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The Calculation of Phase Equilibrium Between Structural Phases with a Magnetic Transition by the Cluster Variation Method

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The phase equilibrium between structural phases with a magnetic transition is investigated using the CV-pair approximation of the cluster variation method (CVM). By the geometric analysis of the grand potential, it is demonstrated that the grand potential and effective chemical potential of the different structural phases with a magnetic transition can be separated into paramagnetic and magnetic terms. In addition, the molar grand potential-effective chemical potential curve can be obtained from the relevant molar energy diagram. A calculation method for the phase equilibrium between structural phases with a magnetic transition is proposed; this method is applied to the α/γ phase equilibrium in the Fe–Mn binary system, and the calculated phase diagram closely approximates the experimental diagram.

KEY WORDS: chemical potential; CVM; free energy; grand potential; magnetic transition; mixing entropy; phase equilibrium.

1. INTRODUCTION

The cluster variation method (CVM), proposed by Kikuchi [1] in 1951, is a statistical mechanics method to calculate the mixing entropy of a solid solution, which takes into account the effects of temperature and interaction energy between atoms on the entropy of mixing. In contrast to the point approximations of Bragg and Williams [2] and Bethe [3], the nearest-neighbor interaction energy described by the pair approximation of

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the CVM is more accurate than that in Refs. 2 and 3. The CVM using the natural iteration method (NIM) with absolute convergence can effectively calculate the phase equilibria between the same structural phases [4]. In recent years the CVM has been given widespread attention by phase diagram researchers and has been developed further and applied in phase equilibrium calculations [5, 6]. It has shown many advantages for order–disorder transitions and miscibility gap calculations [7, 8]. However, so far, it is still not reported that the CVM is applied to the calculation of phase equilibrium between different structural phases with a magnetic transition. This may be because it is very difficult to construct the magnetic transition by the first principle, and it is not suitable to the natural iteration calculation. Sanchez and Lin [9] proposed a magnetic transition model based on the CVM, but this model is suitable only for a fcc structure and has not yet been applied to an actual alloy system. Therefore, we try to combine the CVM with the present magnetic transition free energy models such as the Hillert et al. [10] and Nishizawa et al. [11] models to calculate the phase equilibrium between structural phases with a magnetic transition. In this paper, the free energies of structural phases with a magnetic transition are investigated using the CV-pair approximation of the CVM and the Nishizawa et al. magnetic transition model. Geometrical analysis of the grand potential for a solution with a magnetic transition is first carried out, then a method of calculating the phase equilibrium between the different structural phases with a magnetic transition is proposed. Therefore, the applied range of the CVM is extended, and its practicality is enhanced.

2. MODEL OF ENERGY

Compared to the nonmagnetic solution, the molar free energy of the solution with a magnetic transition is changed. It is assumed that the changed magnetic transition free energy is ΔF_m. The molar free energy of the ferromagnetic phase F_m^m is

$$F_m^m = F_m^p + \Delta F^m \tag{1}$$

where F_m^p is the molar free energy of the paramagnetic phase and the molar free energy equals the sum of the paramagnetic free energy and the magnetic transition free energy.

For the molar free energy of the paramagnetic term, the nearest-neighbor pair interactions are described by the CV-pair approximation of the CVM. The approximations lead to results numerically more accurate than those of Braggs and Willians [2] and of Bethe [3]. With CV-pair approximation, the lattice structure is taken into account through the coordination number 2ω. The molar internal energy U_m^p and molar entropy of mixing S_m^p are

$$U_m^p = N_0\omega \sum_i \sum_l \varepsilon_{ij} y_{ij}, \qquad S_m^p = R\left[(2\omega - 1) \sum_i x_i \ln x_i - \omega \sum_i \sum_j y_{ij} \ln y_{ij} \right] \tag{2}$$

where N_0 is Avogadro's number, R is the gas constant, ε_{ij} is the interaction energy between atom i and atom j, y_{ij} is the probability of the i–j atom pair, x_i is the mole fraction of component i, and $x_i = \sum_j y_{ij}$.

The internal energy in Eq. (2) can be further separated into

$$U_m^p = N_0\omega \sum_y \varepsilon_{ij} y_{ij} = \omega N_0 \left\{ \sum_i \varepsilon_{ii} x_i + \sum_i \sum_{j \neq i} [\varepsilon_{ij} - \tfrac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})]\, y_{ij} \right\} \tag{3}$$

The first term in Eq. (3) expresses the linear sum of internal energies for two components before mixing, and

$$N_0\omega \sum_i \varepsilon_{ii} x_i = \sum_i {}^0U_i x_i = \sum_i {}^0F_i x_i \tag{4}$$

where the ${}^0U_i$ and ${}^0F_i$ are the internal energy and free energy of pure component i, respectively.

