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CALCULATION MORSE POTENTIAL PARAMETERS UNDER TEMPERATURE AND PRESSURE EFFECTS IN EXPANDED X-RAY ABSORPTION FINE STRUCTURE SPECTRA

Nguyen Ba Duc[1,*], *Trinh Phi Hiep*[1], *Vu Quang Tho*[1], *Nguyen Van Thu*[2]

[1] *Tan Trao University, Tuyen Quang, Viet Nam*

[2] *Ha Noi Pedagogical University 2*

[*] *Email: ducnb@daihoctantrao.edu.vn*

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Abstract:

A new method for estimating the effective parameters of Morse potential under thermal disorder and pressure effects for materials has crystals structure developed by using the energy of sublimation, the compressibility, and the lattice constant. Use the Morse potential parameters received to calculate the mean square relative displacement, spring constants, anharmonic interatomic effective potential, and local force constant for silicic and germanium semiconductor crystals, are the materials have diamond structure crystals. The received results suitable for the experimental values and other theories.

1. Introduction

In EXAFS spectra with the anharmonic effects, the anharmonic Morse potential [1] is suitable for describing the interaction and oscillations of atoms in the crystals [2-7]. In the EXAFS theory, photoelectron emitted from an absorber scattered by surrounded vibrating atoms [1,2]. This thermal oscillation of atoms contributes to the EXAFS spectra, especially the anharmonic EXAFS [2-7], which is affected by these spectra's physical information. In the EXAFS spectrum analysis, the parameters of Morse potential is usually extracted from the experiment. Still, experimental data are not available in many cases, so a theory is necessary to deduce Morse's potential value. The only calculation has been carried out for cubic crystals [8]. The results have been used actively for calculations EXAFS thermodynamic parameters [6] and reasonable with those extracted from EXAFS data [9] using anharmonic correlated Einstein model [8]. Therefore, the requirement for calculation of the anharmonic Morse interaction potential due to thermal disorder for other structures is essential.

The purpose of this study is to expand a method for calculating the Morse potential parameters using the energy of sublimation, the compressibility, and the lattice constant with the effect of the disorder of temperature, the application for diamond (DIA) structure crystals. The obtained results applied to the equation of state, mean square relative displacement, spring constants, the effective anharmonic potential, and local force constant. Numerical calculations have carried out for Silicium (Si), Germanium (Ge), and SiGe semiconductor, which are suitable for the experimental values [10], [11].

2. Formalism

The ε(r_{ij}) potential of atoms i and j separated by a distance r_{ij} is given in by the Morse function:

$$\varepsilon(r_{ij}) = D\left\{ e^{-2\alpha(r_{ij}-r_o)} - 2e^{-\alpha(r_{ij}-r_o)} \right\} , \quad (1)$$

where 1/α describes the width of the potential, D is the dissociation energy (ε(r_0) = - D); r_0 is the equilibrium distance of the two atoms.

To obtain the potential energy of a large crystal whose atoms are at rest, it is necessary to sum Eq. (1) over the entire crystal. It is quickly done by selecting an atom in the lattice as origin, calculating its interaction with all others in the crystal, and then multiplying by N/2, where N is the total number of atoms in a crystal. Therefore, the potential E is given by:

$$E = \frac{1}{2} ND \sum_j \left\{ e^{-2\alpha(r_j-r_o)} - 2e^{-\alpha(r_j-r_o)} \right\} . \quad (2)$$

Here r_j is the distance from the origin atom to the jth atom. It is beneficial to describe the following quantities:

$$r_j = \left[m_j^2 + n_j^2 + l_j^2\right]^{1/2} a = M_j a , \quad (3)$$

where m_j, n_j, l_j are position coordinates of atoms in the lattice. Substitute the Eq. (3) into Eq. (2), the potential energy can be rewritten as:

$$E(a) = \frac{1}{2} NDe^{\alpha r_0}\left[e^{\alpha r_0} \sum_j e^{-2\alpha a M_j} - 2\sum_j e^{-\alpha a M_j} \right] (4)$$

