Quasiharmonic *r*–space Computational Scheme for Phonon Dynamics: Case Study of Calcium Oxide

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The role of *phonons* is important in accounting various properties of materials. Crystal potential being an anharmonic function of volume, variations are seen in phonon derived properties with a change in volume. In the present work, we employ an approximate technique of expanding phonon frequencies using Taylor series expansion upto second-order in volume to calculate the volume dependent phonon frequencies of CaO in B1 and B2 phases. Equilibrium properties are obtained by fitting Murnaghan EoS to first principles DFT based results, however. The mode Grüneisen parameter and concavity parameter are computed with the help of present *ab initio* phonon frequencies for both the phases. Their volume dependence are estimated analytically using the proposed scheme. We find that phonon frequencies increase by decreasing volume. Analytically calculated volume dependent phonon frequencies are compared in reasonable agreement with the frequencies obtained directly using DFT for B1-phase. Thus, the present *r*–space computational scheme of deriving volume dependent phonon frequency proves to be an alternative to overcome lengthy phonon calculations.

Keywords: CaO, Phonons, Quasiharmonic.

1. INTRODUCTION

Ample studies have been done at ambient conditions as well as at high pressure on CaO. Calcium oxide and other alkaline earth oxides have been studied largely in geophysical research. CaO is an important material for various technological applications, such as in refractory systems, as a reaction facilitator [1] and in plasma displays [2]. It is one of the abundant material of Earth's lower mantle. Experimentally, B1 to B2 phase transition for CaO was investigated by shock wave [3, 4] and diamond anvil cell compression [5, 4]. Theoretical works include calculations of cohesive energy and structural properties by Cortonay *et al* [6] by *ab initio* calculations and Kalpana *et al* [7] by Linear-muffin-tin-orbitals (LMTO) method. Vibrational, thermodynamic and lattice dynamical properties were determined by Schütt *et al* [8] using density-functional perturbation theory within local density approximation at zero pressure. Louail *et al* [9] and Deng *et al* [10] have studied the effects of pressure on the elastic constants. Method based on an electron-gas approximation has been used to study high-pressure structure and phase stability of CaO [11].

Information about structural instabilities and phase transformations can be obtained by studying the pressure dependence of lattice vibrations. CaO being a significant component in the lower mantle [12], its thermoelasticity is essential for our understanding processes including brittle failure, flexure, and the propagation of elastic waves [13, 14]. Information of phonon is very useful for accounting variety of properties and behaviour of crystalline materials, such as thermal properties, mechanical properties, phase transition, and superconductivity, whereas electronic contribution is less significant in such insulation oxides. It is vital to study the behaviour of phonons as it is also useful in finding whether the material is dynamically stable or not. In the present work, we represent the phonon dispersion curve, mode Grüneisen parameter (γ) and concavity parameter (β) for CaO. Grüneisen parameter is a dimensionless parameter that changes gradually as a function of pressure and temperature. The microscopic definition of Grüneisen parameter is related to the frequency of vibration of atoms in a solid while the macroscopic definition is related to properties such as thermal expansion and heat capacity. Experimental determination of γ is difficult while theoretically it can be determined using phonon dispersion of solid.

Ab initio calculations of lattice dynamics for CaO are important as it is responsible for phase transitions under pressure. DFT allows accurate computation of phonon dispersion on a fine grid of wave vectors covering complete Brillouin zone which is comparable with the data obtained from neutron diffraction.

2. THEORY

Change is observed in phonon properties with change in volume since the crystal potential is anharmonic function of volume. A simple framework is provided by quasi-harmonic approximation, allowing calculation by introducing an explicit dependence on volume of phonon frequencies [15]. The term "quasi-harmonic approximation (QHA)" refers to volume dependence of phonon properties, harmonic approximation being applied at each volume. The phonon frequencies at ambient condition were obtained using density functional theory, which were then expanded using Taylor series upto second-order in volume as shown in Eq.(1) to analytically calculate the volume dependent phonon frequencies:

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$$\omega(n,\vec{q}) = \omega_0(n,\vec{q})\left[1 - \gamma_0(n,\vec{q})\left(\frac{V - V_0}{V_0}\right) - \frac{1}{2}\beta_0(n,\vec{q})\left(\frac{V - V_0}{V_0}\right)^2\right], \tag{1}$$

where, $\omega_0(n,\vec{q})$, $\gamma_0(n,\vec{q})$ and $\beta_0(n,\vec{q})$ are respectively the phonon frequency, Grüneisen parameter and concavity parameter at equilibrium associated with vibrational mode $(n,\vec{q})$ where n is the branch index and $\vec{q}$ is the wave vector. Eq.(1) permits us to calculate the phonon frequencies at any volume provided that the phonon frequencies at equilibrium condition is known [16].

