

COHESIVE ENERGY FOR ALKALI METALS USING THE TB SMA MODEL

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Abstract

In the previous studies of TB-SMA Model, the tight binding model important parameter n was assigned the values of $n=1/2$ or $2/3$ and the four other parameters of the model are fitted to experimental data. This work has outlined another approach where the important parameter n is uniquely obtained for the different alkali metals, and it turns out to vary from one metal to another.

The method outlined here has been employed to study the Cohesive energy of alkali metals using the TB-SMA Model.

Keywords: Tight Binding Second Moment Approximation, Alkaline metals and BCC metals.

Introduction.

Empirical potentials, that include many body interactions terms, beyond a pair potential term, have been developed to overcome the burden posed by the first principle computation [1,2].

In general, semi empirical approaches tackle the many-body problem by determining a functional form for the cohesive energy based on some physical model [3,4,5]. The functional form often contains some parameters, which are to be determined by fitting to the experimental properties.

The main advantage of a many-body potential treatment over the traditional and practically simple pair-potential treatment is the ability to reproduce some basic features of metallic systems. Once these parameters have been obtained, the functional form may then be used to calculate other properties, such as defect energies.

The tight-binding (TB) theory of cohesion in solids [6,7], has been extensively applied to describe the energies of alkali metals. It is well known that the cohesion of alkali metals and their alloys has its main contribution from d-bands [8]. The second moment approximation (SMA) of TB-Theory express the Cohesive energy as a sum of the two terms, one coming from the band energy E_B (the attractive term) and the other term, E_R being a repulsive contribution. In the TB-SMA scheme the interaction between two atoms depends on the atomic distance and also on the local environment around each atom. Improvement over the SMA have been proposed, first by Carlsson [9,10], and later by related approaches of Guevara et al., who added other attractive terms to the cohesive energy [11,12].

The TB-SMA potentials has an advantage that it is simply in mathematical form and are used to estimate the thermodynamic properties of fcc metals whose cohesive properties originates from the large f-band density of states [11,12].

The TB-SMA scheme, contains five model parameters, usually denoted as A , ζ , p , q and n [13-14]. These parameters can be determined by fitting to the experimental values of the cohesive energy, the Monovacancy formation energy, the independent elastic constants, and also by taking the equilibrium condition into account.

In many of the TB-SMA scheme, the model parameter n is often taken as $1/2$ [15,16]. With such a fixed value for n , the other four parameters for alkali metals were determined, by fitting to the experimental cohesive energy E_C ; the bulk modulus B_O , the elastic constants C_{44} and also by taking the equilibrium condition into account. For several metals, the predicted values of the Monovacancy formation energy E_{IV}^f and other elastic constants (C_{11} and C_{12}) disagreed with the experimental values.

In this work, instead of arbitrarily assigning a fixed value for n , the five parameters in the TB-SMA scheme have been determined by fitting to the experimental value of E_C , E_{IV}^f , B_O , C_{12} , C_{44} , and also taking the equilibrium condition into account.

It is shown in this study that the value of parameter, n , was not constant for the alkali metals, Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), and Caesium (Cs) whose potentials are explicitly exhibited. At the same time, the resulting TB potentials lead to a good agreement with experiment in the physical quantities whose values are predicted.

The relevant details of the TB-SMA as we use it are outlined in section 2.0 and 2.1. The results for the determined five TB-SMA parameters and cohesive energy functions

For the four models are presented in section 3.0.

Materials and Methods

2.0 The Basic equations of the EAM

The TB-SMA scheme is formally analogous to the embedded-atom method (EAM). Empirical potentials such as the EAM also describe the atomic interactions by several analytical functions [17,18].

However, we give below the 7 basic equations that regularly arise when working Practically with the EAM.

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$$U_o = 4\phi_1(r_o) + F(\rho_e) \tag{2.1}$$

$$0 = 4\phi_1'(r_o) + F'(\rho_e) \left[\frac{V_{11}}{a} \right] \tag{2.2}$$

$$6aB_o = 4\phi_1''(r_o) + F''(\rho_e) [\rho'(r_o)]^2 + F'(\rho_e) [\rho''(r_o)] \tag{2.3}$$

$$aC_{11} = \left[\frac{-4\phi_1'(r_o)}{3\sqrt{3}a} + \frac{2}{3}\phi_1''(r_o) \right] + \frac{aF'(\rho_e)}{\Omega_o} W_{11} + \frac{aF''(\rho_e)}{\Omega_o} V_{11}^2 \tag{2.4}$$

