IONIC OVERLAP INTERACTION ENERGY, PRESSURE AND BULK MODULUS FOR CUBIC METALS

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Ion-ion overlap interaction plays a dominant role in governing the lattice dynamical behaviour of crystals having significant ionic-size. It is abundantly clear that the ionic interaction is screened out up to a few neighbours due to the presence of the conduction electrons in metallic crystals. In the present communication expressions for ionic-interaction energy (E_I), pressure (P_I) and bulk modulus (B_I) have been derived assuming the screening potential first used by Yukawa and later developed by Krebs. It has been assumed that this screened potential couples first two neighbours of the cubic structure. Computations of these quantities for seven body centered and nine face centered cubic metals suggest that the suitable screening is described by compromised model potential scheme whereas Bohm–Pines and Thomas–Fermi schemes represent the limits.

1. Introduction

The ions of non-simple cubic metals, namely the noble metals, the transition metals and the rare earth metals, possess significant size. Electronic structure of these metals reveals the hybridization of various levels. Obviously the ionic-overlap interaction should play a significant role in determining the lattice dynamical behaviours of these metals. It is difficult to evaluate the overlap interaction between the ion-cores from first principles. Generally Born–Mayer potential is used to represent this interaction but this potential is more suitable for ionic-crystals. Recently Moruzzi et al. [1] have reported that a fairly good explanation for cohesion in metals is given by the electron-screening phenomenon. As a matter of fact the electrons are responsible for the various physical and chemical properties of the metals. The screening among ions due to the conduction electrons has been described by Thomas and Fermi (TF) [2] and Bohm-Pines (BP) [3] schemes. Yukawa [4] has developed a theoretical explanation for the nature of the nuclear forces in terms of an empirical screened nucleonic potential. Similar type of a screened Coulombian potential with suitable parameter has been employed by Bhatia [5], Krebs [6] and Cheveau [7] in their lattice dynamical studies of cubic metals.

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The present communication deals with the derivation of the expressions for the ionic interaction energy and subsequently the expressions for the ionic-pressure and ionic-bulk modulus have been derived for the bcc and fcc metals. The numerical values thus obtained are analysed to decide in favour of the most suitable expression for the ionic screening in cubic metals.

2. Theory

The screening parameter (K_c) limiting the range of the ionic interactions may be expressed as

$$K_c = \beta(\gamma_0/a_0)^{1/2}K_F, \tag{2.1}$$

where K_F is the Fermi-wave vector, γ_0 the radius of the atomic sphere, a_0 the Bohr-radius and β denotes a multiplying factor. Various values to β have been attributed by different workers [2, 3, 8, 9] which may be quoted as

$\beta = 0.814$ Thomas–Fermi [2] scheme,
$\beta = 0.353$ Bohm–Pines [3] scheme,
$\beta = 2/\pi$ Compromised Model Potential [8] Scheme,
$\beta = 0.4$ Ho model Potential [9] scheme.

The screened Coulombian potential ϕ_I coupling the neighbouring ions may be written according to Krebs [6] as

$$\phi_I \sim \frac{1}{\gamma}\exp(-K_c\gamma), \tag{2.2}$$

where γ is the ionic separation. The screening makes this interaction effective up to second neighbours leading to the following expressions for the interaction energy (E_I) per ion

$$E_I = 16e^2/a\sqrt{3}\exp(-K_1a^{1/2})+(6e^2/a)\exp(-K_2a^{1/2}) \text{ bcc}, \tag{2.3}$$

$$E_I = 24e^2/a\sqrt{2}\exp(-K_1'a^{1/2})+(6e^2/a)\exp(-K_2'a^{1/2}) \text{ fcc}, \tag{2.4}$$

where a is the lattice constant, and e is the electronic charges.

