
STRUCTURAL, ELECTRONICS AND PHONON DISPERSION RELATIONS OF BI-III BINARY COMPOUND SEMICONDUCTORS USING DENSITY FUNCTIONAL THEORY

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ABSTRACT: Phonon dispersion relations of semiconductors especially III–Bi binary compounds are of immense importance in the study of structural and vibrational properties of semiconductor materials. In this paper structural and phonon frequencies at high symmetry points using local density and generalized gradient approximations within density functional perturbation theory were calculated and compared with a view to know the influence of pseudopotentials on the investigated properties and variation of acoustic and optics frequencies of the compounds with atomic orbitals of the selected compounds. Our results reveal that only BBi show higher values of both longitudinal and transverse optical frequencies which can be attributed to the fact that BBi binary compound is the only optoelectronic material that has direct energy, in addition acoustic and optical frequencies decrease for local density approximation than the generalized gradient approximation in BBi compound while they are greater for LDA than the GGA frequencies in AlBi compound. The phonon frequencies calculated will be useful in phonon engineering where vibrational properties of materials are employed.

Keywords: Phonon Frequencies, Phonon Engineering, Pseudopotentials Optoelectronic, and Density Functional Perturbation Theory.

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INTRODUCTION

The goal of electronic structure studies is to be able to calculate physical properties which agree favorably well with experimental data. If this is achieved confidence is restored in the calculational methods. This confidence allows an identification and detailed interpretation of the microscopic bases of observed

phenomena, followed by the prediction of new and unexpected properties of the materials. In a situation whereby the work has not been done experimental, the theoretical prediction can be a starting point for the experimental take-off i.e. theoretical calculation can be the starting point for the journey to the expectation. Phonon calculations are of immense

importance in the study of structural and vibrational properties of semiconductor materials. Ab initio methods based on density functional theory (DFT) has been the common and well established tools for studying structural and vibrational properties of real materials. (Bester* & Gabriel, 2009). If DFT formalism is used for systems like atoms, molecules and solids it requires less computational effort unlike Green Function technique. Though DFT formalism was developed by Hohenberg and Kohn, Kohn and Sham, only Kohn-Sham approach to DFT allows an exact description of the interacting N-particle system in terms of an effective non-interacting particle system (Harrison, 2005), (Kohn & Hohenberg, 1961) of the two approximate density functionals, local density approximation is mostly and widely used because it uses the exchange correlation energy density of the homogeneous electron gas, (PICKETT,

1989; Perdew & Mel, 1983). It works for systems with slowly varying densities and surprisingly works well for systems which have very inhomogeneous electron densities such as atoms and molecules. The plane-wave pseudopotentials method and the local density approximation to DFT have provided a simple framework whose accuracy and predictive power have been convincingly demonstrated in a large variety of systems, (CECAM, 2006).

Density Functional Perturbation Theory

Density Functional Perturbation Theory, a suitable technique to calculate vibrational properties of extended materials using a combination of density functional theory and linear response techniques, is a method that gives very accurate phonon frequencies which, in combination with the quasi-harmonic approximation, allows one to study thermal properties of materials.

Theory of Phonon Calculation

In Born-Oppenheimer (adiabatic approximation, the nuclear motion is determined by the nuclear Hamiltonian, H. (Harrison, 2005)

$$H = - \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial R_I^2} + E[\{R\}] \dots \dots \dots (1)$$

Where R_I is the coordinate of the j^{th} nucleus, M_I its mass and $E(\{R\})$ is the ground-state energy of the Hamiltonian, $H_{\{R\}}$ of a system of N interacting electrons moving in the field of fixed nuclei and $\{R\}$ is the set of all the nuclear coordinates. This Hamiltonian is:

$$H_{\{R\}} = - \frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial \bar{r}_i^2} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} + \sum_{i,j} v_I (r_i - R_I) + E_N(\{R\}) \dots \dots \dots (2)$$

$E_N(\{R\})$ is the nuclear electrostatic energy given as

$$E_N(\{R\}) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} \dots \dots \dots (2a)$$

The electron-nucleus Coulomb interaction is

$$v_I = -\frac{Z e^2}{r} \dots \dots \dots (2b)$$

In a pseudopotential scheme, each nucleus is lumped together with its own core electrons known as “frozen ion” which interacts with the valence electrons through a smooth pseudopotential, ($v_I(r)$) (PICKETT, 1989), (CECAM, 2006).