The first and second derivatives of the potential energy of Eq. (4) concerning a, we have:

$$\frac{dE}{da} = -\alpha NDe^{\alpha r_0}\left[e^{\alpha r_0} \sum_j M_j e^{-2\alpha a M_j} + \sum_j M_j e^{-\alpha a M_j} \right] , \quad (5)$$

$$\frac{d^2E}{da^2} = \alpha^2 NDe^{\alpha r_0}\left[2e^{\alpha r_0} \sum_j M_j^2 e^{-2\alpha a M_j} - \sum_j M_j^2 e^{-\alpha a M_j} \right] . \quad (6)$$

At absolute zero T=0, a_0 is the value of a for which the lattice is in equilibrium, then E(a_0) gives the energy of cohesion, $\left[\frac{dE}{da}\right]_{a_0} = 0$, and $\left[\frac{d^2E}{da^2}\right]_{a_0}$ is related to the compressibility [10].

That is,

$$dE(a_0) = E_0(a_0) , \quad (7)$$

where $E_0(a_0)$ is the energy of sublimation at zero pressure and temperature,

$$\left(\frac{dE}{da}\right)_{a_0} = 0 , \quad (8)$$

and the compressibility is given by [8]

$$\frac{1}{\kappa_0} = V_0\left(\frac{d^2E_0}{dV^2}\right)_{a_0} = V_0\left(\frac{d^2E}{dV^2}\right)_{a_0} , \quad (9)$$

where V_0 is the volume at T = 0 and κ_0 is compressibility at zero temperature and pressure.

The volume per atom N/V is related to the lattice constant a by

$$\frac{V}{N} = ca^3 . \quad (10)$$

Substituting Eq. (10) into Eq. (9) the compressibility is formulated by

$$\frac{1}{\kappa_0} = \frac{1}{9cNa_0}\left(\frac{d^2E}{da^2}\right)_{a=a_0} . \quad (11)$$

Using Eq. (5) to solve Eq. (8) we obtain

$$e^{\alpha r_0} = \frac{\sum_j M_j e^{-\alpha a M_j}}{\sum_j M_j e^{-2\alpha a M_j}} . \quad (12)$$

From Eqs. (4, 6, 7, 11) we derive the relation

$$\frac{e^{\alpha r_0}\sum_j e^{-2\alpha a M_j} - 2\sum_j e^{-\alpha a M_j}}{4\alpha^2 e^{\alpha r_0}\sum_j M_j^2 e^{-2\alpha a M_j} - 2\alpha^2 \sum_j M_j^2 e^{-\alpha a M_j}} = \frac{E_0\kappa_0}{9cNa_0} . \quad (13)$$

Solving the system of Eq. (12, 13) we obtain α and r_0. Using α and Eq. (4) to solve Eq. (7) we receive D. The obtained Morse potential parameters D, α depends on the compressibility κ_0, the energy of sublimation E_0 and the lattice constant a. These values of all crystals are available already [12].

Next, apply the above expressions to the equation of state and elastic constants. It is possible to calculate the state equation from the potential energy E. If we assumed that the Debye model could express the thermal section of the free energy, then the Helmholtz energy is given by [8]

$$F = E + 3Nk_B T \ln\left(1 - e^{-\theta_D / T}\right) - Nk_B T D(\theta_D / T) \quad , \tag{14}$$

$$D\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \, , \tag{15}$$

where k_B is Boltzmann constant, θ_D is Debye temperature.

Using Eqs. (14, 15) we derive the equation of state as

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3ca^2}\frac{dE}{da} + \frac{3\gamma_G RT}{V} D\left(\frac{\theta_D}{T}\right) \tag{16}$$

where γ_G is the Grüneisen parameter, V is the volume.

After transformations, the Eq. (16) is resulted as

$$P = \frac{\left[NDe^{\alpha r_0}\alpha \sum_j M_j e^{-\alpha a_0 M_j (1-x)^{1/3}}\right]}{3ca_0^2 (1-x)^{2/3}} - NDe^{2\alpha r_0}\alpha \sum_j M_j e^{-2\alpha a_0 M_j (1-x)^{1/3}} + \frac{3\gamma_G RT}{V_0 (1-x)} D\left(\frac{\theta_D}{T}\right), \tag{17}$$

$$x = \frac{V_0 - V}{V_0}, \ V_0 = ca_0^3, \ R = Nk_B, \ N = 6.02 \times 10^{23} . \tag{18}$$

The equation of state (17) contains the obtained Morse potential parameters, c is a constant and has value according to the structure of the crystal.

