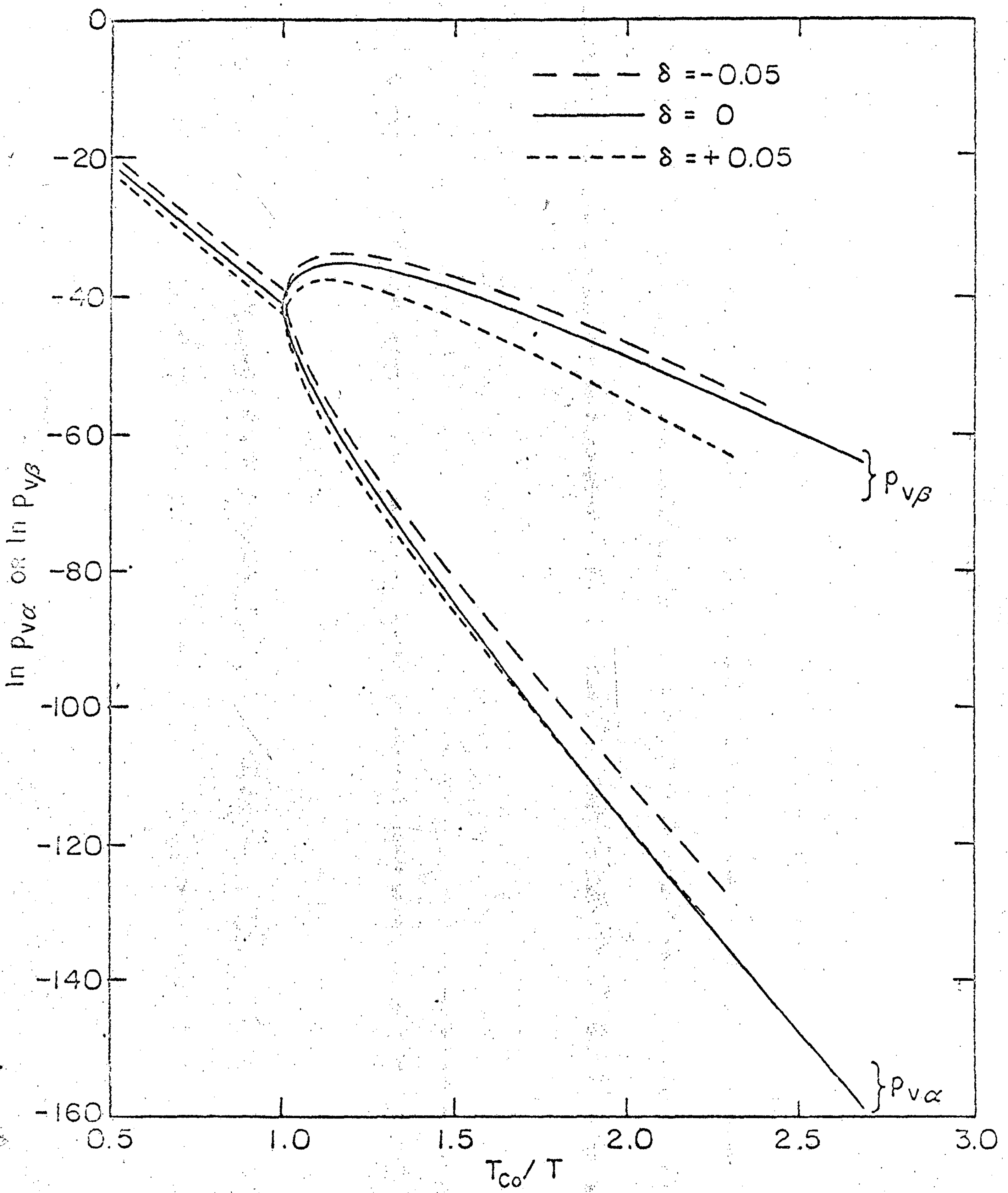

FIG. I PROBABILITIES OF VACANCIES ON α AND β SITES IN THE $L2_0$ ALLOY ACCORDING TO THE SMEARED-DISPLACEMENT MODEL.

