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Materials

Theoretical Analysis of Lattice Parameter Effect on Order-Disorder Transformation Based on Pair Potential

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Abstract: Based on pair potential, the Bragg Williams (B-W) model is modified to take into account the effect of the lattice parameter on theoretical order-disorder transformation analysis. The main purpose of this work is to understand the basic aspects of this effect and related reasonable model on order-disorder transformation. In the present approach, the configuration free energy is chosen as function of the lattice parameter and the long-range order. This energy is calculated through Taylor's expansion, starting from the disordered state. It was found that the configuration free energy has been strongly modified when the lattice parameter is taken into account. It was also found only one type of order-disorder transformation exists in AB alloy and three kinds of order-disorder transformations for non-equiatomic alloy system such as A_3B alloy. This result is in agreement with experiments.

Key words: order-disorder transformation; computer simulation; pair potential; phase transformation

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1 Introduction

The formation of long-range order in alloy systems frequently produces a significant effect on some properties of alloys. Bragg and Williams first produced a rigorous theory of order-disorder (O-D) transitions [1], which involves the following assumptions:

(i) The atoms are at rest on the lattice sites;

(ii) The nearest neighbor interactions are taken into account.

With the B-W theory, two types of order-disorder transformations, first order and second order transformation, can be expected. This theory has been applied to explain the order-disorder transformation in some ordered alloys very successfully. But it is found very difficult to interpret the O-D transformation in Ni-Al system by using the classical B-W model. Recently, Ni et al. has modified B-W model by using EAM potential [2]. From Ni's model, a new type of O-D transformation and a new ordered state could be expected. These new results explain the experimental phenomena observed in the O-D transformation of Ni-Al system.

The classical B-W model did not take into account the change of the lattice parameter during the analysis of the O-D transformation.Based on the pair potential model, it is well known for one atom system, the energy of an atom is proportional to the reference number of the neighbor atoms. This is not true for most of the case. Ni's model found new type O-D transformation is due to taking into account the non-linear relationship between the energy of an atom and it's reference number by using EAM potential [2]. The purpose of this paper is to analyze in a case of a modified B-W model with lattice change, what will be the effect on the O-D transition.

2 Model

With pair potential, the configuration energy for an atom system should be

$$E=\frac{1}{2}\sum_{\alpha}\sum_{\beta(\neq\alpha)}\phi_{i,j}(r_{\alpha\beta}) \tag{1}$$

where ϕ_{ij} is the pair interaction between the type i atom at site α and the type j atom at site β.

Since the probability with α site occupied by an A atom will be reduced to fractions of unity when an order-disorder transition occurs. Bragg and William have used this description to define the long-range order parameter σ as follows:

$$\sigma=\frac{P_i-C_i}{1-C_i} \tag{2}$$

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where $i=\alpha$ or β sublattice and $j=$ A or B atoms, C_i is the atomic composition of type i atom. P_i^j is the probability of type j atom occupying type i sublattice ($i, j=\alpha$ or β).

From equation (2), P_i^j can be written as:

$$P_i^j = C_i\delta_{ij} + C_j(1-\delta_{ij}) + (1-C_i)(\delta_{ij}-1)\sigma \tag{3}$$

where δ_{ij} is the Kronecker delta function, σ is long-range order parameter. The average configuration energy of each atom is defined as follows.

$$E(a,\sigma) = \sum_{\alpha=\mathrm{A,B}} C_i E_i(a,\sigma) \tag{4}$$

where E_i is the energy at the type i site and a is the lattice parameter.

$$E_i(a,\sigma) = \frac{1}{2}\Phi_i(a,\sigma) \tag{5}$$

where Φ_i is the contribution to the total energy for the atom at the type i site respectively.

$$\Phi_i(a,\sigma) = \frac{1}{2}\sum_u^n \sum_v^{n_{i(0)}} \sum_{\beta=\mathrm{A,B}} \sum_{\eta=\mathrm{A,B}} P_i^\eta(\sigma) P_{\delta(i)}^\beta(\sigma) \Phi^{\eta\beta}(r_{v(u)}(a)) \tag{6}$$

where u is the ith neighbor group; v the jth neighbor atom in the uth neighbors group; $\delta_{j(i(0))}$ the sublattice of the vth neighbor in uth group; n the total number of the neighbors group; $n_{i(0)}$ the total number of the neighbor atom in the uth neighbors group; $\Phi^{\eta\beta}(r)$ the pair potential between nA atom and nB atom; $r_{v(u)}$ the distance of vth neighbor atom in uth neighbor group.