The parameters K_1 and K_2 for bcc lattices depend on the screening parameter K_c and the lattice constant a i.e.

$$K_1 = \frac{\sqrt{3}}{2}a^{1/2}K_c; \quad K_2 = a^{1/2}K_c \tag{2.5}$$

For fcc lattice these parameters K_1' and K_2' may be expressed as

$$K_1' = \frac{\sqrt{3}}{2}a^{1/2}K_c; \quad K_2' = a^{1/2}K_c \tag{2.6}$$

The screening parameter K_c may be evaluated using equation (2.1) with different values of β. In the present calculations we have used β's as given in Thomas–Fermi [2], Bohm–Pine [3] and compromised model potential [8] schemes. The pressure (P_I) and the bulk modulus (B_I) are expressed as,

$$P = -\partial E_I/\partial\Omega, \quad B_I = -\Omega\partial P_I/\partial\Omega, \tag{2.7}$$

where Ω is the atomic volume of the lattice concerned. Assuming the validity of the expression (2.7) and the sphericity of the Fermi surfaces we can derive the corresponding expressions for pressure (P_I) and bulkmodus (B_I) associated with each ion. These expressions may be written as:

$$P_I = -e^2[(16K_1/3\sqrt{3}\,a^7)\exp(-K_1a^{1/2})+(32/3\sqrt{3}\,a^4)\exp(-K_1a^{1/2}) +(2K_2/a^{7/2})\exp(-K_2a^{1/2})+(4K_2/a^2)\exp(-K_2a^{1/2})]\ \text{bcc}, \tag{2.8}$$

$$P_I = (-32e^2/\sqrt{2}\,a^3)[(K_1'/2a^{1/2}+1/a]\exp(-K_1'a^{1/2}) -(8e^2/a^3)[(K_2'/2a^{1/2}+1/a)]\exp(-K_2'a^{1/2})\ \text{fcc}, \tag{2.9}$$

$$B_I = (-e^2/3a^4)[(8/3\sqrt{3})\{aK_1^2+9K_1a^{1/2}+16\}\exp(-K_1a^{1/2}) +K_2\{K_2(a+2a^{1/2})+(16+7a^{1/2})\}\exp(-K_2a^{1/2})]\ \text{bcc}, \tag{2.10}$$

$$B_I = (-e^2/3a^4)[\{8aK_1'^2/\sqrt{2}+72K_1'a^{1/2}/\sqrt{2}+128/\sqrt{2}\}\exp(-K_1'a^{1/2}) +\{2aK_2'^2+18K_2'a^{1/2}+32\}\exp(-K_2'a^{1/2})]\ \text{fcc}. \tag{2.11}$$

It may be recalled that most of the pseudo potential approaches for lattice dynamical studies employ the local forms of the potential which are valid in the approximation of nearly spherical Fermi surfaces. Moreover K_c is asumed to be volume independent while deriving the equations (2.8) to (2.11).

3. *Results*

For the three different values of β i.e. 0.814, 0.353 and $2/\pi$ the overlap interaction energy, pressure and bulk-modulus per ion are calculated and are enlisted in Table I, II and III, respectively. The bcc metals chosen for the present study are, V, α-Fe, Mo, W, CR,

TABLE I

Ionic-interaction energies (E_I) per ion for cubic metals in units of 10^{12} ergs

Cubic metals	$\beta = 0.814$	$\beta = 0.353$	$\beta = 2/\pi$	Known values for total E_I	Reference
V	0,868	13.558	2,489	8.290	[19, 26]
α-Fe	1.114	15,771	3,076	6.725	[19, 26]
Mo	0,812	13.029	2.349	10,815	[19, 26]
W	0,795	12.972	2.310	14.021	[19, 26]
CR	0.464	9.318	1.464	5.564	[19, 26]
Nb	0.683	11.742	2.032	—	[19, 26]
Ta	0.679	11.748	2.034	12.860	[19, 26]
Cu	1.138	16.841	3.149	5.647	[19, 26]
Ag	0,746	13.013	2.197	4.789	[19, 26]
Au	0.759	13.149	2.230	5.724	[19, 26]
Pd	0.887	14.464	2.547	6.468	[19, 26]
Ni	1.243	17.787	3.398	7.031	[19, 26]
Al	0.778	13.357	2.278	5.174	[19, 26]
Pb	0.374	8.593	1.223	3.234	[19, 26]
Th	0.339	8.109	1.126	8.694	[19, 26]
Pt	0.861	14.205	2.849	8.457	[19, 26]

