The Study of Lattice Dynamics and Dynamical Elastic Constants for Calcium (Ca) and Strontium (Sr) in bcc Phase Using Pseudopotential Approach

Reshma Nair[1,*], Priyank Kumar[2], N.K. Bhatt[3], P.R. Vyas[1], V.B. Gohel[1]

[1] *Department of Physics, School of Science, Gujarat University, Ahmedabad 380009, Gujarat, India*
[2] *Department of Science & Humanities, Government Polytechnic, Dahod 389151, Gujarat, India*
[3] *Department of Physics, M K Bhavnagar University, Bhavnagar 364001, Gujarat, India*

Pseudopotential methods have been used successfully to understand static, dynamical and transport properties with good degree of agreement in condensed matter physics. In the present communication, we have investigated lattice dynamics of Ca and Sr in bcc phase using local pseudopotential due to George et al. The pseudopotential contains two parameters r_c and β which are determined from zero pressure condition. The computed results of phonon frequencies are in good agreement with experimental finding and maximum deviation for both the metals are about 10 % with experimental findings. Further, we have computed dynamical elastic constants (C_{11}, C_{12} and C_{44}) and bulk moduli (B) which are also comparable with experimental results and other theoretical results. Success of present study reveals that both metals behave as a simple metal rather than early transition metals and extra term for the inclusion of *s-d* hybridization is not required.

Keywords: Lattice dynamics, bcc phase, Pseudopotential, Dynamical elastic constants.

1. INTRODUCTION

Recently, Hiral et al. [1] have studied large number of static and dynamical properties of heavy alkaline earth metals using George pseudopotential [1]. They have concluded that the local form of pseudopotential used in their study itself contains an effect of *s-p-d* hybridization and extra Born-Mayer repulsive potential is not necessary.

Encouraged by the recent observation, we in the present communication have studied static, lattice dynamics and lattice dynamical properties of calcium (Ca) and strontium (Sr) in the bcc phase using same form of pseudopotential. We have carried out theoretical studies of binding energy, equilibrium lattice constants, dynamical elastic constants (C_{11}, C_{12} and C_{44}), bulk moduli (B), phonon frequencies in symmetric direction, phonon density of states ($g(\omega)d\omega$), temperature variations of Debye temperature (θ_D), Debye-Waller factor (W_T) and mean square displacement ($\overline{U}^2$).

Calcium and strontium both are subject of interest for both experimental and theoretical researchers due to their unusual structural behavior [1, 2-4]. At 721 K and 830 K temperature, calcium and strontium undergo a temperature-induced transition from fcc to bcc, respectively at zero pressure [5]. In the case of calcium with an increase in pressure the transition temperature increases while in strontium with an increase in pressure transition temperature decreases and goes to zero at about 35 kbar [5]. Using a second-order simple metal pseudopotential theory structural energy and lattice dynamics of alkaline earth metals (Ca and Sr) were studied theoretically by Animalu [6]. With the inclusion of hybridization effect Moriarity [5] studied phonon spectra of calcium, strontium and barium (Ba). He concluded that the effect of hybridization lowers the longitudinal branch of phonon spectra. The lattice dynamics of the fcc and bcc phases [5] would be useful for a quantitative understanding of phase diagrams of calcium and strontium. He also suggested that for the stabilization of the fcc and bcc phases of calcium and strontium *s-d* hybridization plays an important role. N. Singh [7] has used transition metal pair potential (TMPP) and the effects of *s-d* hybridization and overlap between ion-ion interactions were studied using method suggested by Wills and Harrison [8]. In their calculations, the temperature dependence of pair potential was included with an asymptotic factor for the study of temperature dependency of phonon dispersion curves (for Ca at 721 K and for Sr at 830 K). They also found binding energy and elastic constants for calcium and strontium in the bcc phase. Baria and Jani [2] have studied large numbers of static and lattice dynamical properties using second order perturbation pseudopotential method. They have used model potential with a single parameter (effective core radius r_c) for their studies.

Looking at the aforesaid facts, we in the present study have used a simple form of George pseudopotential [1] to study static and lattice dynamical properties of calcium and strontium in the bcc phase. The paper is organized as follows. Section 2 describes mathematical tools to compute binding energy, phonon dispersion in reciprocal space and dynamical elastic constants. Section 3 is devoted to presentation and comparison of our computed results with experimental results in the form of graphical and tabular forms with necessary discussion. And the paper is concluded with the conclusion in section 4.

