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**DENSITY FUNCTIONAL THEORETICAL CALCULATIONS AND COMPARISONS OF PHONON DISPERSION RELATIONS OF ELEMENTAL SEMICONDUCTORS.**

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**ABSTRACT**

Phonon dispersion relations of semiconductor crystal frequencies at some high symmetry points were reported. A first principles method based on density functional perturbation theory (DFPT) as embedded in the *Quantum Espresso* (QE) simulation software was used. Appropriate equilibrium lattice constants and energy cut-offs needed for the calculations were deduced from the results of convergence tests carried out for the elements used. Effects of the local density approximation (LDA) and generalized gradient approximation (GGA) exchange correlation potentials at each of the high symmetry lines were compared. Our results of the phonon relations compare favourably well with those obtained in similar published researches. The result also showed that magnitude of phonon frequencies (both optical and acoustic) decrease from carbon to tin and in fact the ratio is 3:1 for Carbon: Silicon.

**Keywords:** *Quantum Espresso, dispersion relations, high symmetry points, exchange correlation potentials.*

**INTRODUCTION**

Phonon study is important in solid-state physics and material science because it gives a clear understanding of the physical properties of materials such as the heat capacity, thermal expansion coefficient and electrical conductivities. Phonon dispersion curves of many materials have been measured with high precision, with the development of neutron scattering method (Ashcroft & Mermin, 1976). Majority of interatomic force constant tensors which can match the existing experimental data were described by empirical models with few disposable fitting parameters (Ashcroft & Mermin, 1976). This approach does not however provide a unique set of solution. For better understanding of lattice dynamics in solids, first-principles method is necessary (Giannozzi, 2009). The plane wave pseudo potential method and the LDA to density functional theory (DFT) have provided a simple frame-work whose accuracy and predictive power have been convincingly demonstrated in a large variety of systems (Giannozzi, 2009). Bulk phonon dispersion spectra are interesting not only for their relevance to properties of pure materials, but also ingredients of approximate calculations for complex systems, such as semiconductors alloys, super lattices and other quantum micro-structures. Even, when first principles calculations for the super lattice are available, bulk Phonon dispersions of the constituents are very useful for interpreting the calculated spectra and comparing them with experiment (Gironcoli P. G., 1991). Phonon dispersion relations were calculated for silicon and germanium and their respective phonon frequencies at the high symmetry points were calculated (Gironcoli P. G., 1991). In this paper, we present the first ab initio calculation of full phonon dispersion of elemental semiconductors C, Si, Ge and Sn with procedures in *Quantum Espresso*. Normal mode frequencies and eigenvector components of silicon using a first principle approach that involves ab initio norm conserving non-local pseudopotentials were calculated with procedures in *VisionRes* (Young K, 1997). Due to

translational symmetry  $w_i(k+G) = w_i(k)$ , where  $G$  is a reciprocal lattice vector, only the calculations of phonon frequencies in the first Brillouin zone are necessary. We have calculated and compared Phonon frequencies of LDA and GGA of these elements along some high symmetry lines and compare our results of the similar published researches.

### Density-Functional Perturbation Theory

If we assume that the bare external potential acting on the electrons,  $V_\lambda$  is a continuous function that depends on some parameter  $\lambda$ ,

$$V_\lambda = V(r) + \lambda \frac{\partial V(r)}{\partial \lambda} + \frac{\lambda^2}{2} \frac{\partial^2 V(r)}{\partial \lambda^2} + \dots \quad (1)$$

(all derivatives calculated at  $\lambda=0$ ) and expand the charge density

$$n_0(r) = n(r) + \lambda \frac{\partial n(r)}{\partial \lambda} + \frac{\lambda^2}{2} \frac{\partial^2 n(r)}{\partial \lambda^2} + \dots \quad (2)$$

And the energy functional into power of  $\lambda$ :

$$E_\lambda = E + \lambda \frac{\partial E}{\partial \lambda} + \frac{\lambda^2}{2} \frac{\partial^2 E}{\partial \lambda^2} + \dots \quad (3)$$

The first – order derivative of equation (3) does not depend on any derivative of  $n(r)$ . This is the Hellmann – Feynman theorem: the force associated with the variation of the external parameters is given by the ground – state expectation value of the derivative of  $V_\lambda$ :

$$\frac{\partial E_\lambda}{\partial \lambda_i} = \int n_\lambda(r) \frac{\partial V_\lambda(r)}{\partial \lambda_i} dr \quad (4)$$

$E_\lambda$  is the electron ground-state energy relative to  $\lambda$  parameters, and  $n_\lambda$  is the corresponding electron-density contribution.

