Intermediate Phase Appearing in Nonstoichiometric Compounds

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Intermediate phases appearing in nonstoichiometric compounds are treated statistically using the model of superlattice formation. The condition for occurrence of the phase, relation between the concentration of defects and order parameter, and width of the phase are obtained. Decreasing of fluctuations of the distributed particles is accompanied characteristically with occurrence of the intermediate phase.

1. Introduction

The statistical treatment of nonstoichiometric compounds was done by Anderson (*1*) using solid solution model where a nearly random distribution of the defects is supposed with interactions between them. Subsequently, some improvements have been introduced on the detailed mechanism of the interaction and of the formation of the cluster of defects (*2*)–(*7*).

Some nonstoichiometric compounds have intermediate phases with a definite composition which is given by the ratio of small integers and with narrow composition range such as U_4O_9 appearing in the biphasic mixture of UO_{2+x} and U_3O_8. The origin of the intermediate phase is attributed to the periodic order of defects (excess anions in the case of UO_{2+x}), which is confirmed by the experimental results of the formation of the superlattice structure. The distributed defects must be treated as "liquid" in the solid solution range, while they must be treated as a part of the crystalline solid in the intermediate phase. In the present report we use a model where defects are distributed both in the superlattice position and in the remaining "random" position.

In the present report we discuss the problem of a phase transition with variation of concentration. The boundary of the intermediate phase is mostly parallel to the temperature axis in the phase diagram, and the treatment of the phase transition as a function of temperature is not practical.

2. Thermodynamic Features of the Intermediate Phase

The partial molar free energy of the component X varies with the temperature and the composition in the nonstoichiometric compound such as MX_{2+x}. In the case of occurrence of the intermediate phase in the nonstoichiometric region, the aspect of the partial molar free energy or the chemical potential per mole at a constant temperature is shown schematically in Fig. 1, where we can recognize that the chemical potential increases enormously at the composition of the intermediate phase, $x = x_0$. Unfortunately, we have little information experimentally on the accurate shape of the chemical potential curve at this point because of the extreme narrowness of the intermediate phase range.
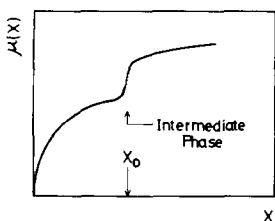
FIG. 1. Variation of the chemical potential of the component X, with the composition x in the nonstoichiometric compound MX_{2+x}. The intermediate phase appears at $x = x_0$.

The features of the chemical potential become more evident by taking the differentiation with x. Now, let us examine the function,

$$\xi(x) = \frac{\partial \mu}{\partial x'} \qquad (1)$$

where μ is the chemical potential of the component X, and x is the concentration of excess anions in the nonstoichiometric compound MX_{2+x}. The function $\xi(x)$ has a sharp peak at the center of the intermediate phase range, $x = x_0$. The peak height $\xi(x_0)$ becomes infinite when perfect order is achieved, as will be discussed in the following sections.

The above feature that the function $\xi(x)$ has a "singularity" is important in order to describe the state of the intermediate phase. The condition $\xi(x) = \infty$ means that an ordered state is achieved and fluctuations vanish in the intermediate phase. In contrast with this, the critical point where the fluctuations become enormous is designated thermodynamically by $\xi(x) = 0$, as we can see in the ordinary order–disorder system. Of course we can recognize the same condition ($\xi(x) = \infty$) at the stoichiometric composition. In general, vanishing of nonstoichiometry is expressed by $\xi(x) = \infty$.

3. Formulation of the Model

We consider a nonstoichiometric system MX_{2+x}, in which excess anions are distributed in the interstitial sites of the parent lattice MX_2. When there is no occurrence of the intermediate phase the excess ions are located nearly randomly as treated by Anderson (1). As the concentration of X approaches to a certain value, $x = x_0$, they begin to locate certain sites and begin to form a superlattice. We call these certain sites superlattice sites in the following. The superlattice sites can be designated in anticipation among the available interstitial sites, whether they are occupied or not, because their locations are determined in the parent lattice. Then the distributed excess anions are divided into two groups; "ordered" anions in the superlattice sites and "random" remainders. Thus we can describe the nonstoichiometric system as the occupied and unoccupied superlattice sites and as the occupied and unoccupied remaining sites.

