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VACANCY MODELS FOR CONCENTRATED BINARY ALLOYS
I. SHORT-RANGE ORDERED AND CLUSTERED ALLOYS

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ABSTRACT

Four 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 environments 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 energy to produce a vacancy depends primarily on the immediate environment of the vacancy.

I. INTRODUCTION

Vacancies are expected to play the same significant role during diffusion, creep, sintering and other kinetic phenomena in 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 numbers 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 desgin 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 authors are 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 concentrations 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 each other and their deficiencies and virtues will be discussed.

In the present paper we shall confine our attention to short-range ordered (or clustered) alloys. Long-range ordered alloys will be discussed in a companion paper. However, a common terminology will be adopted for both papers, as follows: The alloys will contain A and B atoms plus various distinguishable types of vacancies, V, where

n_A = total number of A atoms

n_B = total number of B atoms

n_V = total number of vacancies of all types

n_S = total number of lattice sites

z = coordination number

$N_A = \frac{n_A}{n_A+n_B}$ = atomic fraction of A atoms

$N_B = \frac{n_B}{n_A+n_B}$ = atomic fraction of B atoms

ε_{AA}, ε_{BB}, ε_{AB} = 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

→A-B is

$$\varepsilon = \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}$$

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

II. TERMINOLOGY FOR SHORT-RANGE ORDERED ALLOYS

Either Bethe's[4] or Cowley's[5] 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, subjected to the limitation of considering only nearest-neighbor interactions. Accordingly p_{kj} where k = A, B, V and j = A, B, V will be the probability that the kth species is coordinated about the jth species. Such probabilities are interrelated by the three equations:

$$p_{AA} + p_{BA} + p_{VA} = 1 \tag{1a}$$

$$p_{AB} + p_{BB} + p_{VB} = 1 \tag{1b}$$

$$p_{AV} + p_{BV} + p_{VV} = 1 \tag{1c}$$

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

$$zn_A p_{BA} = zn_B p_{AB} \tag{2a}$$

$$zn_A p_{VA} = zn_V p_{AV} \tag{2b}$$

$$zn_B p_{VB} = zn_V p_{BV} \tag{2c}$$

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

$$\alpha = 1 - \frac{p_{AB}}{\frac{n_A}{n_A+n_B+n_V}} = 1 - \frac{p_{BA}}{\frac{n_B}{n_A+n_B+n_V}} \tag{3}$$

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

$$\begin{aligned} p_{AB} &\simeq N_A\,(1 - \alpha) \\ p_{BA} &\simeq N_B\,(1 - \alpha) \\ p_{AA} &\simeq 1 - p_{BA} = N_A + \alpha N_B \\ p_{BB} &\simeq 1 - p_{AB} = N_B + \alpha N_A \end{aligned} \tag{4}$$

III. SMEARED-DISPLACEMENT MODEL

This model is essentially the short-range order analogue of the model proposed by Krivoglaz and Smirnov[2] 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 site. Since the number of divacancies will always be small relative to the total number of vacancies, $p_{VV} \simeq 0$ and Eqs. (1) and (2) reduce to

$$p_{AA} + p_{BA} + p_{VA} = 1 \tag{5a}$$

$$\frac{n_A}{n_B} p_{BA} + p_{BB} + p_{BV} = 1 \tag{5b}$$

$$n_A p_{VA} + n_B p_{VB} \simeq n_V \tag{5c}$$

Because there are five variables in the three Eqs. (5), 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. (5c) and employ the method of Lagrangian undetermined multipliers to introduce the restrictions of Eqs. (5a) and (5b).

The configurational bond energy of the alloy is simply

$$E_c = \frac{z}{2} (n_A p_{AA} \varepsilon_{AA} + 2 n_A p_{BA} \varepsilon_{AB} + n_B p_{BB} \varepsilon_{BB}) \tag{6}$$

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

$$\Omega_A = \left[\frac{z!}{(zp_{AA})!(zp_{BA})!(zp_{VA})!} \right]^{\frac{n_A}{z}} \tag{7a}$$

$$\Omega_B = \left[\frac{z!}{(zp_{AB})!(zp_{BB})!(zp_{VB})!} \right]^{\frac{n_B}{z}} = \left[\frac{z!}{(\frac{zn_A}{n_B} p_{BA})!(zp_{BB})!(zp_{VB})!} \right]^{\frac{n_B}{z}} \tag{7b}$$

$$\Omega_V = \left[\frac{z!}{(zp_{AV})!(zp_{BV})!(zp_{VV})!} \right]^{\frac{n_V}{z}} = \left[\frac{z!}{(\frac{zn_A p_{VA}}{n_A p_{VA} + n_B p_{VB}})!(\frac{zn_B p_{VB}}{n_A p_{VA} + n_B p_{VB}})!0!} \right]^{\frac{n_A p_{VA} + n_B p_{VB}}{z}} \tag{7c}$$

and where the second equalities follow from Eqs. (2) and (5). 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

