

Total Crystal Energy and Equation of States for Alkaline Earth Metal Using Pseudopotential Approach

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ABSTRACT

In the present paper our well-established model potential describing electron-ion interaction is for alkaline earth metals Ca, Sr and Ba explores to study total energy and equation of states (EOS). The main features of present model potential are single parametric, continues in r-space and weaker within core and Columbic outside the core. The parameter of potential is determined using the equilibrium condition at zero pressure. The total energy, energy-volume (E-V) and pressure-volume (P-V) relation of Ca, Sr and Ba alkaline earth metals are computed using a higher order perturbation theory based on pseudopotential formalism. Numerical values of total energy obtained are found superior than the other theoretical findings. Good agreement is achieved between the presently calculated results of P-V diagram with experimental and other available data found in the literature, confirming the applicability of model potential for such a study. To introduce screening effect different forms of exchange and correlation function are also used.

KEYWORDS: Bulk Metallic Glass, Pseudopotential, Local field correction function, Collective modes, elastic properties

INTRODUCTION

It is recognized that the electronic properties of metals, semiconductors, alloys and compound can be studied using the pseudopotential theory. The total energy of pure metals in the framework of the second order perturbation theory has been a subject of many pseudopotential studies [1-23]. The alkaline-earth metals, group-II in the periodic table, have large compressibility and phase diagrams strongly influenced by a nearly empty d-band lying in close proximity to sp-valance band. The d-band occupation increases with increasing atomic number and with increasing pressure. In effect, pressure converts the alkaline-earth metals from an alkali metal-like to early transition metal-like character. Thus, the study of total energy, energy-volume and pressure-volume relations of these metals, of which Ca, Sr and Ba are the prototype, provides a sensitive test to any theoretical model applied [5, 16-23].

The atomic properties like total crystal energy, pressure, energy – volume relations and pressure – volume relations are computed for Ca (FCC), Sr (FCC) and Ba(BCC) using the reciprocal sum analysis method. Our well tested model potential [24] along with six different forms of local field correction

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functions (LFCF) namely Hartree [3], Taylor [25], Ichimaru-Utsumi [26], Farid et al. [27], Sarkar and Sen [28] and Hubbard Sham [29, 30] to compute the screened form factors, which then used to calculate the total energy and equation of state for Ca, Sr and Ba.

THEORY AND COMPUTATIONAL METHOD

It is difficult to compute static and dynamic properties of crystals such as total energy, pressure, bulk modulus and lattice vibrations using information obtained from the band structure calculation. Second-order perturbation theory based on the pseudopotential formalism is applied to examine the properties of crystals. The total energy of a crystal may be regarded as the sum of two contributions, one of which depends only on the volume of the crystal, and the other, formally, only on the crystal structure. The former includes terms which are independent of the atomic distribution, namely, the kinetic energy of free electrons, and the exchange and correlation energies. The structure dependent energy is the sum of electrostatic energy and the band energy. The total crystal energy per atom of pure metal has been

computed by many workers using pseudopotential calculations up to the third order in the perturbation approach [31].

The first work on the band energy of alloy was done by Hayes and co-workers [32] using a non-local potential. Gurskii and Krasko [33] have reported the total binding energy for all the five alkali metals using a model potential which is continuous in r-space. Soma [5, 16,17] was successful in computing total energy and bulk modulus of some co-valent compounds on the basis of extended perturbation theory. They have used historical model potentials and local Heine-Abarenkov model potential [34] with an additional parameter to ensure minimum energy condition.

The total crystal energy per pseudo-atom, E, of the crystalline solid is obtained in the framework of the usual second order perturbation as [5, 16-20]

$$E = E_i + E_{es} + E_1 + E_2 \tag{1}$$

In equation (2), E_i is the electrostatic energy of point ions immersed in the uniform gas of valence electrons, called the Madelung energy, which is given by

$$E_i = -\frac{\alpha Z^2 e^2}{R_\alpha} \tag{2}$$

With α is the Madelung's constant and $R_\alpha = r_s Z^{\frac{1}{3}}$ and r_s is the radius of the sphere containing one electron.

