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Calculation of Morse Potential for Diamond Crystals. Applification to Anharmonic Effective Potential

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Abstract. Analytical expressions for the Morse potential parameters of diamond crystals have been derived. They contain the energy of sublimation, the compressibility and the lattice constant. Numerical calculations have been carried out for Si and Sn, and the results reflect fundamental properties of this potential. The obtained Morse potential parameters have been used for calculation of the anharmonic correlated effective potentials of these crystals in XAFS theory showing clearly anharmonic effects .

1. Introduction

Interatomic anharmonic potential, especially Morse potential, has been studied widely [1-12]. The parameters of this potential can be extracted from the XAFS (*X-ray Absorption Fine Structure*) [11,12]. They are also used to calculate thermodynamic parameters included in these spectra [4-10]. This potential is successfully applied to calculating the quantities involving atomic interaction, especially, the anharmonic effects contained in XAFS [5-10] which influence on the physical information taken from these spectra. They are also contained in the expressions of equation of state [1]. Therefore, calculation of the Morse potential is very actually desired, especially in XAFS theory. The calculation of Morse potential has been carried out for fcc, bcc [1,22] and hcp [17,22] crystals.

The purpose of this work is to develop a method for calculation of Morse potential parameters of *Diamond,* an interesting crystal structure. Analytical expressions for the parameters of this potential have been derived. They contain the energy of sublimation, the compressibility and the lattice constant which are known already, for example see [13,18,21]. The obtained results are applied to calculating the anharmonic correlated effective potential, contained in the XAFS spectra [4-10,14]. Numerical calculations have been carried out for volume per atom, tructural parameters and Morse potential parameters of Diamond crystals Si and Sn. The obtained Morse potential parameters satisfy all fundamental properties of this potential [19] and have been applied to calculating anharmonic correlated effective potentials of these crystals in XAFS theory.

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2. Procedure for calculation of Morse potential of Diamond crystals

The potential energy $\varphi(r_{ij})$ of two atoms *i* and *j* separated by a distance r_{ij} is given in terms of the Morse function by

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

where α, D are constants with dimensions of reciprocal distance and energy, respectively; r_o is the equilibrium distance of the two atoms. Since $\varphi(r_o) = -D$, *D* is the disociation energy.

In order to obtain the potential energy of the whole crystal whose atoms are at rest, it is necessary to sum Eq. (1) over the entire crystal. This is most easily done by choosing one atom in the lattice as an orgin, calculating its interaction with all the others in the crystal, and then multiplying by $N/2$, where *N* is the total atomic number in the crystal. Thus the total energy Φ is given by

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

Here r_j is the distance from the origin to the *j*th atom. It is convenient to define the following quantities

$$L = \frac{1}{2}ND;\ \beta = e^{\alpha r_o};\ r_j = \left[m_j^2 + n_j^2 + l_j^2\right]^{1/2} a = M_j a, \tag{3}$$

where m_j, n_j, l_j are position coordinates of any atom in the lattice. Applying Eq. (3) to Eq. (2), the energy can be rewritten as

$$\Phi(a) = L\beta^2\sum_j e^{-2\alpha a M_j} - 2L\beta\sum_j e^{-\alpha a M_j}. \tag{4}$$

The first and second derivatives of the energy of Eq. (4) with respect to a are given by

$$\frac{d\Phi}{da} = -2\alpha L\beta^2\sum_j M_j e^{-2\alpha a M_j} + 2L\beta\alpha\sum_j M_j e^{-\alpha a M_j}, \tag{5}$$

$$\frac{d^2\Phi}{da^2} = 4\alpha^2 L\beta^2\sum_j M_j^2 e^{-2\alpha a M_j} - 2\alpha^2 L\beta\sum_j M_j^2 e^{-\alpha a M_j}. \tag{6}$$