The partition function of the whole system is given by,

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

where $K(T)$ is the partition function of the parent crystal MX_2, $Q(T, x)$ is the vibrational partition function due to the excess ions and Z is the configurational partition function on the excess ions. The number of the available interstitial sites is considered to be equal to that of MX_2, N_0, for simplicity. The number of the excess ions is obtained by,

$$N_x = xN_0. \qquad (3)$$

When the size of the unit cell of the superlattice is $(1/\alpha)$ times as large as the original one, the number of the superlattice sites is given by,

$$N_\alpha = \alpha N_0, \qquad (4)$$

and

$$N_\alpha = N_{\alpha A} + N_{\alpha B}, \qquad (5)$$

where $N_{\alpha A}$ and $N_{\alpha B}$ are the numbers of the occupied and unoccupied sites, respectively. The number of remaining interstitial sites is

given by,

$$N_\beta = (1-\alpha)N_0, \qquad (6)$$

and

$$N_\beta = N_{\beta A} + N_{\beta B}, \qquad (7)$$

where $N_{\beta A}$ and $N_{\beta B}$ are the numbers of the occupied and unoccupied sites, respectively.

The configurational partition function of the nonstoichiometry is then obtained by,

$$Z = \frac{N_\alpha!}{N_{\alpha A}!N_{\alpha B}!} \frac{N_\beta!}{N_{\beta A}!N_{\beta B}!} \exp(-E/kT), \quad (8)$$

where E is the interaction energy. In the following treatment we use the Bragg–Williams approximation with variable compositions. Putting the order parameter as s, we have the relations;

$$N_{\alpha A} = x\{\alpha + (1-\alpha)s\}N_0, \qquad (9)$$

$$N_{\alpha B} = \{\alpha - x\alpha - (1-\alpha)sx\}N_0, \quad (10)$$

$$N_{\beta A} = x(1-\alpha)(1-s)N_0 \qquad (11)$$

and

$$N_{\beta B} = (1-\alpha)\{1 - (1-s)x\}N_0. \quad (12)$$

For the case of perfect order $s = 1$, all excess ions are located in the superlattice sites, that is, $N_{\alpha A} = xN_0$ and $N_{\beta A} = 0$. And for the limiting case of disorder $s = 0$, excess ions are distributed in α sites and β sites according to the ratio of both sites as $N_{\alpha A} = x\alpha N_0$ and $N_{\beta A} = x(1-\alpha)N_0$.

The detailed origin of the interaction energy is not discussed here. Hypothetically, we consider that E in Eq. (8) consists of two parts: (i) the repulsive term between excess ions in the ordinary solid solution and (ii) the lowering energy due to formation of the superlattice. They are given by,

$$E = \{-x(1-x)\varepsilon_1 - x^2 s^2 \varepsilon_2\}N_0, \quad (13)$$

where ε_1 is the repulsive energy between adjacent excess ions and ε_2 is the order energy, which depends on materials.

In the following we consider the configurational partition function due to excess ions in Eq. (2); then, the Helmholtz free energy of the system is expressed by,

$$F = -kT \log Z.$$

In the case of solids under ordinary pressure, we can replace this by the Gibbs free energy as,

$$G = -kT \log Z. \qquad (14)$$

Using Eqs. (8)–(14), we have,

$$\begin{aligned}
G = \{&-x(1-x)\varepsilon_1 - x^2 s^2 \varepsilon_2\}N_0 \\
&+ x\alpha(1+\gamma s)N_0 kT \log\{x(1+\gamma s)\} \\
&+ \alpha(1-x-\gamma sx)N_0 kT \log(1-x-\gamma sx) \\
&+ x(1-\alpha)(1-s)N_0 kT \log\{(1-s)x\} \\
&+ (1-\alpha)\{1-(1-s)x\}N_0 kT \\
&\times \log\{1-(1-s)x\}, \qquad (15)
\end{aligned}$$

where we put,

$$\gamma = (1-\alpha)/\alpha. \qquad (16)$$

In the above equations the range of x is limited as $0 \leq x \leq \alpha$. As has been mentioned already, α expresses the portion of the number of available superlattice sites in the number of the available interstitial sites. The intermediate phase occurs near $x = \alpha$ as shown in the following section. When $x > \alpha$, the phase disappears. However, this situation cannot be described by the above model. For a constant temperature, G is expressed as the function of two variables, x and s. However, in the following section it will be found that G is determined uniquely by designating x.