Elastic properties of a crystal described by an elastic tensor contained in the motion equation of the crystal. The non-vanishing elements of the elastic tensor defined as elastic constants. They are given for DIA structure crystals by [13]

$$c_{11} = c_{22} = \sqrt{2} r_0 \left[10\Psi''\left(r_0^2\right) + 16\Psi''\left(2r_0^2\right) + 81\Psi''\left(3r_0^2\right)\cdots\right] - \frac{\left\{\sqrt{\frac{2}{3}}\left[-2\Psi''\left(r_0^2\right) + 16\Psi''\left(2r_0^2\right) - 40\Psi''\left(3r_0^2\right)\cdots\right]\right\}^2}{\sqrt{2} r_0^{-1}\left[4\Psi''\left(r_0^2\right) + 16\Psi''\left(2r_0^2\right) + 12 r_0^{-1}\Psi'\left(2r_0^2\right)\cdots\right]}, \tag{19}$$

$$c_{12} = \frac{\sqrt{2} r_0 \left[10\Psi''\left(r_0^2\right) + 16\Psi''\left(2r_0^2\right) + 81\Psi''\left(3r_0^2\right)\cdots\right]}{3} + \frac{\left\{\sqrt{\frac{2}{3}}\left[-2\Psi''\left(r_0^2\right) + 16\Psi''\left(2r_0^2\right) - 40\Psi''\left(3r_0^2\right)\cdots\right]\right\}^2}{\sqrt{2} r_0^{-1}\left[4\Psi''\left(r_0^2\right) + 16\Psi''\left(2r_0^2\right) + 12 r_0^{-1}\Psi'\left(2r_0^2\right)\cdots\right]}, \tag{20}$$

$$c_{33} = \frac{\sqrt{2}}{3} r_0 \left[32\Psi''\left(r_0^2\right) + 32\Psi''\left(2r_0^2\right) + \frac{512}{3}\Psi''\left(3r_0^2\right) + \cdots\right], \tag{21}$$

$$c_{13} = c_{23} = \sqrt{2} r_0 \left[8\Psi''\left(r_0^2\right) + 32\Psi''\left(2r_0^2\right) + 112\Psi''\left(3r_0^2\right) + \cdots\right], \tag{22}$$

$$\Psi'(r) = -2D\alpha\left[e^{-2\alpha(r-r_0)} - e^{-\alpha(r-r_0)}\right]\frac{1}{r} \ , \tag{23}$$

$$\Psi''(r) = D\alpha^2\left[2e^{-2\alpha(r-r_0)} - \frac{1}{2}e^{-\alpha(r-r_0)}\right]\frac{1}{r^2} + D\alpha\left[e^{-2\alpha(r-r_0)} - e^{-\alpha(r-r_0)}\right]\frac{1}{2r^3} . \tag{24}$$

Hence, the derived elastic constants contain the Morse potential parameters.

Next, apply to calculate of anharmonic interatomic effective potential and local force constant in EXAFS theory. The expression for the anharmonic EXAFS function [2] is described by

$$\chi(k) = A(k)\frac{\exp[-2\Re / \lambda(k)]}{k\Re^2} \operatorname{Im}\left\{e^{i\varphi(k)} \exp\left[2ik\Re + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)}\right]\right\}, \tag{25}$$

where A(k) is scattering amplitude of atoms, φ(K) is the total phase shift of photoelectron, k and λ are wave number and mean free path of the photoelectron, respectively. The $\sigma^{(n)}$ is the cumulants to describe asymmetric of anharmonic Morse potential, and they appear due to being average of the function e^{-2ikr}, in which expanded of the asymmetric terms in a Taylor series around value $\Re$ = <r>, with r is the instantaneous bond length between absorber and backscatter atoms at T temperature.

