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Quasi-chemical Treatment of Intermediate Phases Appearing in Nonstoichiometric Compounds

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A quasi-chemical treatment of the superlattice formation model is applied to intermediate phases appearing in nonstoichiometric compounds. Two kinds of interaction energy are introduced and both the intermediate phase and two-phase separation are described in a single formula. The order parameter and the free energy are obtained as a function of temperature and composition. The boundaries of phases are determined by the common-tangent method.

1. Introduction

Intermediate phases appearing in nonstoichiometric compounds were treated statistically in a previous paper (*1*), using the model of superlattice formation. In that report, using a crude (Bragg–Williams) approximation, it was shown that the ordered state which is supposed to occur at a certain composition of a nonstoichiometric system breaks down rapidly with variation of the composition or of the chemical potential and that the appearance of the intermediate phase can be discussed as the composition-dependent order–disorder phase transition. However, the problem of the relative stability of the intermediate phase or the problem of the phase boundary is left unsolved in the previous paper. To obtain the phase boundary we must analyze both the intermediate phase and adjacent phase, which are usually separated by a miscibility gap in a nonstoichiometric binary system, in a unified model. For this purpose we discuss in the present paper the statistical thermodynamics of the intermediate phase using a quasi-chemical method applied to the superlattice formation model.

The statistical behavior of nonstoichiometric systems with large deviations from stoichiometry have been discussed by Lacher (*2*), Anderson (*3*), and Rees (*4*) on the basis of simplified assumptions, where only the nearest-neighbor interaction is taken into account and where defects are independent thermodynamically of the parent lattice of the compounds. In spite of the simplification, their results can explain well the critical miscibility phenomena observed in both types of nonstoichiometric compounds (interstitial and vacancy types) (*5*). In these models, attractive interactions between defects (a negative interaction energy) imply that defects tend to cluster and that biphasic separation occurs. On the other hand, a positive interaction energy between defects results in formation of the order of defects (*4, 6, 7*). Therefore it is clear that different kinds of energy should be introduced for treatment of biphasic

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separation and ordering of defects in a single formulation.

In the present paper we also adopt the simplified assumptions described above. In the case of intermediate phase, defects are distributed periodically and are incorporated into the parent lattice, and the assumption that defects are independent thermodynamically of the parent lattice may not be exactly valid. However, it is difficult to form a "tight-binding" model where the breakdown of thermodynamical independence is emphasized, so the validity of independence is supposed, and the incorporation is expressed in the present paper by the interaction energy of superlattice formation.

2. Formulation of the Model

Though the present treatment is applicable to both defective structures in glossy nonstoichiometric compounds—vacancies and interstitial atoms, we formulate the model in terms of interstitial atoms, which can be seen typically in the nonstoichiometric compounds such as UO_{2+x}. We consider a hypothetical nonstoichiometric crystalline solid with the chemical formula MX_{2+x}, where the excess atoms of the component X are distributed over the interstitial sites of the parent lattice MX_2. The number of available interstitial sites per mole, N is assumed to be equal to that of MX_2, as in UO_{2+x}. Hereafter we designate the occupied interstitial sites by A, and unoccupied sites by B. The number of occupied sites N_A is equal to that of excess atoms Nx. The number of unoccupied sites is given by $N_B = N(1 - x)$. As we have discussed in the previous paper (*1*), this situation can be treated as the system of the solid solution composed of the component A and B.

In the absence of the intermediate phase, the interaction between excess atoms is rather attractive and two-phase separation occurs in usual binary nonstoichiometric systems, as we have described already. The interaction energy between defects is negative. This can be translated in the AB system by putting the interaction energy as

$$\epsilon_1 = E_{AB} - \tfrac{1}{2}(E_{AA} + E_{BB}). \qquad (1)$$

where ϵ_1 is positive, where E_{AA} is the interaction energy between neighboring excess atoms, E_{BB} is the energy between neighboring unoccupied sites and E_{AB} is the energy between an excess atom and a neighboring unoccupied site. In these terms the interaction energy between unoccupied interstitial sites is physically meaningless and E_{BB} should be put equal to zero in this case.

