JPEDAV (2009) 30:553–558
DOI: 10.1007/s11669-009-9571-5
1547-7037 ©ASM International

Theoretical Investigation of Lattice Thermal Vibration Effects on Phase Equilibria Within Cluster Variation Method

Tetsuo Mohri, Tomohiko Morita, Naoya Kiyokane, and Hiroaki Ishii

(Submitted April 2, 2009; in revised form July 4, 2009)

First-principles phase equilibria calculations often overestimate an order-disorder transition temperature due to the neglect of local lattice distortion effects originated from the mixture of elements of different atomic sizes. The lattice vibration effects introduced through the Debye-Grüneisen theory within the quasi-harmonic approximation has proven to be quite effective in circumventing the inconveniences. With the preferential enhancement of the stability of a disordered phase by introducing the lattice vibration effects, the transition temperature was reduced considerably. In order to gain further insight into the lattice vibration effects, a systematic investigation of the vibrational free energy of the Debye-Grüneisen theory is attempted on the two-dimensional square lattice which constitutes a prototype study prior to the first-principles calculations on realistic alloy systems. A particular focus of the present study is placed on the effects of Debye temperatures of constituent phases on the transition temperature. It is shown that lattice softening by lattice vibration stabilizes the disordered phase by reducing the energy expended to accommodate atoms of different sizes, which is manifested by the reduction of the curvature of the atomic potentials. It is, however, predicted that an opposite case can also take place. When the Debye temperature of an ordered phase is lower than that of the pure metals, the ordered phase is more stabilized and the inclusion of the lattice vibration effects in the free energy raises the resultant transition temperature.

Keywords cluster variation method, Debye-Grüneisen theory, lattice softening, lattice vibration

1. Introduction

First-principles calculation of a phase diagram[1] with the cluster variation method (CVM)[2] to evaluate entropy has attracted broad attention, and recent efforts have been directed toward expanding the applicability to lower symmetry systems as well as multicomponent alloys. One of the serious deficiencies of the CVM-based first-principles calculations is the overestimation of the order-disorder transition temperature, i.e. the overstabilization of the ordered phase. This originates from the neglect of local lattice distortion effects, for the local lattice relaxation alters the crystal symmetry which makes a conventional entropy formula based on CVM not fully justified. Without the local lattice relaxation, atoms of different sizes in a disordered phase encounter one another more frequently and this raises the internal energy. Thus, the disordered phase is destabilized with respect to the ordered phase.

Two schemes have been proposed within CVM to circumvent such an inconvenience. One is to introduce the relaxation explicitly into the free energy formula through a revised entropy expression termed continuous displacement cluster variation method (CDCVM).[3-8] However, the application of CDCVM is still at its infancy and is limited to rather simple systems such as two-dimensional or simple cubic lattices. The details of the CDCVM and comparison with other theoretical methods such as the one proposed by Zunger[9] will be discussed in the separate issue. The other one is to induce lattice softening through lattice thermal vibration effects such that the atoms of different sizes can be accommodated in the lattice without expending much energy at elevated temperatures. In fact, the lattice vibration effects can be rather easily introduced into the theoretical framework of the CVM-based first-principles calculations employing the procedure proposed by Moruzzi et al.[10] and it has been proved[11,12] that the overestimated transition temperatures are reduced to approach the experimental values.

However, the systems investigated using such a scheme are still limited to Fe-based alloys, Fe-Ni, Fe-Pd, and Fe-Pt,[1,11,12] and various roles played by the lattice

---

This article is an invited paper selected from participants of the 14th National Conference and Multilateral Symposium on Phase Diagrams and Materials Design in honor of Prof. Zhanpeng Jin's 70th birthday, held November 3-5, 2008, in Changsha, China. The conference was organized by the Phase Diagrams Committee of the Chinese Physical Society with Drs. Huashan Liu and Libin Liu as the key organizers. Publication in *Journal of Phase Equilibria and Diffusion* was organized by J.-C. Zhao, The Ohio State University; Yong Du, Central South University; and Qing Chen, Thermo-Calc Software AB.

Tetsuo Mohri, Tomohiko Morita, Naoya Kiyokane, and **Hiroaki Ishii,** Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan. Contact e-mail: tmohri@eng.hokudai.ac.jp.

vibration effects in the phase equilibria calculations are not fully grasped yet. Hence, it is deemed necessary to carry out a systematic study of the lattice vibration effects on the phase equilibria by examining lattice thermal properties of the constituent phases. For this, the present study focuses on binary phase equilibria in a two-dimensional square lattice in which a single ordered phase appears. We investigate how different combinations of thermal properties of the constituent phases (pure and ordered phases) affect the order-disorder transition temperature. In particular, the effects of Debye temperature of the constituent phases are studied.