According to B-W model, the configuration energy for an ordered alloy is

$$E = E(\sigma, a) = E_0(a) + W(a)\sigma^2 \tag{7}$$

where

$$E_0(a) = \sum_n^Z \frac{Z_{n0}}{2}[C_{\mathrm{A0}}^2\phi^{\mathrm{AA}}(r_n) + C_{\mathrm{B0}}^2\phi^{\mathrm{BB}}(r_n) + 2C_{\mathrm{A0}}C_{\mathrm{B0}}\phi^{\mathrm{AB}}(r_n)] \tag{8}$$

and

$$W(a) = \sum_n^Z \frac{C_{\mathrm{A0}}(Z_{n0}C_{\mathrm{B0}} - Z_{n\mathrm{B}})}{2}[\phi^{\mathrm{AA}}(r_n) + \phi^{\mathrm{BB}}(r_n) - 2\phi^{\mathrm{AB}}(r_n)] \tag{9}$$

where Z_{n0} is the total number of unlike atomic neighbors in the nth neighbor group for a type A sublattice, r_n is the distance to the nth neighbors group. This distance is a function of lattice parameter. $\phi^{\eta\beta}$ is the pair potential between η atom and β atom, $\eta=$ A, B and $\beta=$ A, B.

The lattice parameter should only be a function of the long-range order parameter (LRO) such for the AB cubic crystal system:

$$a = a(\sigma) \tag{10}$$

By Taylor's expansion, the configuration energy can be written as:

$$E(\sigma, a) = E_0 + \left[\sum_n \frac{1}{n!}\left(\frac{\partial}{\partial\sigma} + \frac{\partial}{\partial a}\frac{\mathrm{d}a}{\mathrm{d}\sigma}\right)^n E|_{\sigma=0}\right]\sigma^n \tag{11}$$

where E_0 is the energy of the totally disordered state.

Using the pair potential energy equation (1) and neglecting the higher order coefficient, the configuration energy can be expressed as:

$$E(\sigma, a) = E_0 + E_1\sigma + E_2\sigma^2 + E_3\sigma^3 + E_4\sigma^4 \tag{12}$$

$$E_2 = W + \frac{1}{2}\frac{\partial E_0}{\partial a}\frac{\mathrm{d}^2 a}{\mathrm{d}\sigma^2} + \frac{1}{2}\frac{\partial^2 E_0}{\partial a^2}\left(\frac{\mathrm{d}a}{\mathrm{d}\sigma}\right)^2 \tag{13}$$

where E_2 is the function of ordering energy and lattice derivative functions.

$$E_3 = 2\frac{\partial W}{\partial a}\frac{\mathrm{d}a}{\mathrm{d}\sigma} \tag{14}$$

$$E_4 = \frac{1}{2}\left(\frac{\partial^2 W}{\partial a^2}\left(\frac{\mathrm{d}a}{\mathrm{d}\sigma}\right)^2 + \frac{\partial W}{\partial a}\frac{\mathrm{d}^2 a}{\mathrm{d}\sigma^2}\right) \tag{15}$$

It is found that the coefficient E_1 will always turn zero. For the structure with the equal number of sublattices, i.e. B_2 structure, the replacement of σ by $-\sigma$ will not alter the configuration energy, so all the odd coefficient should equal to zero.

The ordering energy is defined as follows.

$$\triangle E(\sigma, a) = E(\sigma, a) - E(0, a) \tag{16}$$

The ordering condition is $\triangle E<0$. For AB ordered alloy, E_2+E_4 must be less than zero.

The equilibrium value of σ is determined by minimizing the free energy with respect to a change in σ, then:

$$\frac{\partial G(\sigma)}{\partial\sigma}\Big|_{T=0} = 2\sigma(E_2 + E_4\sigma^2) = 0 \tag{17}$$

The configurational part of the free energy at temperature T can be calculated using the following equation:

$$G(\sigma) = E(\sigma) - TS(\sigma) \tag{18}$$

where E is the configurational part of energy and the average configuration entropy S can be approximated as:

$$S(\sigma) = -k\sum_{i=\alpha,\beta}\sum_{j=\alpha,\beta}\{C_i[C_i\delta_{ij} + C_j(1-\delta_{ij}) + (1-C_i)\cdot (\delta_{ij}-1)\sigma]\ln[C_i\delta_{ij} + C_j(1-\delta_{ij}) + (1-C_i)(\delta_{ij}-1)\sigma]\} \tag{19}$$

3 Theoretical Analysis of Order-Disorder Transformation

For the equilibrium, it is necessary that $\frac{\partial G(\sigma,a)}{\partial\sigma}$ should be zero.