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

whereas the ways suggested above are

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

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

$$S = k\ell n\Omega \tag{8a}$$

where Ω is closely approximated by

$$\Omega = \Omega_A \cdot \Omega_B \cdot \Omega_V \frac{[\Omega_{AB}]_R}{[\Omega_A \cdot \Omega_B]_R} \tag{8b}$$

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

$$F_c = E_c - TS_c \tag{9}$$

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. (5a) and (5b). Using $kT\ell n\lambda_A$ and $kT\ell n\lambda_B$ 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. (5a) and (5b), namely

$$-kT\ell n\lambda_A(p_{AA}+p_{BA}+p_{VA}-1) = 0 \tag{10a}$$

and

$$-kT\ell n\lambda_B(\frac{n_A}{n_B}\, p_{BA}+p_{BB}+p_{VB}-1) = 0 \tag{10b}$$

can be added directly to Eq. (9). Minimizing the resulting expression with respect to each of the now independently variable quantities gives the results,

$$p_{AA} = \frac{1}{e}\,\lambda_A^{\frac{1}{n_A}}\, e^{-\frac{z\varepsilon_{AA}}{2kT}} \tag{11a}$$

$$p_{BB} = \frac{1}{e}\,\lambda_B^{\frac{1}{n_B}}\, e^{-\frac{z\varepsilon_{BB}}{2kT}} \tag{11b}$$

$$p_{BA} = \frac{1}{e}\,(\frac{n_B}{n_A})^{\frac{1}{2}}\,\lambda_A^{\frac{1}{2n_A}}\,\lambda_B^{\frac{1}{2n_B}}\, e^{-\frac{z\varepsilon_{AB}}{2kT}} \tag{11c}$$

$$p_{VA} = \frac{1}{e}\,\lambda_A^{\frac{1}{n_A}} + \frac{1}{e}\,(\frac{n_B}{n_A})^{\frac{1}{2}}\,\lambda_A^{\frac{1}{2n_A}}\,\lambda_B^{\frac{1}{2n_B}} \tag{11d}$$

$$p_{VB} = \frac{1}{e}\,\lambda_B^{\frac{1}{n_B}} + \frac{1}{e}\,(\frac{n_A}{n_B})^{\frac{1}{2}}\,\lambda_A^{\frac{1}{2n_A}}\,\lambda_B^{\frac{1}{2n_B}} \tag{11e}$$

Consequently, from Eqs. (11a), (11b) and (11c)

$$\frac{p_{BA}^{\ 2}}{p_{AA}p_{BB}} = \frac{n_B}{n_A}\, e^{\frac{z(\varepsilon_{AA}+\varepsilon_{BB}-2\varepsilon_{AB})}{2kT}} \tag{12}$$

Since the vacancy concentrations are small, the probabilities can be expressed very accurately in terms of Eqs.(4). Therefore

$$\frac{(1-\alpha)^2}{(\frac{N_A}{N_B}+\alpha)(\frac{N_B}{N_A}+\alpha)} = e^{-\frac{z\varepsilon}{kT}} \tag{13}$$

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. (11a), (11b), (11d) and (11e) into Eq. (5c) in such a way as to eliminate the activities, illustrates that the vacancy concentration is given by

$$\frac{n_v}{n_A+n_B} = N_A^{\ 2}\, e^{\frac{z\varepsilon_{AA}}{2kT}} + 2N_AN_B\, e^{\frac{z\varepsilon_{AB}}{2kT}} + N_B^{\ 2}\, e^{\frac{z\varepsilon_{BB}}{2kT}}$$

$$+ \alpha N_AN_B \left(e^{\frac{z\varepsilon_{AA}}{2kT}} + e^{\frac{z\varepsilon_{BB}}{2kT}} - 2\, e^{\frac{z\varepsilon_{AB}}{2kT}} \right) \tag{14}$$

IV. SIMPLE-DISPLACEMENT MODEL

This vacancy model is an internally consistent short-range ordering

analogue of that proposed by Girifalco[3] 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

$$\Delta E_c = -\frac{z}{2}\left(p_{AA}\epsilon_{AA}+p_{BA}\epsilon_{AB}\right) n_V^{(A)} - \frac{z}{2}\left(p_{AB}\epsilon_{AB}+p_{BB}\epsilon_{BB}\right) n_V^{(B)} \qquad (15)$$

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

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

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

$$F(\alpha, n_V^{(A)}, n_V^{(B)}) = F(\alpha, 0, 0) + \Delta E_c - T\Delta S_c \qquad (17)$$