At absolute zero T = 0, a_o is value of a for which the lattice is in equilibrium, then $\Phi(a_o)$ gives the energy of cohesion, $[d\Phi/da]_{a_0} = 0$, and $\left[d^2\Phi/da^2\right]_{a_0}$ is related to the compressibility [1]. That is,

$$\Phi(a_0) = U_0(a_0), \tag{7}$$

where $U_0(a_0)$ is the energy of sublimation at zero pressure and temperature, i., e.,

$$\left(\frac{d\Phi}{da}\right)_{a_0} = 0, \tag{8}$$

and the compressibility is given by [1]

$$\frac{1}{K_{00}} = V_0\left(\frac{d^2U_0}{dV^2}\right)_{a_0} = V_0\left(\frac{d^2\Phi}{dV^2}\right)_{a_0}, \tag{9}$$

where V_0 is the volume at T = 0, and K_{00} is compressibility at zero temperature and pressure. The volume per atom $v = V / N$ is related to the lattice constant a by the relation [1]

$$V / N = ca^3 \; . \tag{10}$$

Substituting Eq. (10) in Eq. (9) the compressibility is expressed by

$$\frac{1}{K_{00}} = \frac{1}{9cNa_0}\left(\frac{d^2\Phi}{da^2}\right)_{a=a_0} . \tag{11}$$

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

$$\beta = \sum_j M_j e^{-\alpha a M_j} / \sum_j M_j e^{-2\alpha a M_j} . \tag{12}$$

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

$$\frac{\beta \sum_j e^{-2\alpha a M_j} - 2\sum_j e^{-\alpha a M_j}}{4\alpha^2 \beta \sum_j M_j^2 e^{-2\alpha a M_j} - 2\alpha^2 \sum_j M_j^2 e^{-\alpha a M_j}} = \frac{U_0 K_{00}}{9cNa_0} . \tag{13}$$

Solving the system of Eqs. (12, 13) we obtain α, β. Substituting the obtained results into the second of Eq. (3) we derive r_0. Using the obtained α, β and Eq. (4) to solve Eq. (7) we obtain L. From this L and the first of Eq. (3) we obtain D. The obtained Morse potential parameters D, α depend on the compressibility K_{00}, the energy of sublimation U_0 and the lattice constant a. These values of about all crystals are known already [13,16,18,21].

3. Application to calculation of anharmonic correlated effective potential in XAFS

Figure 1 shows Fourier transform magnitudes of XAFS of Sn (Diamond), measured at 77K and 300K at HASYLAB (DESY, Germany) [20]. They are different at these temperatures by the shift of the curves showing anharmonic effects in XAFS. For describing these effects an anharmonic XAFS theory is necessary.

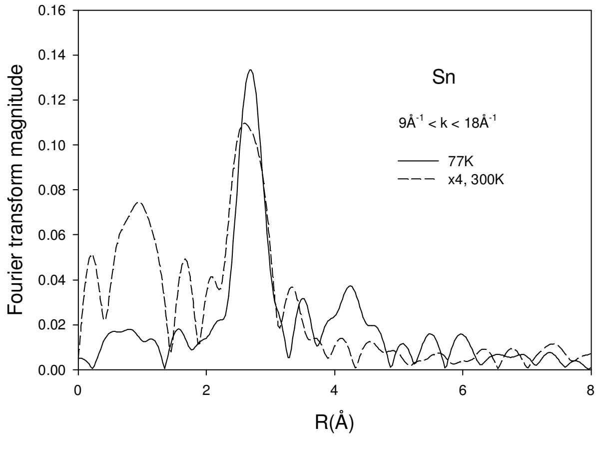

Fig. 1 Fourier transform magnitudes of XAFS of Sn at 77K and 300K.

The expression for the K-edge anharmonic XAFS function [10] is described by

$$\chi(k) = F(k)\frac{e^{-2R/\lambda(k)}}{kR^2}\mathrm{Im}\left\{e^{i\Phi(k)}\exp\left[2ikR + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)}\right]\right\}, \tag{15}$$

where $F(k)$ is the real atomic backscattering amplitude, Φ is net phase shift, k and λ are the wave number and the mean free path of the photoelectron, respectively, and $\sigma^{(n)}$ (n = 1,2,3, …) are the cumulants. The expression for the cumulants in XAFS theory is derived based on the anharmonic correlated Einstein model [9] which is considered, at present, as "the best theoretical framework with which the experimentalist can relate force constants to temperature dependent XAFS" [15]. According to this theory the effective interaction Einstein potential of the system is given by

$$V_{eff}(x) \cong \frac{1}{2}k_{eff}x^2 + k_3x^3 + \cdots = V(x) + \sum_{j\neq i} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}.\hat{\mathbf{R}}_{ij}\right),\ \mu = \frac{M_1M_2}{M_1+M_2},\ \hat{\mathbf{R}} = \frac{\mathbf{R}}{|\mathbf{R}|}. \tag{16}$$

Here k_{eff} is effective force constant, and k_3 the cubic parameter giving an assymmetry in the pair distribution function, r is bondlength and r_0 is its equilibrium value. The correlated Einstein model may be defined as a oscillation of a pair of atoms with masses M_1 and M_2 (e.g., absorber and backscatterer) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left-hand side of Eq. (16), where the sum i is over absorber ($i = 1$) and backscatterer ($i = 2$), and the sum j is over all their near neighbors, excluding the absorber and backsctterer themselves. The latter contributions are described by the term $V(x)$.