So, the equilibrium value of σ is determined by:

$$\frac{\partial G(\sigma,a)}{\partial\sigma} = 0 \tag{20}$$

The free energy difference can be approximated as follows:

$$\Delta G(\sigma, a, T) = G(\sigma, a, T) - G(0, a, T) \tag{21}$$

The order-disorder temperature is defined by:

$$T_{od} = \frac{E(0, a) - E(1, a)}{S(0) - S(1)} \tag{22}$$

The conditions for the critical point are:

$$\frac{\partial G}{\partial \sigma}\Big|_{\sigma \to 0} = 0 \tag{23}$$

and

$$\frac{\partial^2 G}{\partial \sigma^2}\Big|_{\sigma \to 0} = 0 \tag{24}$$

From these conditions, we found the critical point corresponds to

$$T_c = \frac{E_2}{k} \tag{25}$$

where k is a Boltzmann constant.

Using equations (23)–(25), we can write:

$$\frac{2\sigma}{\ln\frac{1+\sigma}{1-\sigma}} = \frac{T}{T_c} \tag{26}$$

For the binary alloy with $C_A \neq C_B$ (A_3B or AB_3), $C \neq 0$,

$$\Delta E_{od}(\sigma, a) = E(0, a) - E(1, a) \tag{27}$$

It means $E_2 + E_3 < 0$ or $E_3 < -E_2$ (28)

From the equilibrium condition, $\frac{\partial G(\sigma, a)}{\partial \sigma}$ must be zero.

Therefore, $\sigma = 0$ (disorder state) or $\sigma = -\frac{E_2}{3E_3}$ (order state) at $T = 0$ K,

$$\frac{\partial^2 G}{\partial \sigma^2}\Big|_{T \to 0} = 0 \text{ if } \sigma = -\frac{E_2}{3E_3} \tag{29}$$

4 Results and Discussion

For AB alloy, at $T = 0$ K, E_3 must also equal zero.

Therefore

$$\Delta E(\sigma, a) = E_2(\sigma^2 - 1) \tag{30}$$

$$\Delta E_{od}(\sigma, a) = E(0, a) - E(1, a) = -E_2 \tag{31}$$

E_2 must be negative.

Figure 1 shows the free energy variation with long-range order for different temperatures. When $T = 0$ K, the stable state corresponds to the completely ordered phase. When T increases and is less than the critical temperature, this state become a minimum between 0 and 1.

As can be seen from figure 1, below the critical temperature, the free energy decreases as σ increases. The free energy difference is positive for the temperature $T < T_{od}$ and negative for $T > T_{od}$. When $T = T_c$, the completely disordered state is stable.

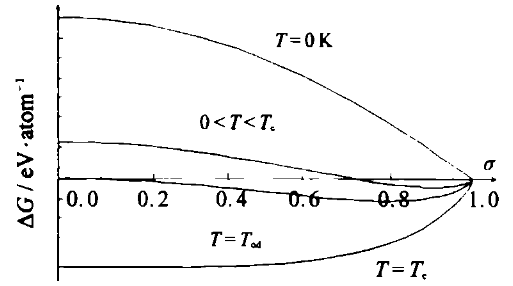

Figure 1 Free energy variation with long-range order at various temperature for AB alloy based on EAM.

Figure 2 shows the variation of the equilibrium long-range order parameter with the reduced temperature T/T_c. As can be seen from the curves σ decreases with the increasing temperature. It is means the order-disorder transformation is a second-order transition.