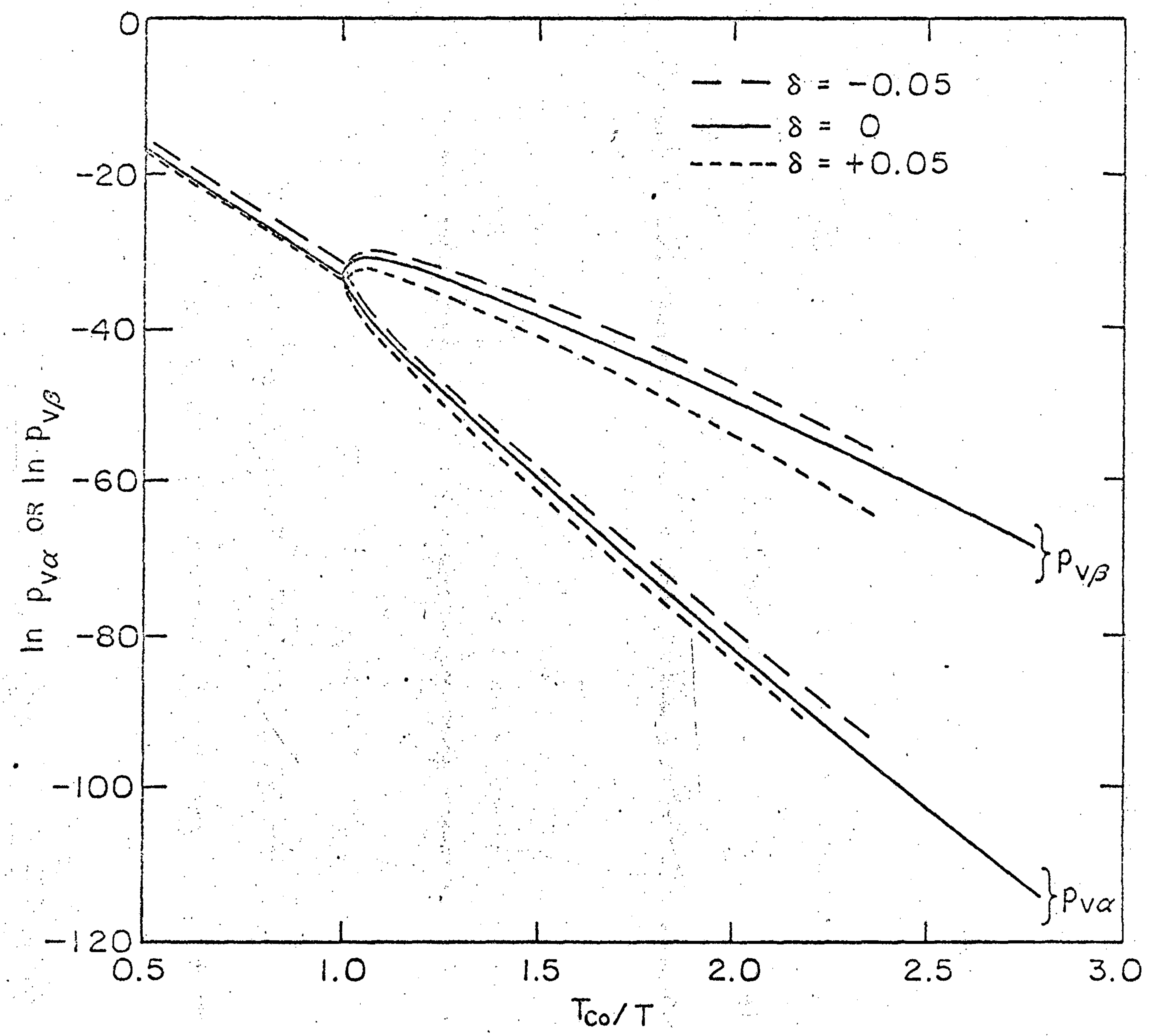

FIG. 2 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE $L2_0$ ALLOY ACCORDING TO THE SIMPLE-DISPLACEMENT MODEL.

