

## EAM Analysis of the Lattice Parameter Effect in Order-Disorder Transformation

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**Abstract:** The embedded atom method (EAM) was used to theoretically analyze the effect of the lattice parameter variation on the order-disorder transformation in binary alloys. Based on EAM, it is found that only one kind of order-disorder transition (second-order transition) exists for AB alloy. Three groups of order-disorder transformation can be observed for the A<sub>3</sub>B or AB<sub>3</sub> compounds. For group I, the order-disorder is a completely first-order transition. For group II, the order-disorder transformation is a classical first-order transition. For group III, the order-disorder transformation is found to be a second-order transition. The lattice parameter variations have a significant effect on  $E_s$  coefficient, which is related to the ordering energy. These results are in good agreement with experiments.

**Key words:** order-disorder transformation; embedded atom method (EAM); phase transformation; binary alloy

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### 1 Introduction

In developing a theory of order-disorder transitions, two approaches of treatment are possible.

A concrete model of an alloy can be considered, and the energy corresponding to different arrangements of atoms on the crystal lattice sites can be calculated. Then the statistical partition function and the free energy of the alloy can be determined. From the free energy global minimum the equilibrium properties of alloys may be determined, in particular, the values of the degree of long-range order and correlation parameters at given temperatures.

The treatment of order-disorder transition that employs statistical theory is difficult because of serious mathematical problems arising from the construction of a statistical theory of order-disorder transitions and the choice of a very crude model and approximate methods of calculation. Such procedure produces some results that agree with experimental data.

Another approach to the development of a theory of order-disorder transitions may be based on general thermodynamical relations, on the calculation of the properties of the crystal, and by assuming that certain thermodynamic quantities can be expanded into series. Thus, a theory of order-disorder transition can be developed without using a specific model for alloy. We chose the EAM presented by Daw and Baskes [1, 2] as

an approximated method that has been developed in the last ten years and successfully used in quite extensive fields involving materials science [3–12]. The purpose of this work is to investigate the effect of lattice parameter variation at various temperatures in binary alloys on order-disorder transformation characteristics combining the EAM with the thermodynamical theory. The utilization of such combination of methods for the qualitative and/or semi-quantitative study to elucidate the order-disorder characteristics has already been established [13] and satisfactory results have been obtained for AB and A<sub>3</sub>B or AB<sub>3</sub> compounds, but it has not taken into the account the lattice constant effect yet.

### 2 Embedded Atom Method (EAM)

Since the probability with  $\alpha$  site occupied by an atom will be reduced to fractions of unity when an order-disorder transition occurs, Bragg and Williams have used this description to define the long range order parameter  $\sigma$ .

$$\sigma = \frac{P_i - C_j}{1 - C_j} \quad (1)$$

where  $i = \alpha$  or  $\beta$  sites and  $j = A$  or  $B$  atoms;  $C_j$  is the atomic composition of type  $j$  atom;  $P_i$  the probability of type  $j$  atom occupying type  $i$  sublattice.

The EAM is a technique for the construction of many body potential models for metals developed recently by Daw and Baskes [14, 15].

The total energy of the system of atoms,  $E_{\text{tot}}$ , in EAM is given by:

$$E_{\text{tot}} = \sum_i E_i \quad (2)$$

$$E_{\text{tot}} = \sum_i (F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij})) \quad (3)$$

$$\rho_i = \sum_{j \neq i} f_j(r_{ij}) \quad (4)$$

where the sums are over the atoms  $i$  and  $j$  (the subscripts denote either an atom at a particular site or the type of that atom); the embedding function  $F_i$  is the energy needed to embed an atom into the background electron density at site  $i$ ;  $\rho_i$  is the total electron density at site  $i$  due to all the atoms in the system except the embed one;  $\phi_{ij}$  is a pair interaction between atoms  $i, j$  whose separation is given by  $r_{ij}$ ; the total energy is the total internal energy of an assembly of atoms;  $f_j(r_{ij})$  is the contribution to the electron density at site  $i$  due to atom at the distance from atom  $i$ .

