

CALCULATION OF MORSE POTENTIAL OF HCP CRYSTALS AND APPLICATION TO EQUATION OF STATE AND ELASTIC CONSTANTS

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Abstract. A new procedure for calculation of the Morse potential parameters of hexagonal closed packed (hcp) crystals has been developed using the energy of sublimation, the compressibility and the lattice constant. The derived equation of state and the elastic constants computed using the obtained Morse parameters agree with the experimental ones. This shows that the Morse function can be applied validly to the problems involving any type of deformation and of atomic interaction in the hcp crystals.

1. Introduction

Morse potential is an anharmonic potential [1] which is suitable for describing the atomic interaction and vibration in the crystals [2-9]. In X-ray Absorption Fine Structure (XAFS) technique photoelectron emitted from an absorber is scattered in a cluster of vibrating atoms [1, 2]. This atomic thermal vibration contributes to the XAFS spectra especially to the anharmonic XAFS [2 - 9] influencing on physical information taken from these spectra. The parameters of this empirical potential are often extracted from the experiment. The only calculation has been carried out for cubic crystals [10]. Its parameters have been used successfully for XAFS calculations [3-5,8] and agree well with those extracted recently from XAFS data [11] using anharmonic correlated Einstein model [8].

The purpose of this work is to develop a method for calculation of the Morse potential parameters of hcp crystals using the energy of sublimation, the compressibility and the lattice constant. The obtained results are applied to the equation of state and the elastic constants. Numerical calculations have been carried out for Zn and Cd. The calculated Morse potential parameters agree with the experimental values [12]. The derived equation of state and the elastic constants computed using the obtained Morse parameters agree with the experimental ones [13].

2. 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

$$\varphi(r_{ij}) = D \left\{ e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)} \right\}, \quad (1)$$

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where α, D are constants with dimensions of reciprocal distance and energy, respectively; r_0 is the equilibrium distance of approach of the two atoms. Since $\varphi(r_0) = -D$, is D the disociation energy.

In order 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. 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

$$\Phi = \frac{1}{2}ND \sum_j \left\{ e^{-2\alpha(r_j-r_0)} - 2e^{-\alpha(r_j-r_0)} \right\}, \quad (2)$$

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

$$L = \frac{1}{2}ND; \beta = e^{\alpha a_0}; r_j = [m_j^2 + n_j^2 + l_j^2]^{\frac{1}{2}}a = M_j a, \quad (3)$$

where m_j, n_j, l_j are position coordinates of any atom in the lattice. Using (3) in (2), the energy can be written

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

The first and second derivatives of (4) with respect to α are given by

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

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

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

$$\Phi(a_0) = U_0(a_0), \quad (7)$$

where $\Phi(a_0) = U_0(a_0)$ is the energy of sublimation at zero pressure and temperature,

$$\left[\frac{d\Phi}{da} \right]_{a_0} = 0 \quad (8)$$

and the compressibility is given by [10]

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

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

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

Calculating the distribution of atoms in the cells we obtain $c = 2$ for bcc, $c = 4$ for fcc and $c = \frac{1}{\sqrt{2}}$ for hcp structure. Substituting (10) in (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

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

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

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

Solving the system of Eqs. (12, 13) we obtain α, β . Substituting them 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 available already [14].

3. Application to equation of state and elastic constant

It is possible to calculate the equation of state from the energy. If it is assumed that the thermal part of the free energy can be adequately represented by the Debye model, then the Helmholtz energy is given by [10]

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

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

where k_B is Boltzmann constant, θ_D is Debye temperature.

Using Eqs. (14, 15) we derive the expression for pressure P leading to the equation of state as

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{1}{3ca^2} \frac{d\Phi}{da} + \frac{3\gamma_D RT}{V} D \left(\frac{\theta_D}{T} \right), \quad (16)$$

where γ_G is Gruneisen parameter, V is the volume. After some transformations the equation of state (18) is resulted as

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

where

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

Hence, the equation of state (18) contains the obtained Morse potential parameters.

Elastic properties of a crystal is described by an elastic tensor contained in the motion equation of the crystal. The non-vanishing components of the elastic tensor are defined as elastic constants. They are given for hcp crystals by [15].