The organization of the present report is as follows. In the next section, the configurational free energy within the pair approximation of the CVM is introduced for the sake of completeness. In the third section, the Debye-Grüneisen model proposed by Moruzzi et al. is briefly reviewed and it is discussed how the lattice vibration effects are renormalized in the pair interaction energies. In order to avoid unnecessary complications arising from various parameters to describe the vibrational free energy, normalized pair interaction energies are introduced in the fourth section. In the final section, calculated results are demonstrated and discussed.

2. Configurational Free Energy Within Cluster Variation Method

In the ordered phase considered in the present study, A and B atoms are arranged alternatively in the nearest neighbor lattice points. The entire lattice points are divided into two sub-lattices α and β, where $\alpha(\beta)$-sublattice is defined as the preferential lattice point for $A(B)$ atom. Then, the long range order parameter (LRO), η, is conveniently defined as

$$\eta = \frac{x_A^{\alpha} - x_A^{\beta}}{x_A} \qquad \text{(Eq 1)}$$

where x_A is the mole fraction of A atom in the entire lattice and x_A^{γ} is the fraction of A atom in the sublattice designated by γ. The stoichiometric composition of the present ordered phase is 1:1, but the LRO parameter, η, defined in Eq 1 provides unity for the maximum ordered state at any composition.

Although the introduction of the lattice thermal vibration effects into the higher order approximation of the CVM is performed in a straightforward manner,[1,11,12] for the sake of simplicity, pair approximation within the CVM is employed in the present study to describe configurational entropy given as

$$S = k_{\mathrm{B}} \cdot \left\{ \frac{2\omega - 1}{2} \sum_i \sum_{\gamma} \left(x_i^{\gamma} \cdot \ln x_i^{\gamma} - x_i^{\gamma} \right) - \omega \sum_{i,j} \left(y_{ij}^{\alpha\beta} \ln y_{ij}^{\alpha\beta} - y_{ij}^{\alpha\beta} \right) + (\omega - 1) \right\} \qquad \text{(Eq 2)}$$

where k_{B} is the Boltzmann constant, ω (2 in the two-dimensional square lattice) the one half of the coordination number, x_i and y_{ij} are point and pair cluster probabilities, respectively, and the superscript(s) designates the sublattice(s). The derivation of Eq 2 has been amply demonstrated in a previous publication[1] and is not repeated here. Throughout this article, internal energy, entropy and free energy are defined per lattice point.

The internal energy in the present study is assigned by the nearest neighbor pair approximation and is written as

$$E(r) = \frac{1}{2} \cdot Z \cdot \sum_{i,j} e_{ij}(r) \cdot y_{ij}^{\alpha\beta} \qquad \text{(Eq 3)}$$

where Z is the coordination number and r is the nearest neighbor atomic distance which is equivalent to the lattice constant of the square lattice. It is noted that the introduction of the dependence of internal energy on the atomic distance is essential to take into account the relaxation effects. Hence, together with Eq 2, the configurational free energy is given as

$$F = \omega \cdot \sum_{i,j} e_{ij}(r) \cdot y_{ij}^{\alpha\beta} - k_{\mathrm{B}} \cdot T \left\{ \frac{2\omega - 1}{2} \sum_i \sum_{\delta} \left(x_i^{\delta} \cdot \ln x_i^{\delta} - x_i^{\delta} \right) - \omega \sum_{i,j} \left(y_{ij}^{\alpha\beta} \ln y_{ij}^{\alpha\beta} - y_{ij}^{\alpha\beta} \right) + (\omega - 1) \right\} \qquad \text{(Eq 4)}$$

where T is the temperature.

For the pair potential $e_{ij}(r)$, the following Morse potential is employed,

$$e_{ij}^{\mathrm{M}}(r) = C_1 - 2C_2 \cdot \exp(-\lambda \cdot (r - r_0)) + C_2 \exp(-2\lambda \cdot (r - r_0)) \qquad \text{(Eq 5)}$$

where M stands for the Morse potential, C_1 and C_2 determine the depth of the potential, r_0 is the equilibrium atomic distance in terms of the Wigner-Seitz radius and λ specifies the curvature at r_0. The shape of the potential is demonstrated later.

3. Temperature-Dependent Interaction Energy

It is not a trivial task to incorporate the lattice vibration effects into the free energy. A common practice within the first-principles calculation is to include the additional vibrational free energy into the temperature-dependent effective cluster interaction energies.[1,11,12] This can be performed using the procedure based on the vibrational free energies proposed by Moruzzi et al.[10] in the following manner.