The second term in Eq. (3) expresses the internal energy of mixing of solution, and given $\Delta\varepsilon_{ij} = \varepsilon_{ij} - (\varepsilon_{ii} + \varepsilon_{jj})/2$, then

$$\Delta U_m^p = \omega N_0 \sum_i \sum_{j \neq i} \Delta\varepsilon_{ij} y_{ij} \tag{5}$$

Thus, the molar free energy of the paramagnetic phase in the solution can be generally expressed by the CVM as follows:

$$F_m^p = \sum_i {}^0F_i x_i + \Delta U_m^p - TS_m^p \tag{6}$$

where ΔU_m^p and S_m^p are described by the CVM.

On the other hand, in this paper, the magnetic transition free energy is given in the Nishizawa et al. model,

$$\Delta F^m = \left(1 - \sum m_i x_i\right) \frac{T_c}{{}^0T_c} [\Delta^0 F_{\mathrm{Fe}}(T^*)]^m \tag{7}$$

where m_i is the magnetic coefficient. It is assumed, for simplifying the analysis, that $m_i = 1$ for all the nonmagnetic alloying elements and $m_i = 0$ for Co and Ni. T_c and ${}^0T_c$ are the Curie temperatures of the solution and pure iron, respectively, and $[\Delta^0F_{\mathrm{Fe}}(T^*)]^m$ is the ferromagnetic free energy of pure iron at the temperature T^*, $T^* = ({}^0T_c/T_c)$.

In the binary system, it is assumed the component 1 is Fe, and component 2 is the other nonmagnetic or magnetic element. Then, the magnetic transition energy can be expressed by

$$\Delta F^m = (1 - m_2 x_2) \frac{T_c}{{}^0T_1^c} [\Delta^0F_1(T^*)]^m \tag{7.1}$$

where T_c and ${}^0T_1^c$ are the Curie temperatures of the solution and component 1, respectively.

3. GEOMETRICAL ANALYSIS OF THE GRAND POTENTIAL

In the CVM, the grand potential is regarded as the thermodynamic potential to analyze the phase equilibrium. Our research group has analyzed geometrically the grand potential of a nonmagnetic solution [12] and provided the correlation between the molar free energy diagram and grand potential-effective chemical potential diagram. The present study provides the first geometrical analysis of the grand potential for a solution with a magnetic transition; and determine the effect of the magnetic transition on the grand potential.

For an n-component system, the function of the grand potential is defined by

$$G = F - \sum_{i=1}^{n} N_i \mu_i \tag{8}$$

where F is the Helmholtz free energy and N_i and μ_i are the number of atoms and chemical potential of component i, respectively. However, it is important to note that the chemical potential μ_i in Eq. (8) differs from the actual chemical potential μ_i' of solution corresponding to a certain composition, and in this paper, we call μ_i the effective chemical potential. The following relation exists among the effective chemical potentials,

$$\sum_{i=1}^{n} \mu_i = 0 \tag{9}$$

which indicates that the average value of chemical potentials for each component is chosen as zero.

When both sides of Eq. (8) are divided by the total number of atoms N and multiplied by Avogadro's number, the molar grand potential is obtained:

$$G_m = F_m - \sum_{i-1}^{n} x_i \mu_i \tag{10}$$

where F_m is the molar Helmholtz free energy, μ_i and x_i are the molar effective chemical potential and mole fraction of component i, respectively, and $\sum_{i=1}^{n} x_i = 1$.

Figure 1 shows a molar free energy diagram of a solution with a magnetic transition in a binary system. The shaded part is the free energy caused by the magnetic transition. For composition x_2, the molar free energy in the paramagnetic state, F_m^p, is line $\overrightarrow{ac}$, and the magnetic transition free energy, ΔF^m, is line $\overrightarrow{cc'}$. The molar free energy in the ferromagnetic state at this composition, F_m^m, equals $F_m^p + \Delta F^m$ (line $\overrightarrow{ac'}$). The tangent of