$$\begin{aligned} c_{11} = c_{22} &= P - \frac{Y^2}{Z}; c_{12} = \frac{P}{3} + \frac{Y^2}{Z}; \\ c_{33} = Q; c_{13} = c_{23} = c_{44} = c_{55} &= X; \\ c_{66} &= \frac{P}{3} - \frac{Y^2}{Z} = \frac{c_{11} - c_{12}}{2}, \end{aligned} \quad (19)$$

where

$$\begin{aligned} P &= \sqrt{2}r_0[10\Psi''(r_0^2) + 16\Psi''(2r_0^2) + 81\Psi''(3r_0^2) + \dots] \\ Q &= \frac{\sqrt{2}}{3}r_0[32\Psi''(r_0^2) + 32\Psi''(2r_0^2) + \frac{512}{3}\Psi''(3r_0^2) + \dots] \\ X &= \sqrt{2}r_0[+8\Psi''(r_0^2) + 32\Psi''(2r_0^2) + 112\Psi''(3r_0^2) + \dots] \\ Y &= \sqrt{2/3}r_0[-2\Psi''(r_0^2) + 16\Psi''(2r_0^2) - 40\Psi''(3r_0^2) + \dots] \\ Z &= \sqrt{2}r_0^{-1}[4\Psi''(r_0^2) + 16\Psi''(2r_0^2) + 12r_0^{-1}\Psi'(2r_0^2) + \dots] \\ \Psi'(r) &= -2D\alpha[e^{-2\alpha(r-r_0)} - e^{-\alpha(r-r_0)}] \frac{1}{r} \\ \Psi''(r) &= D\alpha^2[2e^{-2\alpha(r-r_0)} - \frac{1}{2}e^{-\alpha(r-r_0)}] \frac{1}{r} + D\alpha[e^{-2\alpha(r-r_0)} - e^{-\alpha(r-r_0)}] \frac{1}{2r^3}. \end{aligned} \quad (20)$$

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

4. Numerical results

Now we apply the above derived expressions to numerical calculations for hcp crystals Zn and Cd using the energy of sublimation [12], the compressibility [16] and the lattice constants [14], as well as, the values of θ_D and $D\left(\frac{\theta_D}{T}\right)$ [17-19]. The obtained Morse potential parameters are presented in Table I. The values of our calculated α agree well

with the measured ones [12]. First application of our calculated Morse potential parameters is to calculate the elastic constants. The obtained results for Zn and Cd are presented in Table II in comparison with experimental values [13]. They show in many cases good agreement. The second application of our calculated Morse potential parameters is to the calculation of the equation of state of Zn and Cd. The calculated results are shown in Figures 1 compared to the experimental ones [12] represented by an extrapolation procedure of the measured data. They show a good agreement between theoretical and experimental results, especially at low pressure.

Table I. Morse potential parameters D , α and the related parameters β , L , r_0 of hcp crystals Zn and Cd in comparison with some experimental results [12].

Crystal	β	$L(\times 10^{-22} \text{ eV})$	$\alpha (\text{\AA}^{-1})$	$D(\text{eV})$	$r_0(\text{\AA})$
Zn (Present)	117.140	5.11	1.7054	0.1698	2.7931
Zn (Exp. [12])			1.7000		
Cd (Present)	330.500	5.04	1.9069	0.1675	3.0419
Cd (Exp. [12])			1.9300		

Table II: Calculated elastic constants ($\times 10^{-11} \text{ N/m}^2$) using the obtained Morse potential parameters of hcp crystals Zn and Cd in comparison with experimental values [13].

Crystal	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Zn (Present)	1.81	0.60	0.41	2.03	0.41
Zn (Exp. [13])	1.64	0.36	0.53	0.64	0.39
Cd (Present)	1.51	0.50	0.36	1.67	3.55
Cd (Exp. [13])	1.21	0.48	0.44	0.51	0.19

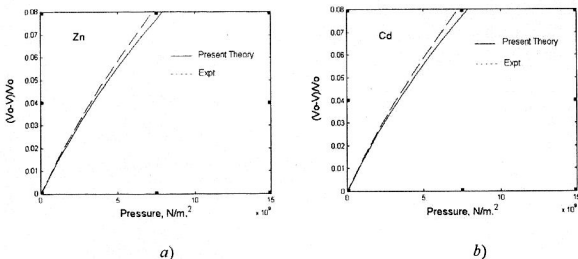


Figure 1: Equation of state calculated by using our calculated Morse potential parameters (solid line) compared to experimental results [12] (dashed line) for Zn (a) and Cd (b). They show very good agreement especially at low pressure.

5. Conclusions

A new procedure for calculation of Morse potential parameters, equation of state and elastic constants have been developed. Analytical expressions have been derived and programed for the calculation of the above physical quantities.

Derived equation of state Equation and elastic constants satisfy all standard conditions for these values, for example, all elastic constants are positive.

Reasonable agreement between our calculated results and the experimental data show the efficiency of the present procedure in calculation of parameters of atomic potential which are important in the calculation and analysis of physical effects in XAFS technique and in solving the problems involving any type of deformation and of atomic interaction in the hcp crystals.

Acknowledgements. This work is supported in part by the basic science research program 410 801 and by the special research project of VNU-Hanoi.

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