

## STUDY OF MORSE POTENTIAL, BINDING ENERGY, THERMAL EXPANSION AND THEIR RELATION

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**Abstract:** Morse potential, binding energy, thermal expansion and their relation have been studied. Analytical expressions for the relation of the binding energy, linear thermal expansion coefficient with the Morse potential parameters have been derived. They lead to the determination of these quantities by using available experimental data. Numerical calculations have been carried out for several crystals, and the results are found to be in good agreement with experiment.

### 1. Introduction

The pairwise potential functions have been used widely in the description of the solid states. One of the most successful function is the Morse potential function. The purpose of this work is to study the relation between the binding energy, the thermal expansion and the parameters of the Morse function. Using these relations we determine the Morse potential parameters.

The paper will be started with determining the average potential per each atom which depends on the Morse parameters and the lattice constant. After showing the dependence of the total potential on the various distance  $a$  between the atoms, we carry out the relation formula of linear thermal expansion with the crystal properties. The calculated results are compared to experiment [3-7].

### 2. Formalism

We consider a certain atom inside the lattice. The total interaction potential of this atom with all the others in the crystal is given by this sum:

$$\sum_i \varphi(r_i), \tag{1}$$

where  $\varphi(r_i)$  is the single-bond potential between that atom and the  $i^{\text{th}}$  atom of crystal,  $i$  runs over all the numbers of atoms of the lattice (except the original atom). Use the Morse function we have:

$$\varphi(r_i) = D.e^{-2\alpha(r_i-r_0)} - 2D.e^{-\alpha(r_i-r_0)} = D.e^{2\alpha r_0} e^{-2\alpha r_i} - 2D.e^{\alpha r_0} e^{-\alpha r_i} = D\beta^2 e^{-2\alpha r_i} - 2D\beta e^{-\alpha r_i}, \tag{2}$$

where,  $D, \alpha, r_0$  are the Morse parameters and

$$\beta = e^{\alpha r_0}. \tag{3}$$

Thus, we can calculate the average potential per each atom by:

$$\varphi = \frac{1}{2} \sum_i (D\beta^2 e^{-2\alpha r_i} - 2D\beta e^{-\alpha r_i}) = \frac{1}{2} D\beta^2 \sum_i e^{-2\alpha r_i} - D\beta \sum_i e^{-\alpha r_i}. \tag{4}$$

For the cubic, *bcc*, *fcc*, *dia* or *hcp* crystals with the lattice constant is  $a$ , the distance  $r_i$  can be taken by the position coordinates  $m_i, n_i, l_i$  (see fig. 1).

$$\Rightarrow r_i = \sqrt{l_i^2 + m_i^2 + n_i^2} \cdot a = M_i a. \quad (5)$$

in which 
$$M_i = \sqrt{l_i^2 + m_i^2 + n_i^2} \quad (6)$$

Therefore, 
$$\varphi = \frac{1}{2} D \beta^2 \sum_i e^{-2\alpha M_i a} - D \beta \sum_i e^{-\alpha M_i a} \quad (7)$$

We can see that, the particular average potential depends on the lattice constant  $a$ :  $\varphi = \varphi(a)$  and its form is similar to the Morse potential form.

When the lattice vibrates, there is small change in the bond distance  $a$  between the atoms, this leads to small change in the potential of lattice. We can expand the potential function in term of Taylor form around the equilibrium distance value  $a_0$ :

$$\begin{aligned} \varphi &= \varphi(a_0) + \left( \frac{\partial \varphi}{\partial a} \right)_{a_0} (a - a_0) + \left( \frac{\partial^2 \varphi}{\partial a^2} \right)_{a_0} (a - a_0)^2 + \left( \frac{\partial^3 \varphi}{\partial a^3} \right)_{a_0} (a - a_0)^3 + \dots \\ &= \varphi(a_0) + 0 \cdot (a - a_0) + K_2 (a - a_0)^2 + K_3 (a - a_0)^3 + \dots \end{aligned} \quad (8)$$

where 
$$U_0 = \varphi(a_0) = \frac{1}{2} D \beta^2 \sum_i e^{-2\alpha M_i a_0} - D \beta \sum_i e^{-\alpha M_i a_0} \quad (9)$$

is the particular cohesion energy of the atoms are at rest, it is the energy of sublimation of one atom.,

and 
$$\left. \frac{\partial \varphi}{\partial a} \right|_{a_0} = -D \alpha \beta^2 \sum_i M_i e^{-2\alpha M_i a_0} + D \alpha \beta \sum_i M_i e^{-\alpha M_i a_0} = 0; \quad (10)$$

$$K_2 = \left. \frac{\partial^2 \varphi}{\partial a^2} \right|_{a_0} = 2 D \alpha^2 \beta^2 \sum_i M_i^2 e^{-2\alpha M_i a_0} - D \alpha^2 \beta \sum_i M_i^2 e^{-\alpha M_i a_0} \quad (11)$$

$$K_3 = \left. \frac{\partial^3 \varphi}{\partial a^3} \right|_{a_0} = -4 D \alpha^3 \beta^2 \sum_i M_i^3 e^{-2\alpha M_i a_0} + D \alpha^3 \beta \sum_i M_i^3 e^{-\alpha M_i a_0} \quad (12)$$

are the expansion coefficients.