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

$$\frac{n_V^{(A)}}{n_A+n_B} = N_A\, e^{\frac{z}{2kT}(p_{AA}\varepsilon_{AA}+p_{BA}\varepsilon_{AB})}$$

$$= N_A\, e^{\frac{z}{2kT}[N_A\varepsilon_{AA}+N_B\varepsilon_{AB}+\alpha N_B(\varepsilon_{AA}-\varepsilon_{AB})]} \tag{18a}$$

and the symmetrical expression

$$\frac{n_V^{(B)}}{n_A+n_B} = N_B\, e^{\frac{z}{2kT}(p_{AB}\varepsilon_{AB}+p_{BB}\varepsilon_{BB})}$$

$$= N_B\, e^{\frac{z}{2kT}[N_B\varepsilon_{BB}+N_A\varepsilon_{AB}+\alpha N_A(\varepsilon_{BB}-\varepsilon_{AB})]} \tag{18b}$$

The total vacancy concentration is given by the sum of Eqs. (18a) and (18b), namely

$$\frac{n_V}{n_A+n_B} = \frac{n_V^{(A)}+n_V^{(B)}}{n_A+n_B} = N_A\, e^{\frac{z}{2kT}[N_A\varepsilon_{AA}+N_B\varepsilon_{AB}+\alpha N_B(\varepsilon_{AA}-\varepsilon_{AB})]}$$

$$+ N_B\, e^{\frac{z}{2kT}[N_B\varepsilon_{BB}+N_A\varepsilon_{AB}+\alpha N_A(\varepsilon_{BB}-\varepsilon_{AB})]} \tag{18c}$$

V. VACANCY-ENERGY MODEL

This model is based on the concepts originally introduced by Lomer[6] for vacancies in extremely dilute solutions and extended more recently

by Dorn and Mitchell[7] 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. 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 ith 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.

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 Mitchell 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 expansion

$$(N_A+N_B)^z = \sum_{i=0}^{z} \frac{z!}{(z-i)!i!} N_A^{z-i} N_B^{i} = 1 \tag{19}$$

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

$$n_{Li} = (n_A+n_B) \frac{z!}{(z-i)!i!} N_A^{z-i} N_B^{i} \tag{20}$$

lattice sites of the ith 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 ith 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 now vacant sites on appropriate equivalent sites on the surface. Thus the free energy change is closely given by

$$\Delta F = \sum_{i=0}^{z} n_i g_i - kT \ln \prod_{i=0}^{z} \frac{n_{Li}!}{n_i!(n_{Li}-n_i)!} \tag{21}$$

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

$$\frac{n_i}{n_S} \simeq \frac{z!}{(z-i)!i!} N_A^{z-i} N_B^{i} e^{-\frac{g_i}{kT}} \tag{22}$$

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

$$(p_{AA}+p_{BA})^z = \sum_{i=0}^{z} \frac{z!}{(z-i)!i!} p_{AA}^{z-i} p_{BA}^{i} = 1 \tag{23a}$$

$$(p_{AB}+p_{BB})^z = \sum_{i=0}^{z} \frac{z!}{(z-i)!i!} p_{AB}^{z-i} p_{BB}^{i} = 1 \tag{23b}$$

gives the probability of having i B atoms and (z - i) A atoms about any A atom, Eq. (23a), and about any B atom, Eq. (23b), respectively. Thus the total number of lattice sites of the ith kind surrounded by i B atoms and (z - i) A atoms is

$$n_{Li} = (n_A p_{AA}^{z-i} p_{BA}^{i} + n_B p_{AB}^{z-i} p_{BB}^{i}) \frac{z!}{(z-i)!i!} \tag{24}$$

Whereas the configurational entropy of mixing n_i vacancies on these sites, where $n_i << n_{Li}$, 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 ith 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 $\bar{\varepsilon}$ is given by

$$\bar{\varepsilon} = N_A p_{AA}\varepsilon_{AA}+N_A p_{BA}\varepsilon_{AB}+N_B p_{AB}\varepsilon_{AB}+N_B p_{BB}\varepsilon_{BB} \tag{25a}$$

Introducing Eqs.(4) reveals that

$$\bar{\varepsilon} = N_A{}^2\varepsilon_{AA}+2N_A N_B\varepsilon_{AB}+N_B{}^2\varepsilon_{BB}-2\alpha N_A N_B\varepsilon \tag{25b}$$

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 ith 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

$$\frac{n_i}{n_s} \simeq \frac{z!}{(z-i)!i!}\left(N_A p_{AA}{}^{z-i}\, p_{BA}{}^{i} + N_B p_{AB}{}^{z-i}\, p_{BB}{}^{i}\right) e^{-\frac{g_i+\alpha N_A N_B g'_i}{kT}} \tag{26a}$$