2. BINDING ENERGY

The total binding energy at 0 K sometimes called cold energy (E_{total}) is given by [9]

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* nairreshma1721997@gmail.com

$$E_{total} = E_0 + E_1 + E_{es} + E_{bs} + E_R. \qquad (2.1)$$

Here, total energy per atom E_{total} is made up of five contributions: uniform electron gas energy (E_0), first order correction to energy (E_1), electrostatic energy (E_{es}), band structure energy (E_{bs}), repulsive or Born-Mayer energy (E_R). In present study, we have not considered contributions of repulsive energy and energy due to local field correction, thus equation (2.1) becomes

$$E_{total} = E_0 + E_1 + E_{es} + E_{bs}. \qquad (2.2)$$

The expressions to compute E_0, E_{es} and E_{bs} are taken from [5]. For the calculation of E_1 and E_{bs} one requires pseudopotential. In the present study, we have used following form of the pseudopotential proposed by George [1] in q-space. The bare-ion pseudopotential has following form in atomic unit system

$$v_{ion}(q) = \frac{1}{\Omega}\left[-\frac{8\pi Z}{q^2} + \beta e^{-q^2 r_c^2}\right], \qquad (2.3)$$

β and r_c are pseudopotential parameters, Ω is atomic volume and Z is valence, E_1 is the first order correction to the energy or the average value of electron ion interaction. It is given by

$$E_1 = \lim_{q\to 0}\left[\frac{8\pi Z}{\Omega q^2} + Z v_{ion}(q)\right], \qquad (2.4)$$

$$E_1 = \frac{\beta Z}{\Omega}. \qquad (2.5)$$

In the present study, we have used the exchange and correlation function due to Hubbard and Sham [6]. The phonon frequencies for $(\boldsymbol{q}, \lambda)$ mode of oscillations in symmetry direction can be obtained by diagonalizing total dynamical matrix $D_{\alpha\beta}(\boldsymbol{q})$.

Following Wallace [5] total dynamical matrix can be written as

$$D_{\alpha\beta}(\boldsymbol{q}) = D_{\alpha\beta}^c(\boldsymbol{q}) + D_{\alpha\beta}^E(\boldsymbol{q}), \qquad (2.6)$$

$D_{\alpha\beta}^c(\boldsymbol{q})$ and $D_{\alpha\beta}^E(\boldsymbol{q})$ represent coulombic and electronic contributions. The expression for $D_{\alpha\beta}^c(\boldsymbol{q})$ and $D_{\alpha\beta}^E(\boldsymbol{q})$ are taken from [5]. In long wavelength limit ($\boldsymbol{q} \to 0$) dynamical elastic constants for bcc crystal are computed using following relation [10]:

$$C_{11} = \frac{1}{12a}\sum_n N(n)\left(x^2 K_{xx}^{(n)} + y^2 K_{yy}^{(n)} + z^2 K_{zz}^{(n)}\right), (2.7)$$

$$C_{44} = \frac{1}{24a}\sum_n \left[\begin{array}{c}(y^2+z^2)K_{xx}^{(n)} + (z^2+x^2)K_{yy}^{(n)} \\ +(x^2+y^2)K_{zz}^{(n)}\end{array}\right], \quad (2.8)$$

$$C_{12} + C_{44} = \frac{1}{6a}\sum_n N(n)\left[\begin{array}{c}yz K_{yz}^{(n)} + zx K_{zx}^{(n)} \\ +xy K_{xy}^{(n)}\end{array}\right], \quad (2.9)$$

a is the lattice constant and $N(n)$ is the co-ordinate number of the nth neighbor. We followed the method used by [10] for the calculation of $K_{\alpha\beta}(R)$.

3. RESULTS AND DISCUSSION

During literature survey, we found that different philosophies are used for the determination of pseudopotential parameters. In most of the methods, researchers determine pseudopotential parameters by favoring some physical quantities while very few have used zero pressure condition called universal condition to determine pseudopotential parameters. In these approaches, one must minimize total binding energy at observed volume. In the present calculation, we have determined two parameters β and r_c (see Eq. (2.3)) using universal condition. The variations of static binding energy against volume variation for bcc calcium and strontium are shown in Fig. 1.

The input data used in calculation and values of pseudopotential parameters determined from zero pressure condition are displayed in Table 1.
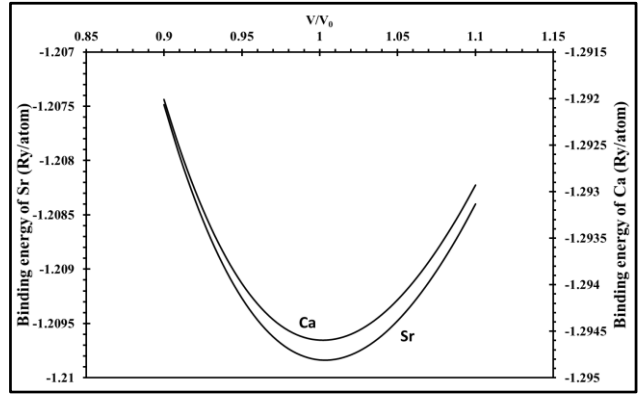

Fig. 1 – The volume variation of binding energy of calcium and strontium

Table 1 – Pseudopotential parameters along with input parameters (all values are in a.u.)