The expression (9) shows that, the general potential function is anharmonic. That is the reason why the crystal has thermal expansion. And we see:  $\langle a \rangle = a_0 + \Delta a \neq a_0$ , where,  $\Delta a$  is the average expansion which we will determine. Define that:  $x = a - a_0 \Rightarrow \langle x \rangle = \Delta a$ .

$$\Rightarrow \varphi = \varphi(a_0) + K_2 x^2 + K_3 x^3 + \dots \quad (13)$$

$$\Rightarrow \text{The external force puts on the atom: } f = -\frac{\partial \varphi}{\partial x} = -2K_2 x - 3K_3 x^2$$

We suppose that, vibration is free so that the average force equals zero (the atom oscillate only around its position).

$$\langle f \rangle = \langle -2K_2 x - 3K_3 x^2 \rangle = 0 \Rightarrow 2K_2 \langle x \rangle = -3K_3 \langle x^2 \rangle \text{ hay } \Delta a = \frac{-3K_3 \langle x^2 \rangle}{2K_2}. \quad (14)$$

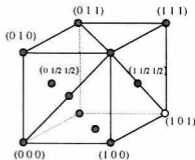


Fig.1. The coordinates positions

The atom vibration energy includes potential and kinetic energy. By approximation, the vibration potential and the kinetic energy have the same value and they equal to one half of the total energy

$$2\langle U \rangle = 2\langle K \rangle = \langle E \rangle \Rightarrow \langle E \rangle = 2\langle U \rangle = 2\langle \phi - \phi(a_0) \rangle = 2\langle K_2 x^2 + K_3 x^3 + \dots \rangle \approx 2K_2 \langle x^2 \rangle \quad (15)$$

$$\Rightarrow \Delta a = \frac{-3K_3 \langle x^2 \rangle}{2K_2} = \frac{-3K_3 \langle E \rangle}{4K_2^2} \quad (16)$$

The thermal expansion coefficient is given by the formula:

$$\gamma = \frac{1}{a_0} \frac{\partial(\Delta a)}{\partial T} = \frac{-3K_3}{4a_0 K_2^2} \cdot \frac{\partial \langle E \rangle}{\partial T} = \frac{-3K_3 C_r}{4a_0 K_2^2} \quad (17)$$

where,  $C_r$ , is the average particular thermal capacity per each atom. It can be determined by the experiment.

Now, let's recall the equations (9-12) and (17). They set up a complete system of relations between the thermal expansion coefficient, the binding energy and the Morse potential parameter.

The eq. (10) leads to:

$$\beta = \frac{\sum_i M_i e^{-\alpha M_i a_0}}{\sum_i M_i e^{-2\alpha M_i a_0}} \quad (18)$$

From (9) we obtain:

$$D = \frac{2U_0}{\beta^2 \sum_i e^{-2\alpha M_i a_0} - 2\beta \sum_i e^{-\alpha M_i a_0}} \quad (19)$$

Eq. (17) has now form:

$$\gamma = \frac{-3K_3 C_r}{4a_0 K_2^2} = \gamma(\alpha, \beta, D) \quad (20)$$

These relations helps us determine the unknown quantities when we have some information about the crystal and the atoms. This work can be executed by a PC (Personal Computer).

### 3. Numerical calculation and conclusion

The first and the second tables give us the results calculated for some kinds of atom and some types of crystal likes examples. In these tables we also give some comparison between the present theory results and the experimental values.

**Table 1.** The thermal expansion coefficient:

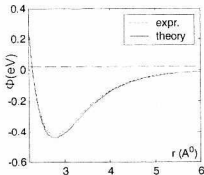
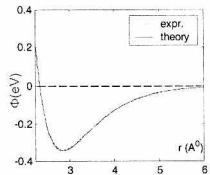
Material	$\alpha$ ( $\text{\AA}^{-1}$ )	$r_0$ ( $\text{\AA}$ )	D (eV)	$\gamma$ ( $10^6 \text{K}^{-1}$ )	$\gamma_{\text{Exp}}$ ( $10^6 \text{K}^{-1}$ )
Pb (fcc)	1.1836	3.733	0.2348	28.4	28.3
Cu (fcc)	1.3588	2.866	0.3429	17.7	17.5
Fe (bcc)	1.3885	2.845	0.4174	11.9	11.9
Ag (fcc)	1.3690	3.115	0.3323	18.9	-

**Table 2.** The Morse potential parameters of some materials.

Material	$\gamma (10^6 \text{ K}^{-1})$	$C_r (10^{23} \text{ J/K})$	$\alpha (\text{\AA}^{-1})$		$\beta$	$r_0 (\text{\AA}^0)$		D (eV)	
			Present	<sup>b</sup> Exp.		Pre.	<sup>b</sup> Exp.	Pre.	<sup>b</sup> Exp.
Ni (fcc)	13.4	3.82	1.417	1.420	51.4	2.780	2.780	0.4425	0.4205
Cu (fcc)	17.5	3.91	1.371	1.359	50.4	2.859	2.866	0.3465	0.3429
Fe (bcc)	11.9	4.16	1.391	1.389	52.6	2,848	2.845	0.487	0.4174
C (dia)	0.91	1.38	7.020	-	$5.10^4$	1.547	-	3.664	-

a: reference [4]; b: reference [7].

The calculated results presented in these tables are found to be in good agreement with experiment. The Morse potentials are shown in Fig. 2 and Fig. 3 compared to experiment [4, 7].

**Fig.2.** The Morse potential function of Ni.**Fig.3.** The Morse potential function of Cu.

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