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THE DIFFUSION IN FCC BINARY INTERSTITIAL ALLOY

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Abstract. We build the theory of diffusion for FCC binary interstitial alloy under pressure based on the statistical moment method, where there are the analytic expressions of the jumping frequency of interstitial atom, the effective jumping length, the correlation factor, the diffusion coefficient, and the activated energy. In limit cases, we can obtain the diffusion theory for FCC metal A under pressure.

Keywords: binary interstitial alloy, jumping frequency, effective jumping length, correlation factor, diffusion coefficient, activated energy, statistical moment method.

1. Introduction

Study on the diffusion of metals and interstitial alloys pays attention to many researchers [1-10]. The phenomenon of the diffusion of atoms in a crystal is one of the very important problems of solid state physics and material science [1-7]. For alloys in general and interstitial alloys in particular, there are two basic mechanisms of diffusion. This is the substitutional mechanism and the interstitial mechanism. The mechanisms of diffusion depend on every material and doped impurity. In studying the process of diffusion, the most important parameters are the activated energy and the diffusion coefficient. Determining the diffusion coefficient of atoms in a crystal is a very complex problem because processes of diffusion depend on many different conditions. In order to obtain exact results of the diffusion coefficient theoretically, it is necessary to solve some basic problems such as the theory of atomic cohesion in crystal, the theory of crystals with defects, the theory of lattice vibration, etc. These problems are studied by many different methods such as the Einstein model, the method of reaction rate, the atomic kinetics method, etc. However, these methods only consider the diffusion qualitatively and meet many mathematical difficulties because exist many approximations especially for alloy models such as interstitial alloys. The structural, thermodynamic, and elastic

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properties, the phase transition, and the diffusion of metals and alloys are investigated by the statistical moment method [11-13].

The statistical moment method is used to study the diffusion in metals, binary substitutional alloys with FCC and BCC structures, binary interstitial alloys, and ternary interstitial and substitutional alloys with BCC structure. The study on diffusion in binary interstitial alloys and ternary interstitial and substitutional alloys with FCC structure is an open problem. Therefore, in this paper, we will build the theory of diffusion for FCC binary interstitial alloys. Concretely by the SMM, we can derive the analytic expressions of the free energy of the interstitial atom, the nearest neighbor distance between two interstitial atoms, the cohesive energy and the alloy parameters for interstitial atom, the diffusion quantities such as the jumping frequency of interstitial atom, the effective jumping length, the correlation factor, the diffusion coefficient, and the activated energy together with the equation of state for FCC interstitial alloy under pressure.

2. Content

2.1. Model of calculation

In the model of interstitial alloy AB with FCC structure, the main atoms A with large size are in peaks and face centers, the interstitial atom B with smaller is in body center of the cubic unit cell with the $c_B << c_A$ (c_A, c_B respectively are the concentrations of atoms A, B). In this model, atom B from the body center (position 1) moves through the middle of the cell side (position 2) to the next body center. In this way, the atom B can move to 12 positions. The free energy of an interstitial atom B in the FCC interstitial alloy AB is determined by [12]

$$\psi \approx U_0 + 3\theta\left[x + \ln\left(1 - e^{-2x}\right)\right] + 3\left\{\frac{\theta^2}{k^2}\left[\gamma_2 x^2 cth^2 x - \frac{2\gamma_1}{3}\left(1 + \frac{xcthx}{2}\right)\right] + \right.$$

$$\left. + \frac{2\theta^3}{k^4}\left[\frac{4}{3}\gamma_2^2 xcthx\left(1 + \frac{xcthx}{2}\right) - 2\left(\gamma_1^2 + 2\gamma_1\gamma_2\right)\left(1 + \frac{xcthx}{2}\right)\left(1 + xcthx\right)\right]\right\} \quad (1)$$

in the anharmonic approximation or

$$\psi = 3\left\{\frac{u_0}{6} + \theta\left[x + \ln\left(1 - e^{-2x}\right)\right]\right\}, U_0 = \frac{u_0}{2} \quad (2)$$

in the harmonic approximation.