$$aC_{12} = \left[\frac{-4\phi_1'(r_o)}{3\sqrt{3}a} + \frac{2\phi_1''(r_o)}{3} \right] + \frac{aF'(\rho_e)}{\Omega_o} W_{12} + \frac{aF''(\rho_e)}{\Omega_o} V_{11}^2 \tag{2.5}$$

$$aC_{44} = \left[\frac{-4\phi_1'(r_o)}{3\sqrt{3}a} + \frac{2\phi_1''(r_o)}{3} \right] + \frac{aF'(\rho_e)}{\Omega_o} W_{12} \tag{2.6}$$

$$E_{Nv}^F = 8F\left(\frac{7\rho_e}{8}\right) - 7F(\rho_e) - U_o \tag{2.7}$$

In the equations above, U_o is the equilibrium energy per atom, i.e. the negative of the experimental cohesive energy. B_o and C_{ij} are, respectively, the bulk modulus, and elastic constants written in Voigt notation Ω_o , is the volume per atom in the solid, r_o is the equilibrium nearest-neighbour distance; and a is the equilibrium lattice constant.

ϕ_1 is a repulsive pair potential whose first and second derivatives with respect to the radial distance r are respectively, ϕ_1' and ϕ_1'' (all quantities being evaluated at $r = r_o$), while F is the embedding function with respect to the density ρ , with F' and F'' being the first two derivatives; again all quantities being evaluated at the equilibrium density ρ_e . E_{Nv}^F is the mono vacancy formation energy. In all the previous applications of the EAM [17], V_{11} , W_{11} and W_{12} have been considered as free parameters to be consistently determined so that the basic equations of the EAM are satisfied. Such an approach enables us to surmount the problem of the elastic constants not being correctly reproduced theoretically. Here, we shall introduce a slightly different approach since it is often desirable to predict several physical quantities from a minimum set of parameters.

For BCC lattice, $r_o = \frac{a(\sqrt{3})}{2}$, $\Omega_o = \frac{a^3}{2}$ and expressions for V_{11} , W_{11} and W_{12} in terms of the derivatives of the density are in the form [1]

It is obvious from equation (2.1) to (2.7) above that the EAM has three basic functions, i.e.: $\phi_1(r)$, $F(\rho)$ and $\rho(r)$ which generate the 8 EAM parameters: $\phi_1(r_o)$, $\phi_1'(r_o)$, $\phi_1''(r_o)$, $F(\rho_e)$, $F'(\rho_e)$, $F''(\rho_e)$, $\rho'(r_o)$, and $\rho''(r_o)$.

2.1 The Basic Functions of the TB-SMA Scheme

In an obvious correspondence with the EAM scheme, the expressions for the cohesive energy U_o , in the TB-SMA scheme is the sum of the two terms [19]

$$U_o = E_R + E_B \tag{2.9}$$

The functions E_R and E_B are usually written in the form

$$E_R = 6\phi_1(r_{ij}) = A \sum_j \exp \left[-p \left(\frac{r_{ij}}{r_o} - 1 \right) \right] \tag{2.10}$$

And

$$E_B = F(\rho) = -\xi \left\{ \sum_j \exp \left[-2q \left(\frac{r_{ij}}{r_o} - 1 \right) \right] \right\}^n \tag{2.11}$$

It is clear that

$$\rho(r_{ij}) = \left\{ \sum_j \exp \left[-2q \left(\frac{r_{ij}}{r_o} - 1 \right) \right] \right\}^n \tag{2.12}$$

Density as a function of the atomic distance ij .

Equations (2.10), (2.11), and (2.12) are the equations for the three basic functions of the TB-SMA scheme.

The sum over j in equations (2.10) to (2.12) is actually a sum over neighbours, r_{ij} , being the distance between atoms i and j and r_o , is the bulk nearest neighbour distances.