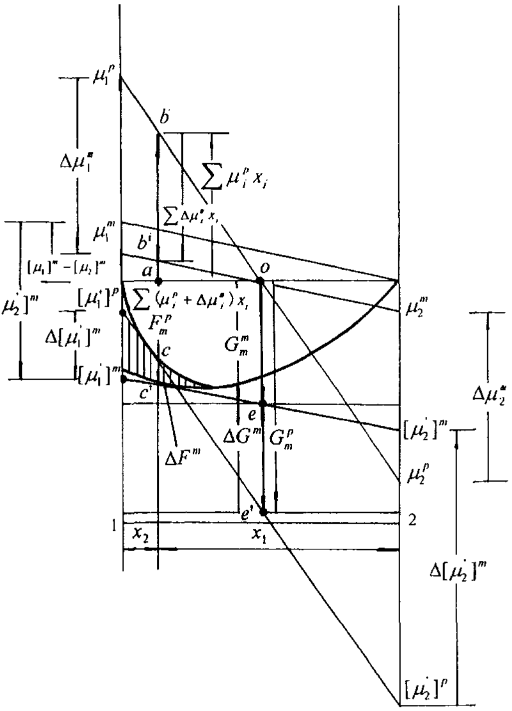

Fig. 1. Expression of the grand potential in the molar free energy diagram.

the free energy curve in the paramagnetic state is made through point c; then the chemical potentials in the paramagnetic state, $[\mu'_1]^p$ and $[\mu'_2]^p$, are obtained. A line, which is parallel to the connected line between $[\mu'_1]^p$ and $[\mu'_2]^p$, is made through the middle point o of the abscissa ($x = 0.5$); then the effective chemical potentials of the paramagnetic state for two components, μ_1^p and μ_2^p, which satisfy Eq. (9), are obtained, and line $\overrightarrow{ab}$ equals the $\sum x_i \mu_i^p$. According to the definition of the grand potential, the grand potential of the paramagnetic state at this composition is

$$G_m^p = F_m^p - \sum_{i=1}^{n} x_i \mu_i^p = \overrightarrow{ac} - \overrightarrow{ab} = \overrightarrow{ac} + \overrightarrow{ba} = \overrightarrow{bc}$$

It can be seen from Fig. 1 that line $\overrightarrow{bc}$ equals line $\overrightarrow{oe'}$. This means that the G_m^p equals the distance from the middle point o to the cross point e' between the connected line $\overline{[\mu'_1]^p [\mu'_2]^p}$ and line $\overrightarrow{oe'}$, and the following equation is obtained.

$$G_m^p = \frac{[\mu'_1]^p + [\mu'_2]^p}{2} \tag{11}$$

For an n-multicomponent system,

$$G_m^p = \sum_{i=1}^{n} [\mu'_i]^p / n \tag{11.1}$$

This is an important equation of the grand potential, which reveals the relation between the grand potential and the chemical potential.

The relationships for the paramagnetic state among the effective chemical potentials, the chemical potentials, and the grand potential can also be obtained

$$\mu_1^p = \frac{[\mu'_1]^p - [\mu'_2]^p}{2}, \qquad \mu_2^p = \frac{[\nu'_2]^p - [\mu'_1]^p}{2}, \qquad G_m^p = [\mu'_i]^p - \mu_i^p \tag{12}$$

The tangent of the free energy curve of the ferromagnetic state is made through point c'; then the chemical potentials in the ferromagnetic state are

$$[\mu'_1]^m = [\mu'_1]^p + \Delta[\mu'_1]^m, \qquad [\mu'_2]^m = [\mu'_2]^p + \Delta[\mu'_1]^m \tag{13}$$

Using the above method, we can obtain

$$\overrightarrow{ab'} = \sum_i \mu_i^m x_i = \overrightarrow{ab} - \overrightarrow{b'b} = \sum_i (\mu_i^p + \Delta\mu_i^m)\, x_i$$

and the $\Delta[\mu'_i]^m$ and $\Delta\mu_i^m$, are the chemical potential and effective chemical potential caused by the magnetic transition. Here they are called the magnetic chemical potential and the magnetic effective chemical potential, respectively. Thus, the grand potential in the ferromagnetic state of solution at the composition x_2 can be analyzed as follows:

$$\begin{aligned}
G_m^m &= F_m^m - \sum \mu_i^m x_i = \overrightarrow{ac'} - \overrightarrow{ab'} = (\overrightarrow{ac} + \overrightarrow{cc'}) - (\overrightarrow{ab} - \overrightarrow{b'b}) \\
&= F_m^p + \Delta F^m - \sum (\mu_i^p + \Delta\mu_i^m)\, x_i = (\overrightarrow{ac} - \overrightarrow{ab}) + (\overrightarrow{cc'} + \overrightarrow{b'b}) \\
&= F_m^p - \sum \mu_i^p x_i + \Delta F^m - \sum \Delta\mu_i^m x_i = G_m^p + \Delta G^m = \overrightarrow{oe'} + \overrightarrow{e'e} = \overrightarrow{oe} \qquad (14)
\end{aligned}$$

