

A METHOD FOR CALCULATION OF MORSE POTENTIAL FOR FCC, BCC, HCP CRYSTALS APPLIED TO DEBYE-WALLER FACTOR AND EQUATION OF STATE

NGUYEN VAN HUNG

Dept. of Physics, College of Natural Sciences

Hanoi National University

Abstract. *Analytical expressions for the Morse potential parameters for fcc, bcc and hcp crystals have been developed. They contain the energy of sublimation, the compressibility and the lattice constant. Numerical results for Cu (fcc), W (bcc) and Zn (hcp) agree well with the measured values. Debye-Waller factors in X-ray absorption fine structure (XAFS) and equation of state computed using the obtained Morse potential parameters agree well with the experimental results.*

I. INTRODUCTION

Interatomic anharmonic potential, especially Morse potential, has been studied widely [1-12]. The parameters of this potential can be extracted from the XAFS [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. Therefore, calculation of the Morse potential is very actually desired, especially in XAFS theory.

The purpose of this work is to develop a method for calculating the Morse potential parameters of *fcc*, *bcc* and *hcp* crystals. 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, 21]. The obtained results are applied to Debye-Waller factors contained in the XAFS spectra [4-10,14] and to equation of state. Numerical calculations have been carried out for *Cu (fcc)*, *W (bcc)* and *Zn (hcp)*. The calculated Morse potential parameters agree well with the measured values [11, 12, 15] and with the other theory results [1]. Debye-Waller factors and equation of state computed using the obtained Morse potential parameters are found to be in good agreement with experiment [17, 18-21].

II. PROCEDURE FOR CALCULATION OF MORSE POTENTIAL

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

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

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 origin, 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

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

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

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

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

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

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

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

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

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, $[d\Phi/da]_{a_o} = 0$, and $[d^2\Phi/da^2]_{a_o}$ is related to the compressibility [1]. That is,

$$\Phi(a_o) = U_0(a_o), \quad (7)$$

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

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

and the compressibility is given by [1]

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

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

$$V/N = ca^3. \quad (10)$$

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

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

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

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

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

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

Solving the system of Eqs. (12), (13) we obtain α, β . Substituting the obtained results into the second of Eqs. (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 Eqs. (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].

III. APPLICATION TO CALCULATION OF PHYSICAL QUANTITIES

1. Debye-Waller factors in XAFS theory

The expression for the K-edge XAFS function [10]

$$\chi(k, T) \sim e^{-2k\sigma^2(T)} \quad (14)$$

is proportional to the Debye-Waller factor $e^{-2k^2\sigma^2}$ defined by the mean square relative displacement (MSRD) σ^2 in temperature T dependence, k is wave number of the photoelectron. The expression for the MSRD in XAFS theory is derived based on the 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

$$V_{eff}(x) \cong \frac{1}{2}k_{eff}x^2 + k_3x^3 + \dots = V(x) + \sum_{j \neq i} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12} \cdot \hat{\mathbf{R}}_{ij}\right), \quad (15)$$

$$\mu = \frac{M_1 M_2}{M_1 + M_2}, \quad \hat{\mathbf{R}} = \frac{\mathbf{R}}{|\mathbf{R}|}.$$

Here k_{eff} is effective spring constant, and k_3 the cubic parameter giving an asymmetry in the pair distribution function. 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 back-scatterer) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left-hand side of Eq. (15), where the sum i is over absorber ($i = 1$) and back-scatterer ($i = 2$), and the sum j is over all their near neighbors, excluding the absorber and back-scatterer themselves. The latter contributions are described by the term $V(x)$.

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

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \cong D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots), \quad (16)$$

to the effective potential of the system of Eq. (15) (ignoring the overall constant for convenience) we obtain

$$k_{eff} = D\alpha^2 \left(S - \frac{15}{2}\alpha a \right) = \mu\omega_E^2; \quad k_3 = -\frac{5}{4}D\alpha^3; \quad \theta_E = \frac{\hbar\omega_E}{k_B}, \quad (17)$$

where x is the deviation of instantaneous bond length between the two atoms from equilibrium, α , D were defined above; k_B is the Boltzmann constant; ω_E, θ_E are the Einstein frequency and Einstein temperature; a describes the asymmetry of the potential due to anharmonicity.