The TB-SMA expressions for the functions $\phi_1(r)$, $F(\rho)$ and $\rho(r)$ as contained in the equation (2.1) to (2.7) are governed by only 5 parameters (A , p , ξ , q , and n), instead of the 8 parameters ($\phi_1(r_o)$, $\phi_1'(r_o)$, $\phi_1''(r_o)$, $F(\rho_e)$, $F'(\rho_e)$, $F''(\rho_e)$, $\rho'(r_o)$ and $\rho''(r_o)$) which we encountered in the EAM scheme. In the initial development of the TB-SMA scheme, the 5 basic parameters were determined by fitting results from ab initio calculations for high symmetry structures, the only experimental input being the lattice constant. The fitting procedure is quite cumbersome since the ab initio results are not easily available. Physical quantities like the elastic constants, the vacancy formation energy, etc were subsequently predicted by the theory. Unfortunately this ambitious programme [20,21] is yet to reach the much desired perfection stage, since several predicted quantities are in conflict with experiment.

In several applications of the TB –SMA scheme the parameter n is specified. In this situation the four remaining free parameters of the TB-SMA scheme can be determined from the EAM equations either using equation (2.1), (2.2), (2.3), and (2.7) or equation (2.1), (2.2), (2.3) and any one of (2.4) to (2.6).

Cohesive energy $E(r)$ expression (Rose et al.) is:

$$E(r) = -E_C \left[1 + \alpha \left(\frac{r}{r_0} - 1 \right) \right] \exp \left[-\alpha \left(\frac{r}{r_0} - 1 \right) \right] \tag{2.13}$$

Where α , the exponential decay factor is $3 \left(\frac{\Omega \beta}{E_C} \right)^{1/2}$

3.0 Results and Discussion

This model for the Alkali metals requires some physical input parameters. These input parameters are the experimental values of the pure metal properties. They are used as input to determine the functions to be used for this work. These inputs are the three bulk elastic constants (C_{11}, C_{12}, C_{44}), the bulk cohesive energy E_C , Lattice constants a , the Bulk modulus B_0 , and the vacancy formation energy E_{IV}^F . The pure metal inputs used to determine the TB-SMA functions are elastic constants (C_{11}, C_{12}, C_{44}) are in 10^{12}erg/cm^3 . Bulk modulus in 10^{12}erg/cm^3 and cohesive energies are in eV. Elastic constants are in 10^{12}erg/cm^3 . The vacancy formation energy E_{IV}^F is expressed in eV. The values for these parameters are taken from Ref. [11,12]. All these are put together in Table 1.

TABLE 1: Experimental Data used for the Parameters Determination.

Physical Quantity	Li	Na	K	Rb	Cs
E_C (eV), Cohesive Energy.	1.6300	1.1130	0.9340	0.8520	0.8040
E_{IV}^F (eV), Monovacancy.	0.4800	0.3400	0.3400	0.2700	0.2600
a (Å), Equilibrium Lattice.	3.5092	4.2906	5.3200	5.7000	6.1400
B_0 (erg/cm ²), Bulk Modulus.	0.1160E+12	0.0680E+12	0.0320E+12	0.0310E+12	0.0200E+12
C_{11} (erg/cm ²), Elastic Constant.	0.1440E+12	0.0816E+12	0.0415E+12	0.0312E+12	0.0247E+12
C_{12} (erg/cm ²), Elastic Constant.	0.1210E+12	0.0679E+12	0.0340E+12	0.0262E+12	0.0206E+12
C_{44} (erg/cm ²), Elastic Constant.	0.1070E+12	0.0570E+12	0.0284E+12	0.0186E+12	0.0148E+12

TABLE 2: Calculated parameters of TB-SMA from this study up to fourth neighbours.

METALS	A(eV)	ξ (eV)	P	q	n	r_0 (Å)	α
Li	1.2524E-03	0.5798	46.4200	0.2836	0.2840	3.0390	2.0786
Na	8.1485E-04	0.3961	48.4470	0.2821	0.2954	3.7157	2.6038
K	7.9876E-04	0.3325	42.8100	0.2909	0.3537	4.6071	2.6921
Rb	9.9593E-04	0.3041	45.8400	0.4247	0.3087	4.9362	3.0768
Cs	1.1243E-03	0.2874	38.2910	0.42370	0.3163	5.3172	2.8442

Table 3: The calculated minimum Cohesive energy function $E(r)$ of this study (TS), compared with Rose et.al [9].

METALS	THIS STUDY	ROSE ET. AL[9]
Li	-1.6280	-1.6300
Na	-1.1117	-1.1130
K	-0.9326	-0.9340
Rb	-0.8504	-0.8520
Cs	-0.8021	-0.8040

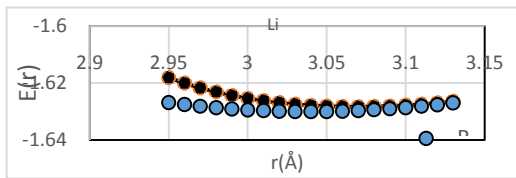


Fig. 1: The Cohesive energy function $E(r)$ of Li, obtained from this study and compared with Rose et. al.[9].

