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Configurational free energy in order-disorder transitions from Monte Carlo calculations for systems under external fields

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A procedure for calculating the configurational free energy with the Monte Carlo simulation is presented, accounting for the case of the application of external fields. First, the free energy for the $L1_0$ ordering systems without any external fields has been evaluated for the various values of the second nearest-neighbor effective interaction, and the feature of this method has been discussed from the viewpoint of the pair correlation. Next, this method has been applied to the case of application of external fields, demonstrating the calculation of the free energy under an external stress field for the $L1_0$ phase that has a tetragonal distortion dependent on the long-range order parameter. [S0163-1829(99)06037-3]

I. INTRODUCTION

Evaluation of free energy is of importance in studies of phase transformations. Recently, the effects of external fields, such as the magnetic field and stress field, on phase equilibrium and kinetics of transformation have been reported.[1–3] In order to discuss quantitatively such effects of external fields, the free energy of the system under external fields should be evaluated.

We shall focus upon the calculation of the configurational free energy in order-disorder transition. In general, there are two kinds of the calculation methods: one is an analytic approximation method such as the cluster-variation method[4] (CVM), and the other is a numerical method such as Monte Carlo (MC) simulation. The analytic CVM is known to describe the features of transitions correctly[5–8] and gives perspectives of the physical problem. On the other hand, the MC simulation is a powerful method of calculating the phase equilibrium. Several studies on the evaluation of the configurational free energy have been reported; the calculation is performed via the thermodynamic integration with the MC simulations (TIMC method).[9–12] However, there are few papers on the calculation of the free energy under external fields.

This paper deals with the calculation of the configurational free energy of a system under external fields within the framework of the TIMC method. Since the uniaxial stress has been reported to enhance significantly the formation of favorably oriented domains for the fcc/$L1_0$ transformations of FePd, CoPt, and AuCu alloys,[2,3] the $L1_0$ ordering system is adopted as the model case of the present calculations. First, the calculations are performed for the case without external fields; one of the advantages of the TIMC method in the calculation of the free energy is described from the viewpoint of the pair-correlation length. Next the configurational free energy under the external compressive stress is calculated for the transition from fcc to $L1_0$ structure, which has a tetragonal distortion dependent on the long-range order parameter.

II. FREE ENERGY OF A SYSTEM UNDER EXTERNAL FIELDS

Let us consider external fields $\{X_i\}$ and their conjugate extensive variables $\{Y_i\}$, where i indicates the species of fields. The total free energy $F_{\text{total}}(T,\{X_i\})$, which is the generalized Gibbs free energy under external fields $\{X_i\}$, is given by

$$F_{\text{total}}(T,\{X_i\})=\left(E-\sum_i X_iY_i\right)-TS$$
$$=F(T,\{Y_i\})-\sum_i X_iY_i, \tag{1}$$

where $F(T,\{Y_i\})$ is the Helmholtz free energy, and $F(T,\{Y_i\})$ and $F_{\text{total}}(T,\{X_i\})$ are connected to each other through the Legendre transformation. The derivative form of the Helmholtz free energy is given by $dF=-SdT+\Sigma_iX_idY_i$, which is derived from the thermodynamic relation $dE=TdS+\Sigma_iX_idY_i$. The Helmholtz free energy $F(T,\{Y_i\})$ is expressed as

$$F(T,\{Y_i(X_i)\})=F(T,\{Y_i(0)\})+\sum_i\int_{Y_i(0)}^{Y_i(X_i)}X_idY_i, \tag{2}$$

where $Y_i(X_i)$ is the extensive variable under the external field X_i. When the dependence of Y_i on X_i is known at a temperature, $F(T,\{Y_i\})$ can be calculated by Eq. (2). This is an ordinary treatment for calculating the Helmholtz free energy.

Here, another approach based on the TIMC method is presented. When the magnitudes of the fields $\{X_i\}$ are fixed, i.e., $dX_i=0$ for all i, the following thermodynamic relation holds:

$$TdS=d\left(E-\sum_i X_iY_i\right). \tag{3}$$

The entropy S under constant fields $\{X_i\}$ can be calculated by the thermodynamic integration:

$$S=\int_{E_r-\Sigma_iX_iY_{i,r}}^{E-\Sigma_iX_iY_i}\frac{1}{T}d\left(E-\sum_i X_iY_i\right)+S_r, \tag{4}$$

where the subscript r indicates the reference state.