If considering the long-range order parameter  $\sigma$ , the average energy of each atom is

$$E(a, \sigma) = \sum_{\alpha=A, B} C_\alpha E_\alpha(a, \sigma) \quad (5)$$

where  $E_\alpha$  is the effective energy of an atom embedded at  $\alpha$  site.

$$E_\alpha(a, \sigma) = \frac{1}{2} \Phi_\alpha(a, \sigma) + F_\alpha[\rho_\alpha(a, \sigma)] \quad (6)$$

where  $F_\alpha$ ,  $\rho_\alpha$ ,  $\Phi_\alpha$  are effective embedding function, effective charge density and effective pairwise energy for the effective atom at the type  $\alpha$  site respectively.

$$F_\alpha[\rho(a, \sigma)] = \sum_{\alpha=A, B} P_\alpha^\sigma(\sigma) F_\alpha^\sigma[\rho_\alpha(a, \sigma)] \quad (7)$$

$$\rho_\alpha(a, \sigma) = \sum_i \sum_{j \in \beta=A, B} P_{\beta(i)}^\sigma(\sigma) \rho^\beta[r_{j(i)}(a)] \quad (8)$$

$$\Phi_\alpha(a, \sigma) = \frac{1}{2} \sum_i \sum_{j \in \beta=A, B} \sum_{\eta \in \beta=A, B} P_\alpha^\sigma(\sigma) P_{\beta(i)}^\sigma(\sigma) \Phi^{\eta\beta}(r_{j(i)}(a)) \quad (9)$$

where  $i$  is the  $i$ th neighbor group;  $j$  the  $j$ th neighbor atom in the  $i$ th neighbors group;  $\delta_{j(i)}$ , the sublattice of the  $j$ th neighbor in  $i$ th group;  $n$  the total number of the neighbors group;  $n_{i(0)}$ , the total number of the neighbor atom in the  $i$ th neighbors group;  $\rho^\beta(r(a))$  the electron density function of  $\beta$  atom;  $F^\beta$  the embedding function of  $\beta$  atom;  $\Phi^{\eta\beta}(r_{j(i)}(a))$  the pair potential between  $\eta$  atom and  $\beta$  atom;  $r_{j(i)}$ , the distance of  $j$ th neighbor atom in  $i$ th neighbor group;  $a$  the lattice parameter.

### 3 Theoretical Analysis of Order-Disorder Transformations

The configuration part of the free energy taking into account the lattice constant effect can be given by the following expression:

$$G(\sigma) = E(\sigma) - TS(\sigma) \quad (10)$$

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

$$S(\sigma) = -k \sum_{i=\alpha, \beta} \sum_{j=\alpha, \beta} \{C_i [C_i \delta_{ij} + C_j (1 - \delta_{ij}) + (1 - C_i)(\delta_{ij} - 1)\sigma] \cdot \ln [C_i \delta_{ij} + C_j (1 - \delta_{ij}) + (1 - C_i)(\delta_{ij} - 1)\sigma] \} \quad (11)$$

where  $k$  is the constant of Boltzmann,  $C_i$  and  $C_j$  are atomic composition, and  $\delta_{ij}$  is Kronecker delta function.

In equation (10), the configurational energy  $E$  can be approximated using the EAM and Taylor's expansion at  $\sigma=0$ . The configurational energy should be a function of the long-range order parameter (LRO),  $\sigma$ , and the lattice parameter,  $a$ . Moreover, the lattice parameter should also be a function of the LRO.