The self – consistent – field (SCF) DFT potential,  $V_{SCF}$ , for a system of electrons moving in the external potential of the ions is given by

$$V_{SCF}(r) = V_{im}(r) + e^2 \int \frac{n(r')}{|r-r'|} dr' + V_{xc}(r) \quad (5)$$

This can be determined by standard technique of self consistent band – structure calculations. These various calculations require a great deal of numerical labor, the stages of which form the basis of the quantum chemistry suite called the quantum espresso package.

### Real space inter-atomic force constants

The range of interatomic force constants in non – polar materials such as elemental semiconductors is short. Interatomic force constants in real – space,  $C_{st}^{\alpha\beta}(R)$  are obtained by

(i) calculating  $\overline{C_{st}^{\alpha\beta}(q)}$  on a discrete  $(n_1, n_2, n_3)$  grid of  $q$  – vectors:

$$\overline{C_{st}^{\alpha\beta}(q)} = \sum_R e^{iq \cdot R} C_{st}^{\alpha\beta}(R) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^\alpha(q) \partial u_t^\beta(q)} \quad (6)$$

$$q_{ijk} = \frac{i-1}{n_1} \mathbf{G}_1 + \frac{j-1}{n_2} \mathbf{G}_2 + \frac{k-1}{n_3} \mathbf{G}_3 \quad (7)$$

$i = 1, \dots, n_1; j = 1, \dots, n_2; k = 1, \dots, n_3$ . These can be calculated from the knowledge of the linear response  $\frac{\partial n(r)}{\partial u_s^{8\alpha}(q)}$  and diagonalized to get phonon modes

at  $\mathbf{q}$ . The Fourier transform of force constant at  $\mathbf{q}$  are second derivatives of the energy with respect to the monochromatic perturbation  $u$ .

(ii) Fourier – transforming to the corresponding real – space grid:  $C(\mathbf{q}_{ijk}) \Leftrightarrow C(\mathbf{R}_{lmn})$

$$\mathbf{R}_{lmn} = l\mathbf{R}_1 + m\mathbf{R}_2 + n\mathbf{R}_3 \quad (8)$$

$l = -\frac{n}{2}, \dots, +\frac{n}{2}$  and like for  $m, n$ . The denser the grid of  $\mathbf{q}$ - vectors, the larger

the vectors  $\mathbf{R}_{lmn}$  for which the interatomic force constants are short – ranged and require a number of calculations at different  $\mathbf{q}$ .

In this paper, equilibrium lattice parameters  $a_0$  (a.u), Born effective charges ( $Z^*$ ) and static dielectric constant ( $\epsilon_\infty$ ) were calculated by phonon code in quantum espresso.

### Methods

The self - consistent charge-density and Kohn – Sham orbitals were calculated. Number of  $k$ -points used was determined by the Monkhorst Pack method. At minimum energy, the required number of  $k$  – points, (kpt), cut off energies (Ecut-off) and lattice parameters ( $a_0$ ) for the phonon calculations were first determined in a convergence test carried out for each element using LDA and GGA pseudo potentials respectively. The graphs were plotted using gnu-plot embedded in QE suite. Phonon calculations of each elemental semiconductor were then calculated using uniform grids ( $nq_1, nq_2, nq_3$ ), where  $n = 4$  in our calculations.

### Results and Analysis

(a) Bulk dispersions compared with experimental values.

In Table 1, we report the values of the lattice parameters, energy cut-offs, Born effective charges and static dielectric constants of C, Si, Ge and Sn. GGA values of these parameters could not be calculated for Ge and Sn because few bands were calculated in the SCF calculation which are not enough for either band structure or phonon calculations. This development might be ascribed to the highly localized 3d orbitals of the semiconductors.