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Since the MC simulation gives the relation between T and $E-\Sigma_i X_i Y_i$, S can be obtained by performing the integration of Eq. (4), and the total free energy $F_{\text{total}}(T,\{X_i\})$ and the Helmholtz free energy $F(T,\{Y_i\})$ can be calculated by Eq. (1).

III. MODEL AND SIMULATION PROCEDURE

The model crystal is an array of 20^3 fcc unit cells, i.e., the number of atoms $N=32\,000$, with periodic-boundary conditions. The interaction energy between atoms i and j at the nth nearest-neighbor sites is denoted as $\epsilon_{ij}^{(n)}$, and the effective interaction energy $v^{(n)}$ is defined as $v^{(n)}=(\epsilon_{\text{AA}}^{(n)}+\epsilon_{\text{BB}}^{(n)})/2-\epsilon_{\text{AB}}^{(n)}$, where $v^{(1)}>0$ for ordering systems. The internal energy E of the system is assumed to be given by

$$E=-\sum_n v^{(n)}q_{AB}^{(n)}-E_0, \tag{5}$$

where $q_{AB}^{(n)}$ is the number of the A-B pairs at the nth nearest-neighbor sites and E_0 is the internal energy of the perfect ordered state at the stoichiometric composition. Without any external fields, the Hamiltonian H of the system equals to the internal energy given by Eq. (5). [Note that $v^{(n)}$ equals $2J^{(n)}$, where $J^{(n)}$ is the spin-spin interaction in the Ising spin ($S_i=\pm 1$) model defined by the Hamiltonian $H=\Sigma_n\{J^{(n)}\Sigma_{\langle nNN\rangle}S_iS_j\}$.]

We have performed canonical simulations for the $L1_0$ alloy system at the stoichiometric composition using the standard Metropolis algorithm with an interchange probability $\min[\exp(-\Delta H/bT),1]$.

IV. RESULTS OF CALCULATION

A. fcc/$L1_0$ transition without external fields

1. Free-energy calculation

First, we consider the case where no external field is applied to the system: $X_i=0$.

The MC simulations were performed to obtain the relation between internal energy and temperature. Appropriate analytic functions were fitted to the discrete results obtained by the simulations: $v^{(1)}/kT$ was expressed as a function of $E/Nv^{(1)}$. According to Eq. (4), the entropy $S(E)/Nk$ can be calculated by numerical integration of $v^{(1)}/kT$ with respect to $E/Nv^{(1)}$, where the reference state was taken as a perfectly random solution at an infinitely high temperature. Since the vibrational entropy is not considered in the present simulations, S consists only of the configurational entropy.

Figure 1 shows the free energy versus temperature curves for $\alpha=0$, -0.2, and -1, where $\alpha=v^{(2)}/v^{(1)}$. The transition temperatures were $kT_c/v^{(1)}\approx 0.882$, 1.47, and 3.57 for $\alpha=0,-0.2$, and -1, respectively, being in reasonable agreement with the results by previous calculations.[13–15] The bold curves indicate the free energies of the equilibrium state, while the light lines indicate those of the super-cooled disordered state given by $F_{\text{dis}}^*(T)=E_{\text{dis}}(T_c)-TS_{\text{dis}}(T_c)$. As seen in insets (i), (ii) and (iii), the difference of the derivatives of the free energies at T_c between the ordered and the disordered phases decreases gradually with increasing $|\alpha|$.

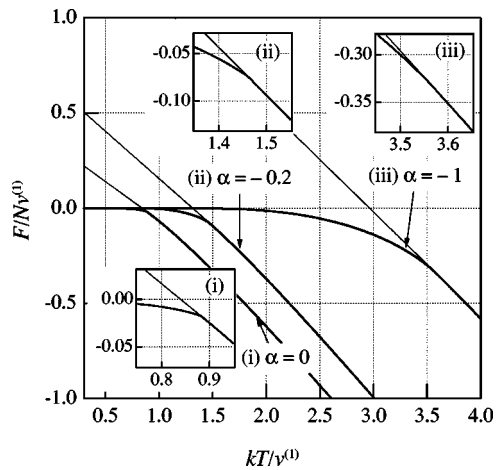

FIG. 1. Free energy versus temperature curves for $\alpha=0,-0.2$, and -1 obtained by the TIMC method for the fcc/$L1_0$ transition.