In EAM, the total energy is given by:

$$E(\sigma, a) = \frac{1}{2} [A(a) + B(a)] \sigma^2 + \frac{C}{3} \sigma^3 \quad (12)$$

where  $a$  is the lattice parameter and

$$A(a) = \sum_i C_A (n_i(0) C_B - n_i(1)) [\phi^{AA}(r_i) + \phi^{BB}(r_i) - 2\phi^{AB}(r_i)] \quad (13)$$

where  $n_i(1)$  is the total number of the unlike atomic neighbors of the  $i$ th neighbor group.

$$B(a) = 2C_A h \left\{ \frac{h}{2C_B} [(F^A(\bar{\rho}))^n + (F^B(\bar{\rho}))^n] + (F^A(\bar{\rho})) + (F^B(\bar{\rho})) \right\} \quad (14)$$

$$C = \frac{3C_A (C_B - C_A) h^2}{2C_B} [F^A(\bar{\rho})^n - F^B(\bar{\rho})^n] \quad (15)$$

are the coefficients to vary with the lattice parameter.  $\rho(a)$  are functions of the lattice parameter,  $a$  which is only a function of  $\sigma$ :

$$a = a(\sigma) \quad (16)$$

Let us consider the configuration energy  $E$  of a given  $a$  and  $\sigma$ . By Taylor's expansion at  $\sigma=0$ ,  $E$  can be written as

$$E(\sigma, a) = E_0 + \left[ \sum_n \frac{1}{n!} \left( \frac{\partial}{\partial \sigma} + \frac{\partial}{\partial a} \frac{da}{d\sigma} \right)^n E|_{\sigma=0} \right] \sigma^n \quad (17)$$

where  $E_0$  is the energy of the totally disordered state.

Using the total energy equation (3) and neglecting the higher order coefficient, the configuration energy can be written as

$$E(\sigma, a) = E_0 + E_2 \sigma^2 + E_3 \sigma^3 \quad (18)$$

where

$$E_2 = \frac{1}{2} (A + B + \frac{\partial^2 A}{\partial a^2} + \frac{\partial^2 B}{\partial a^2}) \quad (19)$$

$$E_3 = C + \left( \frac{\partial A}{\partial a} + \frac{\partial B}{\partial a} \right) \frac{da}{d\sigma} \quad (20)$$

$$\Delta G(\sigma, a) = E(\sigma, a) - E(1, a) = E_2(\sigma^2 - 1) + E_3(\sigma^3 - 1) \quad (21)$$

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

The free energy difference can be approximated as

$$\Delta G(\sigma, a, T) = G(\sigma, a, T) - G(1, a, T) \quad (22)$$

The order-disorder temperature is defined by

$$T_{od} = \frac{E(0, a) - E(1, a)}{S(0) - S(1)} \quad (23)$$

For AB alloy, at  $T=0$  K if  $C_A = C_B$ , it can be seen from equation (16) that  $C$  is equal to zero and  $E_3$  must be also equal to zero. Therefore

$$\Delta E(\sigma, a) = E_2(\sigma^2 - 1) \quad (24)$$

$$\Delta E_{od}(\sigma, a) = E(0, a) - E(1, a) = -E_2 > 0 \quad (25)$$

where  $E_2$  must be negative.

The conditions for the critical point are

$$\left. \frac{\partial G}{\partial \sigma} \right|_{\sigma=0} = 0 \quad (26)$$

and

$$\left. \frac{\partial^2 G}{\partial \sigma^2} \right|_{\sigma=0} = 0 \quad (27)$$

From these conditions, it is found that the critical point corresponds to

$$T_c = -\frac{E_2}{k} \quad (28)$$

Combining the equilibrium condition (equations (26), (27)) and equation (28), the following relation can be found between the long-range order parameter and the reduced temperature:

$$\frac{2\sigma}{\ln \frac{1+\sigma}{1-\sigma}} = \frac{T}{T_c} \quad (29)$$

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

$$\Delta E_{od}(\sigma, a) = E(0, a) - E(1, a) = -(E_2 + E_3) > 0 \quad (30)$$

It means

$$E_2 + E_3 < 0 \text{ or } E_3 < -E_2 \quad (31)$$

Equation (26) 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.