Here, $\theta = k_{Bo}T, k_{Bo} = 1,38.10^{-23}$ J/K $= 1,38.10^{-16}$ erg/K is the Boltzmann constant, $x = \frac{\hbar}{2k_B T}\sqrt{\frac{k}{m}}, \hbar = 1,055096.10^{-34}$ Js $= 1,055096.10^{-27}$ erg.s is the Planck constant, m is the mass of the atom, T is the temperature, u_0 is the cohesive energy, k, γ_1, γ_2 are crystal parameters. Therefore, in order to the free energy of interstitial atom B it is necessary to determine the quantities U_{0B} and k_B at temperature T. To do that, we must calculate the nearest neighbor distances $r_{1B}(0,0)$ and $r_{1B}(0,T)$ between two atoms B in alloy at zero

pressure and zero temperature and at zero pressure and temperature T from the equation of state or from the minimum condition of the cohesive energy.

When the interstitial atom B is in position 1 and in the approximation of three coordination spheres [12, 13]

$$U_{01B} = 6\varphi_{AB}(r_{1B}) + 8\varphi_{AB}(r_{2B}) + 16\varphi_{AB}(r_{3B}), r_{2B} = \sqrt{3}r_{1B}, r_{3B} = \sqrt{5}r_{1B}, \tag{3}$$

$$k_{1B} = \frac{d^2\varphi_{AB}(r_{1B})}{dr_{1B}^2} + \frac{2}{r_{1B}}\frac{d\varphi_{AB}(r_{1B})}{dr_{1B}} + \frac{4}{3}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2} + \frac{8}{3r_{2B}}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}} + \\ + \frac{18}{5}\frac{d^2\varphi_{AB}(r_{3B})}{dr_{3B}^2} + \frac{22}{5r_{3B}}\frac{d\varphi_{AB}(r_{3B})}{dr_{3B}}, \tag{4}$$

$$\gamma_{11B} = \frac{1}{24}\frac{d^4\varphi_{AB}(r_{1B})}{dr_{1B}^4} + \frac{1}{4r_{2B}^2}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2} - \frac{1}{4r_{2B}^3}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}} + \\ + \frac{1}{54}\frac{d^4\varphi_{AB}(r_{2B})}{dr_{2B}^4} + \frac{2}{9r_{2B}}\frac{d^3\varphi_{AB}(r_{2B})}{dr_{2B}^3} - \frac{2}{9r_{2B}^2}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2} + \frac{2}{9r_{2B}^3}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}} + \\ + \frac{11}{100}\frac{d^4\varphi_{AB}(r_{3B})}{dr_{3B}^4} + \frac{6}{25r_{3B}}\frac{d^3\varphi_{AB}(r_{3B})}{dr_{3B}^3} - \frac{1}{20r_{3B}^2}\frac{d^2\varphi_{AB}(r_{3B})}{dr_{3B}^2} + \frac{1}{20r_{3B}^3}\frac{d\varphi_{AB}(r_{3B})}{dr_{3B}}, \tag{5}$$

$$\gamma_{21B} = \frac{1}{2r_{1B}}\frac{d^3\varphi_{AB}(r_{1B})}{dr_{1B}^3} - \frac{3}{4r_{1B}^2}\frac{d^2\varphi_{AB}(r_{1B})}{dr_{1B}^2} + \frac{3}{4r_{1B}^3}\frac{d\varphi_{AB}(r_{1B})}{dr_{1B}} + \\ + \frac{1}{9}\frac{d^4\varphi_{AB}(r_{2B})}{dr_{2B}^4} - \frac{2}{3r_{2B}^2}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2} - \frac{2}{3r_{2B}^3}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}} + \\ + \frac{4}{25}\frac{d^4\varphi_{AB}(r_{3B})}{dr_{3B}^4} + \frac{11}{25r_{3B}}\frac{d^3\varphi_{AB}(r_{3B})}{dr_{3B}^3} + \frac{1}{5r_{3B}^2}\frac{d^2\varphi_{AB}(r_{3B})}{dr_{3B}^2} - \frac{1}{5r_{3B}^3}\frac{d\varphi_{AB}(r_{3B})}{dr_{3B}}, \tag{6}$$

$$\gamma_{1B} = 4(\gamma_{11B} + \gamma_{21B}). \tag{7}$$

When the interstitial atom B is in position 2 and in the approximation of three coordination spheres,

$$U_{02B} = 6\varphi_{AB}(r_{1B}) + 8\varphi_{AB}(r_{2B}) + 16\varphi_{AB}(r_{3B}), r_{2B} = \sqrt{3}r_{1B}, r_{3B} = \sqrt{5}r_{1B}, \tag{8}$$