Within the quasi-harmonic approximation of the Debye-Grüneisen model, the vibrational free energy of an ordered phase or a pure metal designated by n is given as

$$F_{\mathrm{vib}}^{(n)} = E_{\mathrm{vib}}^{(n)}(r, T) - T \cdot S_{\mathrm{vib}}^{(n)}(r, T) \qquad \text{(Eq 6)}$$

where the vibrational energy, $E_{\mathrm{vib}}^{(n)}(r,T)$, and the vibrational entropy, $S_{\mathrm{vib}}^{(n)}(r,T)$, are further written as

$$E_{\mathrm{vib}}^{(n)}(r,T) = \frac{9}{8}k_{\mathrm{B}} \cdot \Theta_{\mathrm{D}}^{(n)} + 3k_{\mathrm{B}} \cdot T \cdot D\left(\frac{\Theta_{\mathrm{D}}^{(n)}}{T}\right) \tag*{(Eq 7)}$$

and

$$S_{\mathrm{vib}}^{(n)}(r,T) = 3k_{\mathrm{B}} \cdot \left[\frac{4}{3}D\left(\frac{\Theta_{\mathrm{D}}^{(n)}}{T}\right) - \ln\left\{1 - \exp\left(-\frac{\Theta_{\mathrm{D}}^{(n)}}{T}\right)\right\}\right] \tag*{(Eq 8)}$$

where $\Theta_{\mathrm{D}}^{(n)}$ is the Debye temperature and $D(x)$ is the Debye function, and the first term of the vibrational energy in Eq 7 represents the *zero-point energy*. Together with the electronic energy contribution, $E^{(n)}(r)$, for the non-vibrational lattice, the free energy of a phase n is written as

$$F_{\mathrm{vib}}^{(n)}(r,T) = E^{(n)}(r) + E_{\mathrm{vib}}^{(n)}(r,T) - T \cdot S_{\mathrm{vib}}^{(n)}(r,T) \tag*{(Eq 9)}$$

Then, Cluster Expansion[13] is performed on the set of vibrational free energies $\{F_{\mathrm{vib}}^{(n)}(r,T)\}$ of a selected set of ordered compounds including pure metals,

$$F_{\mathrm{vib}}^{(n)}(r,T) = \sum_i v_i(r,T) \cdot \xi_i^{(n)}, \tag*{(Eq 10)}$$

where $\xi_i^{(n)}$ is the correlation function[1,14-16] for *i*-cluster contained in the phase *n*. The set of correlation functions, $\{\xi_i^{(n)}\}$, and cluster probabilities $\{x_i, y_{ij}, \ldots\}$ are related through a linear transformation. Then, the effective cluster interaction energies are given not only as a function of atomic distance but also as a function of temperature, *T*,

$$v_i(r,T) = \sum_n F_{\mathrm{vib}}^{(n)}(r,T) \cdot \xi_i^{(n)}. \tag*{(Eq 11)}$$

The total vibrational free energy of a given phase is, therefore, written as

$$F(r,T) = \sum_i v_i(r,T) \cdot \xi_i - k_{\mathrm{B}} \cdot T \cdot S_{\mathrm{C}}(\{\xi_i\}) \tag*{(Eq 12)}$$

where S_{C} is the configurational entropy given by Eq 2. In this scheme, vibrational contribution is effectively renormalized into the effective cluster interaction energies, $\{v_i(r,T)\}$, which proves to be quite useful and fits coherently with the first-principles free energy formula. Hence, the present model inherits the same scheme.

In the present free energy model, however, the internal energy given by Eq 3 is not written in the form of cluster expansion with effective cluster interaction energies, but as a sum of the atomic pair interaction energies, $e_{ij}(r)$. Hence, the vibrational effects are to be renormalized into the atomic pair interaction energies. This is achieved in the following way.

Corresponding to $E^{(n)}(r)$ in Eq 9 is the Morse potential in the present study, and Eq 9 is rewritten as

$$\begin{aligned} F_{\mathrm{vib}}^{(n)}(r,T) &= E^{(n)}(r) + E_{\mathrm{vib}}^{(n)}(r,T) - T \cdot S_{\mathrm{vib}}^{(n)} \\ &= 2e_{ij}^{\mathrm{M}}(r) + E_{\mathrm{vib}}^{(n)}(r,T) - T \cdot S_{\mathrm{vib}}^{(n)} \end{aligned} \tag*{(Eq 13)}$$