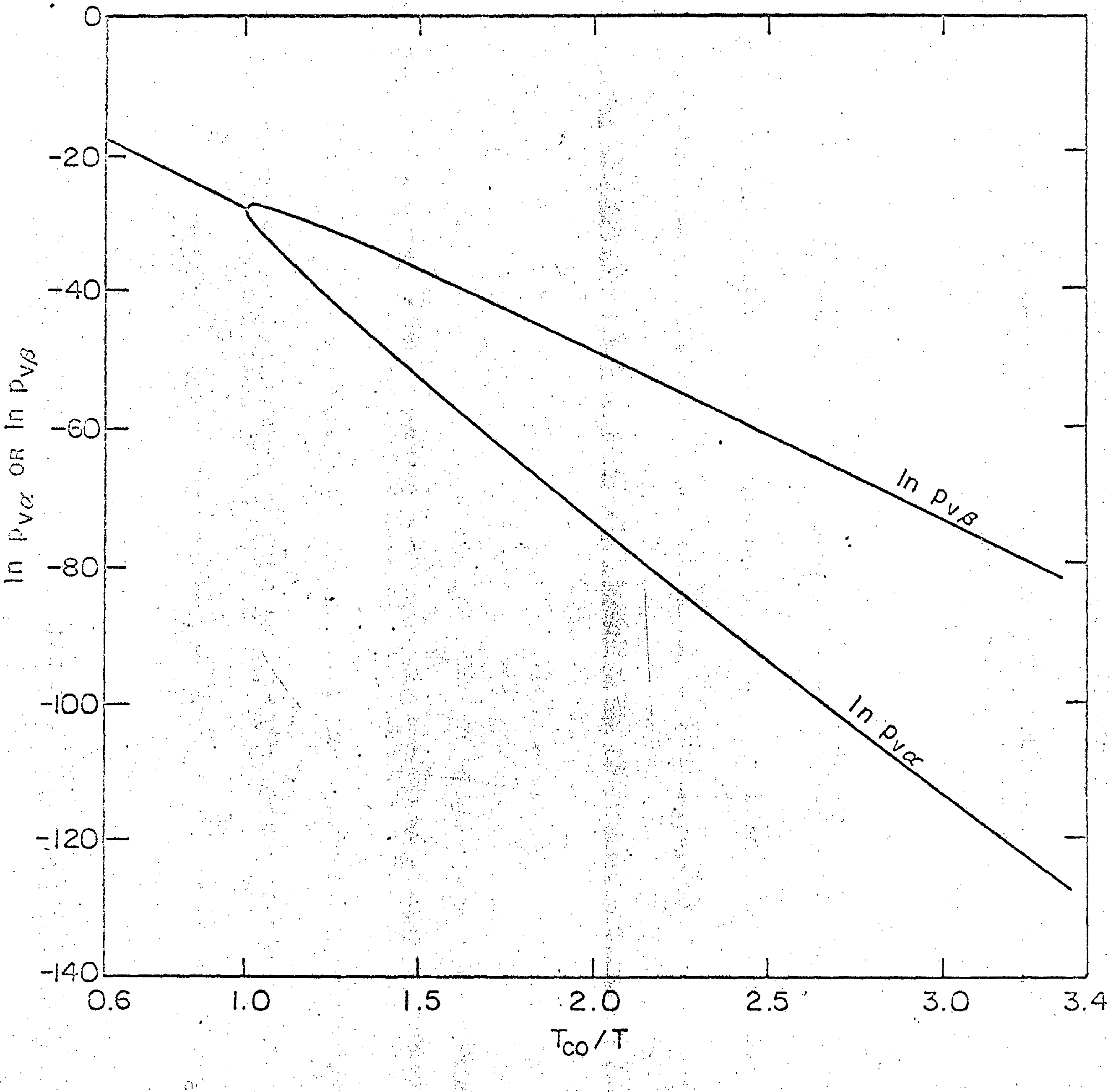

FIG. 3 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY ACCORDING TO THE MODIFIE VACANCY-ENERGY MODEL.

