International Journal of Pure & Applied Physics
ISSN 0973-1776 Vol.1 No.2 (2005), pp. 198-206

http://www.ripublication.com/ijpap.htm

Phase Stability of Less Simple Hexagonal-Close-Packed [*hcp*] Metals at the Nanoscale : Roles of Interatomic Interactions and Coordination

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Abstract

We have investigated the roles of the pair interactions and atomic coordination in the phase stability of a number of less simple hexagonal-close-packed [*hcp]* elemental systems e.g. Zn, Cd and Tl within the nano-crystalline range. The underlying theory is based on the pair wise interactions amenable to the corresponding large crystal with negligible surface effects; this assumption allows the nano-crystal to behave like the bulk crystal immediately below the surface. The corresponding model potential is selected in a way so that it can precisely take care of the sp and d electrons relevant to these systems in terms of the superposition of the states. The prime aim of the present investigation is to invoke the matching condition between the minima in the pair potentials and the first few real vectors in conjunction with the atomic coordination to determine the underlying crystalline phase. The analysis sheds some light on the preliminary aspect of the stability of the phases within the static lattice approximation.

Keywords: Phase stability, elemental metals, pair potentials and atomic coordination.
PACS numbers: 61.66.Bi, 62.50.+p, 64.30.+t

Introduction

Recently there has been a tremendous amount of interest in the production of materials in the nanoscale because of their technological and commercial implications

[1]. It has been observed that when materials are shrunk down to the nanometer scale fabricating nanodots, nanoparticles, nanorods and nanotubes a few dozens of atoms across, a variety of interesting properties appear in these systems. These new properties appearing in these technologically viable materials might add new dimension to their further sophisticated applications [2]. The nanocrystals formed out of the large crystals have been found to adapt a number of interesting features while they come across different environments. For an example, it has been observed that when the semiconducting material ZnS shrunk to nanoscale is brought in contact with water, the entire crystal structure rearranges to become more ordered, closer to the structure of a bulk crystal of ZnS. This phenomenon could have immense implication for our understanding of the extra terrestrial materials and identification of extraterrestrial rocks, especially when the interpretation is done by a robotic probe. A nanoparticle formed in an environment surrounded by water molecule will have different surface and bulk structure than when it is formed in an environment apparently without water. Any replacement of the environment brings along different structural transformation. This environment driven phase transformation in nanoparticles might bring along changing in thermodynamic, atomic and electronic transport properties, optical properties and even in thermomechanical properties e.g. crystal strength in the nanoparticles [3].

The above perspectives might be summarized to the facts that: (a) nanoparticles undergo structural phase transformations induced by the surface perturbation, (b) the dangling bonds of the particle surface induce some types of novel chemical binding that can go down to the surface up to a few atomic layer and (b) the core structure mostly remains unaffected by the environment in many cases.

In the present investigation we are interested to look for the possible structural phase stability within the nanoscale pertaining in a number of less simple *hcp* metallic systems namely, Zn, Cd and Tl. We are primarily interested in the bulk of the nanocrystal that resembles that of the large crystal under normal thermodynamic conditions. The surface effect is taken as a weak perturbation assuming that it does not noticeably affect the bulk of the system. Consequently we invoke a pair wise interaction to describe the ion-ion and electron-ion interactions in the atomic distribution of the crystalline systems. The pair wise interaction might be relatively simple for the systems under consideration, but this certainly gives an average and qualitative description of the binding of the crystalline phases of the systems [4].

Now looking at the electronic structure of the less simple systems under consideration it is noted that the d-shells of these systems are completely filled. This indicates that even though the d-electrons might not be of significant importance in determining the stable crystal structure, the sp-d band hybridization certainly plays an important role in the structural properties of these systems [5,6]. Consequently these systems demand a model which self-consistently incorporates this band hybridization effect in the relevant formalism. The Bretonnet and Silbert (BS) [7] model developed recently is an ideal candidate for this purpose: it can precisely take care of this effect relatively in a simpler way. Essentially this potential is derived from a simple superposition of the s-p and d contributions. The relevant pair potential, which is the prime ingredient of the present calculations, is then calculated in terms of the BS model potential. The calculated pair potential is employed to compute the static lattice energies in the various ranges of lattice shells constructed within the nanoscale. Finally the elastic constants with particular emphasis on the stiffness and compliance constants are calculated.