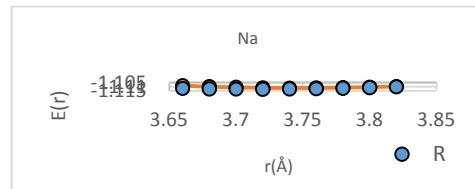


Fig. 2: The Cohesive energy function $E(r)$ of Na, obtained from this study and compared with Rose et. al.[9].

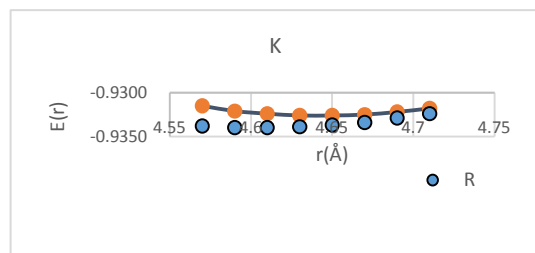


Fig. 3: The Cohesive energy function $E(r)$ of K, obtained from this study and compared with Rose et. al.[9].

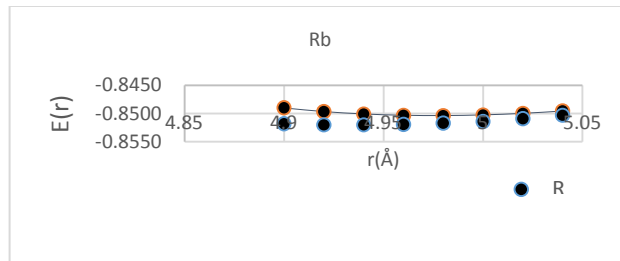


Fig. 4: The Cohesive energy function $E(r)$ of Rb, obtained from this study and compared with Rose et. al.[9].

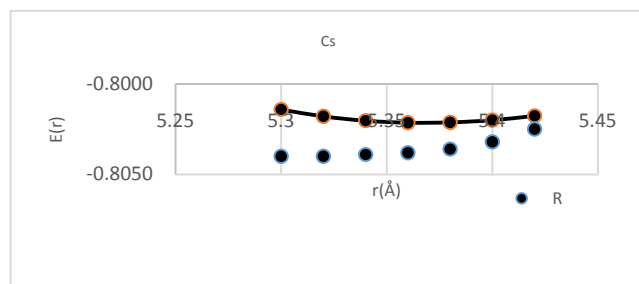


Fig. 5: The Cohesive energy function $E(r)$ of Cs, obtained from this study and compared with Rose et. al.[9].

Results and Discussion

3.0 The experimental data used for the determination of the parameters are shown in Table 1. The parameters of the tight-binding potentials calculated for the five alkali metals up to fourth neighbors with the variation of parameter n , are presented in Table 2.

The cohesive energy function $E(r)$ obtained from this study, in comparison with Rose et.al are illustrated in Fig.1 (Li), Fig.2 (Na), Fig.3 (K), Fig.4 (Rb) and Fig.5 (Cs).

The values of the minimum cohesive energy function $E(r)$ obtained in this study and Rose et.al are illustrated in Table 3.

The percentage differences between the determined values of the minimum cohesive energy function $E(r)$ of this study and Rose et.al are: Li (0.31%), Na (0.12%), K (0.15%), Rb (0.19%) and Cs (0.25%) and both graphs have their minimum cohesive energy points as shown in Table 3.

It was observed from Fig.1 (Li), Fig.2 (Na), Fig.3 (K), Fig.4 (Rb), and Fig.5 (Cs) that the cohesive energy curves of This Study are narrower than the standard curve of Rose et.al [9] and both curves tend to converge as the nearest neighbor distances, $r(\text{\AA})$, increases.

4.0 Conclusion

In this study, the connection between EAM and TB-SMA scheme has been established and utilized to determine the five unknown parameters in the TB-SMA scheme. The parameter n is not constant for all the alkali metals.

This study Cohesive energy function curve and the Rose et.al curve is in good agreement with each other. Therefore, the calculated TB-SMA parameters could be used to obtain other phonon thermodynamics properties of the alkali metals.

5.0References

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