Order of Phase Transition on a Simple Cubic Lattice Determined by Cluster Variation Method

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Detailed analyses of the free energy behavior near the order-disorder transition temperature on a simple cubic lattice are attempted by cluster variation method (CVM). The entropy is formulated within a cubic approximation of the CVM and two kinds of nearest neighbor pair interaction energies are assumed in the internal energy; one is independent of an atomic distance, \( r \), and the other depends on \( r \) through Lennard-Jones type pair potential. In both cases, it is found that the order of the transition is of second order. 

Keywords: cluster variation method, order of phase transition, simple cubic lattice, correlation function

1. Introduction

In general, phase transition is classified into two categories, first order and second order transitions. Among various criteria proposed to define the order of the transition, Ehrenfest’s criterion¹ has been often employed. According to this criterion, the order of the phase transition is defined by the discontinuity of a free energy or its derivative. When a series of derivatives of a free energy function with respect to an independent thermodynamic variable is continuous up to the \((n - 1)\)-th order and the discontinuity appears at the \(n\)-th order derivative, the transition is of the \(n\)-th order. The other criterion which has been equally employed is due to Landau² who claims that the existence and non-existence of a meta-stable phase are a measure of the order of the transition, and the first (second) order transition is characterized by the existence of a meta-stable phase (state). The equivalence of these two criteria has been amply demonstrated by one of the present authors (TM)³, ⁴ for order-disorder transitions based on the temperature dependence of a free energy curve as a function of a long-range order parameter (hereafter abbreviated as LRO parameter). As is shown in the latter, the free energy of an ordering system is generally a function of various configurational variables. By eliminating all those configurational variables except a LRO parameter, one can demonstrate that the existence (non-existence) of a meta-stable state is closely related to the variation of the curvature of the free energy with temperature.

In actual alloy systems, it is often observed that several ordering reactions proceed with decreasing/increasing the temperature at a same composition. One of the typical examples is found in Ni₂MnGa and Ni₂AlTi systems for which L₂₁ and B₂ orderings take place in the low temperature region, and these ordering reactions play a deterministic role in the functional and structural properties such as ferromagnetic shape memory effect, thermoelasticity etc. It is interesting to note that the L₂₁ to B₂ transition for Ni₂MnGa is of the second order as was confirmed by the measurement of a LRO parameter,⁵ while it is of the first order for Ni₂AlTi which is claimed based on the co-existence of two phases in the microstructural observation.⁶ The origin of the different order of the transition between these two alloys has not been clarified yet.

In our previous work,⁷ the phase stability of L₂₁ ordered phase and the transition behavior from L₂₁ to B₂ ordered phase were studied based on the cluster variation method (hereafter CVM).⁸ The entropy is calculated within the tetrahedron approximation of the CVM⁹ and the internal energy is written by the pair interaction model including the nearest and next nearest neighbor pairs. It should be recalled that both the ordered phases degenerate energetically if only the nearest neighbor pair interactions are considered.

We carefully examined the temperature dependencies of the grand potentials of the two ordered phases by changing the combination of the first and second nearest neighbor pair interaction energies, and concluded that the transition is of the second order since the two grand potentials merge into a single grand potential of B₂ ordered phase without intersecting each other as approaching the transition temperature. In these calculations, however, the pair interaction energies are given as fixed values and do not depend on an atomic distance, concentration and all other chemistry of constituent elements. Hence, the main objective of the present study is to examine the ordering behavior by introducing the dependence on the atomic distance into pair interaction energies.

It is anticipated, however, that the analysis of the ternary ordering behavior under the pair interaction energies which depend on an atomic distance is quite cumbersome. Then, by noting the fact that the L₂₁ to B₂ transition of a \(A_2BC\) ternary system can be regarded as the binary ordering of a \(BC\) system on a simple cubic lattice which constitutes a sublattice of the L₂₁ ordered phase, the main focus is placed on the binary ordering on a simple cubic lattice.