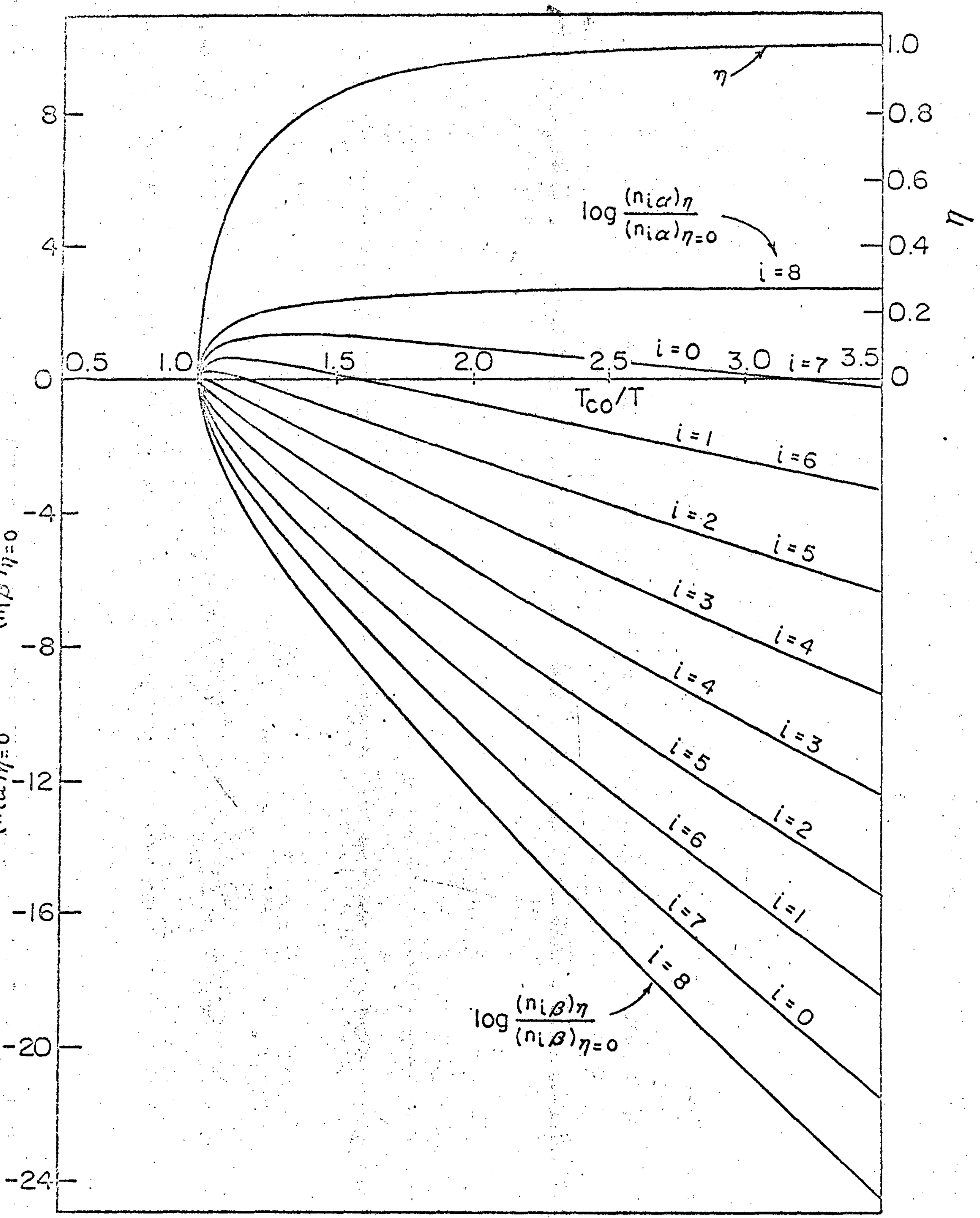

FIG. 4 EFFECT OF ORDERING ON THE DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY.