TABLE II

Ionic pressure (P_I) per ion for cubic metals in units of 10^{12} dyne/cm^2

Cubic metals	$\beta = 0.814$	$\beta = 0.353$	$\beta = 2/\pi$
V	0.0672	0.6370	0.164
Fe	0.1056	0.9083	0.248
Mo	0.06009	0.5805	0.148
W	0.0578	0.5679	0.142
CR	0.0225	0.2688	0.601
Nb	0.0443	0.4562	0.112
Ta	0.0441	0.4567	0.112
Cu	0.1117	0.7718	0.2131
Ag	0.0525	0.4274	0.1074
Au	0.05408	0.4376	0.1104
Pd	0.07145	0.5439	0.142
Ni	0.1312	0.8759	0.247
Al	0.0566	0.4535	0.115
Pb	0.0158	0.1689	0.362
Th	0.0133	0.1487	0.0313
Pt	0.0677	0.5218	0.155

TABLE III

Ionic bulk-moduli (B_I) per ion for cubic metals in units of 10^{12} dyne/cm^2

Cubic metals	$\beta = 0.814$	$\beta = 0.353$	$\beta = 2/\pi$	$B = 1/3$ $(C_{11}+2C_{12})$	Ref. for elastic constants
V	0.1401	1.0763	0.3489	1.552	[20]
Fe	0.2176	1.5016	0.4961	1.679	[21]
Mo	0.1248	0,9824	0.3139	2.619	[22]
W	0.1201	0.9610	0.3031	3.1078	[22]
CR	0.0475	0.4609	0.1298	1.5233	[23]
Nb	0.0923	0.7752	0.2383	1.7133	[20]
Ta	0.0915	0.7760	0.2386	1.919	[24]
Cu	0.2163	1.5676	0.4704	1.371	[25]
Ag	0.1044	0.873	0.2401	1.036	[26]
Au	0.1075	0.894	0.2467	1.729	[27]
Pd	0.1406	1.108	0.3160	1.931	[28]
Ni	0.2525	1.777	0.5430	1.836	[26]
Al	0.1124	0.926	0.2569	0.7607	[28]
Pb	0.0328	0.349	0.07144	0.4816	[26]
Th	0.0279	0.307	0.07144	0.577	[29]
Pt	0.1336	1.0637	0.3445	2.827	[30]

Nb and Ta. The fcc metals for which the above mentioned quantities are calculated are Cu, Ag, Au, Pd, Ni, Al, Pb, Th and Pt. For estimating the electronic contribution towards the binding energy and bulk modulus, the known values of the total cohesion-energy and that for the total bulk-modulus [$B = 1/3\,(C_{11}+2C_{12})$] are recorded in the last columns of the Tables I and III.

4. Conclusions

In the Thomas–Fermi scheme [2] the repulsion between the conduction electrons has not been properly accounted for and therefore it overestimates the screening effect leading to extremely short screening radius [10]. Present author [11] has also reported that this scheme (TF) does not account for the required cohesion in metals. Langer and Vosco [12] have introduced the quantum-mechanical factor $f(t)$ for correcting the TF scheme but the situation is not improved at long wave-lengths. Various studies [13, 14, 15] have reported that the Bohm–Pines [3] scheme based on the collective oscillation approach is suitable for most of the metallic crystals. These workers have pointed out that different values for β are needed for different metals for successful description of their lattice dynamical behaviour.

Numerical results reported here present another comparision of the ionic overlap energies, pressures and bulk-moduli on the basis of three [2, 3, 8] different schemes. This comparison brings out the conclusion that the most suitable values for E_I, P_I and B_I are those obtained using $\beta = 2/\pi$ whereas the Bohm–Pines [3] and Thomas–Fermi [2] schemes represent the limits.

The compromised model potential ($\beta = 2/\pi$) assumes the local version of model potential which amounts to spherical Fermi surfaces, for which the present calculations are made. The values for E_I, P_I and B_I reported here may be employed to estimate the corresponding quantities for the electrons, which can otherwise be given in term of self consistent approximate formalisms [16–18].

The ionic pressure, reported here, plays a dominant role in maintaining the lattice equilibrium, to which an adequate analysis is still needed. Further, these quantities (E_I, P_I and B_I) may be utilised in deriving the various lattice dynamical properties of the crystals.

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