Applying the Morse potential of Eq. (1) in the approximation for weak anharmonicity to the XAFS theory by the expansion

$$V(x) = D\left(e^{-2\alpha x} - 2e^{-\alpha x}\right) \cong D\left(-1 + \alpha^2x^2 - \alpha^3x^3 + \cdots\right),\ x = r - r_0\ , \tag{17}$$

so that the anharmonic effective potential Eq. (16) is transformed as

$$V_{eff}(y) = D\left(c_1\alpha^2 + 3c_3\alpha^3 a\right)y^2 + c_3D\alpha^3y^3,\ y = x - a,\ a = \langle x\rangle\ , \tag{18}$$

with the effective local force constant and cubic parameter

$$k_{eff} = 2D\left(c_1\alpha^2 + 3c_3\alpha^3 a\right),\ k_3 = c_3D\alpha^3, \tag{19}$$

and structural parameters

$$c_1 = 1 + \sum_{j=2}^{N}\frac{\cos^2\alpha_j}{2},\ c_3 = -\left(1 + \sum_{j=2}^{N}\frac{\cos^3\alpha_j}{4}\right). \tag{20}$$

4. Numerical results and discussion

To calculate the above equations to obtain the Morse potential parameters, we have to calculate the parameter c in Eq. (10). The space lattice of diamond is fcc. The primitive basis has two identical atoms at 000, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ associated with each point of the fcc lattice. Thus the conventional unit cube contains eight atoms, so that we obtain the value c = 1/8 for this tructure.

Using the theory derived in the previous section and the calculated parameter c, as well as the energy of sublimation, the compressibility and the lattice constant from [13,16,18,21] we calculated Morse potential parameter D, α, r_0 by our established computing programs and the results are included in Table 1.

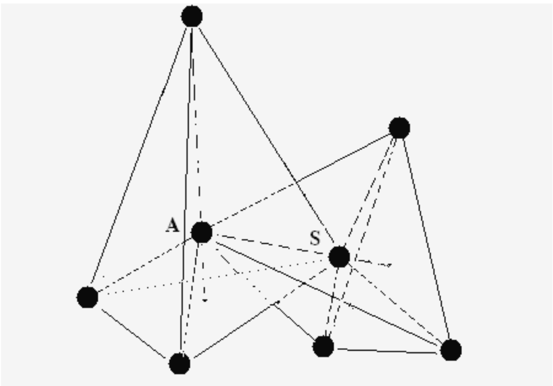

Fig. 2. Nearest neighbors of absorber (A) and backscatterer (S) in XAFS of diamond crystal.

Table 1. Calculated Morse potential parameters for Diamond crystals Si and Sn

Crystal	*D(eV)*	α *(Å^{-1})*	r_0 *(Å)*
Si	0.9956	1.3621	2.8439
Sn	1.3189	2.0504	2.8813

Table 2. Coordinates of neighbors of a central atom in diamond structure

Atomic number	x	y	z	cos($\mathbf{R}_{01}.\mathbf{R}_{ij}$)
1	-1/4	-1/4	-1/4	
2	1/4	1/4	-1/4	-1/3
3	1/4	-1/4	1/4	-1/3
4	-1/4	1/4	1/4	-1/3

Based on the coordinates of neighbors and central atom (Fig. 2) presented in Table 2 we calculated the structural paremeters

$$c_1 = 1 + \cos^2\alpha_2/2 + \cos^2\alpha_3/2 + \cos^2\alpha_4/2 = 7/6.$$
$$c_3 = -\left(1 + \cos^3\alpha_2/4 + \cos^3\alpha_3/4 + \cos^3\alpha_4/4\right) = -35/36. \tag{21}$$

Hence, for diamond the anharmonic correlated effective potential from Eq. (18) is resulted as

$$V_{eff}(x) \cong \frac{7}{6}D\alpha^2x^2 - \frac{35}{36}D\alpha^3x^3 , \tag{22}$$

$$V_{eff}(y) = D\left(\frac{7}{6}\alpha^2 - \frac{105}{36}\alpha^3 a\right)y^2 - \frac{35}{36}D\alpha^3y^3 . \tag{23}$$