### Results

**Table 1:** Equilibrium lattice constants  $a_0$  (a.u), Born effective charges ( $Z^*$ ) and static dielectric constants  $\epsilon_\infty$ .

	LDA				GGA	
	C	Si	Ge	Sn	C	Si
$a_0$ (a.u)	6.74	10.26*,10.2	10.68*,10.67	12.263	6.74	10.2
	0.15	0.07	0.003	0.08	0.14	1.8
$\epsilon_\infty$	5.57	12.66 13.6*	20.24 16.50*	34.0	5.60	10.29

In theory effective charges are prominent and peculiar to polar materials such as AIAs, which has been confirmed by our results (table1) except the GGA value for Si which is

(1.8) greater than unity. Our values of lattice constants in Si and Ge compared well with experimental values (in asteriks) Paolo G. & Stefano, (1990). Also our LDA values of dielectric constants for Si is 0.94 less than the experimental values while it is greater by 3.74 in Ge.

### Phonon calculations

**Table II:** Phonon frequencies (in THz) calculated at high symmetry for C, Si, Ge and Sn) using GGA and LDA pseudopotentials.

High – symmetry points	C		Si		Ge		Sn	
	LDA	GGA	LDA	GGA	LDA	LDA	LDA	LDA
$\Gamma$ - X <sub>TA</sub>	15.00	23.18	4.52	4.30	2.38	1.29		
$\Gamma$ - X <sub>LA</sub>	37.27	36.36	12.30	12.75	6.98	4.43		
$\Gamma$ - X <sub>TO</sub>	46.59	41.82	14.37	14.60	8.85	6.00		
$\Gamma$ - X <sub>LO</sub>	37.27	36.36	12.30	12.75	6.98	4.43		
$\Gamma$ - L <sub>TA</sub>	16.36	16.36	3.26	3.40	1.91	1.03		
$\Gamma$ - L <sub>LA</sub>	33.18	31.82	11.26	11.50	6.64	4.09		
$\Gamma$ - L <sub>TO</sub>	38.64	38.18	14.67	15.20	8.34	5.43		
$\Gamma$ - L <sub>LO</sub>	38.64	38.18	12.44	13.00	6.94	4.51		

### Analysis of Results

We have calculated phonon dispersion relations within the frame work of density functional perturbation theory. The LDA exchange correlation potentials of PE or BHS are used for C, Si, Ge and Sn while the GGA exchange correlations of PW was used for C and Si. Few bands were produced for Ge and Sn. Hence GGA could not produce enough bands for the plotting. The elements are 3d highly localized (Ferhat, 2005). Plane-waves energy cut-offs used, were deduced from the convergence test of each element. These basis sets are complete enough to guarantee a convergence on the calculated phonon frequencies. Dynamical matrices were calculated on to a (444) reciprocal space fcc grid. The bulk phonon dispersions are displayed in the appendix, for the non – polar materials. Some values at the high symmetry points X and L are also reported.

From table II, LDA values decreases with increasing atomic orbitals from carbon down to tin, the greater the number of atomic orbitals, the less is the corresponding phonon frequency. The GGA values decreases greatly (e.g. X<sub>TA</sub>) from 23.18 for carbon to 4.3 for tin. What is unique in the phonon dispersion relations of these elemental semiconductors is that LO and LA meet at same point on X – symmetry, but as the electrons cross from  $\Gamma$  to L, there exists a split between longitudinal acoustic and longitudinal optics. Also in this calculation there is no LO – TO split along  $\Gamma$  – L symmetry line in carbon for both LDA and GGA.