While the fcc/$L1_0$ transition is typical first order for small $|\alpha|$, the transition is close to the second-order transition when the second nearest-neighbor interaction is negatively large. Though the change in the character of the transition agrees with the detailed analysis by the CVM, the difference in the transition temperature between the MC simulation and the CVM increases with increasing $|\alpha|$.[8] This difference is discussed in the next section.

2. Dependence of pair-correlation length and transition temperature on α

The accuracy of the transition temperature in the CVM with small-size cluster has been discussed from the viewpoint of the correlation length for $\alpha=0$.[10] Therefore, the dependence of the correlation function (length) on α just above the transition temperature has been investigated.

The site-occupation variable $s(\boldsymbol{R})$ is defined as $s(\boldsymbol{R})=2[n(\boldsymbol{R})-\bar{n}]$, where $\bar{n}$ is the average concentration and $n(\boldsymbol{R})=1$ or 0 when the site $\boldsymbol{R}$ is occupied by A or by B atom, respectively. The pair-correlation function $g(\mathbf{r})$ can be written as $g(\mathbf{r})=1/N\Sigma_{\boldsymbol{R}}\langle s(\boldsymbol{R})\cdot s(\boldsymbol{R}+\boldsymbol{r})\rangle$. The correlation function $g(r)$ has been calculated up to $r=16a$ (a is the lattice parameter) along the $\langle 100\rangle$ directions by step a in the system with the size of 32^3 fcc unit cells, and has been normalized to be unity at $r=0$.

Figure 2 shows the average correlation functions $g(r)$ in the $\langle 100\rangle$ directions just above the transition temperature for three values of α; $g(r)$ has a functional form of $\exp(-r/\xi)$, where ξ is the correlation length. Clearly, the pair-correlation length ξ increases with increasing $|\alpha|$. According to Mohri *et al.*,[8] the difference in the transition temperature between the CVM and the MC simulation increases with increasing $|\alpha|$. The difference is considered to be due mainly to the long correlation length ξ for large $|\alpha|$.

B. fcc/$L1_0$ transition under uniaxial stress

1. Model system and Hamiltonian

The $L1_0$ ordered structure is tetragonal ($c/a\neq 1$) in its symmetry. The conditions adopted in this calculation are as

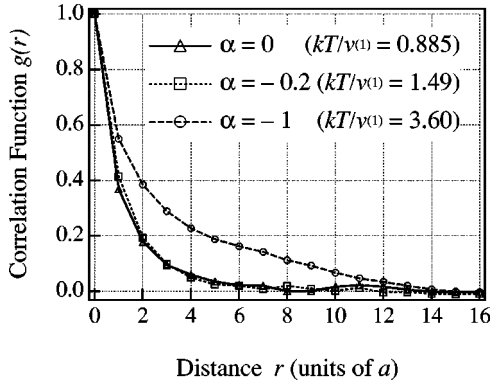

FIG. 2. Dependence of correlation function on α just above the transition temperature for the fcc/$L1_0$ transition.

follows: (i) the strain ϵ_{ij} is given by $\epsilon_{ij}^{o}\eta^2$, where ϵ_{ij}^{o} is the tetragonal distortion in the perfect ordered state and η is the long-range order (LRO) parameter,[16,17] and when the tetragonality appears, (ii) the lattice volume remains constant, and (iii) the effective interaction energies do not change.

In this case, X_i and Y_i in Eq. (1) are replaced by σ_{kl} and $V\epsilon_{kl}$, respectively, where σ_{kl} is the external stress tensor, and V is the volume of the system ($dV=0$). Then, the Hamiltonian H of the system can be written, using the internal energy E given by Eq. (5), as

$$H=E-\sum_{k,l}\sigma_{kl}V\epsilon_{kl}, \tag{6}$$

hereafter, $\Sigma_{k,l}\sigma_{kl}(V\epsilon_{kl})$ is expressed as $\sigma V\epsilon$ briefly.