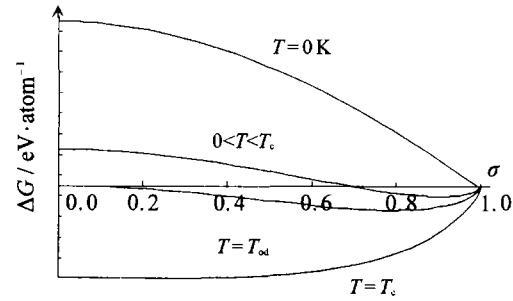
$$\frac{\partial^2 E(\sigma, a)}{\partial \sigma^2} \quad (32)$$

must be positive for the equilibrium condition.

Set  $\sigma=0$  in the equation (32) gives  $E_2 > 0$  for the disordered state. If set  $\sigma_0 = -\frac{2E_2}{3E_3}$  in equation (32), we find that  $E_2$  must always be negative, e.g.  $-E_2$ .

## 4 Results and Discussion

**Figure 1** shows the Gibbs free energy variation with long-range order curves at different temperatures for AB alloy. At  $T=0$  K, The stable state corresponds to the completely ordered phase. When the temperature increases and less than the critical temperature, this state becomes a minimum between 0 and 1. As can be seen from figure 1, below the critical temperature, the free energy decreases as  $\sigma$  increases. The free energy difference is positive for the temperature  $T < T_{od}$  and negative for  $T > T_{od}$ . At  $T=T_c$ , the completely disordered state is stable.



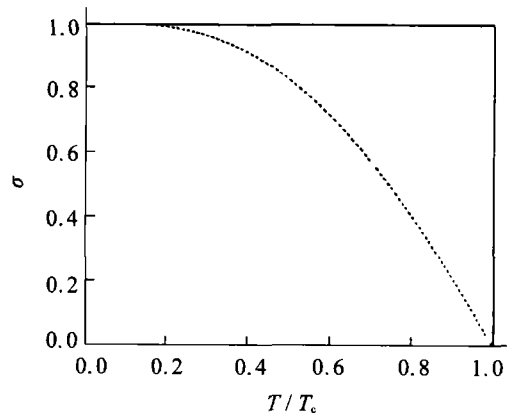
**Figure 1** Gibbs free energy change with long-range order parameter at various temperatures for AB alloy based on EAM.

The equilibrium value of the long-range order parameter in an alloy for a given value of the lattice parameter is determined from a minimum value of the configuration energy with respect to a change in  $\sigma$ .

**Figure 2** shows the variation of  $\sigma$  as a function of  $T/T_c$ .  $\sigma$  decreases monotonously as  $T/T_c$  increases. The order-disorder transformation is a second order transition. According to the values of  $E_2$ ,  $E_3$ , order-disorder transformations for  $A_3B$  or  $AB_3$  alloys can be classified into three categories.

**Group I:**  $E_2 > 0$  and  $E_3 < 0$ .

**Figure 3** shows the calculated results of free energy change as a function of long range order parameter, and



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

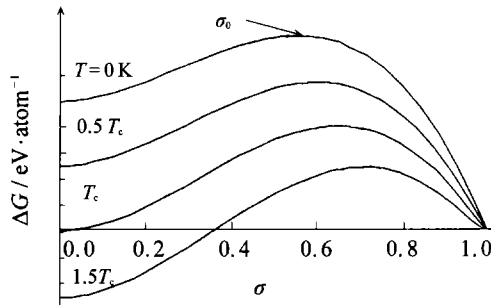


Figure 3 Gibbs free energy change with long-range order parameter (group I:  $E_2 > 0, E_3 < 0$ ) at various temperature for  $A_3B$  alloy based on EAM.

there is a maximum free energy change peak located at  $\sigma_0 = -\frac{2E_2}{3E_3}$ .

It can be seen from figure 3 that the free energy difference value decreases with the increase of the temperature. Above the critical temperature, the free energy change becomes more negative.