In Equation (1), E_{es} is the sum of the kinetic, exchange and correlation energies of the valence electron and is given by

$$E_{es} = Z \left[\frac{3.21}{r_s^2} - \frac{0.916}{r_s} - 0.115 + 0.031 \ln(r_s) \right] \tag{3}$$

E_1 is the First order perturbation energy of the valence electron due to the pseudopotential and is given by,

$$E_1 = \lim_{q \rightarrow 0} \left[\frac{4\pi Z_{eff}^2 e^2}{\Omega_0 q^2} + Z V_B(q) \right] \tag{4}$$

RESULTS AND DISCUSSION

The input parameters used in the present calculations are presented in Table 1. Here parameter of potential r_c has been calculated using the zero-pressure condition (11).

Table 1. Input Parameter and constants

Metals	Z	Ω_0 (a.u) ³	r_c (a.u)					
			H	T	IU	F	S	HS
Ca	2	293.49	1.0459	0.9995	0.99725	0.9909	1.0234	1.0306
Sr	2	380.44	1.1755	1.1241	1.11768	1.1098	1.1513	1.1587
Ba	2	428.56	1.2359	1.1766	1.13559	1.1186	1.1924	1.2175

and E_2 is the second order perturbation energy is the band structure energy.

$$E_2 = \sum_{q \neq 0} F(q) \tag{5}$$

Here $F(q)$ is the normalized energy wave number characteristics and is given by

$$F_{eff}(q) = -\frac{4\pi Z_{eff}^2 e^2}{16\pi} |V_B(q)|^2 \times \frac{[z_H(q)-1]}{(1+z_H(q)-1)[1-f(q)]} \tag{6}$$

Where $V_B(q)$ is the bare ion pseudopotential from factor is given by [24].

$$V_B(q) = -\frac{4\pi Z^2 e^2}{\Omega_0 q^2} \left(\cos(qr_c) - \frac{\exp(-1)}{1+(qr_c)^2} \frac{q r_c}{\Omega_0} (\sin(qr_c) + qr_c \cos(qr_c)) \right) \tag{7}$$

The pseudopotential form factor used to describe the electron-ion interaction in metals of the form (in Rydberg Units). Where Z , Ω_0 , q and r_c are valency, atomic volume, wave vector and parameter of the potential respectively. The potential of this type is representative of self-consistent potentials with single parameter r_c . $\epsilon_H(q)$ is the static Hartree dielectric function and $f(q)$ be the LFCF.

The pressure P is obtained from the first derivative of the total crystal energy per atom E with respect to the atomic volume Ω_0 given by,

$$P = -\frac{dE}{d\Omega_0} \tag{8}$$

$$P_{total} = -\left[\frac{dE_i}{d\Omega_0} + \frac{dE_{es}}{d\Omega_0} + \frac{dE_1}{d\Omega_0} + \frac{dE_2}{d\Omega_0} \right] \tag{9}$$

We can write the above equation as

$$P = P_i + P_0 + P_1 + P_2 \tag{10}$$

By setting the derivative

$$\frac{dE}{d\Omega_0} = -P = 0 \tag{11}$$

The parameter of the potential (7) for metals Ca, Sr and Ba are evaluated.

Total crystal energy**Table 2. Total Crystal Energy (Ryd/atom) at zero pressure for Calcium (Ca)**

LFCF [35]	Various contribution of energy (Ryd)				E (Ryd)	Others [35] [36]
	E _i	E ₀	E ₁	E ₂		
H	-1.7384	-0.3035	0.4629	-0.0381	-1.6172	-1.3917 -1.3366
T	-1.7384	-0.3035	0.4228	-0.0573	-1.6765	
IU	-1.7384	-0.3035	0.4209	-0.0404	-1.6615	
F	-1.7384	-0.3035	0.4159	-0.0426	-1.6690	
S	-1.7384	-0.3035	0.4433	-0.2813	-1.6268	
HS	-1.7384	-0.3035	0.4416	-0.0440	-1.6364	

Table 3. Total Crystal Energy (Ryd/atom) at zero pressure for Strontium (Sr).