For the disordered case this relationship reduces to Eq. (22). When p_{AA} etc. are replaced by the degree of order, Eq. (26a) becomes

$$\frac{n_i}{n_S} \simeq \frac{z!}{(z-i)!i!} \{N_A(N_A+\alpha N_B)^{z-i}[N_B(1-\alpha)]^i + N_B[N_A(1-\alpha)]^{z-i}(N_B+\alpha N_A)^i\} e^{-\frac{g_i + \alpha N_A N_B g'_i}{kT}} \quad (26b)$$

VI. MODIFIED VACANCY-ENERGY MODEL

The Vacancy-Energy Model for equilibrium concentrations 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 the 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. (23a) and (23b) vacancies of the ith 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

$$\frac{n_i^{(A)}}{n_A} = \frac{z!}{(z-i)!i!} p_{AA}^{z-i} p_{BA}^{i} e^{\frac{(z-i)\varepsilon_{AA}+i\varepsilon_{BA}}{2kT}} \tag{27a}$$

and by

$$\frac{n_i^{(B)}}{n_B} = \frac{z!}{(z-i)!i!} p_{AB}^{z-i} p_{BB}^{i} e^{\frac{(z-i)\varepsilon_{AB}+i\varepsilon_{BB}}{2kT}} \tag{27b}$$

respectively.

The total equilibrium number of vacancies of the ith kind is simply

$$\frac{n_i}{n_S} = \frac{n_i^{(A)}+n_i^{(B)}}{n_S} = \frac{z!}{(z-i)!i!} \{N_A p_{AA}^{z-i} p_{BA}^{i} e^{\frac{(z-i)\varepsilon_{AA}+i\varepsilon_{BA}}{2kT}}$$

$$+ N_B p_{AB}^{z-i} p_{BB}^{i} e^{\frac{(z-i)\varepsilon_{AB}+i\varepsilon_{BB}}{2kT}}\} \tag{28}$$

Thus the total number of vacancies is given by

$$\frac{n_V}{n_S} = \sum_{i=0}^{z} \frac{n_i}{n_S} = N_A\{p_{AA} e^{\frac{\varepsilon_{AA}}{2kT}} + p_{BA} e^{\frac{\varepsilon_{BA}}{2kT}}\}^z$$

$$+ N_B\{p_{AB}\, e^{\frac{\varepsilon_{AB}}{2kT}} + p_{BB}\, e^{\frac{\varepsilon_{BB}}{2kT}}\}^z$$

$$= N_A\{(N_A+\alpha N_B)\, e^{\frac{\varepsilon_{AA}}{2kT}} + N_B(1-\alpha)\, e^{\frac{\varepsilon_{BA}}{2kT}}\}^z$$

$$+ N_B\{N_A(1-\alpha)\, e^{\frac{\varepsilon_{AB}}{2kT}} + (N_B+\alpha N_A)\, e^{\frac{\varepsilon_{BB}}{2kT}}\}^z \qquad (29)$$

VII. DISCUSSION

The vacancy models for short-range ordered alloys that were presented in the preceeding 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. Such approximations have been so extensively reviewed in the literature that no further comment on these issues is necessary here.

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 zp_{AA} and zp_{BA} atoms of type A and B respectively, with similar accountings for atoms surrounding each B atom. Thus a more appropriate (i.e. 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. (14) and (18c) 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. (14) and (18c) reduce to

$$\frac{n_V}{n_S} \simeq e^{\frac{z}{2kT}(N_A{}^2\varepsilon_{AA}+2N_AN_B\varepsilon_{AB}+N_B{}^2\varepsilon_{BB}-2\alpha N_AN_B\varepsilon)} = e^{\frac{z\bar{\varepsilon}}{2kT}} \qquad (30)$$

The similarity of deductions based on these two models is illustrated in Fig. 1 for the conditions $z = 8$, $N_A = N_B = 1/2$ and $\varepsilon_{AA} = \varepsilon_{BB}$. 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-Displacement Model but was not made in the Smeared-Displacement Model. As shown in Fig. 1 over the range of $-\varepsilon/2kT$, 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. 1, the Modified Vacancy-Energy Model also follows the same trends and at high temperature it predicts the same result because Eq. (29) reduces to Eq. (30). Here the additional assumption that $N_o\ \varepsilon_{AB} = -14.50$ kcal

and $N_o\varepsilon_{AA} = N_o\varepsilon_{BB} = -14.15$ kcal, where N_o 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. 2, 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. 3, 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. However, this distribution is strongly affected by the values of bond energies. This can be readily shown from the following equation which is reduced from Eqs. (28) and (29) for the case $N_A = N_B = 1/2$ and z = 8.