In this case,  $T_c$  is calculated by  $G(0, T_c) = G(1, T_c)$ . Figure 4 shows the  $\sigma-T/T_c$  curve, from which it can be

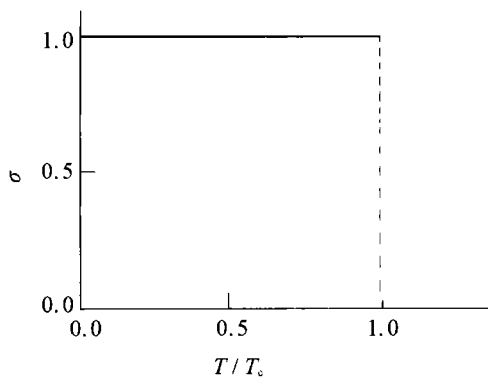
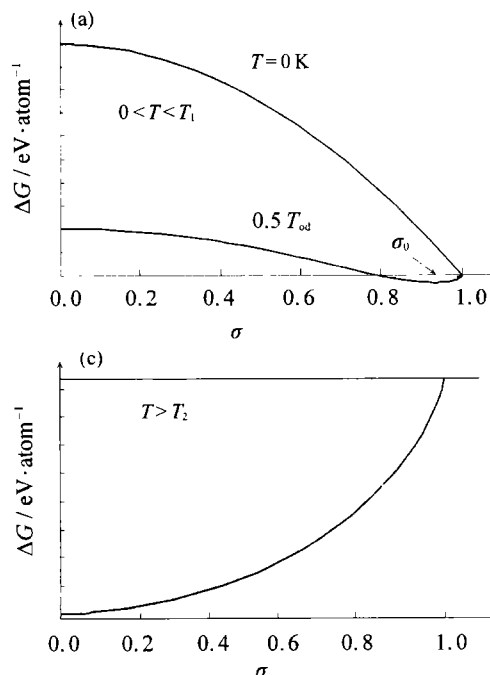


Figure 4 Long-range order variation with  $T/T_c$  for group I of order-disorder transformation  $A_3B$  or  $AB_3$  alloy based on EAM.



seen that when the temperature is below  $T_c$ ,  $\sigma$  is always unit. At  $T_c$ ,  $\sigma$  decreases from 1 to 0 abruptly. The order-disorder transformation is a first order transition.

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

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

In this case,  $T_c$  is calculated by  $G(\sigma_{oc}, T_c) = G(0, T_c)$ . At  $T = 0\text{K}$ , as shown in figure 5 (a), the free energy change decreases monotonously with increasing  $\sigma$ . The stable state is at  $\sigma = 1$ . If  $T_1$  is the minimum temperature to be observed, then  $T_1 < T_{od}$ . When the temperature increases to  $0.5 T_{od} < T_1$ , this state moves to a minimum sited at  $0 < \sigma < 1$  and the free energy change is negative. From this figure, it can be seen that the free energy change of the ordered phase is lower than that of the disordered phase. When  $T_1 < T < T_2$ , figure 5(b) shows one free energy change maximum peak and two minimum ( $\sigma=0$  and  $\sigma_0$ ), the minimum ( $\sigma_0$ ) characterizes the stable phase for  $T = T_{od} < T_2$ . For  $T = T_c$  and  $T_2 > T > T_c$ , the disorder state ( $\sigma=0$ ) will be the stable phase.

Finally in stage III, When the temperature is higher than  $T_c$  and more higher than  $T_2$ , figure 5(c) shows that the minimum and the maximum disappear, and the free energy change  $\Delta G$  increases with the increase of  $\sigma$ .

Figure 6 shows  $\sigma-T/T_c$  curve, when the temperature is below  $T_c$ ,  $\sigma$  decreases monotonously with the increasing temperature. At  $T_c$ ,  $\sigma$  decreases abruptly from  $\sigma_0$  to 0, the order-disorder transformation is a first order transition. Figure 6 shows the characteristic variations of the long-range order (LRO) parameter with the temperature for the stoichiometric  $A_3B$  composition. At  $T=$