Figure 3 shows the calculated Morse potentials of Si and Sn. They satisfy all properties of the Morse potential [19], i. e., it describes repulsive force in short distance when atoms approach each other obeying Pauli exclusion principle, and describes attractive force in long distance when atoms go far from each other. The reason of this attraction is that the atoms have diffusion moments which attract each other in long distance. Figure 4 illustrates the calculated anharmonic and harmonic effective potentials for Si and Sn. They show strong asymmetry of these potentials due to including anharmonic contributions in atomic vibrations of these diamond crystals.

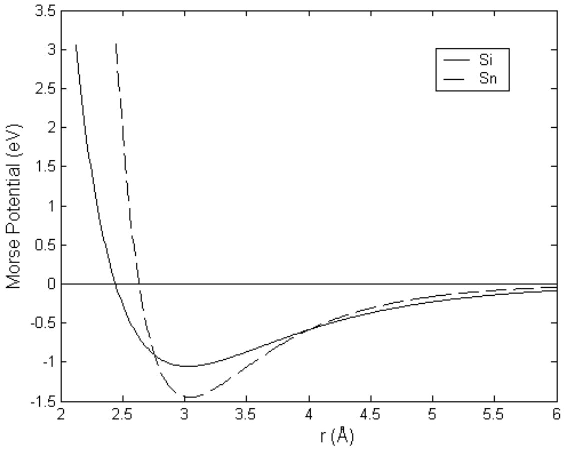

Fig. 3. Calculated Morse potentials for Si and Sn.

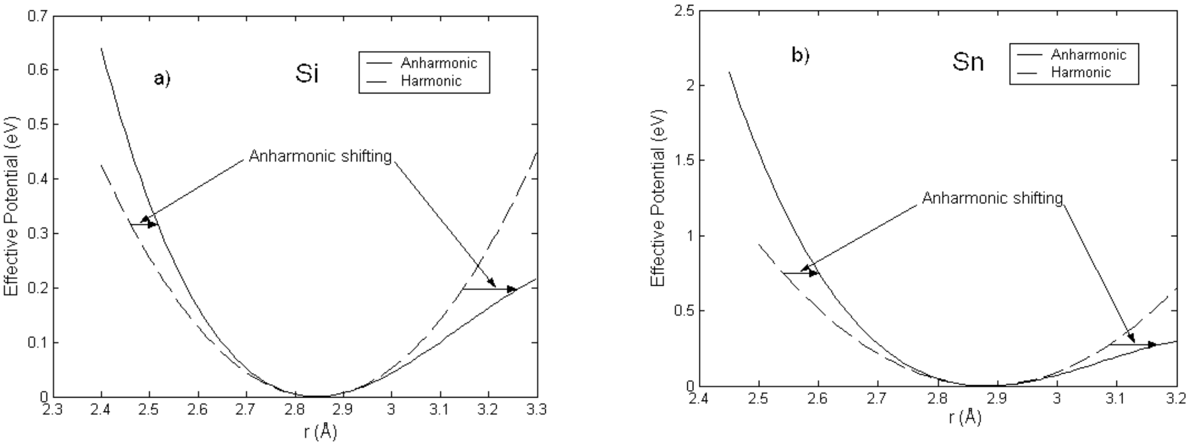

Fig. 4. Calculated anharmonic and harmonic effective potentials for Diamond crystals Si (a) and Sn (b) showing strong anharmonic shifting.

5. Conclusions

A new procedure for calculation of Morse potential parameters for *Diamond* crystals has been developed and the obtained results are applied to calculation of anharmonic and harmonic potential in the XAFS theory. The derived expressions have been programed for the computation of the considered physical quantities.

The derived expressions for Morse potential parameters contain the energy of sublimation, the compressibility and the lattice constant of Diamond crystals which are available in literatures.

The good satisfying of the calculated Morse potential with its fundamental properties, as well as, the good description of the effective potentials and the asymmetry of this potential due to anharmonicity show the efficiency and reliability of the present procedure in computation of the atomic interaction potential parameters as the Morse potential which are important for calculation and analysis of physical effects in XAFS technique and in solving the problems involving any type of atomic interaction in the *Diamond* crystals.

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