Using the definition [9] $y = x - a$ as the deviation from the equilibrium value of x at temperature T and quantum statistical theory [24] the MSRD is described by

$$\sigma^2 = \frac{1}{Z} Tr(\rho y^2) = \frac{1}{Z} \sum_n e^{-n\hbar\omega_E} \langle n | y^2 | n \rangle = \frac{\hbar\omega_E(1+z)}{2k_{eff}(1-z)}, \quad z = e^{-\theta_E/T}, \quad (18)$$

where we express y in terms of annihilation and creation operators, \hat{a} and \hat{a}^+ , i. e.,

$$y = \kappa(\hat{a} + \hat{a}^+); \quad \kappa^2 = \frac{\hbar}{2\mu\omega_E} \quad (19)$$

and use harmonic oscillator state $|n\rangle$ with eigenvalue $E_n = n\hbar\omega_E$ (ignoring the zero point energy for convenience).

Therefore the expression for the MSRD is resulted as

$$\sigma^2(T) = \sigma_o^2 \frac{1+z}{1-z}, \quad \sigma_o^2 = \frac{\hbar\omega_E}{2SD\alpha^2}, \quad (20)$$

where σ_o^2 is the zero-point contributions to σ^2 .

In the derivation of the above expressions we have developed a structural parameter

$$S = 2 + \sum_{j=2}^N \left(\hat{\mathbf{R}}_{01} \cdot \hat{\mathbf{R}}_{0j} \right)^2; \quad \hat{\mathbf{R}} = \mathbf{R}/|\mathbf{R}|, \quad (21)$$

where N is atomic number of the first shell, \mathbf{R}_{01} is directed from absorber located at point 0 to the location of the first scatterer at $j = 1$, and \mathbf{R}_{oj} are from absorber to the other scatterers. This parameter describes the distribution of atoms in the crystal.

2. Equation of state

It is possible to calculate the equation of state from the energy Φ . If it is assumed that the thermal part of the free energy can be adequately represented by the Debye model, then the Helmholtz free energy is given by [1]

$$F = \Phi + 3Nk_B T \ln(1 - e^{-\theta_D/T}) - Nk_B T D(\theta_D/T) \quad , \quad (22)$$

$$D\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx, \quad (23)$$

where θ_D is Debye temperature, the remaining parameters were defined above.

Using Eqs. (22, 23) we derive the expression for pressure P leading to the equation of state as

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3ca_0^2} \frac{d\Phi}{da} + \frac{3\gamma_G RT}{V} D\left(\frac{\theta_D}{T}\right) \quad , \quad (24)$$

where γ_G is Grüneisen parameter, V is the volume.

After some transformations the equation of state (24) is resulted as

$$P = \frac{1}{3ca_0^2(1-x)^{2/3}} \left[2L\beta\alpha \sum_j M_j e^{-\alpha a_0 M_j (1-x)^{1/3}} \right] - \quad (25)$$

$$- 2L\beta^2\alpha \sum_j M_j e^{-2\alpha a_0 M_j (1-x)^{1/3}} + \frac{3\gamma_G RT}{V_0(1-x)} D\left(\frac{\theta_D}{T}\right)$$

where $x = \frac{V_0 - V}{V_0}$, $V_0 = ca_0^3$, $R = Nk_B$, $N = 6.02 \times 10^{23}$. (26) Hence, the equation of state (25) contains the obtained Morse potential parameters.

IV. NUMERICAL RESULTS AND COMPARISON TO EXPERIMENT

Now we apply the above derived expressions to numerical calculations for some *fcc*, *bcc* and *hcp* crystals. Considering the distribution of atoms in the crystals and volume per atom we calculated the values of c in Eq. (10) and structural parameter S according to Eq. (21) for these crystal structures, the results are given in Table 1. Hence, for *fcc* Eq. (20) becomes Eq. (9) in Ref. [10].