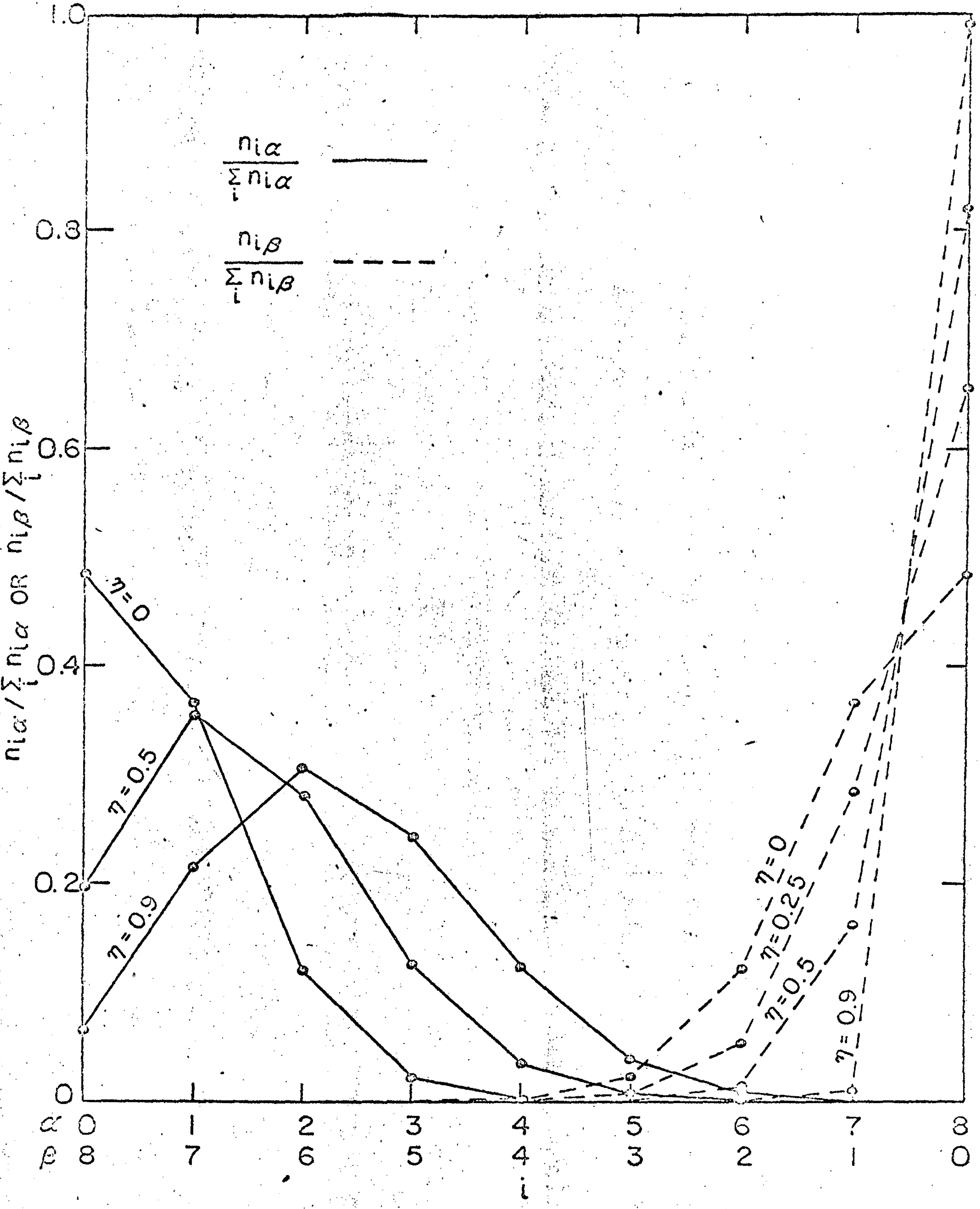

FIG. 5 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY WHERE $N_0\mathcal{E}_{AA}=-7.9$ KCAL, $N_0\mathcal{E}_{BB}=-20.4$ KCAL AND $N_0\mathcal{E}_{AB}=-14.50$ KCAL.