	Calcium	Strontium
Z	2	2
M	40.78	87.62
a	9.604799	10.47313
Ω	443.0318	574.3809
r_0 [7]	4.159	4.535
β	135	156
r_c	0.82	0.925

Table 2 – Binding energy ($-E$) in Ryd/ele for calcium and strontium in bcc phase

Metals	Present (Exp.)	Others
Ca	1.29459 (1.458 [5])	0.963 [7], 1.378 [5]
Sr	1.20984 (1.356 [5])	0.892 [7], 1.200 [5]

We have computed binding energies (cold energies) for calcium and strontium which are compared with the experimental findings and other theoretical results. Our computed results are good with having 12.8 and 10.7 % variation with experimental findings and are better than other theoretical results. The volume and hence lattice constant variations of binding energies for both the metals are graphically shown in Fig. 1.
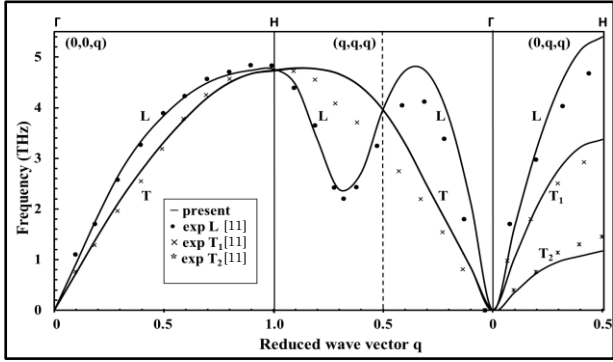
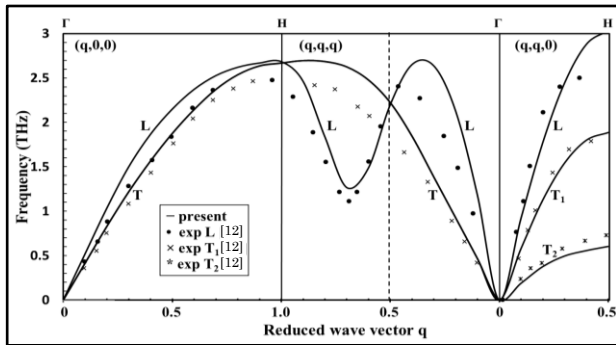**Fig. 2** – Phonon dispersion curves of calcium in symmetry directions

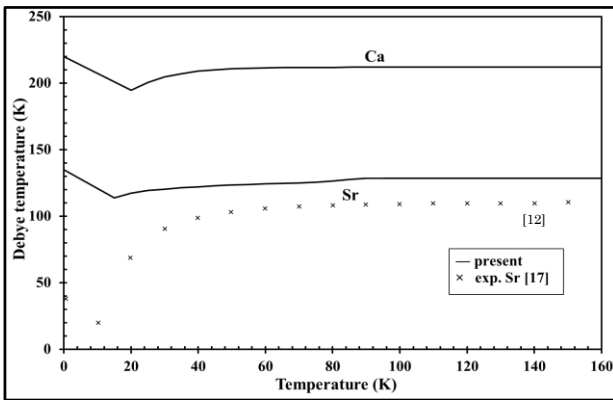**Fig. 3** – Phonon dispersion curves of strontium in symmetry directions

Fig. 4 – Debye temperature as a function of temperature of calcium and strontium

The phonon frequencies for bcc calcium and strontium are displayed along with the experimental results in Fig. 2 and Fig. 3, respectively.

The presently computed results for calcium are very good with having maximum 15 % deviation with experimental findings. Also, in case of strontium the results are good and maximum deviation with observed result is 16.76 %. The present study reveals that the pseudopotential and the method to determine pseudopotential can satisfactorily explain bcc phases of calcium and strontium. It strengthens the conclusion made by Hiral et al. [1] that without inclusion of hybridization effect the present form of pseudopotential are capable for understanding of fcc phases of calcium and strontium. Looking at the success of lattice dynamics, we would like to calcu-