The layout of the paper is as follows: In section 2 we have briefly described the formulation suitable for the bulk of a hypothetical nanocrystal. In section 3 we present and discuss the results and finally some concluding remarks are made in section 4.

Basic Formulation

As indicated in the introduction that our present aim is to investigate the structural stability of a number of less simple elemental metals in terms of the profile of the pair potential in conjunction with the relative position of the lattice vectors of the underlying crystal structures. Consequently we have employed the pair potential φ(r) to calculate the free energies and the elastic constants to look for a microscopic insight into the phase stability of a number of sp-d bonded systems. In view of this, we have presented the basic formulation of the energies in terms of the second order pseudopotential theory combining the pair potential.

Bretonnet and Silbert [BS] Model Potential

As mentioned above the BS local pseudopotential can be constructed by the superposition of sp- and d-band contributions [7] for a metallic system,

$$V(r) = \sum_{m=1}^{2} B_m \exp(-r/ma) \qquad \text{if } r < R_C \tag{1}$$
$$= -Z/r \qquad \text{if } r > R_C$$

where a, R_C and Z stand for softness parameter, core radius and the effective s-electron occupancy number, respectively. The form inside the core is obtained from the concept of d-band inverse scattering approach. Outside the core it is the bare Coulomb interaction between an electron and an ion. The coefficients B_1 and B_2 for the systems depend on their R_C, a and Z values. The unscreened form factor of equation (1) is:

$$v(q) = 4\pi n a^3 \left[\frac{B_1 J_1}{\left(1+a^2q^2\right)^2} + \frac{8B_2 J_2}{\left(1+4a^2q^2\right)^2} \right] - \frac{4\pi Z e^2 n}{q^2} \cos(qR_C) \tag{2}$$

where, n $(= z\rho)$ is the average number density and

$$J_m = 2 - \exp\left(-\frac{R_C}{ma}\right)\left\{\left[\frac{R_C}{ma}\left(1+m^2a^2q^2\right) + \left(1-m^2a^2q^2\right)\right]\frac{\sin(qR_C)}{maq}\right.$$
$$\left. + \left[2 + \frac{R_C}{ma}\left(1+m^2a^2q^2\right)\right]\cos\left(qR_C\right)\right\} \tag{3}$$

Pseudopotential Method : Energetics and Pair Potentials

The binding energy per atom for an sp-d bonded crystalline metal having *N* atoms with valency *Z* contained in a volume *Ω* is given by [8]

$$U(\Omega, g) = U_0(\Omega) + U_E + \sum_{q\neq} |S(q)|^2 \varphi(q)\delta_{q,g} \tag{4}$$

where ***g*** is a reciprocal lattice vector of the underlying lattice. $U_o(\Omega)$ depends on the crystal volume *Ω* and represents the energy of the free electron gas and electrostatic energy of ions embedded in it. The Ewald energy of point ions in a uniform gas of electrons is denoted by U_E and the band structure energy comprising the central interaction *φ(q)* is given by the last term in equation (4). The real space representation of equation (4) takes the form

$$F(\Omega, R) = ZF_{eg} - \Omega K_{eg}^{-1} + \frac{1}{2}\varphi(\Omega, R=0) + \frac{1}{2N}\sum_{R\neq 0}\varphi(\Omega, R) \tag{5}$$

where F_{eg} is the electronic gas contribution, K_{eg} is the compressibility of the free electron gas and ***R*** is a real lattice vector of the underlying lattice. Here *φ(Ω, R=0)* represents the electrostatic interaction between an ion and its own screening cloud of electrons. The central interatomic pair potential is given by

$$\varphi(\Omega, R) = \frac{2Z^2}{R} + \frac{1}{4\pi^3}\int F(q)\frac{\sin qR}{qR}(4\pi q^2)dq \tag{6}$$

The wave number characteristic *F(q)* is given by

$$F(q) = \frac{q^3}{4\pi}\left[\frac{1}{\varepsilon(q)} - 1\right]v^2(q) \tag{7}$$

where *v (q)* is the bare pseudopotential form factor given by equation (2). The screening function *ε(q)* is given by

$$\frac{1}{\varepsilon(q)} = 1 + \frac{(4\pi/q^2)\lambda_o(q)}{1-(4\pi/q^2)(1-G(q))\lambda_o(q)} \tag{8}$$

Here ε(q) and G(q) denote the dielectric function and local field correction, respectively. These functions were taken from Ichimaru and Utsumi [9]. The values of core radii were taken from Harrison [6]. The interatomic pair potentials for the various systems are calculated by using the room temperature number density. Here λ_o is the non-interacting response function.