The geometry of the system in equilibrium is based on the condition that the force acting on all the nuclei vanishes (=0). This force can be calculated by applying Hellmann- Feynman theorem to the Born-Oppenheimer Hamiltonian, $H_{\{R\}}$:

$$F_I = -\frac{\partial E(\{R\})}{\partial R_I} = -\left\langle \psi_{\{R\}} \left| \frac{\partial H}{\partial R_I} \right| \psi_{\{R\}} \right\rangle \dots \dots \dots (3)$$

$\psi_{\{R\}}(r_1, \dots, r_N)$ is the ground state wave function of the electronic Hamiltonian, $H_{\{R\}}$.

In terms of electron charge density, $\rho(r)$,

$$F_I = -\int \rho(r) \frac{\partial v_I(r - R_I)}{\partial R_I} dr - \frac{\partial E_N(\{R\})}{\partial R_I} \dots \dots \dots (4)$$

For the nuclear configuration [R], $\rho(r)$ is:

$$\rho(r) = N \int |\psi_{\{R\}}(r_1, r_2, \dots, r_N)|^2 dr_1, dr_2, \dots, dr_N \dots \dots \dots (5)$$

For a system near equilibrium geometry, the harmonic approximation is applied and the nuclear Hamiltonian equation (28) reduces to the Hamiltonian of a system of independent harmonic

oscillators, called normal modes. The normal mode frequencies ω and the displacement pattern, U_I^α for the α^{th} Cartesian component of the I^{th} atom, are determined by the secular equation:

$$\sum_{I, \beta} (C_{11}^{\alpha\beta} - M_I \omega^2 \delta_{IJ} \delta_{\alpha\beta}) U_J^\beta = 0 \dots \dots \dots (6)$$

One important consequence of variational behavior of DFT is that the Hellmann-

Feynman theorem for forces is still valid in DFT framework. i.e.,

$$F_I^{DFT} = -\sum \rho(r) \frac{\partial V_{\{R\}}(r)}{\partial R_I} dr - \frac{\partial E_N(\{R\})}{\partial R_I} - \int \frac{\delta E(\{R\})}{\delta \rho(r)} \frac{\partial \rho(r)}{\partial R_I} dr \dots \dots \dots (7)$$

For the ground-state charge density, the minimum condition implies that the functional derivative of $E(\{R\})$ equals a constant and the integral of the derivative

of the electron density is zero because of charge conservation, (Paolo & Baroni, 2005). Thus, $F_I^{DFT} = F_I$.

This IFC can be calculated as finite displacements of atoms around the equilibrium positions for finite systems in solid state physics, frozen phonon technique. Alternative method for calculating IFC is the use of density

functional perturbation theory (DFPT) which is used in this research.

Phonon Modes in Crystals

Also, in crystals, normal modes (phonons) are classified by a wave vector \bar{q} and a mode index, ν .

$$\sum_{t,\beta} (\bar{C}_{st}^{\alpha\beta}(q) - M_s \omega^2(q) \delta_{st} \delta_{\alpha\beta}) U_t^\beta(q) = 0 \dots \dots \dots (8)$$

From the secular equation (37), phonon frequencies $\omega(q)$ and displacement pattern $U_s^\alpha(q)$ can be calculated. The dynamical matrix $\bar{C}_{st}^{\alpha\beta}$ is the Fourier transform of the IFC- real-space, $C_{st}^{\alpha\beta}$ where:

$$\bar{C}_{st}^{\alpha\beta}(\bar{q}) = \sum_l e^{iq \cdot \bar{R}_l} C_{st}^{\alpha\beta}(\bar{R}_l) \dots \dots \dots (8a)$$

$$C_{st}^{\alpha\beta}(l, m) = \frac{\partial^2 E}{\partial U_s^\alpha(l) \partial U_t^\beta(m)} = C_{st}^{\alpha\beta}(\bar{R}_l - R_m) \dots \dots \dots (8b)$$

$U_s(l)$ is the derivation from the equilibrium position of atom S in the l^{th} unit cell. The derivatives are evaluated at $U_s(l) = 0$ U_s . Calculation of this derivative in an infinite periodic system is impossible because the displacement of a single atom would break the translational

symmetry of the system. (Giannozz, Gironcoli, Pavone, & Baroni, 1991)

If equation (8a) is written as second derivatives of the energy w.r.t lattice distortion of wave vector \bar{q} the dynamical matrix becomes:

$$\bar{C}_{st}^{\alpha\beta}(\bar{q}) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^\alpha(q) \partial u_l^\beta(q)} \dots \dots \dots (8c)$$

Phonon Dispersion Relations

Phonon Dispersion Relation $\omega(k)$

is not a linear function of k and it

is therefore a dispersion relation. For monatomic lattice,

$$\omega(k) = \text{Sin} \omega_m \text{Sin} \left(\frac{ka}{2} \right) \dots \dots \dots (9)$$