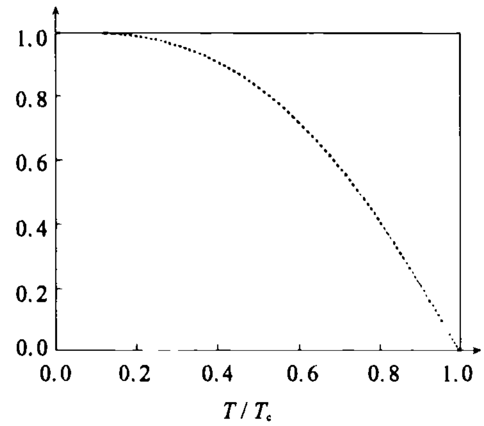

Figure 2 Long-range order parameter variation with reducted temperature for AB alloy based on EAM.

For the A_3B or AB_3 binary alloys, E_3 is different of zero.

The equilibrium value of the degree of long-range order in an alloy for a given value of the lattice parameter is determined by a minimum value of the configuration energy with respect to a change in σ.

$$\frac{\partial E(\sigma, a)}{\partial \sigma} = 0 \tag{32}$$

Equation (32) has the solution $\sigma = 0$ corresponding to a disordered state of the alloy and the solution $\sigma_0 = -\frac{2E_2}{3E_3}$ corresponding to the ordered state.

The equilibrium condition is $\frac{\partial^2 E(\sigma, a)}{\partial \sigma^2} > 0$ (33)

If $\sigma = 0$ in equation (33), $E_2 > 0$ for the disordered state and if

$$\sigma_0 = -\frac{2E_2}{3E_3} \tag{34}$$

in equation (33), $-E_2$ must always be negative.

Following the values of E_2, E_3, three groups of order-disorder transformation must exist.

Group I: E_2>0 and E_3<0.

Figure 3 shows the calculated results of the free energy variation with long-range order parameter for different temperatures and a maximum free energy change peak located at $\sigma_0=-\frac{2E_2}{3E_3}$ for all the temperatures exists.

It can be seen from this figure that the free energy change decreases with the increase of temperature. Above the critical temperature, the free energy change is negative.

In this case, T_c is calculated by $G(0, T_c) = G(1, T_c)$ and $T_c = T_{od}$.

Figure 4 shows the σ variations with the reduced temperature that σ will always be unit and decreases from 1 to 0 at the order-disorder temperature. The order-disorder transformation is a first order transition.

Group II: E_2<0 and $E_3=-\frac{1}{3}E_2$.

For these conditions, the calculated $\Delta G(\sigma, a)$-σ curve is shown in **figure 5**. It presents an energy minimum peak at $\sigma_0=-\frac{2E_2}{3E_3}$.

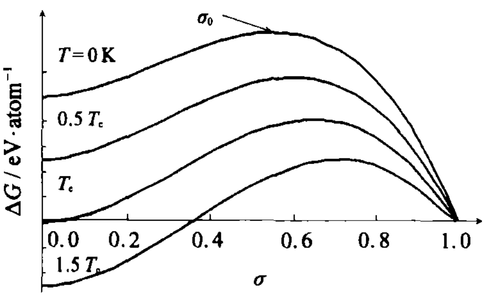

Figure 3 Free energy variation with long-range order parameter (group 1: E_2>0, E_3<0) at various temperature for A_3B alloy based on EAM.

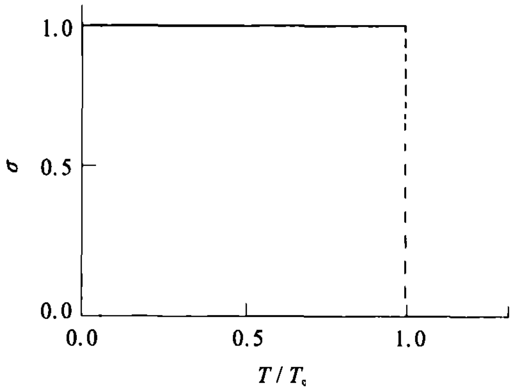

Figure 4 Long-range order variation with T/T_c for group I of order-disorder transformation A_3B or AB_3 alloy based on EAM.