where M stands for the Morse potential, and it should be noted that *i* and *j* indicate *A*(*B*) and *A*(*B*) for pure metal $n = A(B)$ and *A* and *B* for the ordered phase $n = AB$, respectively. It is worth pointing out that no like-pair potentials are included in $E^{(AB)}$. This simplifies the entire analysis. In order to renormalize $F_{\mathrm{vib}}^{(n)}(r,T)$ in the *temperature-dependent* pair interaction energy, $\varepsilon_{ij}(r,T)$, Eq 13 is modified as

$$\begin{aligned} F_{\mathrm{vib}}^{(n)} &= 2e_{ij}^{\mathrm{M}}(r) + E_{\mathrm{vib}}^{(n)}(r,T) - T \cdot S_{\mathrm{vib}}^{(n)} \\ &= 2\left\{e_{ij}^{\mathrm{M}}(r) + \frac{1}{2}\left(E_{\mathrm{vib}}^{(n)}(r,T) - T \cdot S_{\mathrm{vib}}^{(n)}\right)\right\} \\ &= 2\varepsilon_{ij}(r,T) \end{aligned} \tag*{(Eq 14)}$$

4. Numerical Calculations

By substituting Eq 5, 7 and 8 into Eq 14, the explicit form of $\varepsilon_{ij}(r,T)$ is obtained as

$$\begin{aligned} \varepsilon_{ij}(r,T) = {} & C_1^{(n)} - 2C_2^{(n)} \cdot \exp\left(-\lambda^{(n)} \cdot \left(r - r_0^{(n)}\right)\right) \\ & + C_2^{(n)} \exp\left(-2\lambda^{(n)} \cdot \left(r - r_0^{(n)}\right)\right) \\ & + \frac{1}{2} \cdot \left(\frac{9}{8}k_{\mathrm{B}} \cdot \Theta_{\mathrm{D}}^{(n)} - k_{\mathrm{B}} \cdot T \cdot D\left(\frac{\Theta_{\mathrm{D}}^{(n)}}{T}\right)\right. \\ & \left. + 3k_{\mathrm{B}} \cdot T \cdot \ln\left\{1 - \exp\left(-\frac{\Theta_{\mathrm{D}}^{(n)}}{T}\right)\right\}\right) \end{aligned} \tag*{(Eq 15)}$$

One of the essential difficulties of the present approach is the determination of the Debye temperature. In the first-principles calculations, as was described in the previous section, the binding energy curve, $E^{(n)}(r)$, obtained by electronic structure energy calculation is fitted into a Morse potential, and the curvature and the asymmetry of the potential curve uniquely determine the thermal properties of a phase *n* including the Debye temperature and the Grüneisen constant. In fact, it has been demonstrated[10] that the Debye temperature and the Grüneisen constant are related to the curvature λ of a binding energy curve through

$$\Theta_{\mathrm{D}} = (\Theta_{\mathrm{D}})_0 \cdot \left(\frac{r_0}{r}\right)^{3\gamma} \tag*{(Eq 16)}$$

where $(\Theta_{\mathrm{D}})_0$ is the Debye temperature evaluated at the equilibrium Wigner-Seitz radius and γ is the Grüneisen constant given by

$$(\Theta_{\mathrm{D}})_0 = 41.63\left(\frac{r_0 B}{M}\right)^{1/2} \tag*{(Eq 17)}$$

and

$$\gamma = \frac{\lambda r}{2} \tag*{(Eq 18)}$$

where B the bulk modulus in kbar and r_0 is given in atomic unit. In order to apply this procedure, one needs atomic mass M of the constituent elements, which is utterly impossible to obtain from the present model. Moreover, in the strict analysis, modification to the two-dimensional system is indispensable. In view of the lack of these considerations, the Debye temperature $(\Theta_D)_0$ is assigned as a parameter, which, in turns, enables us to perform a systematic study of the dependence of order-disorder transition temperature on the Debye temperature of the constituent phases. Also, the volume (r) dependency of the Grüneisen constant in Eq 18 is neglected and γ_0 evaluated at the Wigner-Seitz radius r_0 is employed as γ in Eq 16.