Next, we consider that a superlattice is formed at a certain value of x. This value depends on the compounds. For instance, in U–O system, the most significant intermediate phase is U_4O_9 and many other phases such as U_2O_5, U_3O_7, and U_5O_{13} are reported (*8*). Departing from the composition and the detailed structure of existing intermediate phases, here we postulate that the superlattice formation occurs at the concentration $x = \frac{1}{2}$, in order to avoid the complexity of the model. Referring to the model proposed previously (*1*), the excess atoms have a tendency to occupy the designated sites (to be called α lattice) and the remaining sites (β lattice) are inclined to be unoccupied at this concentration. This can be achieved by introducing the order energy ϵ_2 ($\epsilon_2 < 0$). The number of sites in the α and β lattices are given by $N_\alpha = N/2$ and $N_\beta = N/2$, respectively, for we have assumed that the intermediate phase occurs at $x = \frac{1}{2}$.

According to the assumption of thermodynamical independence of the defects of the parent lattice, the partition function of the whole system is written as

$$Z_0 = K(T)ZQ(T), \qquad (2)$$

where $K(T)$ is the partition function of the parent lattice, $Q(T)$ is the vibrational partition function due to excess atoms, and Z is the configurational partition function of excess atoms. In the following analysis we restrict our discussion within the treatment of Z and the related thermodynamic quantities are calculated by using the modified quasi-chemical method.

Application of the quasi-chemical method (9) to this problem is carried out as follows. Let us consider the distribution of excess atoms over the sites of the α and β lattices. By using the order parameter, s, we have

$$\langle A\alpha\rangle = (N/2)(1+s)x, \tag{3}$$

$$\langle B\alpha\rangle = (N/2)\{1-(1+s)x\}, \tag{4}$$

$$\langle A\beta\rangle = (N/2)(1-s)x, \tag{5}$$

and

$$\langle B\beta\rangle = (N/2)\{1-(1-s)x\}, \tag{6}$$

where $\langle A\alpha\rangle$ is the number of excess atoms in the α lattice, $\langle B\alpha\rangle$ the number of unoccupied sites in the α lattice, $\langle A\beta\rangle$ the number of excess atoms in the β lattice, and $\langle B\beta\rangle$ the number of unoccupied sites in the β lattice.

Now we count the number of pairs of neighboring sites in the four possible ways by using the parameter θ. When an α site (a site in the α lattice) is supposed to be surrounded by z β sites and when the number of total AB pairs is expressed by $zN\theta$, then

$$\langle A\alpha A\beta\rangle = (z/2)N(x-\theta), \tag{7}$$

$$\langle B\alpha B\beta\rangle = (z/2)N(1-x-\theta), \tag{8}$$

$$\langle A\alpha B\beta\rangle = (z/2)N(\theta+sx), \tag{9}$$

and

$$\langle B\alpha A\beta\rangle = (z/2)N(\theta-sx), \tag{10}$$

where $\langle A\alpha B\beta\rangle$ is the number of pairs of excess atoms on α and β sites, $\langle B\alpha B\beta\rangle$ is the number of pairs of unoccupied α and β sites, $\langle A\alpha B\beta\rangle$ is the number of pairs of atoms on α sites and unoccupied β sites, and $\langle B\alpha A\beta\rangle$ is the number of pairs of atoms on β sites and unoccupied α sites.

According to Takagi (*10, 11*) the number of distinguishable configurations is obtained by counting consistent combinations as

$$g = \frac{\langle\alpha\beta\rangle!}{\langle A\alpha A\beta\rangle!\langle B\alpha B\beta\rangle!\langle A\alpha B\beta\rangle!\langle B\alpha A\beta\rangle!}\left\{\frac{\langle A\alpha\rangle!\langle B\alpha\rangle!}{\langle\alpha\rangle!}\right\}^{z-1}\times\left\{\frac{\langle A\beta\rangle!\langle B\beta\rangle!}{\langle\beta\rangle!}\right\}^{z-1}, \tag{11}$$

where $\langle\alpha\beta\rangle$ is the number of total pairs given by

$$\langle\alpha\beta\rangle = zN/2 \tag{12}$$

and where

$$\langle\alpha\rangle = N_\alpha = N/2 \quad \text{and} \quad \langle\beta\rangle = N_\beta = N/2. \tag{13}$$