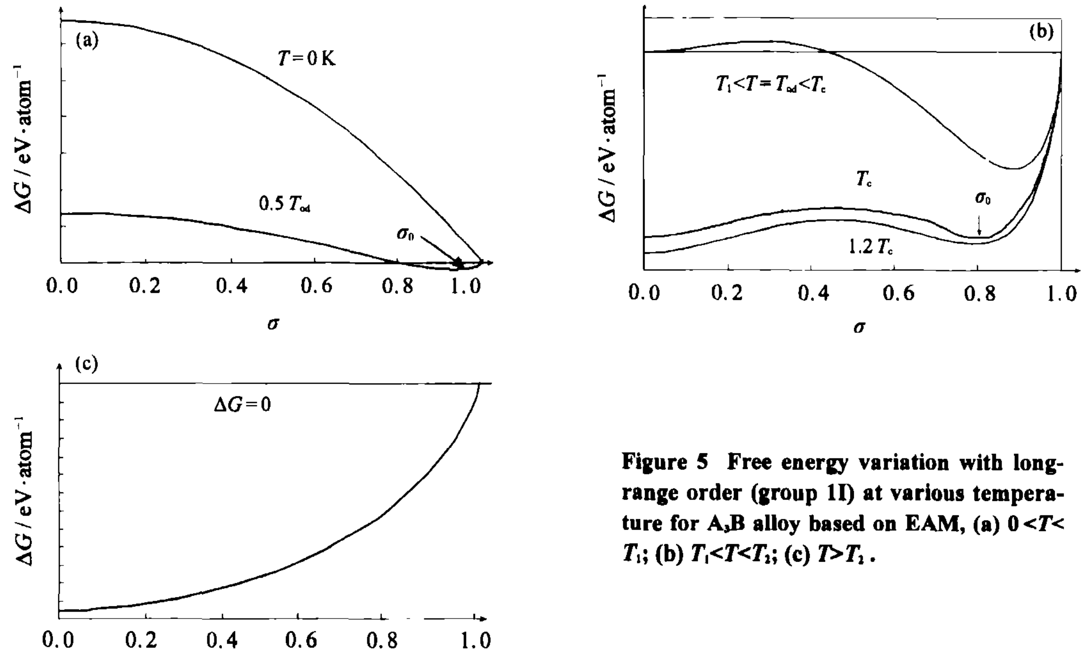

Figure 5 Free energy variation with long-range order (group II) at various temperature for A_3B alloy based on EAM, (a) 0<T<T_1; (b) T_1<T<T_2; (c) T>T_2.

The critical temperature was calculated from the condition $G(\sigma_0, T_c) = G(0, T_c)$.

Condition II involves the formation of 3 stages of order-disorder transformation due to the effect of the increase temperature as can be seen from figure 5.

Figure 5 shows the obtained results for this condition. At T = 0 K, figure 5 (a) shows that the free energy change decreases monotonously with increasing σ. The stable state is at $\sigma = 1$.

When the temperature increases to $0.5T_{od} < T_1$, this state moves to a minimum sited at $0 < \sigma < 1$ and the free energy change is negative for this minimum. From this figure, we can see that the free energy change of the ordered phase is lower than that of the disordered phase. If we call T_1, the temperature of the observed minimum: $T_1 < T_{od}$. When $T_1 < T < T_2$, figure 5 (b) shows a free energy change maximum peak and also the minimum which characterize the stable phase. Finally in stage III, when the temperature is higher than T_c, figure 5 (c) shows that the minimum and the maximum disappear, and the free energy change increases with the increase of σ.

Figure 6 presents the equilibrium value of σ as a function of T/T_c, σ decreases as the temperature decreases until σ_0 for $T < T_c$; this transformation is a second order transition and decreases abruptly from σ_0 to 0 when the temperature reaches the critical value. This second type is a first order transition.

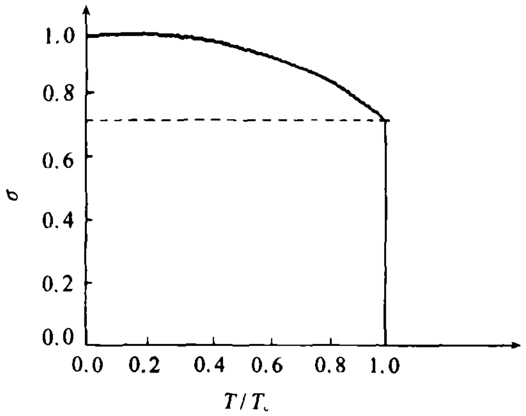

Figure 6 Long-range order variation with T/T_c (groupII) of order-disorder transformation of A_3B alloy.

Group III: $E_2 < 0$ and $-\frac{1}{3}E_2 < E_3 < -E_2$.