LFCF [37]	Various contribution of energy(Ryd)				E (Ryd)	Others [37] [38]
	E _i	E ₀	E ₁	E ₂		
H	-1.5949	-0.3174	0.4512	-0.0338	-1.4944	-1.1621 -1.2770
T	-1.5949	-0.3174	0.4126	-0.0498	-1.5489	
IU	-1.5949	-0.3174	0.4079	-0.0330	-1.5369	
F	-1.5949	-0.3174	0.4022	-0.0352	-1.5448	
S	-1.5949	-0.3174	0.4328	-0.0214	-1.5003	
HS	-1.5949	-0.3174	0.4389	-0.0385	-1.5119	

Table 4. Total Crystal Energy (Ryd/atom) at zero pressure for Barium (Ba)

LFCF [37]	Various contribution of energy (Ryd)				E (Ryd)	Others [37] [38]
	E _i	E ₀	E ₁	E ₂		
H	-1.5325	-0.3214	0.4427	-0.0322	-1.4434	-0.9717 -1.2181
T	-1.5325	-0.3214	0.4014	-0.0483	-1.5008	
IU	-1.5325	-0.3214	0.3738	-0.0419	-1.5220	
F	-1.5325	-0.3214	0.3627	-0.0476	-1.5388	
S	-1.5325	-0.3214	0.4122	-0.0244	-1.4642	
HS	-1.5325	-0.3214	0.4297	-0.0365	-1.4607	

Total crystal energy for Ca, Sr and Ba are shown in Table 2, 3 and 4 respectively. From table 2, 3 and 4 it is observed that the maximum total crystal energy is obtained due to the H screening functions. For Ca metals the total crystal energy, the computed percentile influence with respect to H function are 3.66%, 2.74%, 3.20%, 0.59% and 1.19% for T, IU, F, S and HS screening functions respectively. For Sr metals computed percentile influence with respect to H function are 3.65%, 2.84%, 3.37%, 0.39% and 1.17% for T, IU, F, S and HS screening functions. Similarly, we computed the percentile influence for Ba metals is observed with respect to H function are 3.97%, 5.45%, 6.60%, 1.41% and 1.46 for T, IU, F, S and HS screening functions. From this result we observed that the for pure FCC (Ca, Sr) metals, T screening functions shows the maximum and S screening functions shows the minimum influence with respect to static H screening function than the other five screening functions while F screening function shows the maximum influence with respect to the H functions than the other five screening functions for BCC (Ba) metals. It is also observed that the present values are in good agreement with other values [36-38]. Due to lack of other information we do not put any concert remark for the total energy of Ca, Sr and Ba, but in the absence of other data these results will provide a good set of data for future comparison.

Energy-Volume (E-V) relation

Energy-Volume Relations always serve as a database in the construction of empirical schemes. Both self-consistent and non-self-consistent Harris Foulkes calculation can be done and a connection is made between them and simpler tight binding and classical model of interatomic forces. Energy –Volume relations help us to find equilibrium lattice parameter and also to compute the elastic properties like bulk modulus etc. Here, we evaluate the energy-volume relations of alkaline earth metals along with six local field correction functions. Figure 1, 2 and figure 3 shows the energy-volume relation for the Ca, Sr and Ba metals. The figures 1 to 3, we observed that T screening functions shows the maximum and S screening functions shows the minimum influence with respect to the H function than the other local field correlation functions. In the absence of

experimental data we have computed the percentile influence for these metals with respect to H screening functions. For the energy-volume relation the computed percentile influence with respect to H function are 3.75-4.43%, 2.83-3.24%, 3.23-3.63%, 0.68-0.43% and 1.27-1.44% for T, IU, F, S and HS screening functions respectively for Ca metal. The percentile influence with respect to H in the E-V relation with Sr metals along with other screening functions the values are 3.65-4.49%, 2.85-3.11%, 3.37-3.81%, 0.40-0.094% and 1.18-1.45% of T, IU, F, S and HS functions, respectively. From figure 3, the percentile influence with respect to H screening functions for Ba metal, the values are 3.98-7.73%, 5.44-9.86%, 6.61-11.9%, 1.43-2.82% and 1.12-2.45% of T, IU, F, S and HS functions, respectively.