Substituting Eqs. (3)–(10), and (12) and (13) into Eq. (11), we have

$$g = \frac{(zN/2)!}{\{(z/2)N(x-\theta)\}!\{(z/2)N(1-x-\theta)\}!\{(z/2)N(\theta+sx)\}!\{(z/2)N(\theta-sx)\}!} \times\left[\frac{\{(N/2)(x+sx)\}!\{(N/2)(1-x-sx)\}!}{(N/2)!}\right]^{z-1} \times\left[\frac{\{(N/2)(x-sx)\}!\{(N/2)(1-x+sx)\}!}{(N/2)!}\right]^{z-1}. \tag{14}$$

Using the relations $N_A = Nx$ and $N_B = N(1 - x)$, and putting

$$N_C = N\theta \tag{15}$$

and

$$N_D = Nsx, \tag{16}$$

Eq. (14) can be rewritten as

$$g(N_A,N_B,N_C,N_D) = \frac{\{(z/2)(N_A + N_B)\}!}{\{(z/2)(N_A - N_C)\}!\{(z/2)(N_B - N_C)\}!\{(z/2)(N_C + N_D)\}!\{(z/2)(N_C - N_D)\}!} \times \left[\frac{\{\frac{1}{2}(N_A + N_D)\}!\{\frac{1}{2}(N_B - N_D)\}!}{\{\frac{1}{2}(N_A + N_B)\}!}\right]^{z-1} \times \left[\frac{\{\frac{1}{2}(N_A - N_D)\}!\{\frac{1}{2}(N_B + N_D)\}!}{\{\frac{1}{2}(N_A + N_B)\}!}\right]^{z-1}. \tag{14a}$$

Here N_C is the number of AB pairs (pairs of occupied and unoccupied sites) divided by z, and N_D is the difference in number of the excess atoms between the α and β sites.

The semi-grand partition function of the defects is obtained as the product of Eq. (14a) and energy terms as follows.

$$Z = \sum_{N_C}\sum_{N_D} g(N_A,N_B,N_C,N_D) \exp\left(\frac{-zN_AE_{AA}}{2kT}\right) \exp\left(\frac{-zN_C\epsilon_1}{kT}\right) \exp\left(\frac{-zN_D^2\epsilon_2}{NkT}\right). \tag{17}$$

Here the term $\exp(-zN_BE_{BB}/2kT)$ is neglected, because E_{BB} is zero as we have described already. In the usual formula of the quasi-chemical method the term $\exp(-zN_D^2\epsilon_2/NkT)$ is not written. Either the ordered state or the case of two-phase separation is considered according to the positive or negative sign of ϵ_1 in the usual treatment. The energy terms corresponding to the variables of both N_C (the number of pairs of occupied and unoccupied sites) and N_D (which is related to the number of atoms in the superlattice sites) are included in Eq. (17) and by this formula we can treat the coexisting system of ordered phase and two-phase separation.

In the calculation of Eq. (17), summation is equated to the maximum term. This equilibrium condition is obtained by the following differentiations.

$$\frac{\partial \ln\left\{g(N_A, N_B, N_C, N_D) \exp\left(\frac{-zN_C\epsilon_1}{kT}\right)\right\}}{\partial N_C} = 0 \tag{18}$$

and

$$\frac{\partial \ln\left\{g(N_A, N_B, N_C, N_D) \exp\left(\frac{-zN_D^2\epsilon_2}{NkT}\right)\right\}}{\partial N_D} = 0. \tag{19}$$

Using Eqs. (14a), (15), (16) and Stirling's relation, Eqs. (18) and (19) are calculated as

$$\frac{(x - \theta)(1 - x - \theta)}{(\theta + sx)(\theta - sx)} = \exp\left(\frac{2\epsilon_1}{kT}\right) \tag{20}$$

and

$$\frac{4zsx\epsilon_2}{kT} + z \ln\frac{\theta + sx}{\theta - sx} = (z - 1) \ln\frac{(1 - s)(1 - x + sx)}{(1 - s)(1 - x - sx)}. \tag{21}$$

These are the basic relations in the following analysis.