A free energy curve behaves very sensitively to the change of a LRO parameter around a transition temperature and the determination of the order of the transition requires both the accurate free energy model and careful numerical calculations with high accuracy. In the present study, CVM is employed to describe the free energy together with Lennard-Jones type pair interaction energies. It has been amply demonstrated that such a scheme with a relatively small basic cluster of the CVM provides both the accurate transition
temperatures as well as the order of the transition for both fcc- and bcc-based systems.\(^{10,11}\) It should be noted that the basic cluster which is a largest cluster considered in the entropy formula in the present calculation for a cubic system is a cubic cluster in which numerous independent cluster variables are identified as will be demonstrated in the following section. Therefore, as compared with the tetrahedron approximation which has been most often employed for fcc- and bcc-systems, the number of the configurational variables dealt in the present study is far larger and extra care should be taken in the numerical calculations.

The organization of the present report is as follows. In the next section, for the sake of completeness, the theoretical framework of the present study is briefly described. Prior to the main subject of the binary ordering under the pair interactions which depend on an atomic distance, the results for a simple constant pair interaction model are presented in the third section.

2. Calculation Method

2.1 Free energy

The ordered phase for a simple cubic lattice which is studied in the present report is shown in Fig. 1. The stoichiometric composition of this ordered phase is 50 at\% and the entire lattice consists of two sublattices, \(\alpha\) and \(\beta\), as shown in Fig. 1. When \(B\) and \(C\) species arrange preferentially on \(\alpha\) and \(\beta\) sublattices, respectively, which are surrounded by \(A\) species on the interpenetrating simple cubic lattice, \(L_2\) ordered phase is formed. The free energy is formulated for the BC binary system on a simple cubic lattice.

In the following expression of the Helmholtz energy, \(F\)

\[
F = E - TS, \tag{1}
\]

where \(E\) is the internal energy, \(T\) the temperature and \(S\) is the entropy. The internal energy \(E\) is described as

\[
E = \frac{z}{2} \sum_{i,j} e_{ij} x_{ij}^{\alpha\beta}, \tag{2}
\]

where \(e_{ij}\) is the atomic pair interaction energy between species \(i\) and \(j\), \(x_{ij}\) is a pair cluster probability of finding an atomic neighbor pair cluster and \(z\) is the first nearest neighbor coordination number which is six for a simple cubic lattice. For the sake of simplicity, only pair interaction energies are considered in the present study. This is believed to be quite reasonable since the dominant cohesive mechanism to maintain high symmetric cubic structure is described to central forces (pair interaction energy).

As is described in the introduction, the cubic approximation of the CVM is employed to formulate the entropy term which is written as\(^{9}\)

\[
S = k_B \left[ 3 \sum_{i,j,k,l} L(w_{ijkl}^{\alpha\beta}) + \frac{1}{2} \left( \sum_i L(x_i^\alpha) + \sum_j L(x_j^\beta) \right) - \sum_{i,j,k,l,p} L(v_{ijklmnop}^{\alpha\beta}) - 3 \sum_{i,j} L(y_{ij}^{\alpha\beta}) \right], \tag{3}
\]

where \(L(X)\) is defined as \(X \ln X - X\), \(x_i\), \(w_{ijkl}\) and \(v_{ijklmnop}\) are cluster probabilities of finding atomic arrangements specified by subscript(s) on a point, square and cubic clusters, respectively, and \(k_B\) is the Boltzmann constant. Each cluster is illustrated in Fig. 2. Note that the superscript(s) in the cluster probabilities indicates a sublattice(s). Then, together with the internal energy given by eq. (2), the Helmholtz energy is expressed as

\[
F = 3 \sum_{i,j} e_{ij} x_{ij}^{\alpha\beta} - k_B T \left[ 3 \sum_{i,j,k,l} L(w_{ijkl}^{\alpha\beta}) + \frac{1}{2} \left( \sum_i L(x_i^\alpha) + \sum_j L(x_j^\beta) \right) - \sum_{i,j,k,l,p} L(v_{ijklmnop}^{\alpha\beta}) - 3 \sum_{i,j} L(y_{ij}^{\alpha\beta}) \right]. \tag{4}
\]