Phonon frequencies increase by decreasing volume and the slope of each phonon mode is nearly constant in the wide volume range [17]. Grüneisen parameter which is the normalized slope, is related to the bond strength and vibration mode of phonon, is defined as follows:

$$\gamma_0 = -\frac{V_0}{\omega_0}\left(\frac{\partial \omega}{\partial V}\right)_0. \tag{2}$$

Studies of the Gruneisen parameter yield the information about lattice anharmonicity needed for a fundamental understanding of phonons. It describes how each phonon mode change with the volume of system. The description of the thermoelastic behaviour of materials at high temperature and pressure involves Gruneisen parameter.

The concavity parameter which is equivalent to second order derivative of phonon frequencies is defined as

$$\beta_0 = -\frac{V_0^2}{\omega_0}\left(\frac{\partial^2 \omega}{\partial V^2}\right)_0. \tag{3}$$

Grüneisen and concavity parameter are calculated numerically by energy minimization and phonon calculation at equilibrium V_0, and also at four supplementary volumes in the vicinity of V_0.

3. COMPUTATIONAL DETAIL

The computations were done using density functional theory within generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) as applied in Quantum Espresso package. To represent the electron-ion interactions, a scalar relativistic Vanderbilt-type ultrasoft pseudopotentials were used along with nonlinear core correction (NLCC). The convergence of total energy with cutoff energy and k-points was performed for CaO in B1 and B2 phase. Energy cutoff of 100 Ry and an 11×11×11 Monkhorst-Pack k-point grid was used for both the phases. Dynamical matrices were calculated on a 4×4×4 grid in q-space. The set of dynamical matrices obtained in these calculations were used to construct the force constant matrix via Fourier transformation.

4. RESULTS AND DISCUSSION

The total energy of CaO was calculated at equilibrium volume V_0 for B1 and B2 phases using GGA approximation to decide the equilibrium structural parameters such as equilibrium lattice constant (a), bulk modulus (B) and first pressure derivative (B′).

Table 1 – Equilibrium structural parameters of CaO

Phase	Results	a (Å)	B (GPa)	B′
B1	Present	4.8331	104.3	4.28
	Other[18]	4.836	102.3	4.17
	Exp. [19]	4.8105	115	4.10
B2	Present	2.9357	105.7	4.23
	Other[18]	2.938	104.6	3.98
	Exp. [20]	2.907	130	3.5

It can be seen from the above table that present results are in good agreement with other theoretical and experimental results. Obtained lattice constant for B1 phase differs from theoretical and experimental data by 0.06% and 0.46% respectively; for B2 phase the variation is about 0.07% and 0.98% respectively. The excellent agreement favours the choice of pseudopotentials and the GGA approximation for this study. The equilibrium structure of crystal is determined by minimization of total energy of system as a function of lattice parameter.

Fig. 1 shows the phonon dispersion curve at equilibrium volume. The continuous line represents the DFT calculation, which is compared with the experimental data obtained by Weinstein et al. from neutron data [21] and it is seen that most of the data are well reproduced by our calculations. The phonon frequencies calculated analytically match well with the frequencies obtained from DFT upto $0.8V_0$.
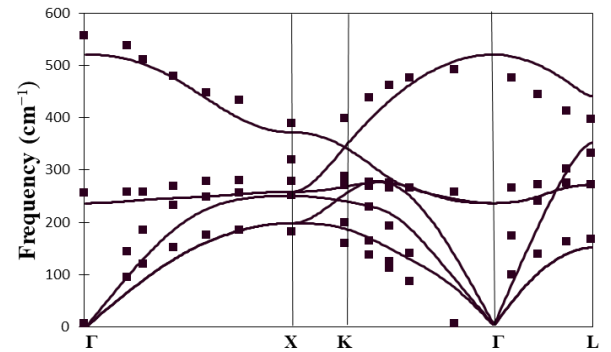

Fig. 1 – Phonon dispersion curve of CaO at equilibrium V_0. DFT (continuous line) and experimental [21] results (square)