### CONCLUSION

In this paper we have calculated complete phonon dispersions of elemental semiconductors using computational method based on density functional perturbation theory (DFPT). We have compared frequencies at high – symmetry points  $\Gamma$  – X, and  $\Gamma$  – L using local density and generalized gradient approximations within density functional

theory. The phonon dispersion relation curves obtained in this work compared well with those in published research work who have used other simulation softwares such as VASP (Zou, 2007). The concept of inter-atomic force constants, as embedded in Quantum espresso (QE), is very useful, not only for interpolating vibrational properties throughout the Brillouin zone but also for using the information gained, in simple systems such as elemental or binary semi – conductors in rather complex ones, such as alloys and quantum structures. (Gironcoli P. G., 1991). Our phonon frequencies, both optics and acoustics are in carbon than others. This is an interesting result. In fact, the frequencies in carbon are about thrice the corresponding frequencies of silicon. Based on our observations, we therefore assert that the Quantum espresso software compete favorably well with other simulation software. From Table II, we also conclude that generalized gradient pseudopotentials produced frequencies, at the high symmetry point, less than that of their local density counterpart. (Giannozzi P, 2009)

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**Phonon Dispersions Relation(PDR) graphs**

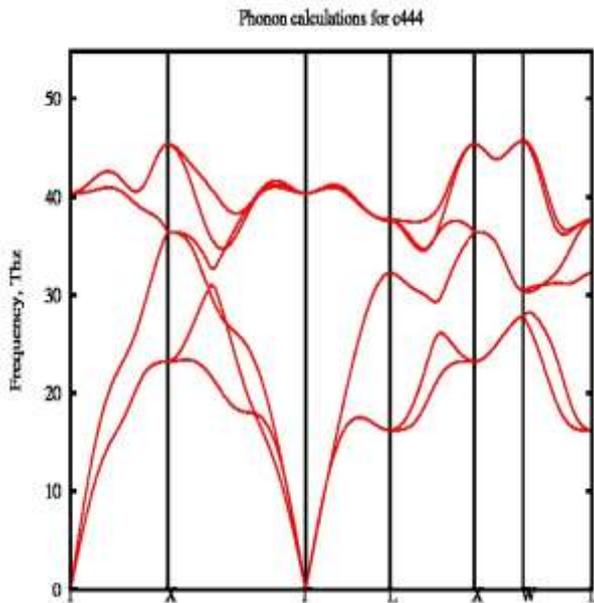
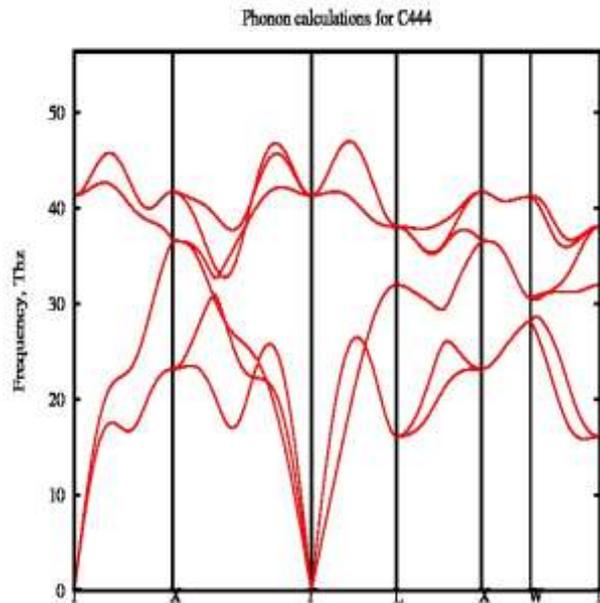