4. Derivation of the Equilibrium Condition

The equilibrium condition is obtained from Eq. (14) and by putting,

$$\frac{\partial G}{\partial s} = 0. \qquad (17)$$

We have,

$$\frac{\partial G}{\partial s} = -2x^2 s\varepsilon_2 N_0 + x(1-\alpha)N_0 kT$$

$$\log\frac{\{1-(1-s)x\}(1+\gamma s)}{\{1-(1+\gamma s)x\}(1-s)}. \quad (18)$$

We obtain the following equation from Eqs. (17) and (18),

$$\frac{2\varepsilon_2 sx}{(1-\alpha)kT} = \log\frac{\{1-(1-s)x\}(1+\gamma s)}{\{1-(1+\gamma s)x\}(1-s)}. \quad (19)$$

Eq. (19) is difficult to solve analytically. Differentiating the right side of the above equation and putting $s = 0$, we obtain the condition that Eq. (19) has the solution except $s = 0$. This condition is,

$$\frac{2\varepsilon_2 x}{(1-\alpha)kT} > \frac{1}{\alpha(1-x)}. \quad (20)$$

The relation between x and s can be obtained with the numerical calculation of Eq. (19). In Fig. 2, the order parameter s is plotted against x for the case of $\alpha = 0.25$ using various values of $(2\varepsilon_2/kT)$. From this we can recognize that the ordered phase is formed as the concentration x approaches to α and that the width of the ordered phase depends on the interaction term $(2\varepsilon_2/kT)$.
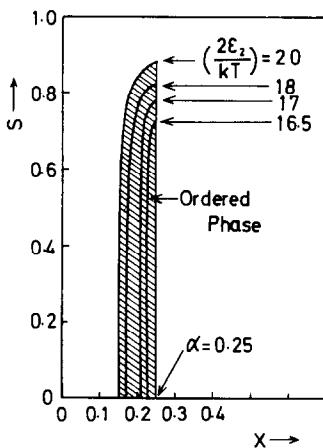

FIG. 2. Plotting the order parameter s against the excess ion concentration x for the case of $\alpha = 0.25$ and using various values of $(2\varepsilon_2/kT)$ in Eq. (19).

The degree of the order at $x = \alpha$ also depends on $(2\varepsilon_2/kT)$. When we describe the width of the ordered phase by,

$$W = \alpha - x_1, \quad (21)$$

x_1 being the value where s increases enormously, W varies as shown in Fig. 3. That is, the width of the ordered phase decreases with decreasing $(2\varepsilon_2/kT)$ and vanishes at the point,

$$\frac{2\varepsilon_2}{kT} = \left(\frac{1}{\alpha}\right)^2. \quad (22)$$

This can be obtained by putting $x = \alpha$ in Eq. (20). The narrow width of the ordered phase which is often observed in nonstoichiometric compounds means that the ordering energy is small.

Next we examine the dependency of the free energy on the concentration x. Differentiating G with N_x we obtain the chemical potential as,

$$\mu(x) = (-1+2x)\varepsilon_1 - 2xs^2\varepsilon_2$$

$$+\{\alpha + s(1-\alpha)\}kT\log\frac{x(1+\gamma s)}{(1-x)-\gamma sx}$$

$$+(1-\alpha)(1-s)kT\log\frac{x(1-s)}{1-(1-s)x}. \quad (23)$$

The function $\xi(x)$ defined in Eq. (1) is also obtained as,

$$\xi(x) = 2\varepsilon_1 - 2s^2\varepsilon_2 + \{\alpha + s(1-\alpha)\}$$

$$kT\left\{\frac{1}{x} + \frac{1+\gamma s}{(1-x)-\gamma sx}\right\}$$

$$+(1-\alpha)(1-s)kT\left\{\frac{1}{x} + \frac{1-s}{1-(1-s)x}\right\}. \quad (24)$$