For describing anharmonic EXAFS, effective anharmonic potential [6] of the system is derived which in the current theory is expanded up to the third - order and given by

$$E_{eff}(x) = \frac{1}{2}k_{eff}x^2 + k_3x^3 + \ldots + = E(x) + \sum_{j\neq i} E\left(\frac{\mu}{M_i}x\hat{\Re}_{12}.\hat{\Re}_{ij}\right), \qquad \mu = \frac{M_1M_2}{M_1+M_2}; \quad \hat{\Re} = \frac{\Re}{|R|}. \tag{26}$$

Here k_{eff} is the effective local force constant, and k_3 is the cubic parameter characterizing the asymmetry in the pair Morse potential, x is the deviation of instantaneous bond length between the two atoms from equilibrium. The correlated model defined as the oscillation of a pair of particles with M_1 and M_2 mass. Their vibration influenced by their neighbours atoms given by the sum in Eq. (24), where the sum i is over absorber (i = 1), and backscatter (i = 2), and the sum j is overall their near neighbours, excluding the absorber and backscatter themselves. The advantage of this model is a calculation based on including the contributions of the nearest neighbours of absorber and backscatter atoms in EXAFS.

For DIA structure crystals, the anharmonic interatomic effective potential Eq. (24) has the form

$$E_{eff}(x) = E_x(x) + 2E_x(-\frac{x}{2}) + 8E_x(-\frac{x}{4}) + 8E_x(\frac{x}{4}). \tag{27}$$

Applying Morse potential given by Eq. (1) expanded up to 4th order around its minimum point

$$E_{eff}(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D\left(-1 + \alpha^2x^2 - \alpha^3x^3 + \frac{7}{12}\alpha^4x^4\ldots\right). \tag{28}$$

From Eqs. (26)-(28), we obtain the anharmonic effective potential E_{eff}, effective local force constant k_{eff}, anharmonic parameters k_3, k_4 for DIA crystals presented in terms of our calculated Morse potential parameters D and α.

3. Numerical results and discussion

To receive the Morse potential parameters, we need to calculate the parameter c in Eq. (10). The space lattice of the diamond is the fcc. The primordial basis has two identical atoms at 0 0 0, ¼ ¼ ¼ connected with each point of the fee lattice. Thus, the conventional unit cube contains eight atoms so that we obtain the value c = 1/4 for this structure.

Apply the above-derived expressions to numerical calculations for DIA structure crystals (Si, Ge and SiGe) using the energy of sublimation [10], the compressibility [14] and the lattice constants [11], as well as, the values of θ_D and D [10,15,16].

The numerical results of Morse potential parameters showed in Table 1. The theory values of α fit well with the measured experiment [10]. The elastic constants calculated by Morse potential parameters for Si and Ge are presented in Table 2 and compared to the experimental values [11].

Table 1: *Morse potential parameters D, α and the related parameter r_0 of Si, Ge and SiGe in comparison to some experimental results [10].*

Crystal	β	α (Å^{-1})	D(eV)	r_0 (Å)
Si (Present)	120.110	1.3642	0.9862	2.8429
Si (Expt.)	-	1.3106	-	2.7503

Ge (Present)	327.210	1.5569	0.9675	2.8319
Ge (Expt.)	-	1.4105	-	2.7442
SiGe (Present)	-	1.4606	0.9769	2.7934

Table 2: *Elastic constants ($\times 10^{-11}$N/m) of Si and Ge have calculated by Morse potential and comparison to experimental values [11].*

Crystal	c_{11}	c_{12}	c_{13}	c_{33}
Si (Present)	1.85	0.64	0.55	2.13
Si (Expt.)	1.77	0.41	0.61	1.54
Ge (Present)	1.46	0.57	0.46	1.63
Ge (Expt.)	1.35	0.52	0.52	0.57

The next application is to calculate the state equation. The computed results illustrated in Figure 1 for Si crystal, Figure 2 for Ge crystal, and compared with the experimental ones (dashed line) [10] represented by an extrapolation procedure of the measured data. The results show they suitable very good, especially at low pressure.