$$k_{2B} = \frac{d^2\varphi_{AB}(r_{1B})}{dr_{1B}^2} + \frac{2}{r_{1B}}\frac{d\varphi_{AB}(r_{1B})}{dr_{1B}} + \frac{4}{3}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2} + \frac{8}{3r_{2B}}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}} + \\ + 2\frac{d^2\varphi_{AB}(r_{3B})}{dr_{3B}^2} + \frac{6}{r_{3B}}\frac{d\varphi_{AB}(r_{3B})}{dr_{3B}}, \tag{9}$$

$$\gamma_{12B} = \frac{1}{24}\frac{d^4\varphi_{AB}(r_{1B})}{dr_{1B}^4} + \frac{1}{4r_{1B}^2}\frac{d^2\varphi_{AB}(r_{1B})}{dr_{1B}^2} - \frac{1}{4r_{1B}^3}\frac{d\varphi_{AB}(r_{1B})}{dr_{1B}} + \\ + \frac{1}{54}\frac{d^4\varphi_{AB}(r_{2B})}{dr_{2B}^4} + \frac{2}{9r_{2B}}\frac{d^3\varphi_{AB}(r_{2B})}{dr_{2B}^3} - \frac{2}{9r_{2B}^2}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2} + \frac{2}{9r_{2B}^3}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}} +$$

$$+\frac{17}{300}\frac{d^4\varphi_{AB}(r_{3B})}{dr_{3B}^4}+\frac{4}{25r_{3B}}\frac{d^3\varphi_{AB}(r_{3B})}{dr_{3B}^3}+\frac{7}{20r_{3B}^2}\frac{d^2\varphi_{AB}(r_{3B})}{dr_{3B}^2}-\frac{7}{20r_{3B}^3}\frac{d\varphi_{AB}(r_{3B})}{dr_{3B}}, \tag{10}$$

$$\gamma_{22B}=\frac{1}{2r_{1B}}\frac{d^3\varphi_{AB}(r_{1B})}{dr_{1B}^3}-\frac{3}{4r_{1B}^2}\frac{d^2\varphi_{AB}(r_{1B})}{dr_{1B}^2}+\frac{3}{4r_{1B}^3}\frac{d\varphi_{AB}(r_{1B})}{dr_{1B}}+$$
$$+\frac{1}{9}\frac{d^4\varphi_{AB}(r_{2B})}{dr_{2B}^4}+\frac{2}{3r_{2B}^2}\frac{d^2\varphi_{AB}(r_{2B})}{dr_{2B}^2}-\frac{2}{3r_{2B}^3}\frac{d\varphi_{AB}(r_{2B})}{dr_{2B}}+$$
$$+\frac{4}{25}\frac{d^4\varphi_{AB}(r_{3B})}{dr_{3B}^4}+\frac{1}{25r_{3B}}\frac{d^3\varphi_{AB}(r_{3B})}{dr_{3B}^3}+\frac{7}{5r_{3B}^2}\frac{d^2\varphi_{AB}(r_{3B})}{dr_{3B}^2}-\frac{7}{5r_{3B}^3}\frac{d\varphi_{AB}(r_{3B})}{dr_{3B}}, \tag{11}$$

$$\gamma_{2B}=4(\gamma_{12B}+\gamma_{22B}). \tag{12}$$

If knowing the interaction potentials $\varphi_{AA},\varphi_{BB}$, we can determine the interaction potential φ_{AB} in the alloy AB as follows:

$$\varphi_{AB}=\frac{1}{2}(\varphi_{AA}+\varphi_{BB}). \tag{13}$$

Approximately, the mean nearest neighbor distance between two atoms in the alloy is equal to one in the pure metal A.

The equation of state for metal A with FCC structure at pressure *P* and temperature *T* is described by [12]

$$Pv=-r_1\left(\frac{1}{6}\frac{\partial u_0}{\partial r_1}+\theta xcthx\frac{1}{2k}\frac{\partial k}{\partial r_1}\right), \tag{14}$$

where $v=\frac{r_1^3\sqrt{2}}{2}$ a nd using $\frac{\partial x}{\partial r_1}=\frac{x}{2k}\frac{\partial k}{\partial r_1}$. At 0K, the eq. (14) has the form

$$Pv=-r_1\left(\frac{1}{6}\frac{\partial u_0}{\partial r_1}+\frac{\hbar\omega_0}{2k}\frac{\partial k}{\partial r_1}\right). \tag{15}$$

If knowing the form of potential, the eq. (15) allows us to calculate the nearest neighbor distance between two atoms in the alloy at 0K and pressure *P*.