β is the interatomic force constant, IFC. For diatomic lattice,

$$\omega^2 = \beta \left(\frac{M+m}{Mm} \right) \left[1 \pm \left\{ 1 - \frac{4Mm}{(M+m)^2} \text{Sinka} \right\}^{\frac{1}{2}} \right] \dots \dots \dots (10)$$

This equation shows that there are two dispersion relations and therefore two dispersion branches are associated with diatomic lattices. (Kittel, 2005). The

lower curve called acoustic branch corresponds to the negative sign of eq (10), which begins at $q=0$ and as q increases the curve rises linearly at first

and later saturates at $q = \frac{\pi}{2a}$ at frequency $\left(\frac{2\beta}{M}\right)^{\frac{1}{2}}$.

The upper curve; the optical branch starts at $q=0$ with a finite frequency, decreases slowly and saturates at $q=\pi/2a$ with frequency $(2\beta/m)^{1/2}$

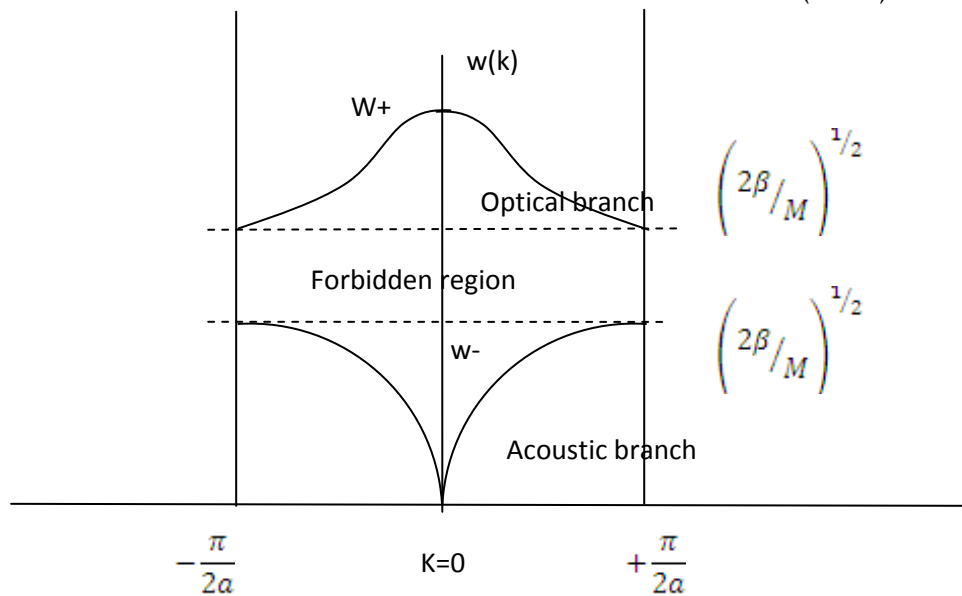


Fig. 1 Dispersion Curve for Diatomic system

Frequency of the optical branch does not vary appreciably over the entire q -range and it is in fact approximated to a constant.

LITERATURE REVIEW

Among the previous work on phonon calculations of binary semiconductor compounds are ab-initio (VASP) calculation of phonon dispersion relation of c-BN using the direct method and the hellmann-feynman forces generated by 0.5% of displacement of boron, and 0.5% of displacement of nitrogen atoms, (Parlinski, 2001). Investigation of a variety of ground state properties of the 3C, 2H and 4H poly types of silicon carbide and lattice dynamical properties

of cubic SiC K. Karch, et al (1996), using plane-wave pseudopotentials within local density approximation of the density functional theory and density functional perturbation theory (Karc, Pavone, Windi, Schutt, & Strauch, 1994). Investigations of Phonon dispersions of elemental Si and Ge, AlAs, AlSb, GaAs, GaSb binary compounds semiconductors (Giannozz, Gironcoli, Pavone, & Baroni, 1991), the result show that force constant is less for materials that differ by their anions than those that differ by their cations.

MATERIAL AND METHOD

Since one of the objectives of this work is to assess the influence of pseudopotentials, LDA and GGA, on the investigated properties, GGA-PBE

pseudopotentials were constructed for Indium, Silicon and Germanium using Dar Corso method in quantum espresso package (Giannozzi, 2009). First-principles total energy calculations were performed within the local density approximation (LDA-PZ) and generalized gradient approximation (GGA-PBE) using plane-wave self-consistent field (PWscf) method, as embedded in Quantum Espresso Simulation package. Convergence tests were performed to obtain suitable number of k-points, kinetic energy cut offs and lattice constants. For each compound

convergence test results showed that MP 444 was suitable for the total energy self-consistence field calculation. Equilibrium structural parameters for each compound were calculated using the standard procedure by fitting total energy-volume to a Murnaghan's equation of states and displayed in table II.