In order to simplify the analysis, length scale is normalized with respect to the Wigner-Seitz radius of A, $r_0^{(A)}$, and all the energy parameters, $C_1^{(n)}$, $C_2^{(n)}$ and $k_B \cdot \Theta_D^{(n)}$ are normalized by the Debye temperature of A, $k_B \cdot \left(\Theta_D^{(A)}\right)_0$. Hence, the final expression of the interaction energy is given as

$$\begin{aligned}\varepsilon^{(n)}(r,T) = {} & C_1^{(n)} - 2C_2^{(n)} \cdot \exp\left(-\lambda^{(n)} \cdot \left(r - r_0^{(n)}\right)\right) \\ & + C_2^{(n)} \exp\left(-2\lambda \cdot \left(r - r_0^{(n)}\right)\right) \\ & + \frac{1}{2} \cdot \left(\frac{9}{8} \cdot \tau_2^{(n)} + \tau_1 \cdot D\left(\frac{\tau_2^{(n)} \cdot \left(r_0^{(n)}/r\right)^{3\gamma_0}}{\tau_1} \right) \right. \\ & \left. + 3\tau_1 \cdot \ln\left\{ 1 - \exp\left(-\frac{\tau_2^{(n)} \cdot \left(r_0^{(n)}/r\right)^{3\gamma_0}}{\tau_1} \right) \right\} \right)\end{aligned} \qquad \text{(Eq 19)}$$

where the normalized energies $\varepsilon_{ij}(r,T)/k_B \cdot (\Theta_D^A)_0$, $C_1^{(n)}/(\Theta_D^A)_0$ and $C_2^{(n)}/(\Theta_D^A)_0$ are redefined as $\varepsilon^{(n)}(r,T)$, $C_1^{(n)}$ and $C_2^{(n)}$, respectively, in Eq 19. Likewise, the normalized lengths $r_0^{(n)}/r_0^{(A)}$, $r/r_0^{(A)}$ and $\lambda^{(n)} \cdot r_0^{(A)}$ are redefined as $r_0^{(n)}$, r and $\lambda^{(n)}$, respectively. Furthermore, $\tau_1 = k_B \cdot T/k_B \cdot (\Theta_D^A)_0$ and $\tau_2^{(n)} = k_B \cdot \left(\Theta_D^{(n)}\right)_0 \Big/ k_B \cdot (\Theta_D^A)_0$ are normalized temperature and normalized Debye temperature of a phase n, which are the main variables in the analysis.

5. Results and Discussion

Shown in Fig. 1 are the atomic pair potentials for A-A, A-B and B-B pairs assigned by the Morse potential given by Eq 5. The parameters employed in the present study are tabulated in Table 1. By setting $C_1 = C_2$, the bottom of the potential curves of A-A and B-B is set to 0, which defines the energy reference state. In order to stabilize the ordered phase, the unlike-pair potential, A-B, is assigned to be deeper than the like-pair potentials. These pair potentials determine the ground state of the system without the lattice vibration effects.

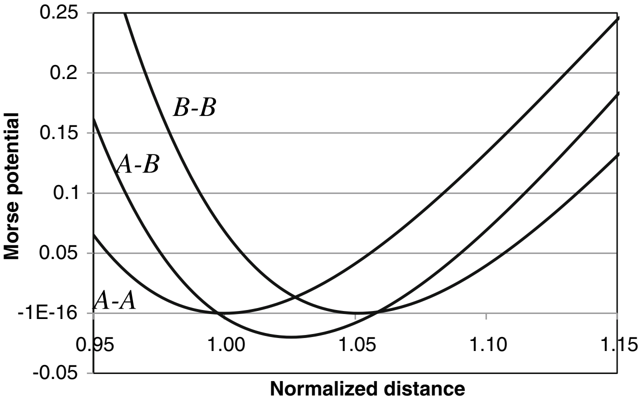

Fig. 1 Atomic potentials for A-A, A-B and B-B pairs assigned by the Morse potential. The energy parameters are tabulated in Table 1

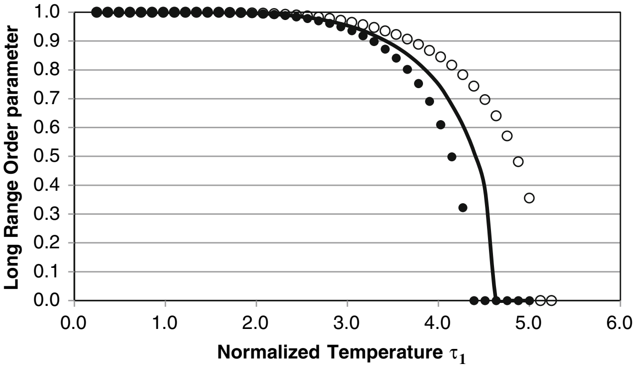

Fig. 2 Temperature dependences of long range order parameter, η in Eq 1, at a fixed composition of 50%. Solid line corresponds to the one without lattice vibration effects while solid and open circles indicate the ones with vibrational effects. The Debye temperatures, τ_2, corresponding to solid circles and open circles are tabulated in Table 2

Table 1 Morse potential parameters employed to calculate potential curves in Fig. 1

	C_1	C_2	r_0	λ
A-A	1.00	1.00	1.00	1.66
A-B	1.06	1.08	1.03	1.66
B-B	1.00	1.00	1.05	1.66

Note that actual values employed for $C_1^{(A)}$ and $C_2^{(A)}$ in the calculations are 96.15 and other values of C_1 and C_2 are normalized by this value

The calculated temperature dependence of LRO parameter, $\eta(T)$, at a fixed composition of 50% is shown by a solid line in Fig. 2. This indicates a typical second-order transition behavior and the transition temperature, $\tau_t = 4.76$, is determined as the temperature at which $\eta(T)$ falls 0.