3. Order Parameter in Temperature–Composition Space

When we put

$$r = x - \theta, \qquad (22)$$

Eq. (20) can be solved with respect to r in the form,

$$r = \frac{(2x + A - 2xA) \pm ((2x + A - 2xA)^2 - 4(1 - A)(1 - s^2)x^2)^{1/2}}{2(1 - A)}, \qquad (23)$$

where A is given by

$$A = \exp\left(\frac{-2\epsilon_1}{kT}\right). \qquad (24)$$

As this analysis is restricted near the intermediate phase, the variable of concentration x is replaced by neighborhood concentration δ defined by

$$\delta = \tfrac{1}{2} - x, \qquad (25)$$

the value of which is zero at the central concentration of the intermediate phase. The composition range of the intermediate phase is extremely narrow. For example, the width of the phase is about 0.02 in U_4O_9, which can be classified into rather wide range group (*8*). In many cases the width of the phase should be about 0.001. So we can assume $\delta \ll 1$. From the conditions that $1 > A > 0$ and $x(1 - s) > r > 0$, we adopt the negative sign in Eq. (23) and this is rewritten as

$$r = \frac{\kappa'(1 - s^2)}{2(1 + q)}, \qquad (26)$$

where

$$\kappa' = \frac{(1 - 2\delta)^2}{1 - 2(1 - A)\delta}, \qquad (27)$$

$$q = (1 - (1 - A)\kappa^2(1 - s^2))^{1/2}, \qquad (28)$$

and

$$\kappa = \frac{1 - 2\delta}{1 - 2(1 - A)\delta}. \qquad (29)$$

As the value of δ is extremely small (10^{-2}–10^{-3}) and as the value of A is small ($1 > A > 0$), κ' can be approximated in the form

$$\kappa' \sim (1 - 4\delta)\{1 + 2(1 - A)\delta\}$$
$$\sim 1 - 2(1 + A)\delta \sim 1 - 2\delta. \qquad (30)$$

Substituting Eqs. (22), (25), (26), and (30) into Eq. (21), we attain a final formula which designates the value of the order parameter s of the ordered phase near $x = \frac{1}{2}$ ($\delta = 0$), as a function of temperature T and concentration δ as

$$\ln\frac{q + s}{q - s} = \left(\frac{z - 2}{z}\right)\ln\frac{1 + s}{1 - s} + \left(\frac{z - 1}{z}\right)\ln\left\{\frac{1 + [2\delta(1 - s)/(1 + s)]}{1 + [2\delta(1 + s)/(1 - s)]}\right\} - \frac{2s\epsilon_2}{kT} + \frac{4s\delta\epsilon_2}{kT}, \qquad (31)$$

where q is given by Eq. (28).

Let us examine Eq. (31) numerically for given values of z, ϵ_1 and ϵ_2. ϵ_1 has the same physical meaning as the interaction energy between interstitial atoms, $-E_{ii}$ in the treatment by Anderson (*3*) and determines the critical miscibility temperature of two-phase separation. For the U–O system, with very high critical miscibility temperature, this has been calculated as 5.03–5.56 kcal/mole (*12*). For nonstoichiometric oxides with lower critical temperatures such as the Pr–O system, ϵ_1 may be obtained as about 1 kcal/mole. In order to clarify the influence of the intermediate phase on two-phase separation, we had better use a small value of ϵ_1 compared with that of ϵ_2. We put $\epsilon_1 = 0.25$ kcal/mole (this corresponds to the critical miscibility temperature about 500 K) and $\epsilon_2 = -0.80$ kcal/mole. The coordination number z is given by 6, 8, and 12 for simple cubic, body-centered, and facecentered structure, respectively. The essential part of the result may not be affected by these values of z. Here we use $z = 8$.

The calculations were carried out by a FACOM 230-75 computer. The curve of s against T at $\delta = 0$ coincides with that of the usual order–disorder phase transition with the critical temperature $T_c = 1060$ K. The critical temperature decreases with increasing absolute value of δ as shown in Fig. 1. A set of solutions of Eq. (31) form a surface in s, T, δ space. Another set of solutions designated by A in Fig. 1 appears, which seems to have no relation with the intermediate phase in this case.