It is essential to realize that the cluster probabilities appearing in eq. (3) are mutually dependent through normalization and geometrical conditions given by

\[
1 = \sum_i x_i^\alpha = \sum_j x_j^\beta = \sum_{ij} y_{ij}^{\alpha\beta} = \sum_{ijkl} w_{ijkl}^{\alpha\beta} = \sum_{ijklmnop} v_{ijklmnop}^{\alpha\beta}, \tag{5}
\]

and

\[
x_i^\alpha = \sum_{j,k,l,...,p} w_{ijklmnop}^{\alpha\beta}, \quad x_j^\beta = \sum_{i,j,k,...,p} w_{ijklmnop}^{\alpha\beta}, \quad y_{ij}^{\alpha\beta} = \sum_{k,l,...,p} w_{ijklmnop}^{\alpha\beta}, \quad w_{ijkl}^{\alpha\beta} = \sum_{m,n,o,...,p} v_{ijklmnop}^{\alpha\beta}, \tag{6}
\]

respectively. Under such constraints, the minimization of the Helmholtz energy is carried out by employing Natural Iteration Method.\(^{9}\) In the present study, however, cluster probabilities are transformed to a set of correlation functions\(^{12-14}\) which forms independent configurational

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Fig. 1 Ordered phase in the simple cubic structure.

Fig. 2 Illustration of sub-clusters contained in the basic cluster, a cubic cluster.
variables and Newton-Raphson procedure is employed to minimize the Helmholtz energy. The definition of the correlation functions has been amply demonstrated in the previous publication and is not reproduced in this report, but it is noted that 34 kinds of independent correlation function are identified in the present study and these are tabulated in Table 1. The Helmholtz energy in eq. (4) is, therefore, formally rewritten as

\[
F = F(T : \xi_1^a, \xi_1^b, \xi_2^a, \xi_3^a, \xi_4^a, \xi_5^a, \ldots, \xi_{34}^{a\alpha\beta\gamma\delta\epsilon\zeta}).
\]

Among these correlation functions, the point correlation function, \(\xi_1^a\), on the sublattice, describes the difference of the concentration of species A (or B) between the two sublattices and, therefore, serves as a LRO parameter, while others are short-range order (SRO) parameters. The unity of \(\xi_1^a\) (\(\xi_1^a = 1.0\)) indicates a fully ordered state which is realized only at 0 K, while a complete disordered state is described by null value (\(\xi_1^a = 0.0\)).

Then, the Helmholtz energy is minimized with respect to SRO parameters under a given set of temperature and a LRO parameter through Newton-Raphson procedure, which yields the Helmholtz energy written in the following form,

\[
F = F(T : \xi_1^a, \xi_3^a, \xi_4^a, \xi_6^a, \xi_7^a, \xi_9^a, \xi_{11}^a, \xi_{13}^a, \xi_{14}^a, \xi_{15}^a, \xi_{17}^a, \xi_{19}^a, \xi_{20}^a, \xi_{22}^a, \xi_{24}^a, \xi_{26}^a, \xi_{28}^a, \xi_{30}^a, \xi_{31}^a, \xi_{32}^a, \xi_{34}^a).
\]

Among these 34 correlation functions, at 1:1 stoichiometric composition which is the main concern of the present study, the number of independent variables is reduced due to the following conditions originating from the symmetry (anti-symmetry) of exchanging the species on a cluster which consists of even (odd) number of lattice points,

\[
\xi_1^a = -\xi_2^a, \quad \xi_3^a = -\xi_4^a, \quad \xi_5^a = -\xi_6^a, \quad \cdots.
\]

Then, the number of independent correlation functions is reduced to 21 and the Helmholtz energy is further rewritten as

\[
F^* = F(T, \xi_1^a).
\]

By plotting \(F^*\) as a function of \(\xi_1^a\) for various temperatures \(T\), one can analyze the Helmholtz energy behavior to determine the order of the transition.