Elastic Constants from Pair Potential

In the nearest neighbor approximation the elastic constants C_{ij} are related to the derivatives of the pair potential *φ (r)* constituting the force constants *g* and *T* [10]

$$T = \left(\frac{1}{r}\frac{d\varphi}{dr}\right)_{r=R} \qquad \text{[tangential]} \qquad \text{(a)} \tag{9}$$

$$g = \left(\frac{d^2\varphi}{dr^2}\right)_{r=R} \qquad \text{[radial]} \qquad \text{(b)}$$

For a face-centred-cubic [*fcc*] lattice the two elastic constants are given by

$$C_{44} = \frac{(g+3T)}{(4\Omega_0)^{1/3}} \qquad \text{[stiffness constant]} \qquad \text{(a)} \qquad (10)$$

$$\frac{1}{2}(C_{11} - C_{12}) = \frac{(g/2 + 7T/2)}{(4\Omega_0)^{1/3}} \qquad \text{[compliance constant]} \qquad \text{(b)}$$

where Ω_0 is the equilibrium atomic volume of the crystalline system. These for the body-centred-cubic [*bcc*] lattice are

$$C_{44} = \frac{(g/3 + 2T/3)}{(2\Omega_0)^{1/3}} \qquad \text{(a)} \qquad (11)$$

$$\frac{1}{2}(C_{11} - C_{12}) = \frac{T}{(2\Omega_0)^{1/3}} \qquad \text{(b)}$$

The elastic constants for the hexagonal-close-packed [*hcp*] structure are given by

$$C_{44} = \frac{(2g/3 + 10T/3)}{(4\Omega_0)^{1/3}} \qquad \text{(a)}$$

$$\frac{1}{2}(C_{11} - C_{12}) = \frac{(5g/6 + 10T/6)}{(2\Omega_0)^{1/3}} \qquad \text{(b)} \qquad (12)$$

$$\frac{1}{6}(C_{11} - C_{12} + 2C_{33} - 4C_{13}) = \frac{1}{(\Omega_o)^{1/3}}(g+3T) \qquad \text{(c)}$$

Results and Discussions

The input parameters used in the calculations are presented in Table 1. The calculated pair potentials φ (r) for Zn, Cd and Tl are shown in Figures 1 (a-c). The values of the first three lattice vectors for each structure corresponding to these elemental systems along with the pair potential minima $\varphi_{min}(r)$ are shown in Table 2.

Table 1: Input parameters used in the calculations. Here Ω_a is the atomic volume, n the number density, R_c the core radius, a the softness parameter and Z the effective valence associated with the BS potential [7]. The units are indicated with the quantities.

Parameter/ System	Ω_a(Å^3)	n(Å^{-3})x10^{-2}	R_c(au)	a (au)	Z
Zn	15.20	6.58	1.27	0.285	1.8
Cd	21.61	4.63	1.23	0.253	1.4
Tl	28.64	3.49	1.13	0.218	1.5

Table 2: The first three real vectors *R* for the *fcc, bcc* and *hcp* structures for Zn, Cd, Tl. The minima in the pair potentials $\varphi_{min}(r)$ (au) are presented in the last column. All the quantities are in atomic units.

R/ System	Real lattice vectors *R* (au)									
	fcc			*bcc*			*hcp*			$\varphi_{min}(r)$ (au)
Zn	5.25	7.42	9.09	5.10	5.88	8.33	5.02	7.10	8.21	5.03
Cd	5.91	8.36	10.24	5.75	6.63	9.39	5.63	7.96	9.20	5.60
Tl	6.49	9.18	11.24	6.31	7.28	10.31	6.54	9.24	10.68	5.77