4. The Boundary of the Ordered Phase

To determine the boundary of the ordered phase, one must compare the free energy of the ordered phase with that of adjacent phases. In the case of solid under ordinary pressure, one can approximate the Gibbs free energy by

$$G = -kT \ln Z. \tag{32}$$

Under the conditions expressed by Eqs. (20) and (21), summations in the partition function can be replaced by the maximum term $g^*(x, s, \theta)$, so we have

$$Z = g^*(x, s, \theta) \times (\text{energy terms}). \tag{33}$$

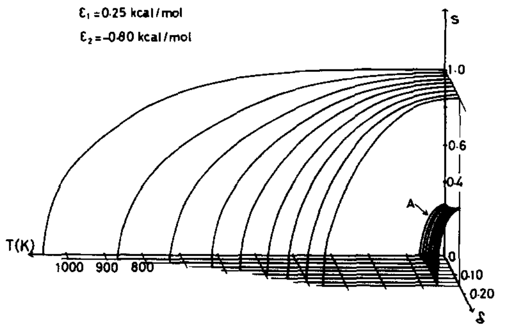

FIG. 1. The order parameter s versus temperature T and composition δ near the composition where the intermediate phase appears.

From the relation $N_A = Nx$ and $N_B = N(1 - x)$ and Eqs. (14a), (15), and (16) and using Stirling's relation, we have

$$\begin{aligned} \ln g^*(x, s, \theta) = {} & (zN/2)\{x - \theta) \ln (x - \theta) \\ & + (1 - x - \theta) \ln (1 - x - \theta) \\ & + (\theta + sx) \ln (\theta + sx) \\ & + (\theta - sx) \ln (\theta - sx)\} \\ & + [(z - 1)N/2]\{x + sx) \ln (x + sx) \\ & + (x - sx) \ln (x - sx) \\ & + (1 - x + sx) \ln (1 - x + sx) \\ & + (1 - x - sx) \ln (1 - x - sx)\}. \end{aligned} \tag{34}$$

From Eqs. (32), (33), and (34), and referring the energy terms in Eq. (17), the free energy of the system is given by

$$\begin{aligned} G = {} & G_0 + \epsilon_0 xN + \epsilon_1 zN\theta + \epsilon_2 zs^2x^2N \\ & + (zNkT/2)\{(x - \theta) \ln (x - \theta) \\ & + (1 - x - \theta) \ln (1 - x - \theta) \\ & + (\theta + sx) \ln (\theta + sx) \\ & + (\theta - sx) \ln (\theta - sx)\} \\ & + [(z - 1)NkT/2]\{x + sx) \ln (x + sx) \\ & + (x - sx) \ln (x - sx) \\ & + (1 - x + sx) \ln (1 - x + sx) \\ & + (1 - x - sx) \ln (1 - x - sx)\}, \end{aligned} \tag{35}$$

where G_0 is the constant term and $\epsilon_0 xN$ is the first-order term.

In the absence of the intermediate phase, two-phase separation occurs, the free energy of which is obtained by putting $s = 0$ in Eq. (35) as

$$\begin{aligned} G = {} & G_0 + \epsilon_0 xN + \epsilon_1 z\theta N + (zNkT/2) \\ & \{(x - \theta) \ln (x - \theta) + (1 - x - \theta) \\ & \ln (1 - x - \theta) + 2\theta \ln \theta\} \\ & - (z - 1)NkT\{x \ln x \\ & + (1 - x) \ln (1 - x)\}. \end{aligned} \tag{36}$$

This equation coincides with that obtained by application of the usual quasi-chemical method to two-phase separation in the binary solid solution or to the system of localized monolayers (9). Eqs. (35) and (36) can be calculated numerically by using the values of s and θ which are obtained according to the treatment described already. For given temperatures the values of free energy are shown in Fig. 2 as a function of the composition x. Here free energy when $z = 8$, $\epsilon_1 = 0.25$ kcal/mole, $\epsilon_2 = -0.80$ kcal/mole is plotted for temperatures $T = 400$ and 800 K. The term $(G_0 + \epsilon_0 xN)$ in both equations is dropped here for convenience. The dotted line expresses the free energy in the absence of the intermediate phase. To determine phase boundaries we use the common-tangent method. Common tangents are also shown in the same figure.