2.2 Pair interaction energy

In the pair interaction energy \(e_{ij}\) in eq. (2), the dependence on the atomic distance, \(r\), is introduced through Lennard-Jones type potential,

\[
e_{ij}(r) = e_{ij}^0 \left( \frac{r_0}{r} \right)^{m} - \frac{m}{n} \left( \frac{r_0}{r} \right)^{n},
\]

where \(e_{ij}^0\) and \(r_0\) describe the depth of the potential and equilibrium atomic separation, respectively, and the exponents \(m\) and \(n\) are related with stiffness of the lattice against the compression and expansion. In the present study, \(m = 12\) and \(n = 6\) are assigned and the values employed for \(e_{ij}^0\) and \(r_0\) are summarized in Table 2. Because \(|e_{AB}|\) is larger than \(|e_{AA}|\) and \(|e_{BB}|\), ordering reaction can be expected. Then, the internal energy is written as

\[
E = \sum_{i,j} e_{ij}(r) \cdot y_{ij}^{\rho\delta}\n
= \sum_{i,j} e_{ij}^0 \left( \frac{r_0}{r} \right)^{m} - \frac{m}{n} \left( \frac{r_0}{r} \right)^{n} \cdot y_{ij}^{\rho\delta}.
\]

It is noted that due to the introduction of the dependence of the atomic distance into the Helmholtz energy, additional minimization of the Helmholtz energy should be carried out with respect to \(r\), which yields the equilibrium atomic distance, \(r^*\).

\[
\frac{\partial E}{\partial r} \bigg|_{r=r^*} = 0.
\]
3. Results and Discussion

Prior to introducing the dependence of the atomic distance into the pair interaction energy, the Helmholtz energy behavior in the vicinity of the disordered state ($\xi^c = 0$) is analyzed under a set of constant pair interaction energies, $\epsilon_{AA} = \epsilon_{BB} = -\epsilon_{AB} = 0.25$. The dependencies of the Helmholtz energy on the LRO parameter for various temperatures are depicted in Figs. 3(a)–(d). The Helmholtz energy and temperature are normalized with respect to the effective pair interaction energy which is defined by $W_{AB} = (\epsilon_{AA} + \epsilon_{BB}) - 2\epsilon_{AB}$. The change of the Helmholtz energy shown in Figs. 3(a) and (b) are not smooth, which is caused by numerical processing within a very small scale as one can realize in the vertical axis. However, the discontinuous change of the Helmholtz energy is negligibly small and no significant effects are anticipated in determining the order of the transition.

As shown in Fig. 3(a), the Helmholtz energy minimum appears at the disordered state ($\xi^c = 0$), and with decreasing temperature, the minimum shifts in the right hand side direction, and at the lower temperatures (2(c) and (d)). Helmholtz energy minima are realized in the finite values of the LRO parameter. During this transition, the Helmholtz energy curves are kept to be flat without forming a local minimum at the disordered state, which confirms the second order nature of the order-disorder transition on a simple cubic lattice. Equivalently, as shown in Figs. 3(c) and (d), the equilibrium LRO parameter of an ordered state shifts towards the null value ($\xi^c = 0$) continuously with increasing the temperature, which is a different expression of the second order transition. The flatness of the Helmholtz energy curve which is mathematically described by the vanishing of the second order derivative suggests that the small amount of configurational fluctuation is amplified significantly. This is directly related to the short range order diffuse intensity scattering associated with the spinodal ordering.

Within the accuracy of the present calculation, the transition temperature is located between 1.145500 and 1.145225, which agrees quite well with previous result.