It is known from Eq. (14) that the grand potential in the ferromagnetic state can be expressed by the sum of the grand potential in the paramagnetic state (paramagnetic grand potential) and the grand potential caused by the magnetic transition (magnetic grand potential). The chemical potential can also be separated into paramagnetic and magnetic terms, i.e., for the effective chemical potential, $\mu_i^m = \mu_i^p + \Delta\mu_i^m$, and $\sum \Delta\mu_i^m = 0$, and for the chemical potential $[\mu'_i]^m = [\mu'_i]^p + \Delta[\mu'_i]^m$. Similarly, the following equations for the ferromagnetic state can also be obtained,

$$\begin{aligned}
G_m^m &= \frac{[\mu'_1]^m + [\mu'_2]^m}{2}, \qquad & G_m^m &= [\mu'_i]^m - \mu_i^m \\
\mu_1^m &= \frac{[\mu'_1]^m - [\mu'_2]^m}{2}, \qquad & \mu_2^m &= \frac{[\mu'_2]^m - [\mu'_1]^m}{2}
\end{aligned} \qquad (15)$$

The molar grand potential and effective chemical potential of solution at a fixed composition can be directly obtained from the molar free energy $(F_m - x_i)$ diagram by the analysis given above. As shown in Fig. 2, the grand-potential, effective chemical-potential $(G_m - \mu_i)$ diagram of a solution with a magnetic transition can be drawn by the geometrical method presented here. The correlation of grand potentials between ferromagnetic and paramagnetic states at the same composition is also given in Fig. 2. Figure 2a gives the molar free energy diagram and the correlative $G_m - \mu_i$ curve. It can be seen that due to the magnetic transition, the effective chemical potential of the ferromagnetic state is lower than that of the paramagnetic state for a solution at the same composition, and the grand potential of the ferromagnetic state is lower than that of the paramagnetic state at the same effective chemical potential. Thus, there is a difference in the grand potential between the ferromagnetic and the paramagnetic states for a solution at the same composition, and the larger is the free energy caused by the magnetic transition, the larger is this difference. For example, when the composition of a solution is at point a on the $F_m - x_i$ curve, the ferromagnetic and paramagnetic states are points a and a', respectively, on the $G_m - \mu_i$ curve. Figure 2b shows the case where the solution in a paramagnetic state is in the single phase, and the miscibility gap is formed due to the magnetic transition. At this temperature, the equilibrium compositions are at points b' and f.

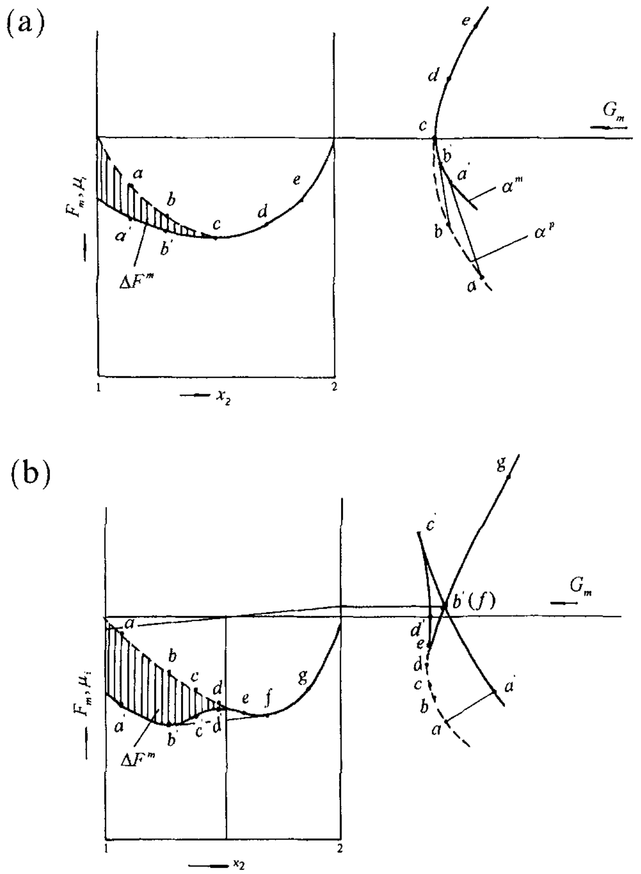

Fig. 2. Correlation between the $F_m - x_i$ and the $G_m - \mu_i$ diagrams. (a) Correlation between the $F_m - x_i$ and the $G_m - \mu_i$ diagrams in the case without miscibility; (b) the miscibility gap is formed due to the magnetic transition; (c) the miscibility gap increases because of the magnetic transition; (d) the phase equilibrium is between structural phases.