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

$$= \frac{\frac{8!}{(8-i)!\,i!}\left\{(1+\alpha)^{8-i}(1-\alpha)^{i}\, e^{\frac{(8-i)\varepsilon_{AA}+i\varepsilon_{BA}}{2kT}} + (1-\alpha)^{8-i}(1+\alpha)^{i}\, e^{\frac{(8-i)\varepsilon_{AB}+i\varepsilon_{BB}}{2kT}}\right\}}{\left\{(1+\alpha)\, e^{\frac{\varepsilon_{AA}}{2kT}} + (1-\alpha)\, e^{\frac{\varepsilon_{BA}}{2kT}}\right\}^{8} + \left\{(1-\alpha)\, e^{\frac{\varepsilon_{AB}}{2kT}} + (1+\alpha)\, e^{\frac{\varepsilon_{BB}}{2kT}}\right\}^{8}} \qquad (31)$$

If the bond energies $N_o\varepsilon_{AA} = -7.9$ kcal, $N_o\varepsilon_{BB} = -20.4$ kcal and $N_o\varepsilon_{AB} = -14.50$ kcal (where N_o is Avogadro's number) are assumed, the second term inside the braces are negligible with respect to the first term and the exponentials become the predominant factor. Therefore, as shown in Fig. 4, at low temperatures the i = 0 type of vacancy is most populous.

The assumption, common to the Shared-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 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 further modify 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. (27a) and (27b) 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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FIGURE CAPTIONS

Figure 1. Temperature effect on the equilibrium vacancy concentrations and the short-range order parameter for the case $N_A = N_B = 1/2$, $\varepsilon_{AA} = \varepsilon_{BB}$ and $z = 8$.

Figure 2. Effect of ordering on the distribution of the various vacancy concentrations according to the Modified Vacancy-Energy Model.

Figure 3. Distribution of the various vacancy concentrations for the case $N_A = N_B = 1/2$, $N_o\varepsilon_{AA} = N_o\varepsilon_{BB} = -14.15$ kcal, $N_o\varepsilon_{AB} = -14.50$ kcal and $z = 8$.

Figure 4. Distribution of the various vacancy concentrations for the case $N_A = N_B = 1/2$, $N_o\varepsilon_{AA} = -7.9$ kcal, $N_o\varepsilon_{BB} = -20.4$ kcal, $N_o\varepsilon_{AB} = -14.50$ kcal and $z = 8$.