Thus determined phase-boundary composition for each temperature is shown in the form of the phase diagram in Fig. 3, where the intermediate phase coexists with two-phase separation. The dotted line expresses the phase boundary of two-phase separation in the absence of the intermediate phase. One can recognize that occurrence of the intermediate phase influences the boundaries of the adjacent phases. The width of the intermediate phase is found to be extremely narrow and is scarcely dependent upon the order energy ϵ_2. The value of ϵ_2 determines rather the high-temperature limit of the boundary of the ordered phase. The limiting temperature is about 980 K in this case. This is slightly lower than the critical temperature $T_c = 1060$ K as described in the previous section.

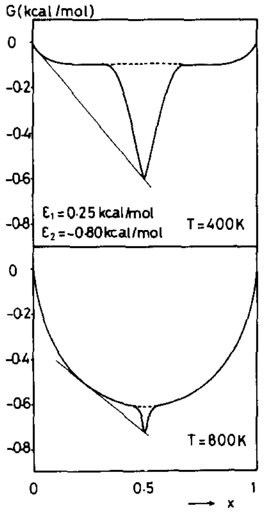

FIG. 2. Free energy of the intermediate and adjacent phase as a function of composition x in MX_{2+x}. To determine the phase boundaries, the common tangent is drawn. Dotted line indicates the free energy in the absence of the intermediate phase.

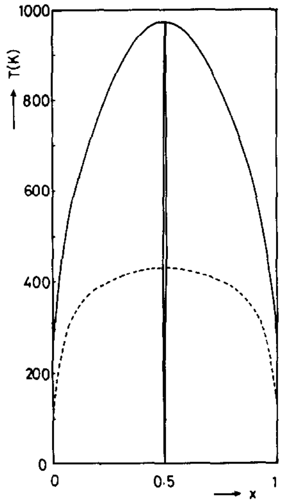

FIG. 3. Phase diagram of the intermediate and adjacent phases for interaction energies, $\epsilon_1 = 0.25$ kcal/mole and $\epsilon_2 = -0.80$ kcal/mole. Dotted line expresses two-phase separation in the absence of the intermediate phase.

Minimum values of free energy for various values of the interaction energy ϵ_2 are shown in Fig. 4 as a function of temperature. The dotted line indicates the minimum values of free energy of two-phase separation in the absence of the intermediate phase. The intermediate phase appears in the phase diagram when its minimum value of free energy locates in lower position than the dotted line in the figure. For $\epsilon_1 = 0.25$ kcal/mole, the absolute value of ϵ_2 is necessary to be larger than 0.50 kcal/mole for

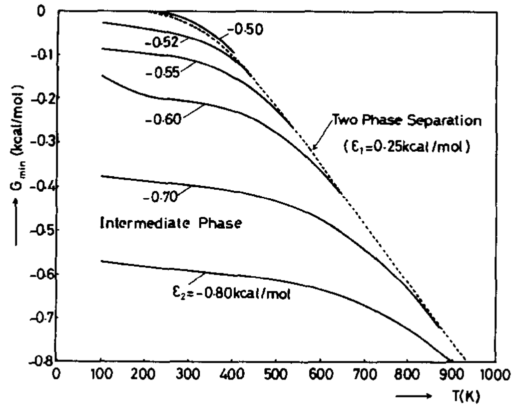

FIG. 4. The minimum values of free energy for various order energies of the intermediate phases. Dotted line is the minimum value of free energy of two-phase separation with $\epsilon_1 = 0.25$ kcal/mole.

occurrence of the intermediate phase. In general this condition is given by $\epsilon_2 > -2\epsilon_1$.