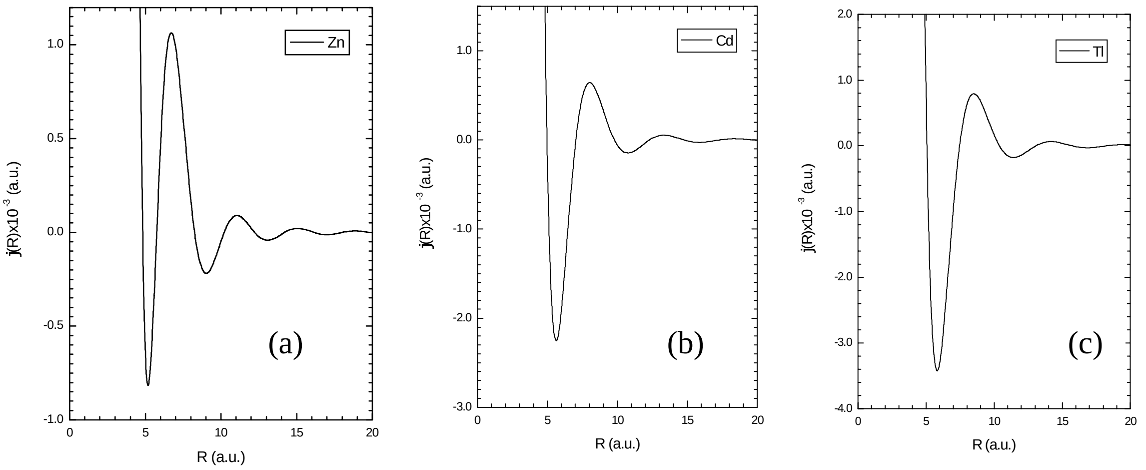

Figure 1. Pair potentials for (a) Zn, (b) Cd and (c) Tl calculated by using the Bretonnet-Silbert [BS] pseudopotential [7]. The input parameters used in the calculations are presented in Table 1.

Results for the energy differences *ΔE* between *bcc-fcc* and *bcc-hcp* for all the three systems are shown in Figures 2(a-c). Within all the shells the calculations overwhelmingly predict an *hcp* structure for all the systems. The energy differences, however, exhibit an oscillatory profile over the entire range of lattice shells. Now if we look at Figure 1 (a) for Zn, it is observed that the first *hcp* [*c/a* = 1.85] lattice vector is in the closest vicinity of the pair potential minimum followed respectively by the first *bcc* and *fcc* lattice vectors. The second minimum which is very shallow appears immediately after 8.8 au which corresponds to the second *bcc* lattice vector and obviously this situation can not alter the phase stability. For Cd the situation is much more subtle: looking at Figure 1 (b) it is noted that the first *hcp* [c/a = 1.89] lattice vector is the most relevant one to the corresponding pair potential minimum generating the minimum energy for this structure. Other lattice vectors are not visibly relevant so far the structural prediction is concerned; this is noted clearly in the energy differences ΔE in Figure 2 (b). Consequently the experimentally observed *hcp* [*c/a* = 1.89] has been seen to be stable over the entire nanoscale range. For Tl, the experimental *hcp* [*c/a* = 1.6] structure is also predicted by the present calculations; even though first lattice vector for the *hcp* structure is not the most relevant one, but the next few hcp shells and the higher coordination are assumed to favor this prediction. For all the three crystalline systems the structural prediction follows the sequence *hcp-bcc-fcc*.