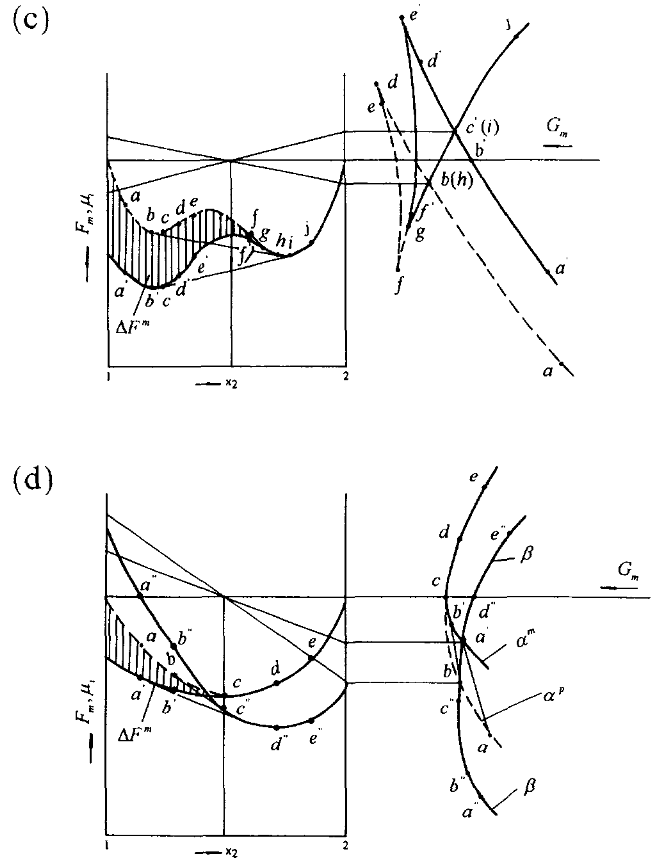

Fig. 2. *(Continued)*

It can also be seen from the $G_m - \mu_i$ diagram that the grand potential for the paramagnetic state is the curve abcd, and there is not a cross point on this curve; the grand potential in the ferromagnetic state is the curve $a'b'c'd'$, and there is a cross point $b'(f)$ which corresponds to the phase equilibrium. Figure 2c shows the case where the solution is in a paramagnetic state with a miscibility gap, and the miscibility increases because of the magnetic transition. Two phase equilibria exist in the $F_m - x_i$ diagram; one is a metastable phase equilibrium between point b and point h, and the other is a stable phase equilibrium between point c' and point i. These points correspond, respectively, to two cross points, $b(h)$ and $c'(i)$, in the $G_m - \mu_i$ diagram. It can be seen that the grand potential of point $c'(i)$ is lower than that of point $b(h)$. Figure 2d shows the case where the phase equilibrium is between different structural phases; the α phase is the solution with a magnetic transition, and the β phase is nonmagnetic. In the $G_m - \mu_i$ diagram, the points b and a' correspond to the phase equilibrium between the β and the α phases in the paramagnetic state and the phase equilibrium between the β and the α phases in the ferromagnetic state, respectively. The grand potential of point a' is lower than that of point b, which indicates that the phase equilibrium between the β and the α phases in the ferromagnetic state is stable.

4. METHOD OF PHASE EQULLIBRIUM CALCULATION

If the α and β phases are nonmagnetic, for the calculation of the phase equilibrium between the α and the β phases, it is assumed that the free energies of pure component i for the α and β phases are ${}^0F_i^\alpha$ and ${}^0F_i^\beta$, which are equal to zero and $\Delta^0F^{\alpha\to\beta}({}^0F_i^\beta - {}^0F_i^\alpha)$, respectively. Thus, the molar free energies for α and β can be expressed, respectively, by

$$F_m^\alpha = \Delta U_m^\alpha - TS_m^\alpha, \qquad F_m^\beta = \sum_i \Delta^0F_i^{\alpha\to\beta} x_i^\beta + \Delta U_m^\beta - TS_m^\beta \tag{16}$$

and the molar grand potentials for the α and β phases can be given as follows:

$$\begin{aligned} G_m^\alpha &= \Delta U_m^\alpha - TS_m^\alpha - \sum_i \mu_i^\alpha x_i^\alpha \\ G_m^\beta &= \sum_i \Delta^0F_i^{\alpha\to\beta} x_i^\beta + \Delta U_m^\beta - TS_m^\beta - \sum_i \mu_i^\beta x_i^\beta \end{aligned} \tag{17}$$