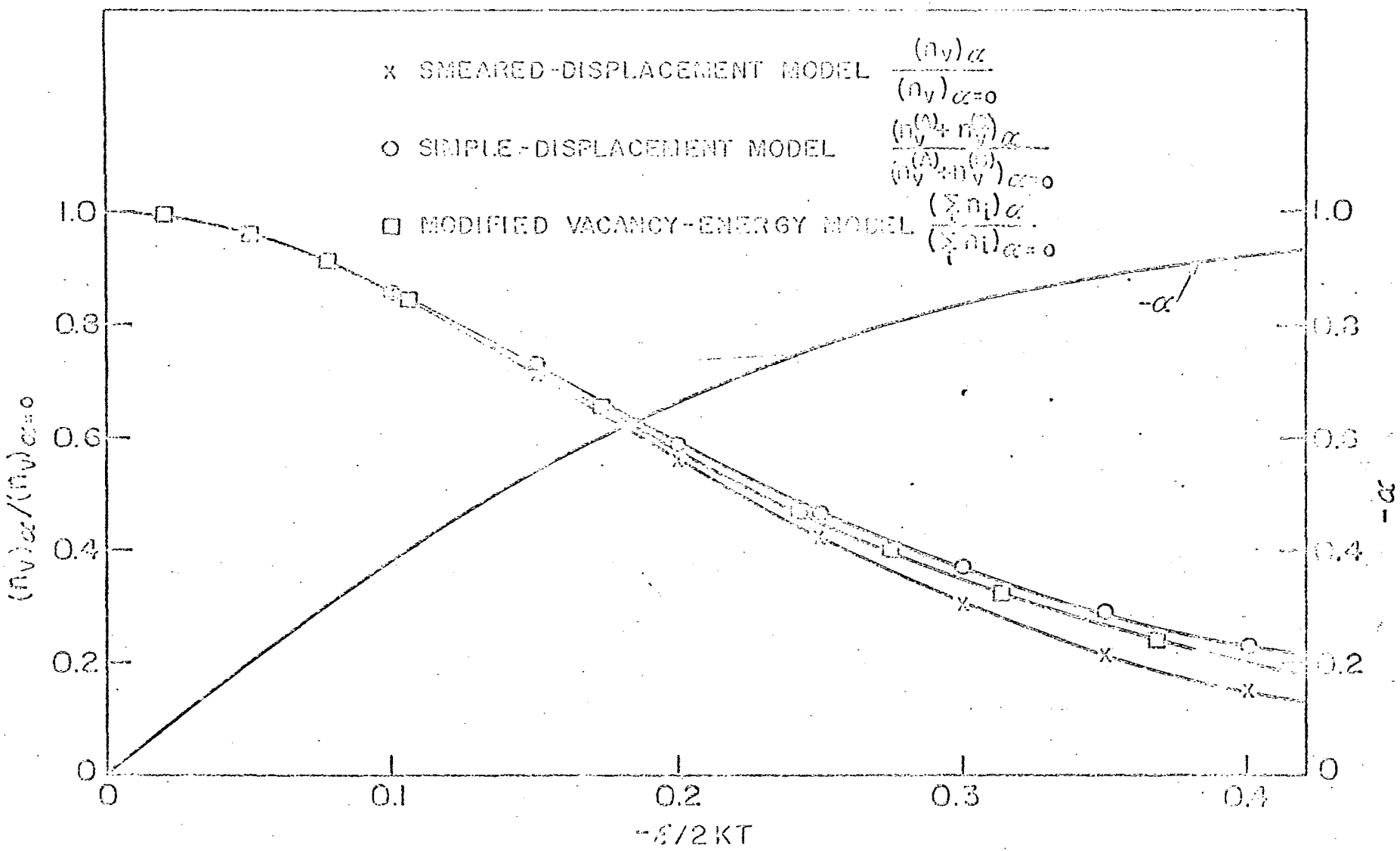

FIG. 1 TEMPERATURE EFFECT ON THE EQUILIBRIUM VACANCY CONCENTRATIONS AND THE SHORT-RANGE ORDER PARAMETER FOR THE CASE $N_A = N_B = \frac{1}{2}$, $\varepsilon_{AA} = \varepsilon_{BB}$, AND $Z = 8$.