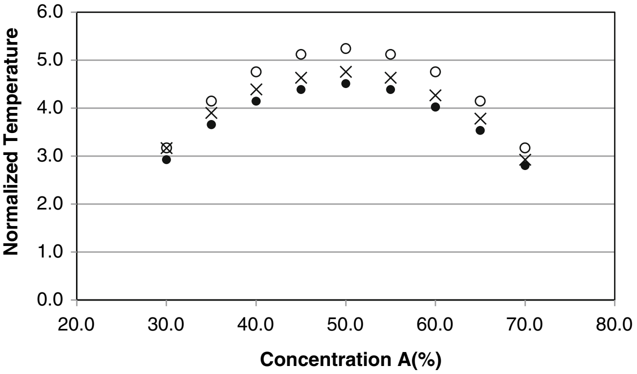

Fig. 3 Phase boundaries calculated with and without lattice vibration effects. Cross marks (×) correspond to the one without lattice vibration effects, while open and solid circles are obtained with lattice vibration effects. The Debye temperatures of the ordered phase assigned for the calculations with lattice vibration effects (open and solid circles) are tabulated in Table 2

Table 2 Morse potential parameters and Debye temperature τ_2 employed to calculate temperature dependences of LRO in Fig. 2 and phase diagrams in Fig. 3

	C_1	C_2	r_0	λ	τ_2
A	1.00	1.00	1.00	1.66	1.00
AB	1.06	1.08	1.03	1.66	1.00 (●) 0.93 (○)
B	1.00	1.00	1.05	1.66	1.00

● and ○ correspond to the same marks in Fig. 2 and 3

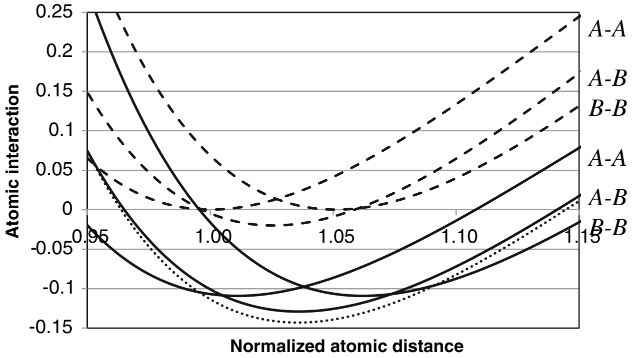

Fig. 4 Atomic pair potentials with and without lattice vibration effects. Broken lines are a reproduction of Fig. 1 and indicate the ones without lattice vibration effects. Solid lines are calculated at temperature $\tau_1 = 4.0$ with parameters tabulated in Table 2. τ_2 is the same for all $n = A$, AB and B. The dotted line indicates the *A-B* pair potential calculated at $\tau_1 = 4.0$ with the same parameters except for the Debye temperature of *AB*, $\tau_2 = 0.80$

By repeating the same procedure for different compositions, one can obtain a phase diagram. Shown in Fig. 3 by cross marks is the calculated phase boundary without the vibrational effects. The phase boundary is slightly asymmetric around 50% and a disordered region is wider in the *B*-rich region than in the *A*-rich region. This is due to the shape of the Morse potential from which a smaller atom (*A*) in the *B*-rich solution expends less energy than the opposite case in the uniformly deformable lattice, which is a natural consequence of the fact that the repulsive potential is steeper than that of the attractive potential. Although the equilibrium lattice constants of *A* and *B* in the present study do not differ appreciably (see Table 1), the asymmetry should be more pronounced with a larger difference of atomic sizes in the constituent atoms.

By keeping the same Morse potential parameters for the calculations above, the lattice vibration effects are introduced through temperature-dependent terms in Eq 19 with the same Debye temperatures ($\tau_2^{(n)} = 1.0$) for all $n = A$, AB and B (see Table 2). The temperature dependence of LRO parameter at 50% and the entire phase boundary are shown by solid circles in Fig. 2 and 3, respectively. One can clearly see that the transition temperature decreases, indicating the stabilization of the disordered phase. It is noted that such preferential stabilization (destabilization) of the ordered (disordered) phase is induced despite the fact that the temperature-dependent terms of pair interaction energies are the same for all the phases. This is explained by the lattice softening effects in the following manner.