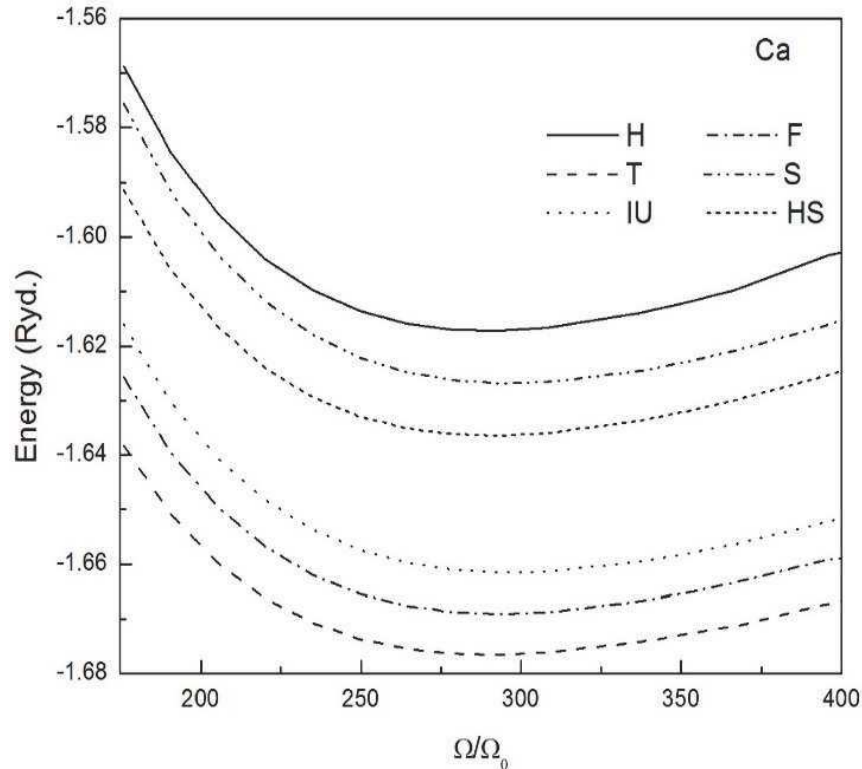


Figure 1. Energy-Volume relation for Ca.

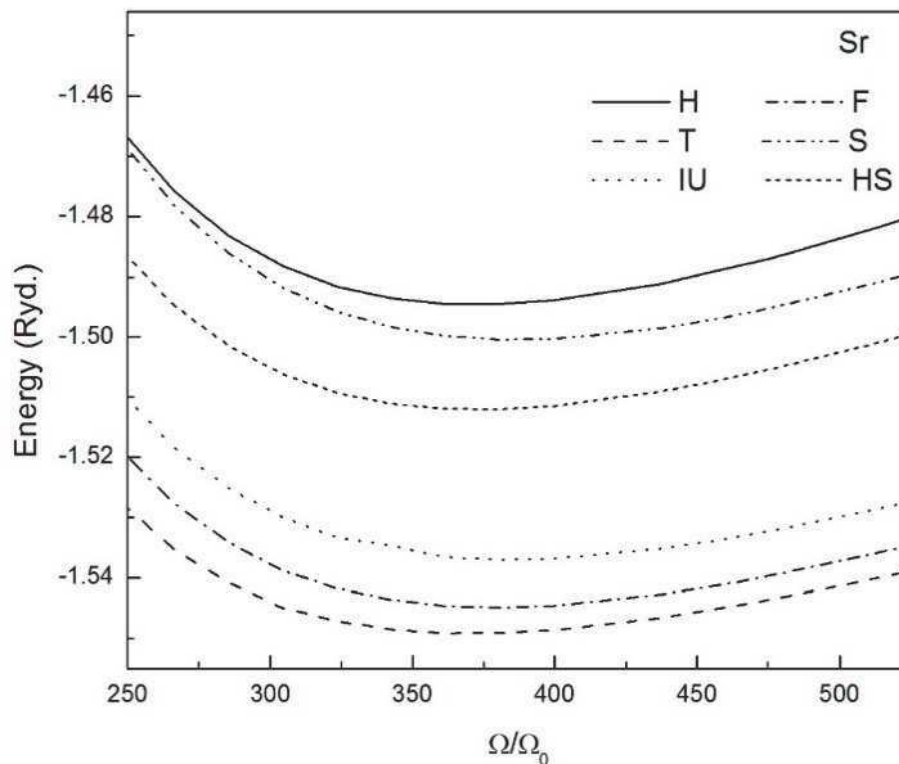


Figure 2. Energy-volume relation for Sr.