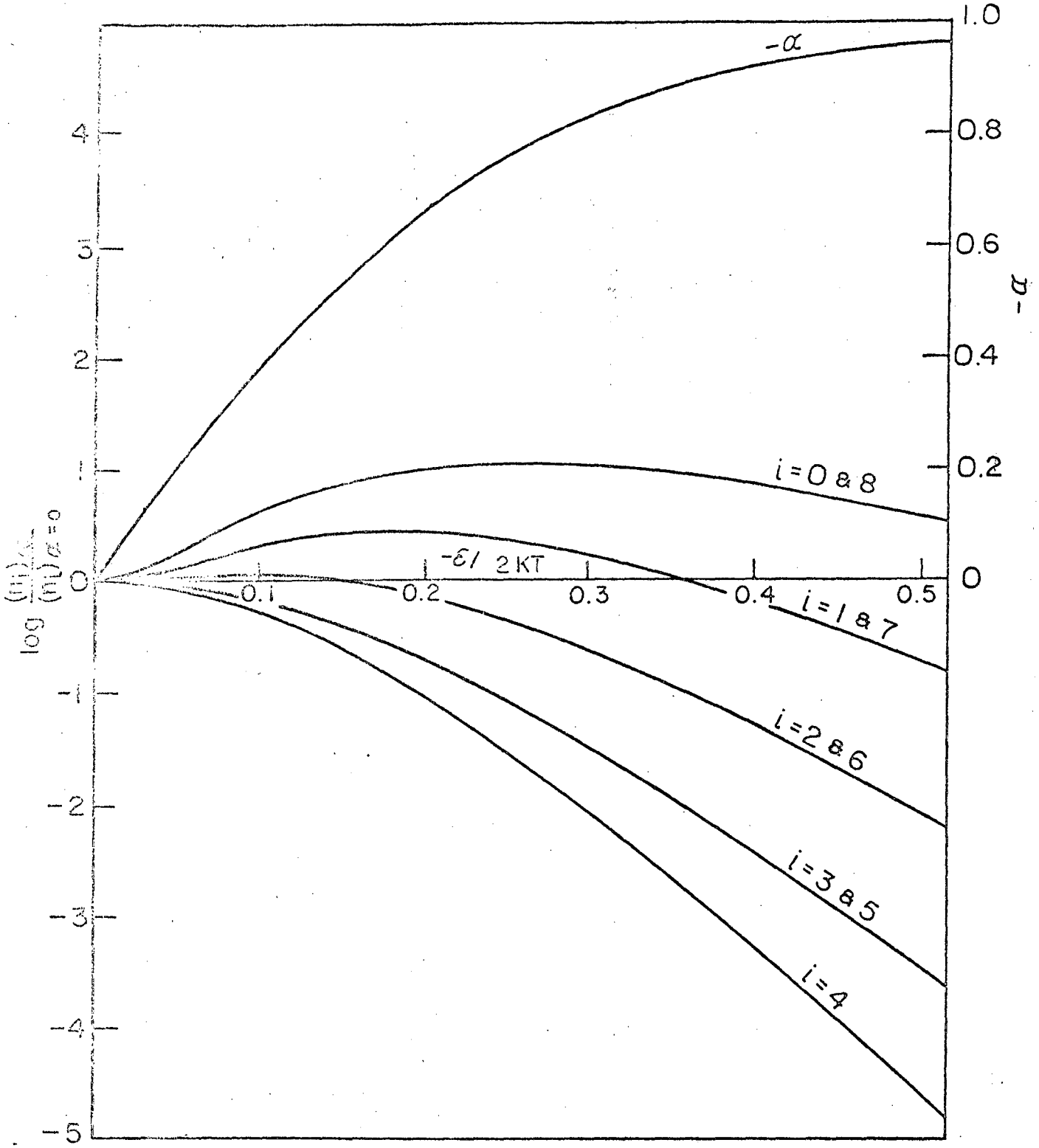

FIG. 2 EFFECT OF ORDERING ON THE DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS ACCORDING TO THE MODIFIED VACANCY-ENERGY MODEL.

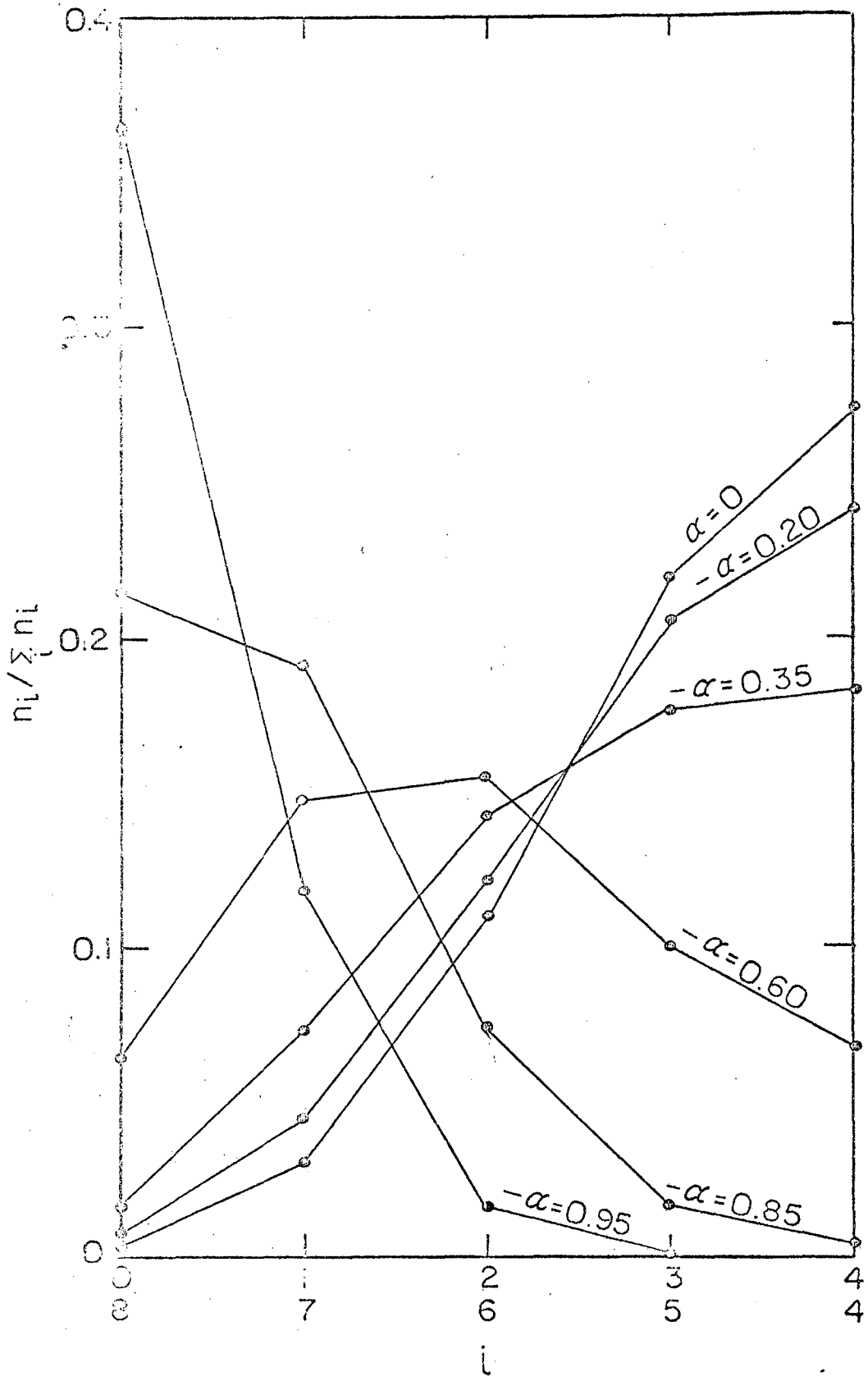

FIG. 3 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS FOR THE CASE $N_A = N_B = 1/2$, $N_0\mathcal{E}_{AA} = N_0\mathcal{E}_{BB} = -14.15$ KCAL, $N_0\mathcal{E}_{AB} = -14.50$ KCAL AND $z = 8$.