If ΔU_m and S_m are described by the CV-pair approximation, the molar free energy of mixing is

$$\begin{aligned} \Delta F_m &= \Delta U_m - TS_m \\ &= \omega N_0 \sum_i \sum_{j\neq i} \Delta\varepsilon_{ij} y_{ij} - RT\left[(2\omega - 1)\sum_i x_i \ln x_i - \omega \sum_i \sum_j y_{ij} \ln y_{ij}\right] \end{aligned} \tag{18}$$

In the equilibrium condition, $\partial G_m/\partial y_{ij} = 0$

$$y_{ij}^\alpha = (x_i x_j)^{(2\omega^\alpha - 1)/2\omega^\alpha} \exp\left(-\frac{\Delta\varepsilon_{ij}^\alpha}{RT} + \frac{\mu_i + \mu_j}{2\omega RT} + \frac{\lambda}{\omega RT}\right), \qquad i \neq j$$

or

$$y^{\alpha}_{ij}=(x_ix_j)^{(2\omega^{\alpha}-1)/2\omega^{\alpha}}\exp\left(\frac{\mu_i+\mu_j}{2\omega RT}+\frac{\lambda}{\omega RT}\right), \qquad i=j$$

$$y^{\beta}_{ij}=(x_ix_j)^{(2\omega^{\beta}-1)/2\omega^{\beta}}\exp\left(-\frac{\Delta^0F_i^{\alpha\to\beta}+\Delta\varepsilon^{\beta}_{ij}}{RT}+\frac{\mu_i+\mu_j}{2\omega RT}+\frac{\lambda}{\omega RT}\right), \qquad i\neq j$$

or

$$y^{\beta}_{ij}=(x_ix_j)^{(2\omega^{\beta}-1)/2\omega^{\beta}}\exp\left(-\frac{\Delta^0F_i^{\alpha\to\beta}}{RT}+\frac{\mu_i+\mu_j}{2\omega RT}+\frac{\lambda}{\omega RT}\right), \qquad i=j \qquad (19)$$

From Eqs. (18) and (19), it can be seen that the phase transformation free energy of the pure component, $-\Delta^0F_i^{\alpha\to\beta}/RT$, increases only in the pair probability of the β phase for the phase equilibrium calculation of two-phase equilibrium by the CVM, and other terms are the same as for the calculation of phase equilibrium between the same structural phases.

In the calculation of phase equilibrium between the α and the β phases, the curves of grand potentials for the two phases are calculated by the NIM, and the cross point of grand potentials for the α and β phases is determined by the dichotomous natural iteration method (DNIM) [13]. After doing this, the equilibrium compositions of the α and β phases can be obtained.

For the solution with a magnetic transition, the method of phase equilibrium calculation is presented in detail for the following two cases, i.e., the phase equilibrium between ferromagnetic and nonmagnetic phases and the phase equilibrium between two ferromagnetic phases.

If the phase equilibrium is between ferromagnetic and nonmagnetic phases, it is assumed that the α phase is ferromagnetic, and the β phase is nonmagnetic. According to the geometric analysis of the grand potential above, the molar grand potential of the α phase, ${}^{\alpha}G^{m}_{m}$, can be separated into paramagnetic and magnetic terms, ${}^{\alpha}G^{p}_{m}$ and $\Delta^{\alpha}G^{m}$, respectively.

$${}^{\alpha}G^{m}_{m}={}^{\alpha}G^{p}_{m}+\Delta^{\alpha}G^{m} \qquad (20)$$

The molar grand potentials for the α phase in the paramagnetic state and the β phase are described by the CVM, and the magnetic grand potential of the α phase is derived from the Nishizawa et al. [11] model. For the α phase, the equilibrium composition is not directly obtained from Eq. (20) by the NIM; this is because that there is no symmetric form in Eq. (20) due to the magnetic grand potential, $\Delta^{\alpha}G^{m}$, and the absolute convergence of the

NIM cannot be assured. Therefore, we propose a calculation method of phase equilibrium between structural phases with a magnetic transition by combining the NIM with the present magnetic transition free energy model. The calculation procedure of this method is introduced as follows.