For these conditions, the $\Delta G(\sigma, a)$-σ curve is shown in **figure 7** and shows the variation of the free energy change with long-range order parameter. There is an energy minimum peak at $\sigma_0 = -\frac{E_2}{3E_3}$.

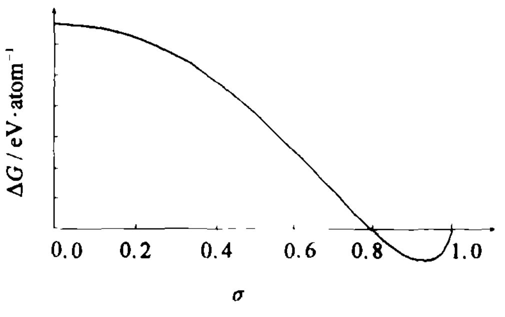

Figure 7 Free energy variation with long-range order (semi-ordered alloy) at T=0 K based on EAM.

The order-disorder transformation is also a second-order as in the case of AB alloy.

For the condition of $-\frac{2}{3}E_2 < E_3 < -E_2$, **figure 8** shows a minimum, this phase was interpreted as a partially ordered state [2].

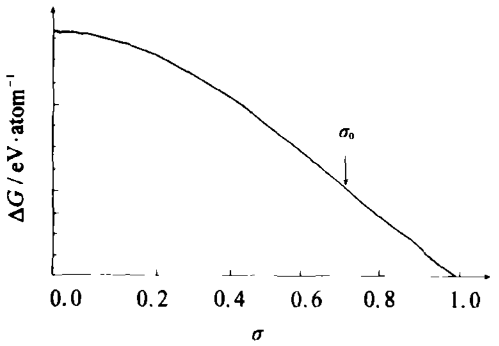

Figure 8 Free energy variation with long-range order (group III) at T = 0 K for A_3B alloy based on EAM.

As can be seen through the expansion coefficients, the effect of the lattice parameter leads all the coefficients to vary with the lattice parameter and its derivatives.

This work has developed a simple model based on pair potential to analyse what kind of order-disorder transformation is possible when the lattice parameter effect is taken into account. The first important result is the lattice parameter has a very strong effect on the configuration energy. It was found that the expansion coefficients of the configuration energy depend strongly on the lattice parameter and its derivatives. It was also found that the E_2 coefficient has a very strong effect on the order-disorder transformation in the case of A_3B alloys.

The theoretical analysis of this work, takes into account the restriction condition of the lattice parameter, indicated that the order-disorder transformation is a continuous second-order transformation for AB alloys. For other alloy systems (A_3B alloys), three kinds of order-disorder transformations were found to be possible.

These results are the same as those obtained by EAM potential [2]; and can be expected by taking into account the contributions of the tetrahedron pair correlation energy in the expansion of the configuration energy. Daw and Baskes [3] have pointed out that, if the embedded function is completely linear, the contribution from the embedding function can always be converted into a contribution from a two body potential.

Comparing with the previous generation of pair potentials, other authors [4–7] have taken into account the lattice parameter relaxation but never found the same result. We know that EAM potential have been known as one of the more powerful potential. In the case of the binary alloys the local relaxation is of considerable importance, especially where there is a large discrepancy between atomic sizes but has no much influence on the order-disorder analysis. The agreement of our calculation with EAM suggests that the used model has some physical significance and the model represents a very reliable way of exploring the properties of alloys. The model presented here is apparently simple and has the ability to expect the order-disorder transformation in binary alloys from the restriction condition of the lattice parameter.

4 Conclusions

The effect of the lattice parameter on the order-disorder transformation was analyzed theoretically. A simple model has been developed through Taylor's expansion. It was found that the effect of the lattice parameter leads all the coefficients of configuration energy expansion to vary with the lattice parameter and its derivatives. The E_2 coefficient was found to have a very strong effect on order-disorder transformation. It was found that only one type of order-disorder transformation exists in AB alloy. It gives the same result as that of the classical B-W model.

It was also indicated that there are three kinds of order-disorder transformations for non-equi-atomic alloy system such as A_3B alloy for pair potential when the lattice parameter is taken into account. This result is the same as that obtained by using EAM, because our model has been extended until the fourth term of configuration energy in the Taylor's expansion. The limitation of other previous model, which takes into account the local relaxation, is perhaps due to the non-contribution of the higher order near neighbor.

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