As was described in the previous section, in order to introduce the dependence on the atomic distance into the pair interaction energies, Lennard-Jones type pair potential given by eq. (12) is employed. The Lennard-Jones parameters are tabulated in Table 2. The behavior of the Helmholtz energy in the vicinity of the disordered state is calculated for four temperatures and demonstrated in Figs. 4(a)–(d). In these calculations, the equilibrium atomic distance is determined by eq. (13) for each temperature and LRO parameters. It was confirmed that the magnitude of the equilibrium lattice constants do not change appreciably within the narrow range of LRO parameters considered in Figs. 4(a)–(d). Note that both the Helmholtz energy and temperature are normalized with respect to $\epsilon_{AB}$. Throughout these temperatures, the numerical convergence was a serious problem and the obtained Helmholtz energy curves are not smooth except at $k_BT/\epsilon_{AB} = 0.96100$ (3(d)). The maximum discontinuity (jump) of the Helmholtz energy is plotted as a function of the convergence parameter $\epsilon_c$ in Fig. 5. The convergence criterion adopted in the present study is as follows; when the value of $\epsilon = \sum |\xi_i^{\text{input}} - \xi_i^{\text{output}}|$, where $i$ specifies a cluster and the sum is taken over 21 correlation functions, is smaller than $\epsilon_c$, the convergence is attained. One can confirm in Fig. 5 that the magnitude of the discontinuity tends to go to null value with smaller convergence parameter. The convergence parameter employed in the present study is $\epsilon_c = 10^{-15}$ which is strict enough to examine the detailed behavior of the Helmholtz energy and to determine the order of the transition.

The behavior of the Helmholtz energy curve in the vicinity of a disordered state across the transition temperature $k_BT/\epsilon_{AB} = 0.9612$ is quite similar to the one with constant...
Fig. 4 Helmholtz energy change as a function of LRO parameter under Lennard-Jones pair interaction energies at $k_B T/e_{AB} = 0.96150$ (a), $k_B T/e_{AB} = 0.96120$ (b), $k_B T/e_{AB} = 0.96110$ (c) and $k_B T/e_{AB} = 0.96100$ (d). The Helmholtz energy and temperature are normalized with respect to $e_{AB}$.

Fig. 5 Relationship between discontinuous Helmholtz energy change vs convergence condition of Newton-Raphson method.

Equation (16) indicates that, in the case of a constant pair interaction energy model, two atomic species $A$ and $B$ cannot be energetically distinguished, since $W_{AB}$ is symmetric with respect to the exchange of $A$ and $B$. While under the Lennard-Jones type pair potential, difference of atomic species is reflected in the effective pair interaction energy $W_{AB}$ through Lennard-Jones parameters, $e_{ij}$ and $r_{ij}$. General arguments of the order of the transition are based on the symmetry of the superlattice points without referring to the constituent elements. The constant pair interaction model falls into this category. Whereas the present study suggests that order-disorder transition on the simple cubic Lennard-Jones lattice is of the second order no matter what the constituent elements are, although the possibility that the different choice of the Lennard-Jones parameters may lead to the first order transition is not completely excluded.

The present calculations are carried out for the binary transition on a simple cubic lattice and these are regarded as the preliminary analysis to investigate more realistic ternary ordering on the L21 lattice. It is stressed that the second order transition confirmed in the present study for the simple cubic lattice is not directly applicable to L21 to B2 transition on the parent lattice. In particular, the experimental observation of the first order transition in Ni$_2$AlTi implies that the order of the transition on two interpenetrating lattices is seriously affected by the configurational interference between the two lattices through the chemistry of constituent elements. This
implication motivates the further investigation based on the first-principles investigation based on electronic structure total energy calculation which remains as a future investigation.

4. Conclusions

In the present study, the order of phase transition of a binary system on a simple cubic lattice which undergoes the order-disorder transition was determined. We investigated two systems with different type of pair interaction energies; one is the system with constant pair interaction energies like Ising system and the other is Lennard-Jones system for which the pair interaction energies depend on an atomic distance. In both cases, it is confirmed that the order of the transition is of the second order.

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