A chemical potential is chosen as the effective chemical potential of the α phase in the paramagnetic state ${}^{\alpha}\mu_2^p$, and the equilibrium composition x_2 and the molar grand potential of the paramagnetic state ${}^{\alpha}G_m^p$ corresponding to the ${}^{\alpha}\mu_2^p$ can be obtained by means of the NIM. According to the geometric analysis of the grand potential above, the magnetic grand potential is expressed as

$$\Delta^{\alpha}G^m = \Delta^{\alpha}F^m - \Sigma\Delta^{\alpha}\mu_i^m x_i^{\alpha} = \frac{\Delta[{}^{\alpha}\mu_1']^m + \Delta[{}^{\alpha}\mu_2']^m}{2} \tag{21}$$

The $\Delta[{}^{\alpha}\mu_i']^m$ is the magnetic chemical potential of the α phase. According to the Nishizawa et al. magnetic transition free energy model for the binary system, the $\Delta[{}^{\alpha}\mu_i']^m$ can be derived as

$$\Delta[{}^{\alpha}\mu_1']^m = \frac{T_c}{{}^0T_1^C}[\Delta^0F_1^{\alpha}(T^*)]^m - x_2(1-m_2x_2)\frac{dT_c}{dx_2}\frac{[\Delta^0H_1^{\alpha}(T^*)]^m}{{}^0T_1^C} \tag{22}$$

$$\begin{aligned}\Delta[{}^{\alpha}\mu_2']^m = {} & (1-m_2)\frac{T_c}{{}^0T_1^C}[\Delta^0F_1^{\alpha}(T^*)]^m \\ & + (1-x_2)(1-m_2x_2)\frac{dT_c}{dx_2}\frac{[\Delta^0H_1^{\alpha}(T^*)]^m}{{}^0T_1^C}\end{aligned} \tag{23}$$

where $[\Delta^0H_1^{\alpha}(T^*)]^m$ is the ferromagnetic enthalpy of component 1 at the temperature T^*. Based on Eqs. (21) to (23), the magnetic grand potential at composition x_2 is obtained. Thus, the grand potential in the ferromagnetic state at the composition $x_2, {}^{\alpha}G_m^m$, can be calculated.

From the Eq. (15), the magnetic effective chemical potentials are

$$\Delta^{\alpha}\mu_1^m = \frac{\Delta[{}^{\alpha}\mu_1']^m - \Delta[{}^{\alpha}\mu_2']^m}{2} = -\Delta^{\alpha}\mu_2^m \tag{24}$$

Then the effective chemical potential is obtained,

$${}^{\alpha}\mu_i^m = {}^{\alpha}\mu_i^p + \Delta^{\alpha}\mu_i^m \tag{25}$$

When the above procedure is repeated, the entire curves of grand potentials for the α and β phases are obtained.

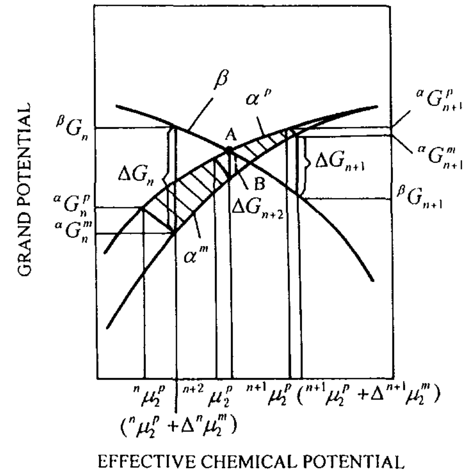

Fig. 3. Schematic diagram of the DNIM used in the phase equilibrium calculation between a ferromagnetic phase and a nonmagnetic phase.

Finally, the cross point of $^{\alpha}G_m^m$ and $^{\beta}G_m$ is sought by the DNIM. The DNIM used in this paper, which is used to determine the cross point of grand potentials for a solution with magnetic transition, is slightly different from the DNIM in Ref. 13. As shown in Fig. 3, in the nth iteration, if the iteration direction sign $\Delta G_n (= {}^{\alpha}G_n - {}^{\beta}G_n)$, $\Delta G_{n+1} (= {}^{\alpha}G_{n+1} - {}^{\beta}G_{n+1})$ are unequal, this indicates that the cross point of grand potential is between ${}^{n}\mu_2^p + {}^{n}\mu_2^m$ and ${}^{n+1}\mu_2^p + {}^{n+1}\mu_2^m$. But in the next iteration, the input value of the effective chemical potential, ${}^{n+2}\mu_2^p$, is $({}^{n}\mu_2^p + {}^{n+1}\mu_2^p)/2$ rather than $[({}^{n}\mu_2^p + \Delta^{n}\mu_2^m) + ({}^{n+1}\mu_2^p + {}^{n+1}\mu_2^m)]/2$.

If the phase equilibrium is between two ferromagnetic phases, i.e., both the α and the β phases are ferromagnetic, the grand potential can be expressed as

$$ {}^{\alpha}G_m^m = {}^{\alpha}G_m^p + \Delta^{\alpha}G^m, \qquad {}^{\beta}G_m^m = {}^{\beta}G_m^p + \Delta^{\beta}G^m \tag{26} $$

The paramagnetic grand potentials for the α and β phases, ${}^{\alpha}G_m^p$ and ${}^{\beta}G_m^p$, are calculated by the CVM with the NIM, and the magnetic grand potentials for the α and β phases are derived from the magnetic transition model.