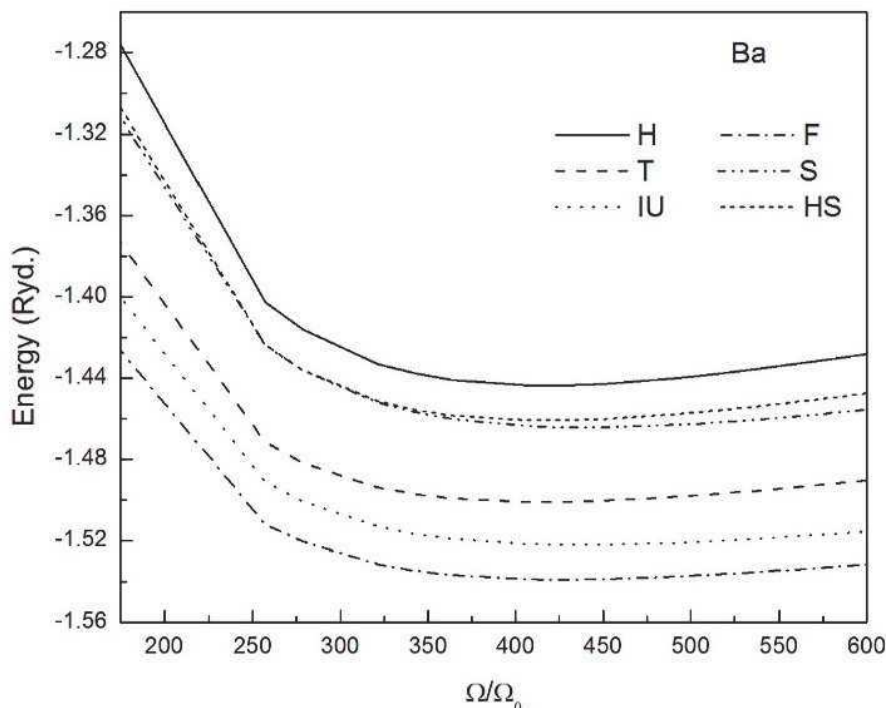


Figure 3. Energy-volume relation for Ba.

Pressure – Volume (P-V) relations

As shown in figure 3, the computed P-V relation for Ca along H and S screening functions lie along with experimental data [39,40] and hence this screening functions show good agreement with experimental data than the other screening function computed due to present potential. It is observed that present results computed using the model potential along with Hartree (H)[3] and Sarkar et al [24] screening functions shows the better agreement with Bhatt et al [40] and available other data reported by Bhatt et al [40]. They are reported P-V relation using local pseudopotential and they have used the local pseudopotential proposed by Fiolhais et al [40]. Figure 2, Shows the P-V relation for Sr compared along with experimental data due to Budy and Strong [39, 41] other data reported by Vyas et al.[42, 43]. It is observed that present results computed using the model potential along with Hartree (H) screening functions shows the better agreement with the available of experimental data and obtained due to Vyas et al.[43] results. To include the effect of temperature, Vyas et al. [43] have reported on empirical EOS with the adjustable parameter and deduce EOS at room temperature. Inflections in their EOS at pressures 24 and 63.5 Kbar indicating structural phase transition cannot be reproduced by the present scheme. On other hand, results on high-pressure [43] EOS predict SPT at about 35Kbar a first-order transition from one crystal structure (fcc-cF4) into another (bcc-cI2) [43] is observed. Figure 3 shows the P-V relation for the Ba metal compared with available experimental data [41]. At a first sight it is noted that the present results computed using local model potential is in excellent agreement with the observational outcomes. It is also observed that the outcome of the present results calculated using the present model potential using with T-function shows good agreement with experimental data computed other screening functions. Our present approach for alkaline earth metals (Ca, Sr, Ba) is found to be good agreement with available experimental and other results.

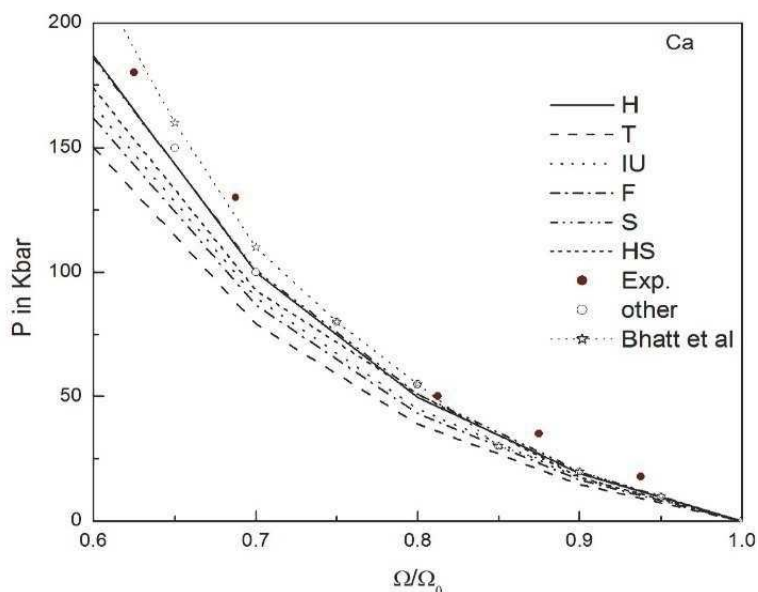


Figure 4. P-V relation for Ca along with Exp.[39], other available data and Bhatt et al [40].