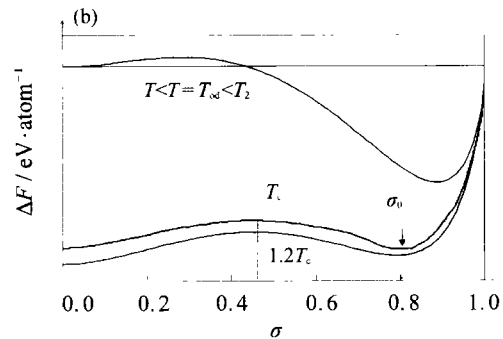
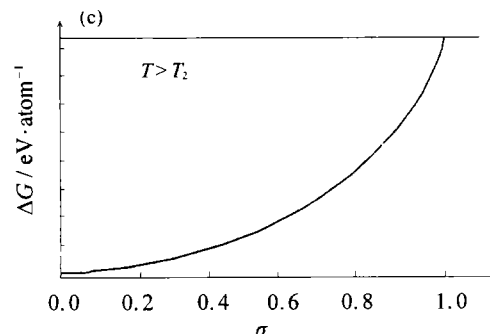


Figure 5 Free energy change with long range order parameter (group II:  $E_2 < 0, E_3 < -1/3E_2$ ) at various temperature for  $A_3B$  alloy based on EAM, (a)  $0 < T < T_1$ ; (b)  $T_1 < T < T_2$ ; (c)  $T > T_2$ .



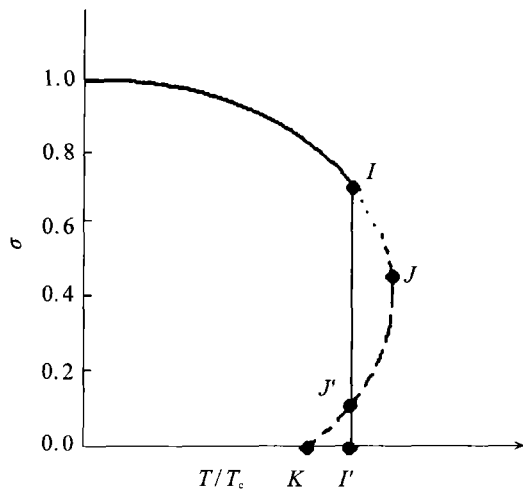


Figure 6 Variation of long-range order parameter ( $\sigma$ ) with reduced temperature ( $T/T_c$ ) for group II order-disorder transformation for  $A_3B$  or  $AB_3$  alloy based on EAM.

$T_c$ , the ordered state  $I$  ( $\sigma \neq 0$ ) is in thermodynamic equilibrium with the disordered state  $I'$  ( $\sigma = 0$ ), this equilibrium can be describe by Landau's Theory [ 15 ].

If we consider  $T_2 = 1.2 T_c$  as the temperature of the  $J$  point in figure 6, from  $I$  to  $J$  there exists a metastable ordered state  $\sigma \neq \sigma' \neq 0$ , and the disordering of the superheated ordered phase must occur by heterogeneous process involving nucleation and growth of the disordered phase within the metastable ordered phase.

At point  $J$ ,  $T = T_2$ , the superheated ordered phase is unstable with respect to disordering and this condition. Thus  $T_2$  is a disordering instability temperature and for  $T \geq T_2$ , a superheated ordered alloy will disorder homogeneously or continuously.

Similarly, on cooling a disordered alloy below  $T_c$ , for temperature  $T_1 < T < T_c$ , the free energy change as function of  $\sigma$  curve exhibits a thermodynamic barrier between the undercooled disordered state ( $\sigma = 0$ ) and the ordered state ( $\sigma = \sigma' \neq 0$ ) as shown in figure 5. The locus from  $J$  to  $K$  in figure 6 is the value of  $\sigma$  at the maximum point ( $\sigma_{max}$ ).

In the temperature range  $T_1 < T < T_c$ , an undercooled disordered phase can only order heterogeneously by nucleation and growth. At  $T_1$  (the ordering instability), the barrier vanishes and the free energy is monotonically decreasing from  $\sigma = 0$  to  $\sigma = \sigma'$ , the equilibrium ordered state.