The calculated procedure of the grand potential is shown in Fig. 4. A chemical potential is given as the paramagnetic effective chemical potential of the α phase, ${}^{\alpha}\mu_2^p$, the ferromagnetic grand potential of the α phase corresponding to ${}^{\alpha}\mu_2^p + \Delta^{\alpha}\mu_2^m$ is calculated, and then the ${}^{\alpha}\mu_2^p + \Delta^{\alpha}\mu_2^m$ is regarded as the paramagnetic effective chemical potential of the β phase.

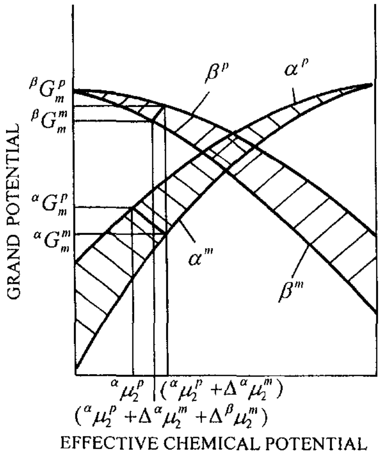

Fig. 4. Schematic diagram of phase equilibrium calculation between two ferromagnetic phases.

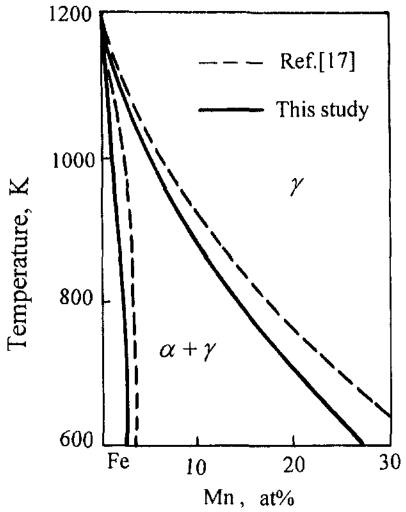

Fig. 5. The calculated α/γ phase equilibrium in the Fe–Mn system in this paper. The calculated α/γ phase boundaries using the CV-pair approximation of the CVM for energy are given by solid lines. The experimental boundaries from Ref. 17 are given by dashed lines.

Similarly, the ferromagnetic grand potential of the β phase corresponding to ${}^{\alpha}\mu_2^p + \Delta^{\alpha}\mu_2^m + \Delta^{\beta}\mu_2^m$ is calculated. The above procedure is repeated, through a series of ${}^{\alpha}\mu_2^p$, to determine the cross points of grand potentials for the two phases, and the equilibrium compositions can be obtained.

In this paper, the α/γ phase equilibrium in the Fe–Mn binary alloy is calculated by CV-pair approximation according to the above method. The interaction energies between Fe and Mn for the α and β phases are estimated from the interaction parameters of the α and β phases [14], $[\varepsilon^{\alpha}_{\mathrm{FeMn}}]^{\mathrm{para}} = -344.9\ \mathrm{J \cdot mol^{-1}}$, $\varepsilon^{\beta}_{\mathrm{FeMn}} = -646.8 + 21.6(x_{\mathrm{Mn}} - x_{\mathrm{Fe}})\ \mathrm{J \cdot mol^{-1}}$. The phase transition free energies for pure Fe and Mn are taken from Refs. 15 and 16 respectively. The calculated result is shown in Fig. 5, and a comparison with the experimental result [17] is made. It can be seen that the two results are in good agreement, which indicates that the above method is suitable to calculate the phase equilibrium between the different structural phases with a magnetic transition.

5. CONCLUSION

For the structural phases with a magnetic transition, the molar free energy can be well described by the CV-pair approximation of the CVM combined with the Nishizawa et al. magnetic transition free energy model. The molar grand-potential effective chemical-potential curve can be obtained from the relevant molar free energy diagram by geometric analysis of the grand potential, and the grand potential and chemical potential can be separated into paramagnetic and magnetic terms, respectively, i.e., $G_m^m = G_m^p + \Delta G^m$ and $\mu_i^m = \mu_i^p + \Delta\mu_i^m$. A calculation method of the phase equilibrium between the structural phases with a magnetic transition by the CVM is proposed, and it is applied to the α/γ phase equilibrium in the Fe–Mn binary system. The result shows that this method is reliable.

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