late phonon density of states ($g(\omega)d\omega$) and lattice mechanical properties like temperature variations of Debye temperature (θ_D), Debye-Waller factor (W_T) and mean square displacement ($\bar{U}^2$). The computed results of temperature variations of Debye temperature (θ_D) against temperature with available experimental results for calcium and strontium is shown in Fig. 4 [12].
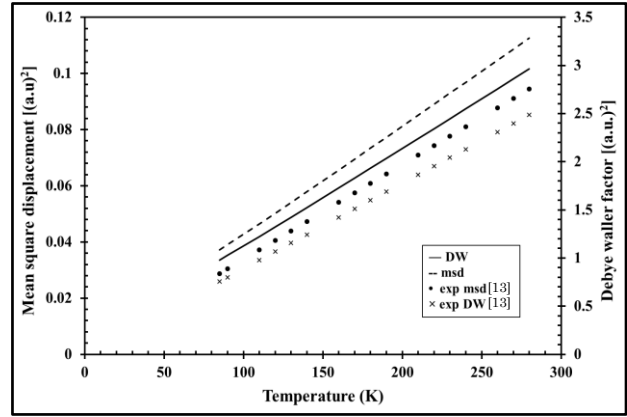

Fig. 5 – Debye-Waller factor (W_T) and mean square displacement ($\bar{U}^2$) of calcium
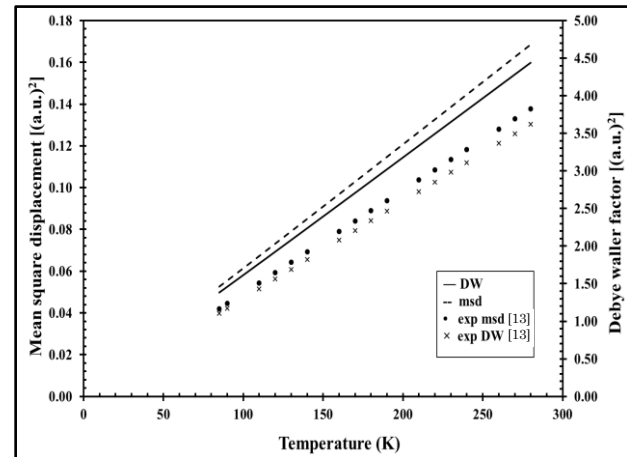

Fig. 6 – Debye-Waller factor (W_T) and mean square displacement ($\bar{U}^2$) of strontium

The expressions to compute Debye-Waller factor (W_T) and mean square displacement ($\bar{U}^2$) are taken from [14]. The computed results of both the physical quantities along with the experimental results due to Peng et al. [13] are displayed in Fig. 5 and Fig. 6 for calcium and strontium, respectively.

The overall agreement of both the physical quantities with experimental findings are very good with having maximum deviation 22 % for strontium and 19 % for calcium in case of Debye-Waller factor (W_T) at 300 K.

The computed dynamical elastic constants using set of Eqs. (2.7)-(2.9) are displayed in Table 3 along with experimental findings and other theoretical results computed using different methods. The dynamical bulk modulus is computed by using relation

$$B = \tfrac{1}{3}(C_{11} + 2C_{12}). \qquad (2.10)$$

Presently computed results of C_{11}, C_{12} and bulk

modulus (B) for calcium are in excellent agreement with experimental results while C_{44} for calcium is also good with deviation of 16 %. Our results are better than other reported theoretical results.

For strontium, the computed results are good for C_{11} and C_{44} with 25 % and 23 %, respectively. But for C_{12} our results are not good as other theoretical results.

Table 3 – The second order elastic constants for calcium and strontium (all the quantities are in 10^{12} dyne/cm^2). The values in parenthesis are percentage variation with experimental results

	Calcium			Strontium		
	Present	Exp.	Other results	Present	Exp.	Other results
C_{11}	0.228 (0.291)	0.228 [11]	0.317 (39) [7]	0.137(25)	0.109 [7]	0.109 (0) [2], 0.136 (24.7) [7]
C_{12}	0.193 (1.29)	0.196 [11]	0.234 (19.38) [7]	0.125(65)	0.077 [7]	0.071 (7.79) [2], 0.089 (15.5) [7]
C_{44}	0.143 (16)	0.12 [11]	0.187 (55.83) [7]	0.0904(22.5)	0.074 [7]	0.069 (6.75) [2], 0.111 (50) [7]
B	0.205 (0.89)	0.207 [11]	0.262 (26.5) [7]	0.124	0.025 [12]	0.195 [12]

4. CONCLUSIONS

The present form of pseudopotential and approach used to determine pseudopotential parameters are found to be successful for the theoretical investigations of large numbers of static, lattice dynamics and thermodynamic properties of both the phases (bcc and fcc) of calcium and strontium. We also agree with Hiral et al. [1] that the parameter β of the pseudopotential contains the effect of hybridization and no extra term is required for the inclusion of hybridization effect. Looking to the success of present study, we would like to extend such simple form of pseudopotential (with two adjustable parameters only) for some transition metals when it changes its phase. Such work is in progress and results are quite encourag-ing and will be published elsewhere.

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