Table 1. Calculated values of c (Eq.10) and structural parameters S for *fcc*, *bcc*, *hcp* crystals.

Crystal structure	<i>fcc</i>	<i>bcc</i>	<i>hcp</i>
Value of c	2	4	$1/\sqrt{2}$
Structural parameter S	5	11/3	5

Table 2. Calculated Morse potential parameters for *Cu* (*fcc*), *W* (*bcc*), *Zn* (*hcp*) in comparison to experiment and to other theory

Crystal	$D(\text{eV})$	$\alpha(\text{\AA}^{-1})$	$r_o(\text{\AA})$
<i>Cu</i> (present)	0.337	1.358	2.868
<i>Cu</i> (other [1])	0.343	1.359	2.866
<i>Cu</i> (Expt. [11])	0.330	1.380	2.802
<i>W</i> (present)	0.992	1.385	3.035
<i>W</i> (other [1])	0.991	1.412	3.032
<i>W</i> (Expt. [12])	0.990	1.440	3.092
<i>Zn</i> (present)	0.170	1.705	2.793
<i>Zn</i> (Expt. [21])		1.700	

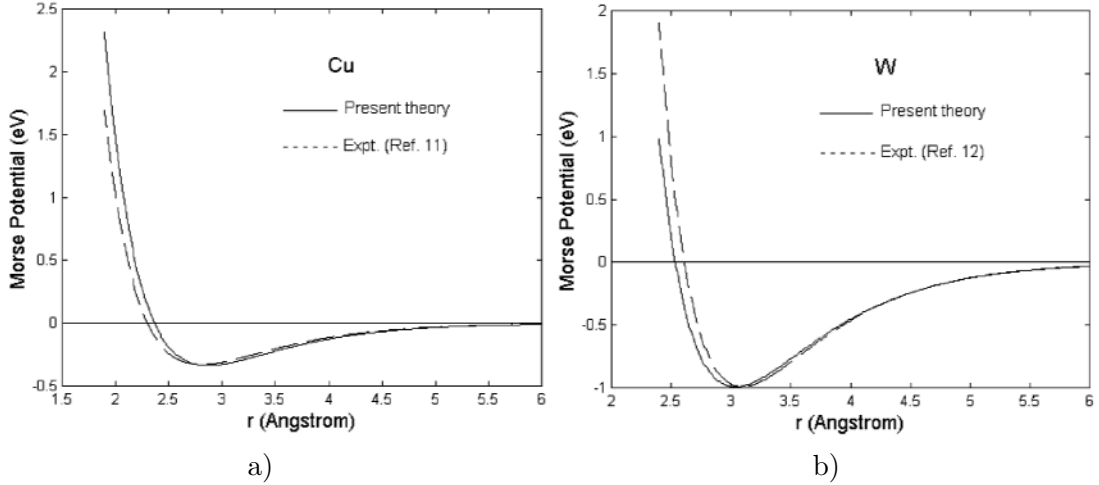


Fig. 1. Morse potentials calculated by present procedure in comparison to experiment (dashed) for *Cu* (a) and for *W* (b)

Using the energy of sublimation, the compressibility and the lattice constants [13, 21, 22] we calculated the Morse potential parameters for *Cu* (*fcc*), *W* (*bcc*) and *Zn* (*hcp*). The results are presented in Table 2 in comparison to those of other theory [1] and of experiment [11, 12]. The accuracy of our results compared to experiment is about 2% for D ; 1.6% for α of *Cu*; 0.2% for D , 3.8% for α of *W* and 0.3% for α of *Zn*. They also agree well with those for *Cu* and *W* of the other theory [1].

Comparison of our calculated Morse potential to experiment is illustrated in Fig. 1a for *Cu* and Fig. 1b for *W*. The temperature dependent MSR D calculated by using our above calculated Morse potential parameters are compared to the ones measured at HASYLAB, DESY (Germany) for *Cu* [17, 19] (Fig. 2a) and for *Zn* [20] (Fig. 2b) providing very good agreement.