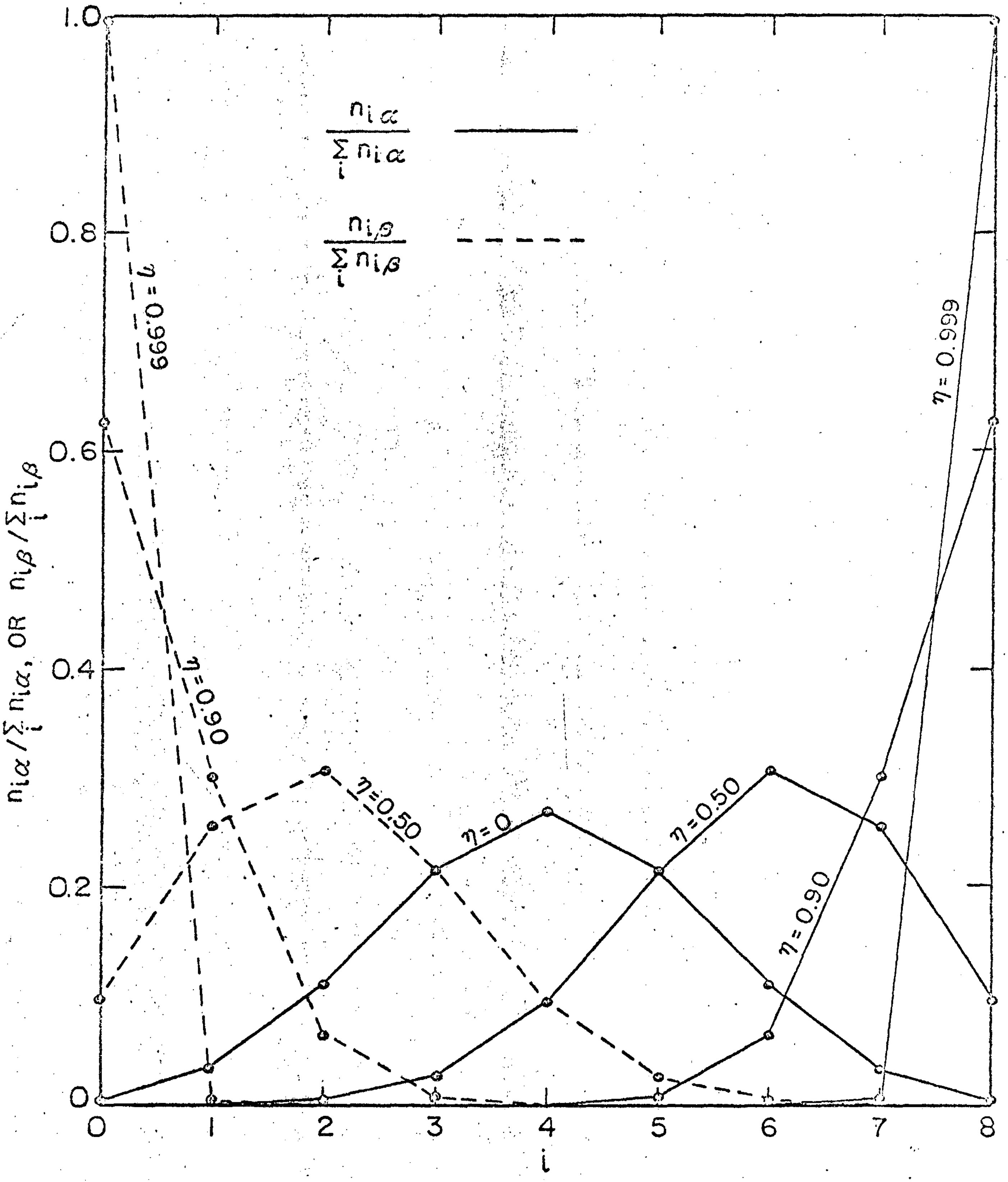

FIG. 6 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L2_0$ ALLOY WHERE $N_0\mathcal{E}_{AA} = N_0\mathcal{E}_{BB} = -14.15$ KCAL AND $N_0\mathcal{E}_{AB} = -14.50$ KCAL.