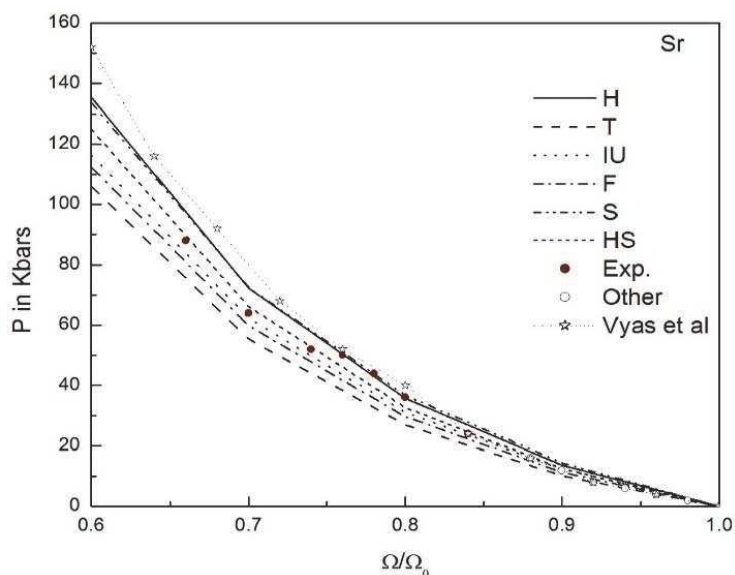


Figure 5. P-V relation for Sr along with Exp.[39], other available data and Vyas et al[42, 43].

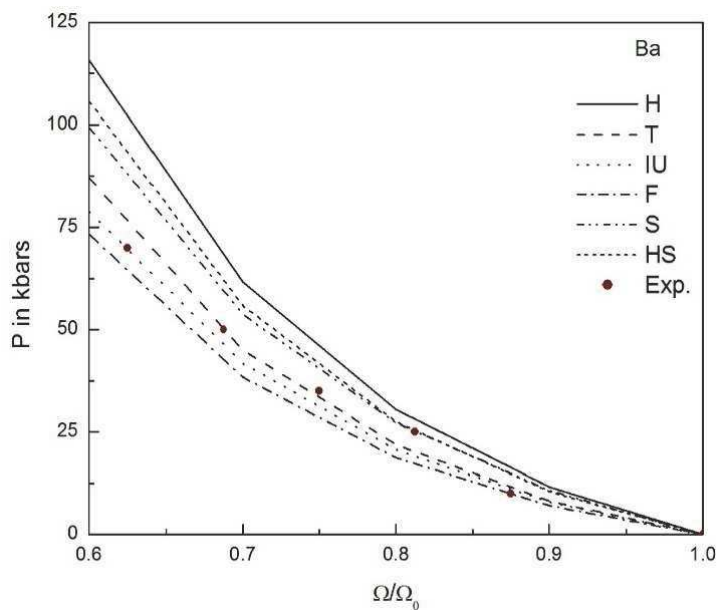


Figure 6. P-V relation for Ba along with Exp.[40].

Overall, the results of total energy, energy-volume relation and equation of state computed here for Ca, Sr and Ba metals suggests that the proper choice of exchange and correlation function is essential for the present study.

Conclusion

Finally, we conclude that the total energy computed using present model potential along with Sarkar et al. screening function is found to be in better agreement with experimental data than the other available theoretical data and H function is found to generate overall higher total energy than the other screening functions. P-V relations found in the alkaline earth metals show good correspondence with experimental data and other available information. The FCC metals Ca and Sr using model potential along with the T screening function shows the maximum influence with respect to H function than the other five local field correction functions. For BCC (Ba) metal using model potential along with the F function shows the maximum influence with respect to the H functions than the other five screening functions. Present study is going to provide important information regarding the E-V, P-V relations and also give the proper choice of model potential for present system. Overall, total energy and equation of state (EOS) for all alkaline earth metals we achieve the good agreement with respect to the experimental data and other data.

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