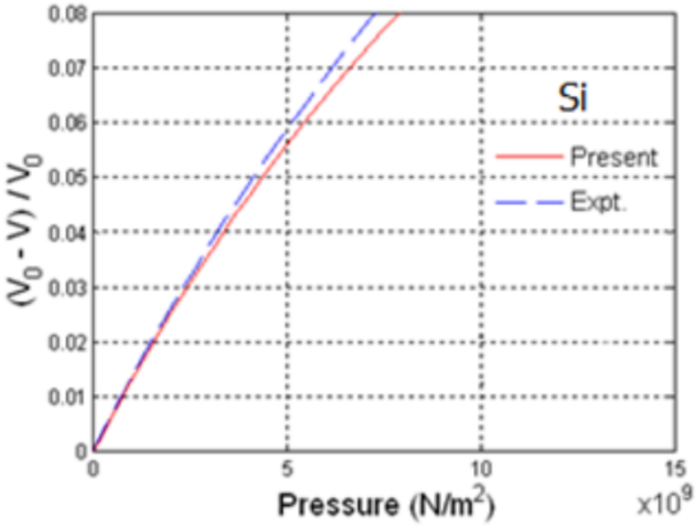

Figure 1. State equation for Si

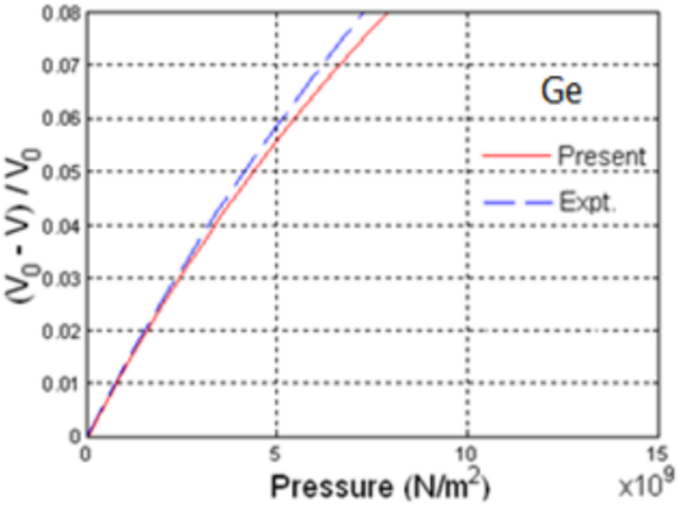

Figure 2. State equation for Ge

Figures 3 and 4 illustrate good agreement of the anharmonic interatomic effective potentials for Si, Ge and SiGe semiconductor calculated using the present theory (solid line). The Morse potential parameters presented in Table 1 and compared to experiment obtained from Morse potential parameters of J. C. Slater (symbol ☐) [10], and simultaneously shows strong asymmetry of these potentials due to the anharmonic contributions in atomic vibrations of these DIA structure crystals illustrate by their anharmonic shifting from the harmonic terms (dashed line).