From Eq. (19) we have concluded that the order parameter s reaches 1 as x goes to α, whenever the energetic condition is satisfied. Applying this to Eq. (24), the term $(1+\gamma s)/\{(1-x)-\gamma sx\}$ becomes infinite, when
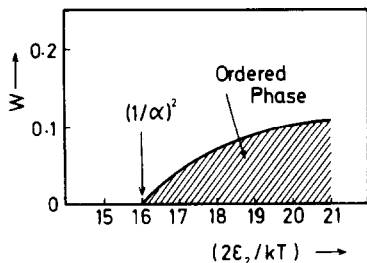
FIG. 3. The width of the intermediate phase depending on the interaction term $(2\varepsilon_2/kT)$ for the case of $\alpha = 0.25$.

$x \to \alpha$, (and $s \to 1$). Thus $\xi(x)$ is shown to be divergent in the region of the intermediate phase.

$\xi(\alpha)$ has finite value in some cases. The reason is that perfect order is not achieved $(s < 1)$ as has been described above. For instance, as we can see in Fig. 2, s $(x = \alpha)$ is only 0.725 for $\alpha = 0.25$ and for $(2\varepsilon_2/kT) =$ 16.5. This gives $\xi(\alpha) = 2\varepsilon_1 + 0.92\varepsilon_2$. Thus the value of $\xi(\alpha)$ expresses the degree of order in the intermediate phase.

Hitherto we have used s for expressing the degree of order. For this purpose we can also use the ratio $N_{\alpha A}$ to $N_{\beta A}$, which are the numbers of excess ions in superlattice sites and in remaining sites, respectively. We have,

$$\eta = N_{\alpha A}/N_{\beta A}, \qquad (25)$$

and using Eqs. (9) and (11),

$$\eta = \alpha + (1 - \alpha)s. \qquad (26)$$

Eq. (24) is rewritten using Eq. (26) by,

$$\xi(x) = 2\varepsilon_1 - 2\left(\frac{\eta - \alpha}{1 - \alpha}\right)^2 \varepsilon_2 + \frac{kT}{x} + \frac{kT\eta^2}{\alpha - \eta x}$$

$$+ \frac{kT(1 - \eta)^2}{1 - \alpha - (1 - \eta)x}. \qquad (27)$$

Finally we must point out that the intermediate phase often appears in the immiscibility gap or in the two-phase region. On the other hand we suppose that the intermediate phase appears in the single and homogeneous phase where excess ions are distributed nearly randomly. However, it depends on the term $2\varepsilon_1 x$ in Eq. (23) whether the "background" phase is the biphasic mixture or the single one. The condition for the phase separation is given by $2\varepsilon_1 > kT$. Thus the case that the intermediate phase appears in the biphasic mixture is also included in the treatment described above.

5. Fluctuations of the System

In the preceding section we obtain the result that the function $\xi(x)$ increases enormously at $x = \alpha$ and becomes infinite in some cases, by using the model where excess ions are distributed both in the superlattice sites and in the random sites. Here we examine the physical meaning of the result from the viewpoint of fluctuations of the system.

When we express the average number of the solute molecules in a small volume v of a solution by $\langle n \rangle$, the mean square fluctuations is given by,

$$\langle \Delta n^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2. \qquad (28)$$

According to the statistical theory of fluctuations (8), this quantity is given by the relation as,

$$\langle \Delta n^2 \rangle = \frac{kT}{(\partial \mu/\partial n)_{P,T}}. \qquad (29)$$

This equation relates the local fluctuations of the distributed particles in a solution and is applicable to the solid solution system too. And the local fluctuations of the concentration is obtained by dividing by N_0^2, that is,

$$\langle \Delta x^2 \rangle = \frac{kT}{N_0(\partial \mu/\partial x)_{P,T}}. \qquad (30)$$