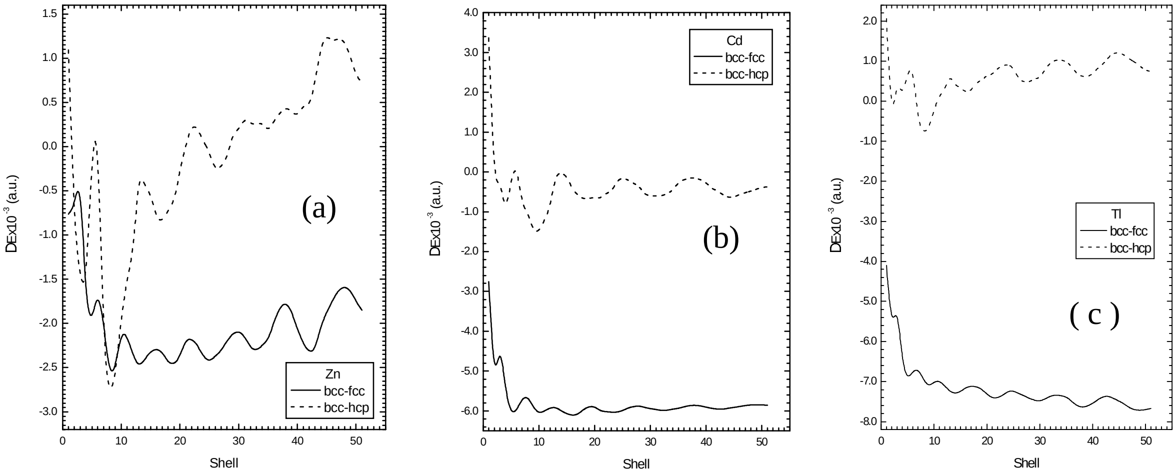

Figure 2: Energy differences between *bcc – fcc* and *bcc-hcp* for (a) Zn, (b) Cd and (c) Tl calculated by using the Bretonnet-Silbert [BS] pseudopotential [7]. The input parameters used in the calculations are presented in Table 1.

Finally we display the calculated results of the elastic constants for the elemental systems in Table. 3 corresponding to the various phases. Among these the stiffness constant C_{44} is assumed to be a measure of the strength of crystal binding [11]. Looking at the numerical values of the results, it might be concluded that for all of the systems C_{44} rightly represents the *hcp* structure having the highest value. Normally the first coordination is employed to calculate the elastic constants; in our calculations we have used up to 10 shells to see the roles of the higher order shells. It is noted that the results converge rather rapidly after the first few shells for all cases.

Now the results for elastic constants C_{ij} are an indication that the stability of a crystalline phase is some what related to the matching between the minima of the pair potentials and the positions of the first few real lattice vectors of the underlying structures. Thus the conclusions that we made in the calculations of the energy differences are along the lines that we have observed in the elastic constant calculations.

Table 3: Calculated elastic constants for Zn, Cd and Tl corresponding to *bcc, fcc* and *hcp* structures. All units are in x10^{11} Nm^{-2}.

System	*bcc*		*fcc*		*hcp*		
	C_{44}	$\frac{1}{2}C_{112}$[a]	C_{44}	$\frac{1}{2}C_{112}$[a]	C_{44}	$\frac{1}{2}C_{112}$[a]	$1/6C_{123}$[b]
Zn	0.097	0.105	0.067	0.093	0.117	0.224	0.007
Cd	0.062	0.073	0.052	0.044	0.078	0.093	0.078
Tl	0.062	0.015	0.09	0.013	0.067	0.017	0.036

[a] $\frac{1}{2}C_{112}$ corresponds to $\frac{1}{2}(C_{11}-C_{12})$ and

[b] $1/6C_{123}$ corresponds to $1/6[C_{11}-C_{12}+2C_{33}-4C_{13}]$

Conclusions

We make the following conclusions in the light of the present calculations:

(1) The calculations have correctly predicted the crystal structure for all the *hcp* lattices with the observed *c/a* ratio. Within the nanoscale, the structural prediction is not over turned as more and more contributions from higher order lattice shells are added to the crystal sums.

(2) The correct matching between the minima of the pair potential and the positions of the first few lattice vectors in conjunction with the respective coordination numbers dominates the phase stability of these systems within the nanoscale.

(3) Going beyond the pair interactions [12] might improve the quantitative nature of the predictions, but our early experience indicates that this inclusion will merely supplement the predictions made by the pair wise interactions.

(4) The calculated stiffness and compliance constants have supplemented supports for the structural prediction. This indicates that the pair wise interaction employed in the calculations has successfully reproduced at least this aspect of the thermomechanical properties.

The present calculations have been done for static lattice approximation. Presently we are involved with calculations considering the lattice vibrations in the formalism to estimate the roles of lattice dynamics in the phase stability of the systems concerned. Roles of entropy with a realistic model are also under consideration.

Acknowledgments

We would like to acknowledge the financial supports under the research grant no # IG/SCI/PHYS/02/02 of the Sultan Qaboos University. AZZA is particularly grateful to the Sultan Qaboos University for extending him all possible supports. Mr Mohammed Al-Rawahi is acknowledged for his logistic supports during the process of the work.

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