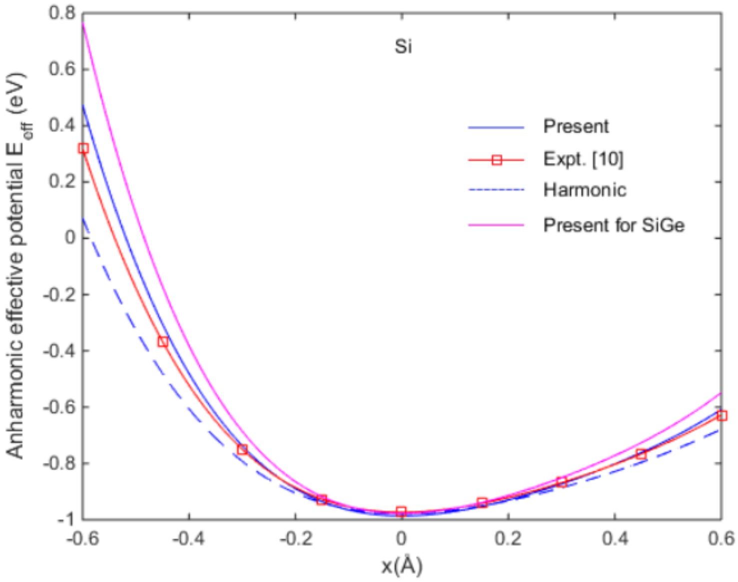

Figure 3. Anharmonic effective potential for Si, and SiGe semiconductor

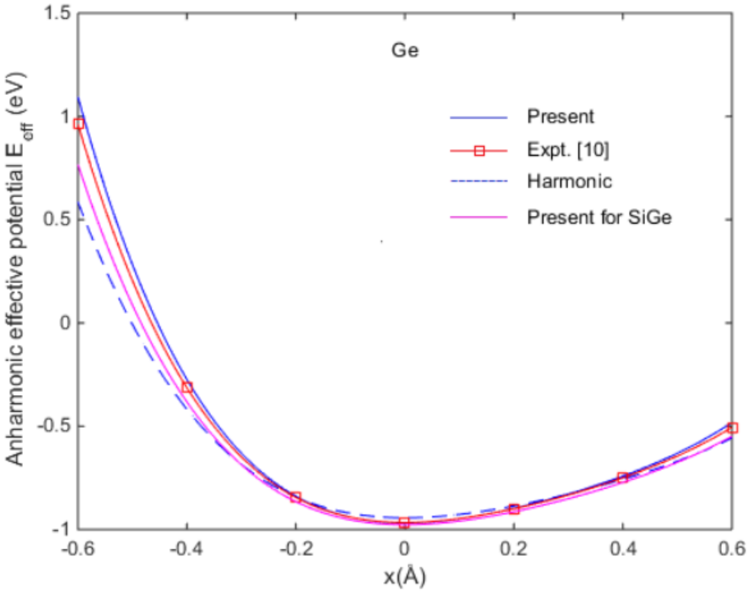

Figure 4. Anharmonic effective potential for Ge, and SiGe semiconductor

Figures 5, 6 shows the temperature and pressure dependence of mean square relative displacement σ2(T) and mean square displacement u2(T) for Si and Ge crystals. They show linear proportional to the temperature T at high temperatures, and the classical limit is applicable. At low temperatures, the curves for Si and Ge contain zero-point energy contributions - a quantum effect. Simultaneously, the values of σ2(T) are greater than the values of u2(T). The calculated results of σ2(T), u2(T) for the Si, Ge crystals fitting well with the experimental values [10]. Thus, it is possible to deduce that the calculation results of the present method for diamond structure crystals such as Si, Ge crystals are reasonable.