Using Eq. (1), we rewrite the above equations as,

$$\langle \Delta x^2 \rangle = \frac{kT}{N_0 \xi(x)} \quad \text{and} \quad \langle \Delta n^2 \rangle = N_0 \frac{kT}{\xi(x)}.$$

$$\qquad (31)$$

From Eqs. (27) and (31), we have,

$$\langle \Delta n^2 \rangle = \left\{ \frac{2\varepsilon_1}{kT} - 2\left(\frac{\eta - \alpha}{1 - \alpha}\right)^2 \left(\frac{2\varepsilon_2}{kT}\right) \right.$$

$$\left. + \frac{1}{x} + \frac{\eta^2}{\alpha - \eta x} + \frac{(1-\eta)^2}{1 - \alpha - (1-\eta)x} \right\}^{-1}.$$
$$(32)$$

From the above equation we can recognize the effect on the local fluctuation of the distributed particles, here related to the distribution of excess ions, by occurrence of the intermediate phase. Fluctuations decrease by occurrence of the intermediate phase. For the limiting case of order, that is, $x = \alpha$, and $s = 1$ or $\eta = 1$, the term $\eta^2/(\alpha - \eta x)$ becomes infinity and fluctuations vanish. This states that excess ions are all ordered in the super-lattice positions and that no particle exists in the irregular positions. When there is no superstructure, that is, $s = 0$ or $\eta = \alpha$, we have

$$\langle \Delta n^2 \rangle = N_0 \left\{ \frac{2\varepsilon_1}{kT} + \frac{1}{x} + \frac{1}{1-x} \right\}^{-1}. \quad (33)$$

Specifically, for the perfectly random distribution where the interaction vanishes, $\varepsilon_1 = 0$, we have,

$$\langle \Delta n^2 \rangle = N_0 x(1 - x). \quad (34)$$

This corresponds to fluctuations of the distribution probability in the model as described in the following.

We divide the whole space of the system into small cells with volume v which contain $(1/\alpha)$ available interstitial sites. This cell corresponds to the unit cell of the super-structure. For convenience we take $\alpha = 0.25$ in the following discussion. Some cells contain no excess ion and some contain one ion. The number of the cells which contain m ions is expressed by $C(m)$, where $0 \le m \le 4$. According to probability theory this number is obtained by (9),

$$C(m) = N_0 \binom{r}{m} p^m q^{r-m}, \quad (35)$$

where r is the number of available sites in the cell and p and q are the concentrations of the excess ion and the vacancy, respectively. In our case the equation is rewritten as,

$$C(m) = N_0 \binom{4}{m} x^m (1-x)^{4-m}. \quad (36)$$

Above relations can be applied for only random distribution. From the probability theory, fluctuations of the number of ions in the cell is given by,

$$\langle \Delta m^2 \rangle = N_0 pq = N_0 x(1 - x), \quad (37)$$

which corresponds to Eq. (34).

When x approaches α, most cells contain one ion, that is, $C(1)$ increases. When x becomes larger than α, $C(1)$ decreases again. With increasing $C(1)$, the cells containing one ion become adjacent with each other. We have not referred to the position of the ion in the cell. However, when cells containing one ion are adjacent, the interaction energy lowers by orientation of these cells, unless there is spherical symmetry on the internal structure. The cell behaves like the spin and a new order is formed among cells containing one ion. By the "separating" of ordered cells, $C(1)$ remaining in the random orientation decreases compared with the number such as given by Eq. (36). Redistribution occurs such as,

$$\complement(0) + \complement(2) \to 2\complement(1), \quad (38)$$

where $\complement(m)$ expresses the cell which contains m excess ions. Thus $C(0)$, $C(2)$, $C(3)$ and $C(4)$ which mean local fluctuations of the number of particles are also decreasing in proportion to the orientation. This is another model on formation of the intermediate phase.

6. Conclusion

We derive the necessary condition for occurrence of the intermediate phase, the relation between the order parameter and concentration, the relation between the

width of the phase and the interaction energy and so on, on the basis of a simple model where excess ions are distributed both in the "ordered" sites and "random" sites. However, practically, the intermediate phase such as U_4O_9 has more complicated structure. Comparison of the obtained result with the experimental one should be done carefully. The function $\xi(x)$ which is related to fluctuations of the system should be useful to distinguish stoichiometric "compound" from nonstoichiometric "solution."

Acknowledgment

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