Analogously, we can find the nearest neighbor distance beween two interstitial atoms $r_{1B}(P,0)$ and $r_{1B}(P,T)$, the free energy of interstitial atom at pressure *P* and temperature *T* and the alloy parameters for interstitial atom in the positions 1, 2 in the alloy AB at 0K and pressure *P*.

When the diffusion happens in the interstitial mechanism, the diffusion coefficient of the alloy AB has the form [11]

$$D=g\Gamma a^2, \tag{16}$$

where Γ is the jumping frequency, *a* is the effective jumping length and *g*is the factor depending on the crystal structure, temperature, diffusion mechanism and is determined by

$$g=n_1 f \tag{17}$$

where f is the correlation factor and n_1 is the number of nearest positions where the diffusion atom (interstitial atom) B can jump in. If positions, where the interstitial atom B can jump in, have the same probabilities, $f = 1$. Because near positions where the interstitial atom B can jump in have larger probabilities than far positions, $f < 1$ and approximately f is determined by

$$f \approx \left(1-\frac{1}{n_1}\right)^2 \approx 1-\frac{2}{n_1}. \tag{18}$$

For FCC lattice, $n_1 = 12$, $f = 0.83$.

The jumping frequency of the interstitial atom C is given by

$$\Gamma = \frac{\omega}{2\pi}\exp\left(-\frac{\Delta\psi}{k_{Bo}T}\right), \omega = \sqrt{\frac{k_B}{m_B}}, \Delta\psi = \psi_B^* - \psi_B, \tag{19}$$

where ψ_B^* is the free energy of the interstitial atom B in position 1 and ψ_B is the free energy of the interstitial atom B in position 2.

The effective jumping length for FCC lattice is equal to

$$a = r_1 + r_2 \tag{20}$$

The diffusion coefficient has the form [8]

$$D = D_0 \exp\left(-\frac{E}{k_{Bo}T}\right), \tag{21}$$

where

$$D_0 = n_1 f a^2 \frac{\omega}{2\pi} \tag{22}$$

and

$$E = \Delta\psi \tag{23}$$

is the activated energy.

When the concentration of interstitial atoms B changes, the effective jumping length of a changes and the pre-exponential of D_0 changes. Approximately,

$$r_B = c_A r_A^* + c_B r_B^* = (1-c_B) r_A^* + c_B r_B^*, r_A^* = \frac{r_A}{\sqrt{2}} \tag{24}$$

where c_A, c_B are the concentrations of atoms A, B, r_A is the nearest neighbor distance between two atoms A in pure metal, r_A^* is the nearest neighbor distance between two atoms A in the alloy AB, r_B^* is the nearest neighbor distance between the atom B and the atoms A in the alloy AB, r_B is the nearest neighbor distance between two atoms B. From that, we can calculate the quantities r_{1B}, r_{2B} corresponding to positions 1, 2, and the effective jumping length $a = r_{1B} + r_{2B}$. Then we find the dependence of the factors D_0, D on the concentration of interstitial atoms B.

After calculating the nearest neighbor distances in positions 1, 2, we can find the diffusion quantities such as the effective jumping length, the jumping frequency, the activated energy, the pre-exponential factor, and the diffusion coefficient.

In the case when the concentration of interstitial atoms is equal to zero, we obtain the diffusion theory for the FCC main metal A [11].

3. Conclusions

By SMM we derive the analytic expressions of the free energy of the interstitial atom, the nearest neighbor distance between two interstitial atoms, the cohesive energy and the alloy parameters for interstitial atom, the diffusion quantities such as the jumping frequency of interstitial atom, the effective jumping length, the correlation factor, the diffusion coefficient, and the activated energy together with the equation of state depending on temperature, pressure and constitution concentration for FCC interstitial AB. In limit cases, we can obtain the diffusion theory for the metal A with FCC structure under pressure.

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