We used the following parameters corresponding to the equiatomic FePd alloy: the lattice parameter is 3.81 Å, the transition temperature is 923 K for $\boldsymbol{\sigma}=0$ and the tetragonal strain components ϵ_{ij}^{o} are $\epsilon_{11}^{o}=\epsilon_{22}^{o}=0.01$, $\epsilon_{33}^{o}=-0.02$, and $\epsilon_{ij}^{o}=0$ for $i\neq j$. Only the first nearest-neighbor interaction is considered: $v^{(1)}=923k/0.882$. Note that the change of the free energy of the high-temperature fcc phase is negligible for a stress of small magnitudes, because the tetragonal strain induced by the stress is quite small.

2. Calculation of free energy under stress

Canonical simulations are started from the perfectly ordered state under an external compressive stress along its c axis. The transition temperature increases with increasing the magnitude of the uniaxial compressive stress; the $L1_0$ phase is stabilized under the compressive stress. As an example, the configurational free energies, F_{total} and F, under a stress of 200 MPa is presented. For this case, the transition temperature has been determined to be about 935 K ($kT_c/v^{(1)}\approx 0.894$).

Figure 3 shows the temperature dependence of the LRO parameter η, the total free energy $F_{\text{total}}(T,\sigma)$ (bold curve) and the Helmholtz free energy $F(T,\epsilon)$ (solid curve) for $\sigma_{33}=-200$ MPa; those (dashed curves) for $\boldsymbol{\sigma}=0$ are also shown. Since the degree of order of the $L1_0$ phase is raised by the compressive stress, the Helmholtz free energy is also raised. However, the total free energy, which includes the stress effect $-\sigma V\epsilon$, is lowered, leading to the higher transition temperature.

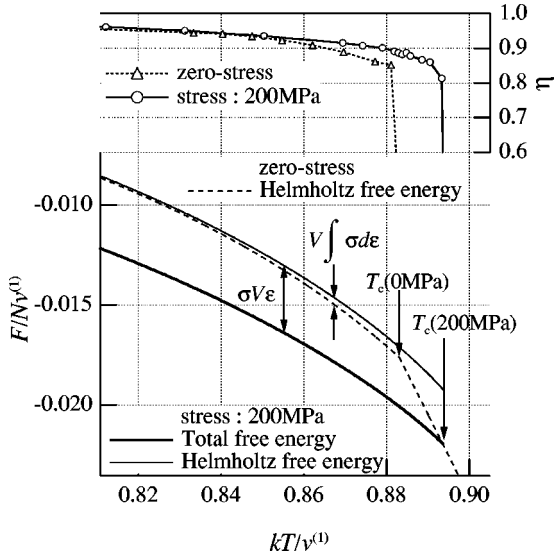

FIG. 3. The LRO parameter, the total free energy and the Helmholtz free energy under an uniaxial compressive stress (200 MPa) obtained by the TIMC method for the fcc/$L1_0$ transition. The Helmholtz free energy under zero stress are also displayed for comparison.

Though the free energy can be calculated also using Eq. (2), the calculation via the thermodynamic integration using Eq. (4) is more convenient, since it does not require the calculation of the free energy for zero external field.

V. CONCLUSIONS AND REMARKS

The procedure of calculating the free energy of a system under external fields has been presented within the framework of the thermodynamic integration with MC simulation (TIMC method).

The configurational free energy can be estimated accurately with this method, if the model system is large enough in comparison to the correlation length; the TIMC method is suitable for handling the weakly first-order or the second-order transitions where the correlation length tends to be divergent at the critical point. In evaluating the configurational entropy by the integration, the state at an infinitely high temperature can be chosen as the reference state, also for the case of the off-stoichiometry and multicomponent systems.

The calculation of the free energy under external fields has been demonstrated, applying this method to the $L1_0$ phase with a tetragonal distortion under an external stress. With the presented method, one can deal with also the case of the external magnetic field and the magnetization.

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