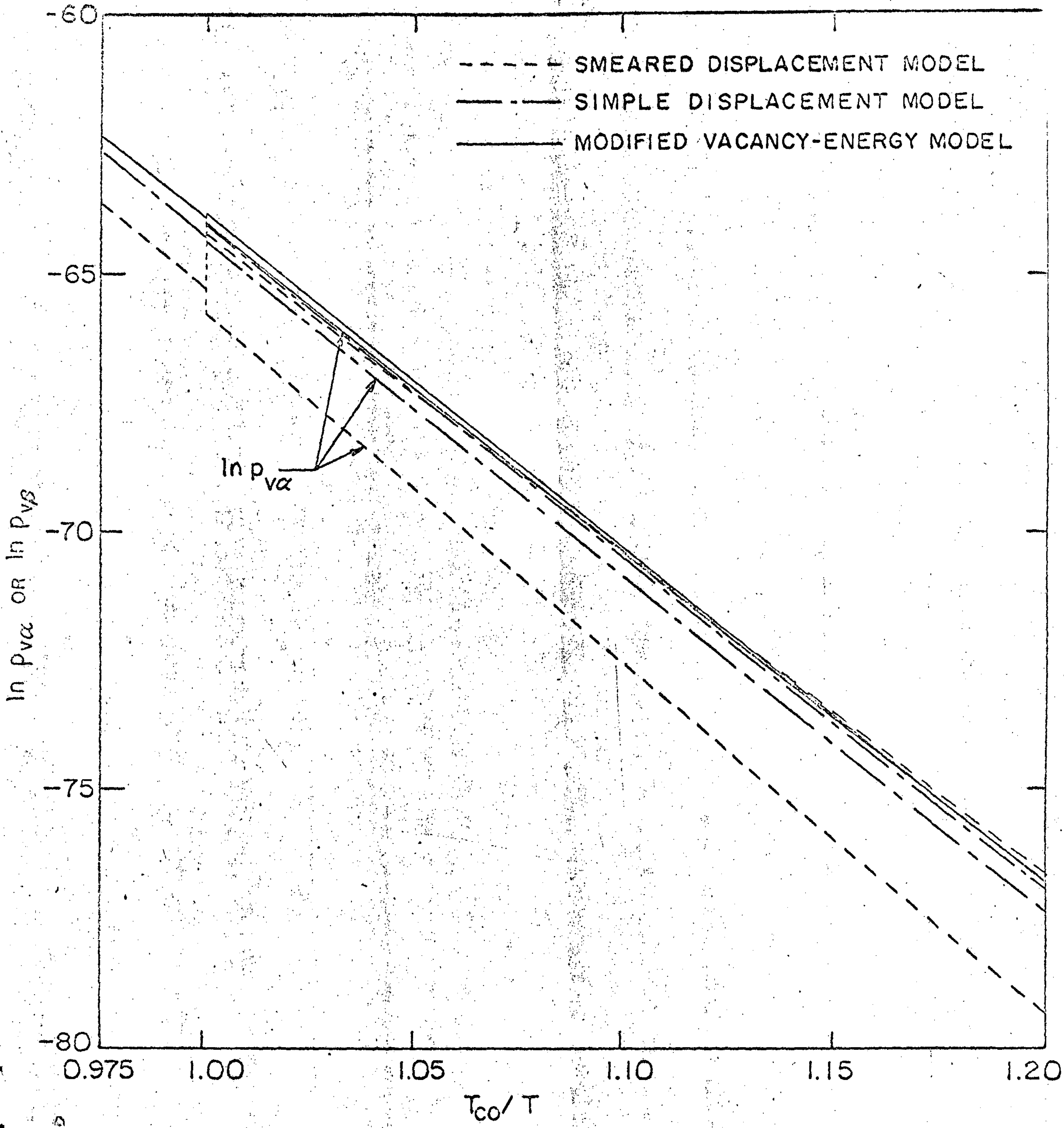

FIG. 7 PROBABILITIES OF VACANCIES ON α AND β SITES IN THE STOICHIOMETRIC, $L1_2$ ALLOY.

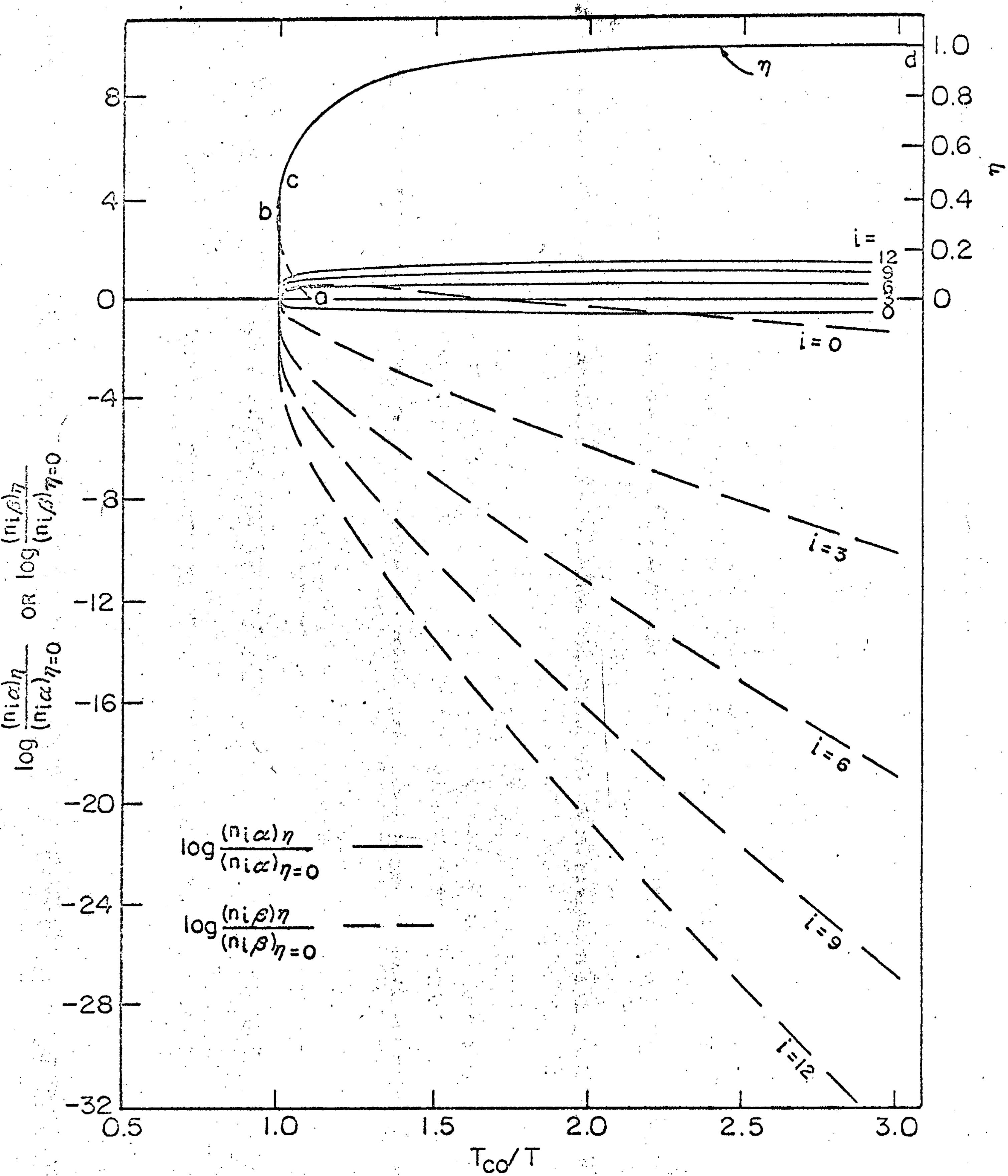

FIG. 8 EFFECT OF ORDERING ON THE DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, LI_2 ALLOY.