Fig. 2 shows the phonon dispersion curve at $0.64V_0$. Phase transition is expected around $0.64V_0$, hence this particular volume is chosen for comparison. It is seen from the figure that analytically calculated volume dependent phonon frequencies are in reasonable agreement with the frequencies obtained directly from DFT. With decreasing volume, the optical phonon modes shift to higher frequencies, while the acoustic phonon modes at the zone boundary of X point decrease in frequency. Further decrease in volume may show imaginary frequency, resulting in structural instability.
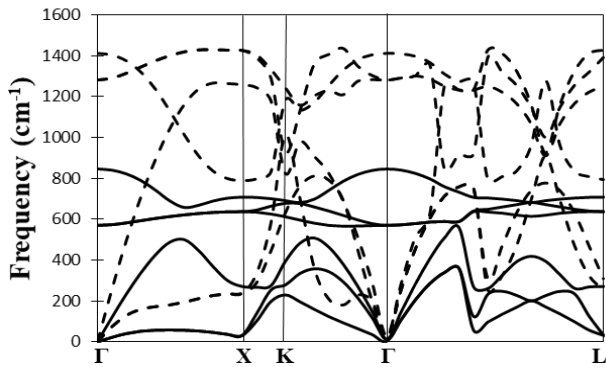
Fig. 2 – Phonon dispersion curve of CaO at $0.64V_0$. Dashed line (present results) and DFT (continuous line)
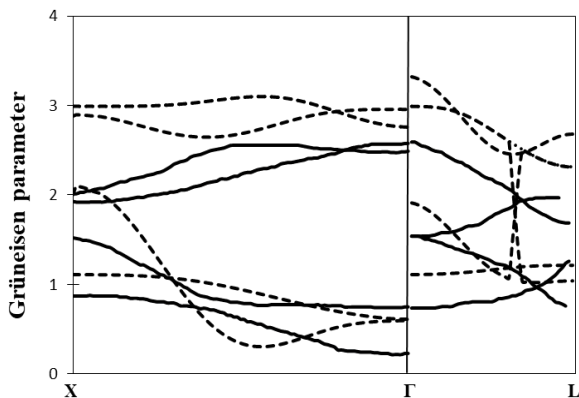

Fig. 3 – Grüneisen parameter of CaO. Dashed line (present results) and experimental [22] (continuous line)
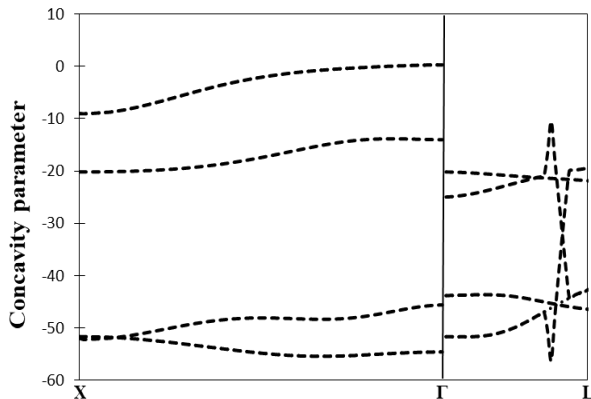

Fig. 4 – Concavity parameter of CaO

Fig. 3 shows the Grüneisen parameter of CaO in two high symmetry directions. Dashed line shows the present result while continuous line shows the experimental result [22] calculated from a pressure dependent shell model. The magnitude of our Grüneisen

parameter differ from experimental result, however the trend is similar. The Grüneisen parameter are positive throughout the Brillouin zone for all branches indicating that there's no softening of any mode with compression and particular phase of CaO is dynamically stable.

Fig. 4 shows the concavity parameter of CaO. The concavity parameter show discontinuity at Γ point. As seen from the figure, β remains negative throughout the Brillouin zone. From Γ to X point, the value of concavity parameter remains almost the same. To our knowledge, no comparison for concavity parameter of CaO is available.
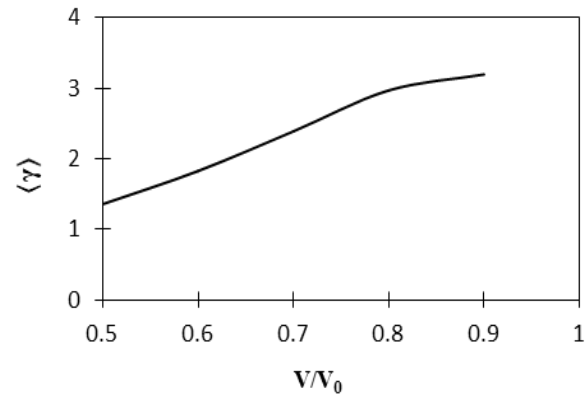

Fig.5 – Volume dependence of $\langle\gamma\rangle$

Fig. 5 shows the volume dependence of average Grüneisen parameter. As seen from the graph, the average value decreases with the decrease in volume. This behaviour agrees with the fact that for crystalline phases, γ always decreases with compression [23].

5. CONCLUSION

Present technique provides a substitute to long phonon calculations. Phonon frequency at any volume can be computed without lengthy phonon calculation, provided the frequency at ambient condition are known. Volume dependent Grüneisen and concavity parameter can be computed with the help of equilibrium quantities and volume dependent phonon frequencies. Increase in phonon frequency is observed with the decreasing of cell volume, because there is increase in the force constants between atomic pairs in the crystal structure due to the volume compression. Thus, γ remains positive.

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