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

For these conditions, the free energy change as function of long-range order parameter curve is shown in figure 7 and shows a turning point at  $\sigma = -\frac{E_2}{3E_3}$ .

The class III appears to show the same results as in

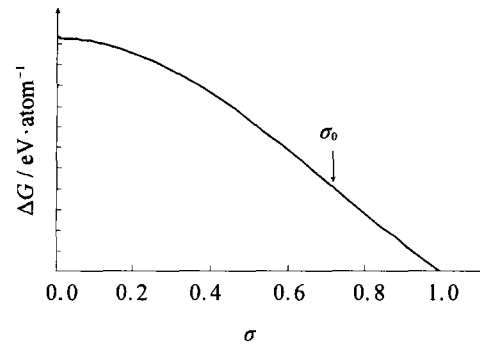


Figure 7 Gibbs free energy variation with long-range order parameters of group III at  $T = 0$  K for  $A_3B$  alloy based on EAM.

$AB$  alloy, the order-disorder transformation is a second-order transition. This results is in good agreement with those calculated by Fontaine using CVM [16 ].

It is known that in the  $A_3B$  phase described by a single order parameter, the transition would necessarily be first order, the coefficient  $E_3$  being non-zero. In the CVM calculations, Fontaine [17] used two order parameters to describe the  $A_3B$  compound and found that the presence of these two order parameters allows the transition to be second-order.

For the conditions  $-\frac{2}{3}E_2 < E_3 < -E_2$ , figure 8 shows a minimum, this phase was interpreted as a partially ordered state and named as semi-ordered state [13].

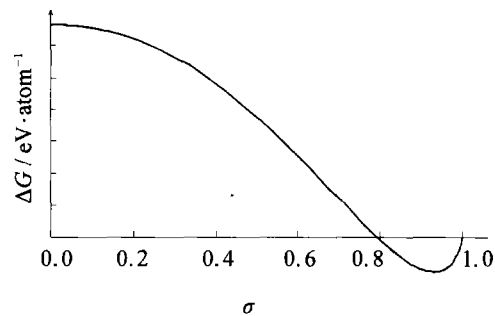


Figure 8 Gibbs free energy change with long-range order (semi-ordered alloy) parameters at  $T = 0$  K based on EAM.

It is found that the  $E_2$  coefficient has a significant effect on the characteristics of order-disorder transformation and as it can be seen from equations (14) and (20),  $E_2$  has a very straight relation with the ordering energy. It has been shown that the ordering energy is highly sensitive to the variation of the lattice parameter [14]. This would tend to suggest that the lattice parameter variation have specific effects on the order-disorder transition.

### 5 Conclusions

- (1) For  $AB$  alloy, the order-disorder transformation

is a second order transition.

(2) For  $A_3B$  or  $AB_3$  alloys following the values of  $E_2$ ,  $E_3$ , three kinds of order-disorder transformation must be considered:

For group I, the order-disorder transformation is a completely first-order transition;

For group II, condition II involves the formation of 3 stages of order-disorder transformation due to the effect of increasing temperature. The order-disorder transformation is a classical first-order transition. At  $T = T_c$ , as the ordered state  $I$  ( $\sigma \neq 0$ ) is in thermodynamic equilibrium with the disordered state  $I'$  ( $\sigma = 0$ ), this equilibrium can be described by Landau's Theory [15].

If we consider  $T$  greater than  $T_c$  there exists a metastable ordered state  $\sigma = \sigma' \neq 0$ . Below  $T_c$ , for temperature  $T_1 < T < T_c$ , the free energy change as function of  $\sigma$  curves exhibits a thermodynamic barrier between the undercooled disordered state ( $\sigma = 0$ ) and the ordered state ( $\sigma = \sigma' \neq 0$ ). In the temperature range  $T_1 < T < T_c$ , an undercooled disordered phase can only order heterogeneously by nucleation and growth.

For group III, the order-disorder transformation is a second-order transition. The  $E_2$  coefficient has a significant effect on the type of order-disorder transition, this result is in agreement with that obtained by Taylor

and Jones [14].

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