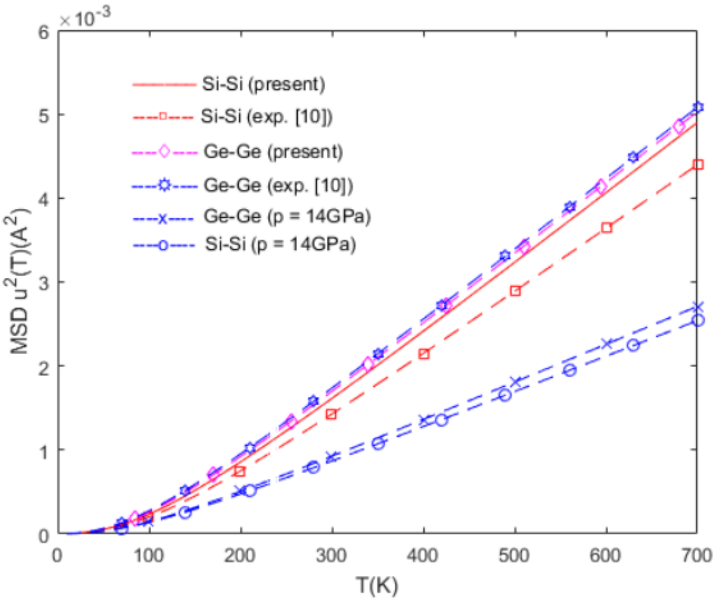

Figure 5. Mean square displacement dependence on temperature and pressure

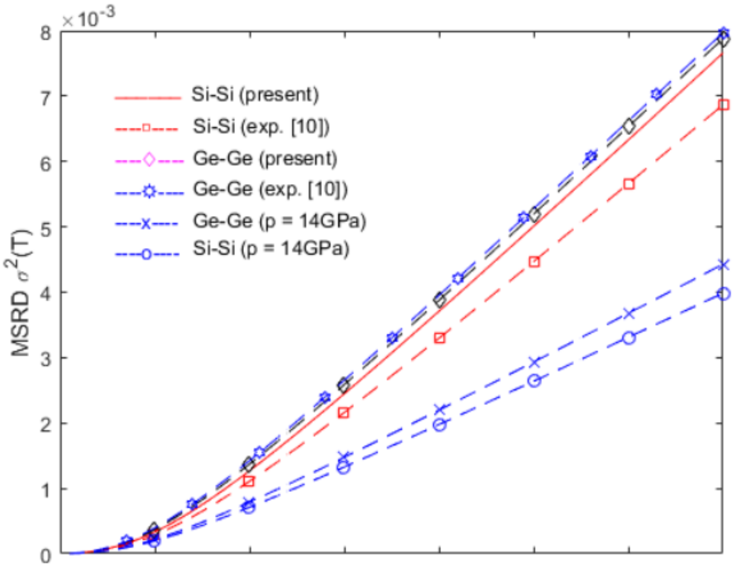

Figure 6. Mean square relative displacement dependence on temperature and pressure

4. Conclusions

In this work, a calculation method of Morse potential parameters and application for diamond structure crystals have been developed based on the calculation of volume and number of an atom in each basic cell and the sublimation energy, compressibility, and lattice constant. The results applied to the mean square relative displacement, mean square displacement, the state equation, the elastic constants, anharmonic interatomic effective potential, and local force constant in EXAFS theory. The derived expressions have programmed for the calculation of the above physical quantities.

Derived equation of state and elastic constants satisfy all standard conditions for these values, for example, all elastic constants are positive. The Morse potentials obtained satisfy all their basic properties. They are reasonable for calculating and analyzing the anharmonic interatomic effective potentials describing anharmonic effects in EXAFS theory. This procedure can be generalized to the other crystal structures based on calculating their volume and number of an atom in each elementary cell.

Reasonable agreement between our calculated results and the experimental data show the efficiency of the present procedure. The calculation of potential atomic parameters is essential for estimating and analyzing physical effects in the EXAFS technique. It can solve the problems involving any deformation and of atom interaction in the diamond structure crystals.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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TÍNH TOÁN CÁC THAM SỐ THẾ MORSE DƯỚI ẢNH HƯỞNG CỦA NHIỆT ĐỘ VÀ ÁP SUẤT TRONG PHỔ CẤU TRÚC TINH TẾ HẤP THỤ TIA X MỞ RỘNG

Nguyễn Bá Đức, Trịnh Phi Hiệp, Vũ Quang Thọ, Nguyễn Văn Thụ

Thông tin bài viết

Ngày nhận bài:
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Từ khóa:

Tham số thế Morse, phương trình trạng thái, hằng số lực hiệu dụng, hệ số đàn hồi, độ dịch chuyển tương đối trung bình phương

Tóm tắt

Một phương pháp mới để ước tính các tham số hiệu dụng của thế Morse dưới ảnh hưởng của rối loạn nhiệt và áp suất đối với các vật liệu có cấu trúc tinh thể được phát triển bằng cách sử dụng năng lượng thăng hoa, khả năng nén và hằng số mạng. Sử dụng các tham số thế Morse đã nhận được để tính toán độ dịch chuyển tương đối trung bình bình phương, hằng số đàn hồi, thế hiệu dụng phi điều hòa và hằng số lực đối với tinh thể bán dẫn silicic và germani, là những vật liệu có cấu trúc tinh thể kim cương. Các kết quả nhận được phù hợp với các kết quả của thực nghiệm và các lý thuyết khác.