The atomic potentials at an elevated temperature (solid line), for instance at $\tau_1 = 4.0$, are compared with those without the lattice vibration effects (broken lines) in Fig. 4. One observes that the minimum of each potential shifts toward the right-hand side, indicating thermal expansion. The downward shifting is due to the vibrational entropy effects. The other noticeable point is that the curvature at the equilibrium distance of each curve, which manifests the bulk modulus, becomes smaller, indicating the softening of the lattice. In fact, the curvature of *A-A* potential at $\tau_1 = 4.0$ is about 86% of that without the lattice vibration effects.

The most primitive estimation of the transition temperature, T_t, is attempted by the simple Bragg-Williams approximation[17] (equivalent to the regular solution model) which claims that the transition temperature is proportional to the ordering energy defined as $\Delta E_{\mathrm{ord}} = e_{AA} + e_{BB} - 2 \cdot e_{AB}$. It is reasonable to assume that e_{AB} takes minimum at 50%, and we define the corresponding atomic distance as r^*_{AB}. Then, the ordering energy at 50% is given as

$$\begin{aligned}
&\Delta E_{\mathrm{ord}}(50\%)\\
&\quad = e_{AA}\left(r^*_{AB}\right) + e_{BB}\left(r^*_{AB}\right) - 2 \cdot e_{AB}\left(r^*_{AB}\right)\\
&\quad = \left\{e_{AA}\left(r^*_{AB}\right) - e_{AB}\left(r^*_{AB}\right)\right\} + \left\{e_{BB}\left(r^*_{AB}\right) - e_{AB}\left(r^*_{AB}\right)\right\}\\
&\quad = \Delta E_A\left(r^*_{AB}\right) + \Delta E_B\left(r^*_{AB}\right) \qquad \text{(Eq 20)}
\end{aligned}$$

where $\Delta E_n\left(r^*_{AB}\right)$ is defined as $e_{nn}\left(r^*_{AB}\right) - e_{AB}\left(r^*_{AB}\right)$ ($n = A$ or B) which is equivalent to the distance between the bottom of the *A-B* potential and the intersection of the vertical line at r^*_{AB} with the potential curve $e_{nn}(r)$. Hence, a decrease of the curvature of both $e_{AA}(r)$ and $e_{BB}(r)$ at an elevated

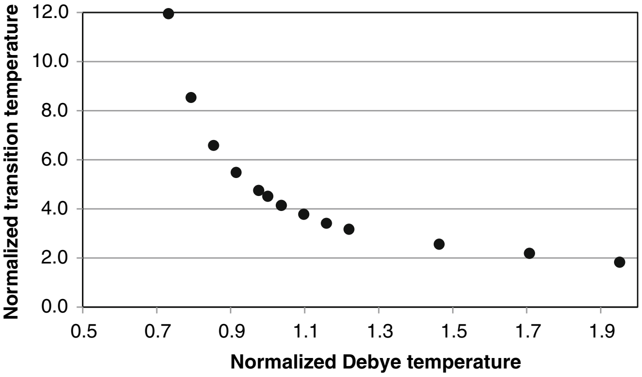

Fig. 5 Dependence of the transition temperature τ_t on the Debye temperature of *AB*, $\tau_2^{(AB)}$, at a fixed composition of 50%

temperature due to the lattice vibration effects reduces both $\Delta E_A\left(r^*_{AB}\right)$ and $\Delta E_B\left(r^*_{AB}\right)$, resulting in a lower transition temperature. A reduction of the curvature of *A*-*A* (*B*-*B*) potential curve indicates that the energy expended to accommodate *B*(*A*) atom in *A*(*B*)-rich solid solution is lowered. This is a typical lattice vibration effect on phase equilibria, and the reduction of the transition temperature by the introduction of the lattice vibration effects reported in the first-principles calculations is ascribed to this effect.

Shown in Fig. 4 by a dotted line is the *A*-*B* pair potential calculated at $\tau_1 = 4.0$ when $\tau_2^{(AB)}$is reduced to 0.8. Apparently, the relative depth of the unlike pair is deepened and, therefore, the stabilization of the ordered phase is expected. As one observes in Fig. 2 and 3 by open circles which are calculated for $\tau_2^{(AB)} = 0.93 \cdot \tau_2^{(A)} \left(= \tau_2^{(B)}\right)$, the transition temperature increases and the phase boundary shifts upward. The dependence of the transition temperature at 50% on $\tau_2^{(AB)}$ is further summarized in Fig. 5. It can be clearly seen that the transition temperature increases monotonically with decreasing Debye temperature of *AB*. According to the vibrational entropy formula given in Eq 8, both the Debye function and the second logarithmic term monotonically decrease with decreasing Debye temperature, $\Theta_D^{(n)}$, at a constant temperature *T*. Hence, with an increase of temperature, the vibrational free energy decreases in favor of a phase with a lower Debye temperature. This is the significance of the stabilization of the ordered phase realized in the present study.