5. Chemical Potential and Related Quantities

In the previous paper (*1*) it was pointed out that the differentiation of the chemical potential with respect to x has a singularity at the intermediate phase. Let us examine this relation in this treatment. The chemical potential of the system is obtained by

$$\mu = \left(\frac{\partial G}{\partial x}\right)_{T,V}. \tag{37}$$

We have recognized that parameter s and θ are determined by designating x and T. So differentiation of G in Eq. (35) is carried out by considering that s and θ are functions of x. Rearranging the result by using Eqs. (20) and (21), we have

$$\mu = \epsilon_0 N + \frac{zNkT}{2} \ln \frac{x-\theta}{1-x-\theta} + \frac{(z-1)NkT}{2} \ln \frac{(x+sx)(x-sx)}{(1-x+sx)(1-x-sx)}. \tag{38}$$

Next we examine the function

$$\xi = \frac{\partial \mu}{\partial x}. \tag{39}$$

Carrying out the differentiation we have

$$\xi = \frac{zNkT}{2}\left\{\frac{1-\theta'}{x-\theta} + \frac{1+\theta'}{1-x-\theta}\right\} + \frac{(z-1)NkT}{2}\left\{\frac{1+s+s'x}{(x+sx)(1-x-sx)} + \frac{1-s-s'x}{(x-sx)(1-x+sx)}\right\}, \tag{40}$$

where

$$\theta' = \frac{\partial \theta}{\partial x} \quad \text{and} \quad s' = \frac{\partial s}{\partial x}. \tag{41}$$

Function ξ which one may call the "chemical susceptibility" from thermodynamic considerations, can be divided into two parts. The first terms are related to biphasic separation, and the last two are related to the intermediate phase. The latter is rewritten as

$$\xi_2 = \frac{(z-1)NkT\{x(1-x) + s^2x(1+x) + s'sx^2(1+2x)\}}{x^2(1+s)(1-s)(1-x-sx)(1-x+sx)}. \tag{42}$$

The feature of this function near $x = \frac{1}{2}$ is shown in Fig. 5. When x approaches $\frac{1}{2}$, s' becomes zero and s becomes 1 at $T = 400$ K. ξ_2 becomes infinite in the order of $(a + s^2)/(1 - s^2)^2$, where a is a constant. At higher temperature such as $T = 800$ K, ξ_2 increases enormously and attains a large value as 10^3. This feature of the function ξ_2 may propose an important key in the treatment of the intermediate phase as a concentration-dependent phase transition.

6. Conclusion

Using the superlattice formation model of the intermediate phase, the order param-

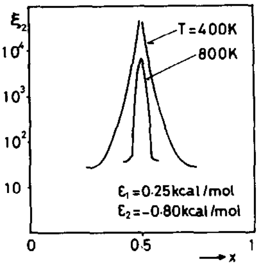

FIG. 5. Singularity of function ξ_2 in the case of the intermediate-phase occurrence.

eter and the free energy are calculated numerically for given values of z, ϵ_1, and ϵ_2. The phase boundary is determined for the intermediate phase and adjacent phases. As the calculation was carried out in order to obtain the general feature of the model, the values of z, ϵ_1, and ϵ_2 do not necessarily coincide with those of existing phases. The model may be applicable to existing phases by some alternations in these points. The most significant difference between the model and existing phases is the number of "molecules" contained in a unit cell. In the present model simple structure is postulated and the unit cell contains one M_2X_5. On the other hand, in U_4O_9, for instance, the unit cell is proposed to contain 64 U_4O_9 "molecules" (*13–15*). The formation of the superlattice with a complicated structure as in U_4O_9 can be described by the cluster formation and ordering of the clusters as has been pointed out in the previous paper (*1*).

In spite of this difference the result of this treatment agrees well with the feature of the existing intermediate phases. The width of the intermediate phase is extremely narrow and is scarcely affected by the magnitude of the order energy ϵ_2. The value of ϵ_2 determines the high-temperature limit of the intermediate phase. The complicated feature of the phase diagram containing intermediate phases might be explained by our conclusion that occurrence of intermediate phases affects the boundaries of adjacent phases and shift them in a large scale. Some problems such as origin of ordering energy and selection of the composition where the intermediate phase occurs are left unsolved in the present paper.

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