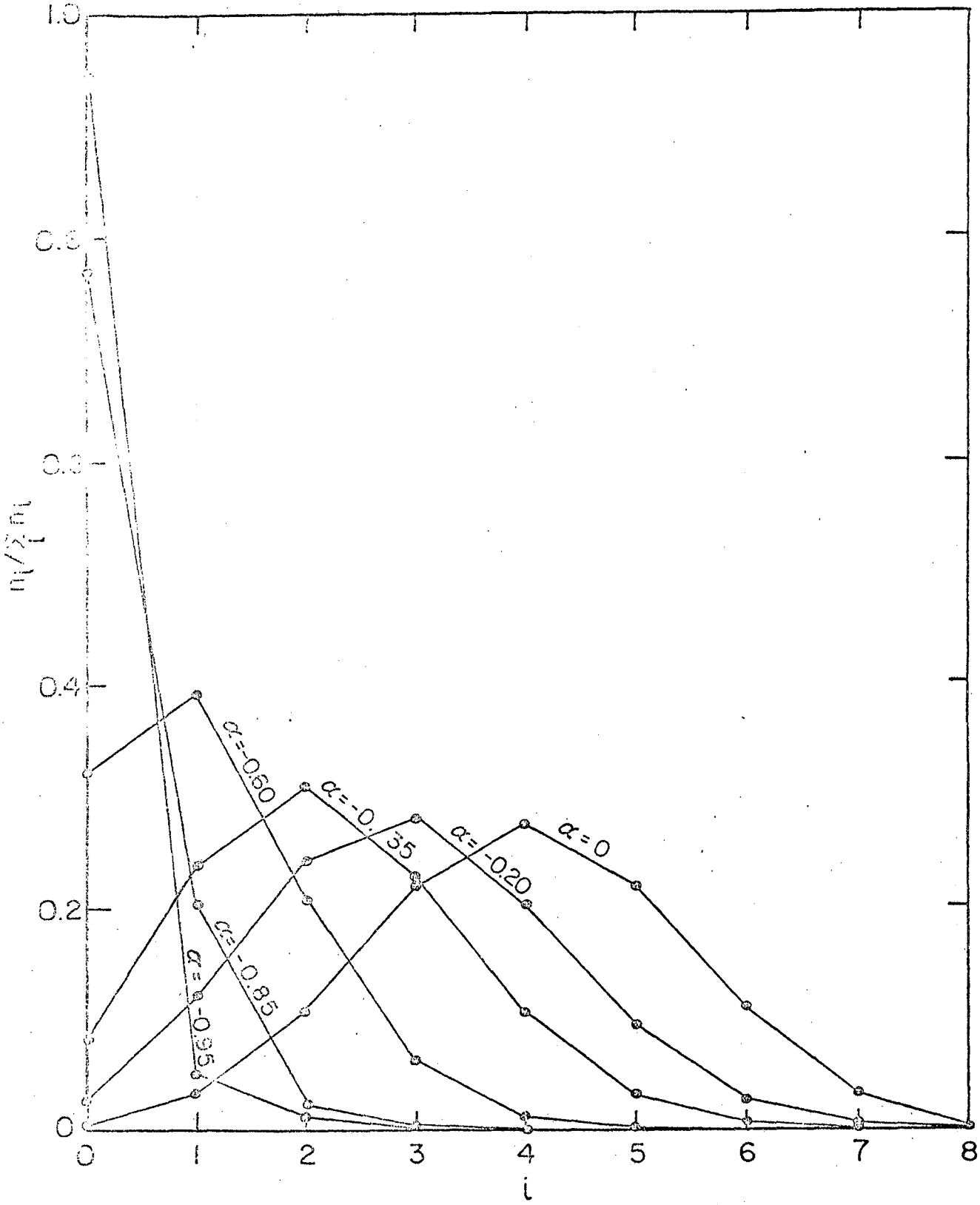

FIG. 4 DISTRIBUTION OF THE VARIOUS VACANCY CONCENTRATIONS FOR THE CASE $N_A = N_B = \frac{1}{2}$, $N_0 \varepsilon_{AA} = -7.9$ KCAL, $N_0 \varepsilon_{BB} = -20.4$ KCAL, $N_0 \varepsilon_{AB} = -14.50$ KCAL AND $z = 8$.

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