In fact, most discussions of lattice vibration effects on phase equilibria are centered around the stabilization of a disordered solid solution enhanced by the lattice softening which renders easier accommodation of atomic species of different sizes. However, when the Debye temperature of an ordered phase is lower than that of pure phases, the stabilization of an ordered phase is expected, which oppositely results in the increase of the transition temperature.

Finally, it is suggested that the technical significance of the present study is that in the choice of a finite set of ordered phases in the Cluster Expansion given by Eq 9-11, an extra care should be taken in the selection of the hypothetical ordered phases.

Acknowledgment

The present work was partly supported by Next Generation Supercomputing Project, Nanoscience Program, MEXT, Japan.

References

1. T. Mohri, Statistical Thermodynamics and Model Calculations, *Alloy Physics*, Chap. 10 and references therein, W. Pfeiler, Ed., Wiley-VCH, 2007, p 525-588
2. R. Kikuchi, A Theory of Cooperative Phenomena, *Phys. Rev.*, 1951, **81**, p 998-1003
3. R. Kikuchi, Space is Continuous-Continuous-Displacement Treatment of Phase-Separating Diagrams, *J. Phase Equilib.*, 1998, **19**, p 412-421
4. R. Kikuchi and A. Beldjenna, Continuous Displacement of Lattice Atoms, *Physica A*, 1992, **182**, p 617-634
5. R. Kikuchi and K. Masuda-Jindo, Calculation of Alloy Phase Diagrams by Continuous Cluster Variation Method, *Comp. Mater. Sci.*, 1999, **14**, p 295-310
6. H. Uzawa and T. Mohri, Calculation of Short-Range-Order Diffuse Intensity for a Two Dimensional Square Lattice Within Cluster Variation Method, *Mater. Trans.*, 2001, **42**, p 422-424
7. H. Uzawa and T. Mohri, Continuous Displacement Cluster Variation Method in Fourier Space, *Mater. Trans.*, 2002, **43**, p 2185-2188
8. T. Mohri, Theoretical Investigation of Phase Equilibria by the Continuous Displacement Cluster Variation Method, *Int. J. Mater. Res.*, 2009, **100**, p 301-307
9. A. Zunger, First-Principles Statistical Mechanics of Semiconductor Alloys and Intermetallic Compounds, *Statics and Dynamics of Alloy Phase Transformations*, P.E.A. Turchi and A. Gonis, Ed., Plenum Press, New York, 1994, p 361-419
10. V. Moruzzi, J.F. Janak, and K. Schwarz, Calculated Thermal Properties of Metals, *Phys. Rev. B*, 1988, **37**, p 790-799
11. T. Mohri and Y. Chen, First-Principles Calculation of $L1_0$-Disorder Phase Boundary in Fe-Pd System, *Mater. Trans.*, 2004, **45**, p 1478-1484
12. T. Mohri and Y. Chen, First-Principles Investigation of $L1_0$-Disorder Phase Equilibria of Fe-Ni, -Pd, and -Pt Binary Alloy Systems, *J. Alloys Compd.*, 2004, **383**, p 23-31
13. J.W. Connolly and A.R. Williams, Density-Functional Theory Applied to Phase-Transformations in Transition-Metal Alloys, *Phys. Rev. B*, 1983, **27**, p 5169-5172
14. J.M. Sanchez and D. de Fontaine, The Fee Ising Model in the Cluster Variation Approximation, *Phys. Rev. B*, 1978, **17**, p 2926-2936
15. J.M. Sanchez, F. Ducastelle, and D. Gratias, Generalized Cluster Description of Multicomponent Systems, *Physica (Utrecht)*, 1984, **128A**, p 334-350
16. T. Mohri, J.M. Sanchez, and D. de Fontaine, Short-Range Order Diffuse Intensity Calculations in the Cluster Variation Method, *Acta Metall.*, 1985, **33**, p 1463-1474
17. W.L. Bragg and E.J. Williams, The Effect of Thermal Agitation on Atomic Arrangement in Alloys, *Proc. R. Soc. Lond. A*, 1934, **145**, p 699-730