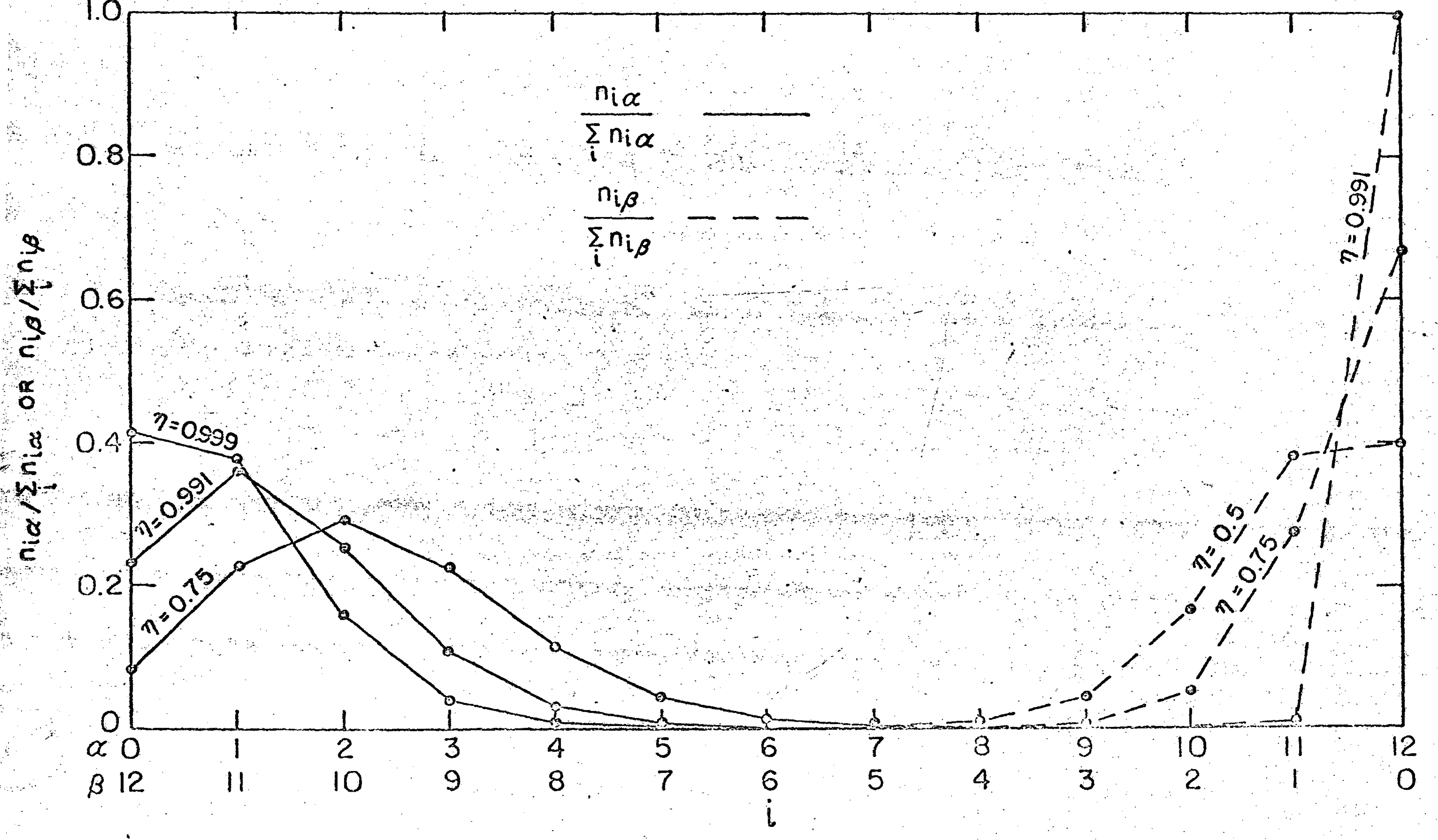

FIG. 9 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ON α AND β SITES IN THE STOICHIOMETRIC, $L1_2$ ALLOY