Fig 4.1 PDR of (a) Carbon with LDA



(b) Carbon with GGA

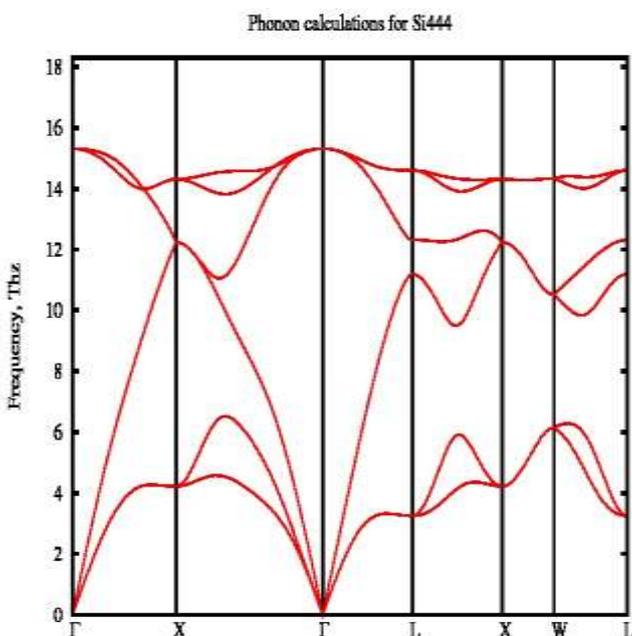
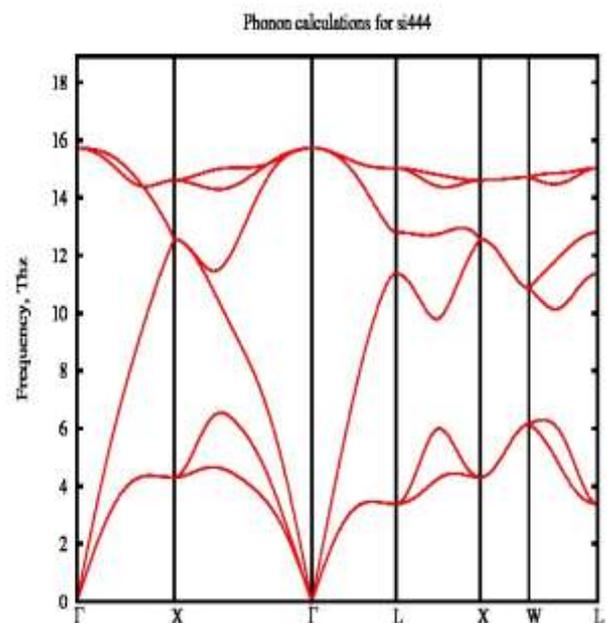


Fig4.2 PDR of (a)Silicon with LDA



(b) silicon with GGA

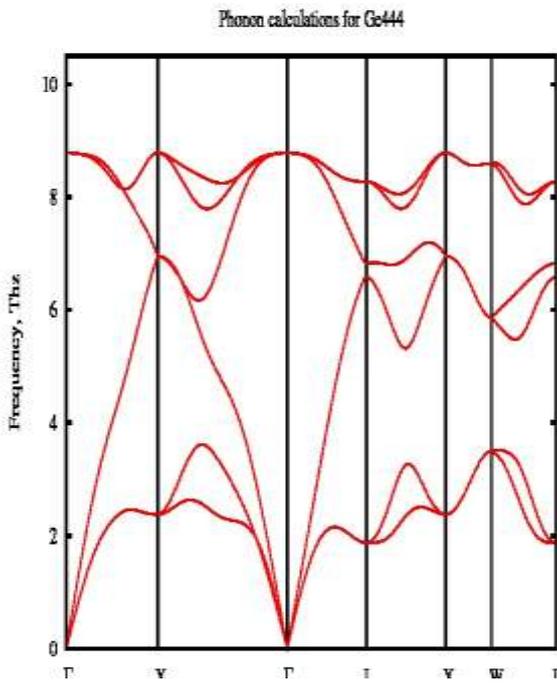
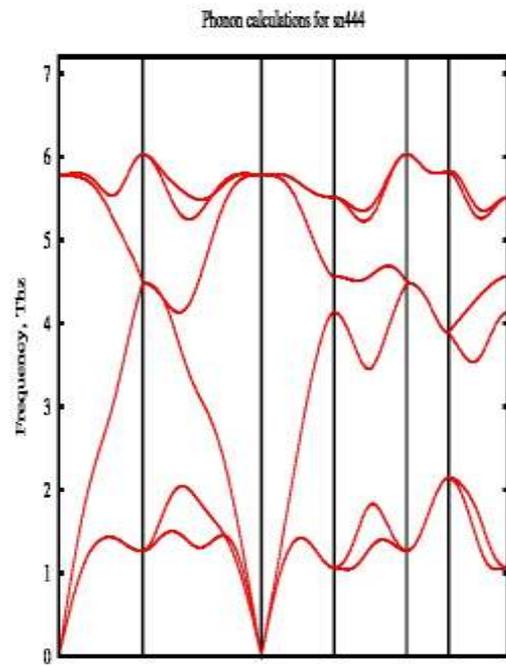


Fig 4.3 PDR of (a) Germanium with LDA



(b) Tin with LDA