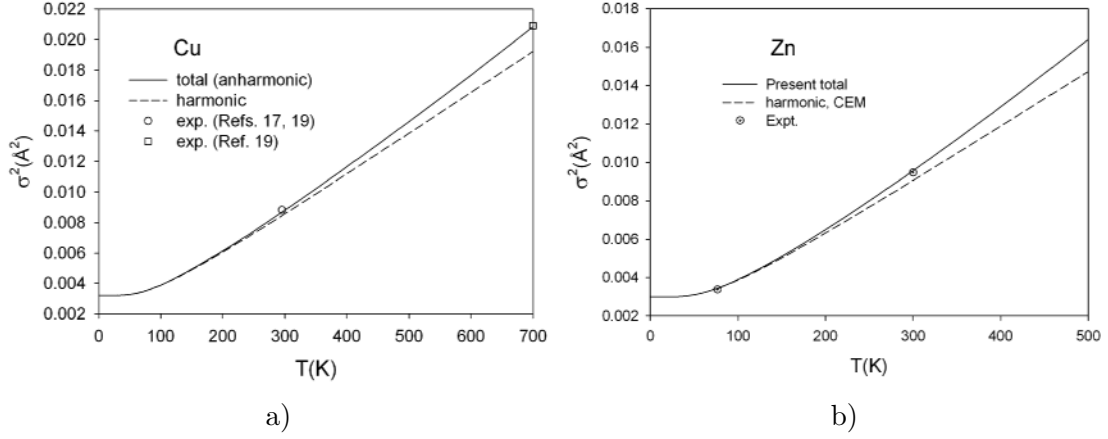


Fig. 2. Temperature dependence MSRD $\sigma^2(T)$ calculated by using our calculated Morse potential parameters in comparison to experiment [17,19] for Cu (a) and [20] for Zn (b).

The next application of our calculated Morse potential parameters is to the calculation of the equation of state for *Zn*. The values of θ_D and $D(\theta_D/T)$ were taken from [23]. The calculated results are shown in Fig. 3 in comparison to the experimental values [21] represented by an extrapolation procedure of the measured data. They show a good agreement between theoretical and experimental results, especially at low pressure.

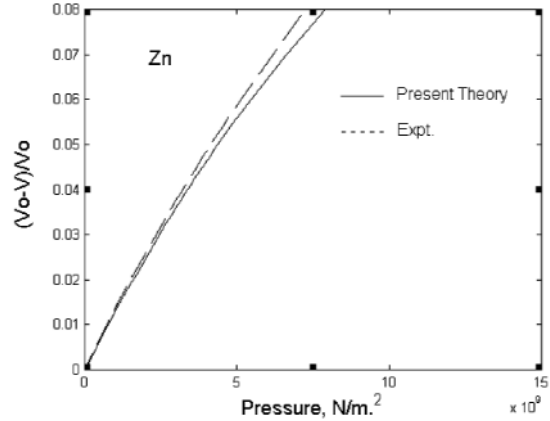


Fig. 3. Equation of state for Zn calculated by using our calculated Morse potential parameters (solid line) in comparison to experimental results [21] (dashed line).

V. CONCLUSIONS

A new procedure for calculation of Morse potential parameters for *fcc*, *bcc* and *hcp* crystals has been developed and the obtained results are applied to calculation of Debye-Waller factors in the XAFS theory and to the equation of state. The derived expressions have been programed for the computation of the considered physical quantities.

The calculated Debye-Waller factor and equation of state satisfy all standard conditions for the considered quantities such as Debye-Waller factors are linearly proportional to temperature at high temperature and contain zero-point contribution at low temperature.

Reasonable agreement of our results with the respective experimental and other theory values 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 *fcc*, *bcc* and *hcp* crystals.

ACKNOWLEDGMENTS

The authors thank Prof. R. R. Frahm and Dr. L. Tröger for providing the measured values of MSRD of *Zn* and *Cu*. This work is supported in part by the special research project of VNU-Hanoi QG. 03.02 and by the Basic Science Research Program No. 41.10.04.

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Received 13 October 2003