RESULTS AND DISCUSSION

Table I. Acoustic, Optical Phonon-frequencies and LO-TO Splitting at high symmetry points in III-Bi Binary Compound Semiconductors

Sym.Pts	BBi		AlBi		GaBi		InBi	
	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
LO-TO	0.20	1.15	0.38	0.32	0.15	0.11	0.16	0.13
Γ -X _{TA}	2.10	2.51	1.46	1.26	1.17	1.06	0.96	0.90
Γ -X _{LA}	3.96	4.57	3.02	3.19	3.40	2.94	2.84	3.10
Γ -L _{ΓA}	1.55	1.71	1.14	1.03	1.00	0.92	0.81	0.80
Γ -L _{LA}	3.70	9.27	3.02	2.77	3.40	2.92	2.81	3.00
Γ -X _{ΓO}	12.2	13.92	7.05	7.32	5.28	4.43	4.02	4.17
Γ -X _{LO}	14.05	16.23	8.98	9.19	5.91	5.23	4.23	4.30
Γ -L _{TO}	12.05	15.03	7.56	7.87	5.62	4.91	4.32	4.03
Γ -L _{LO}	12.80	15.89	8.51	8.65	5.62	4.92	4.06	4.13

DISCUSSIONS AND CONCLUSION

LO-TO splitting increases from BBi to AlBi and decreases from GaBi to InBi using local density approximations (LDA) while the reverse is the case for generalized gradient approximations (GGA). This

result shows that pseudopotentials LDA and GGA have great impact on LO-TO splitting and that d-orbital presence might be responsible for the non linear dependence from BBi to InBi compounds. The long range electric fields associated

with long-wave longitudinal phonons are responsible for the phenomenon of LO-TO splitting, that is, the removal of degeneracy between the LO and TO phonons at the Brillouin zone centre (Karc, Pavone, Windi, Schutt, & Strauch, 1994), (Bester* & Gabriel, 2009), (Parlinski, 2001) observed in the dispersion relation curves. Only BBi show higher values of both longitudinal and transverse optical frequencies. Perhaps this might be attributed to the fact that BBi binary compound is the only

optoelectronic material that has direct energy, (Amusa R. A., 2015) and (Madouri & Ferhat, 2005). In conclusion, acoustic and optical frequencies decrease for local density approximation than the generalized gradient approximation in BBi compound while acoustic frequencies are greater for LDA than the GGA frequencies in AlBi compound. However there is degeneracy in optical frequencies of the d-orbital GaBi and InBi binary compounds.

Phonon Dispersion Relations of III-Bismuth Semiconductors

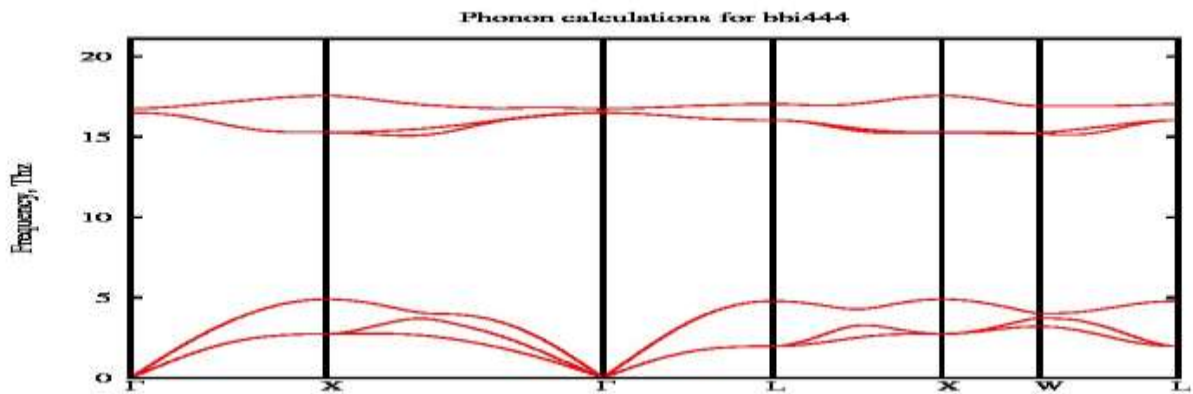


Fig 4.7a (i) Phonon Dispersion relation of Boron Bismuth (LDA)

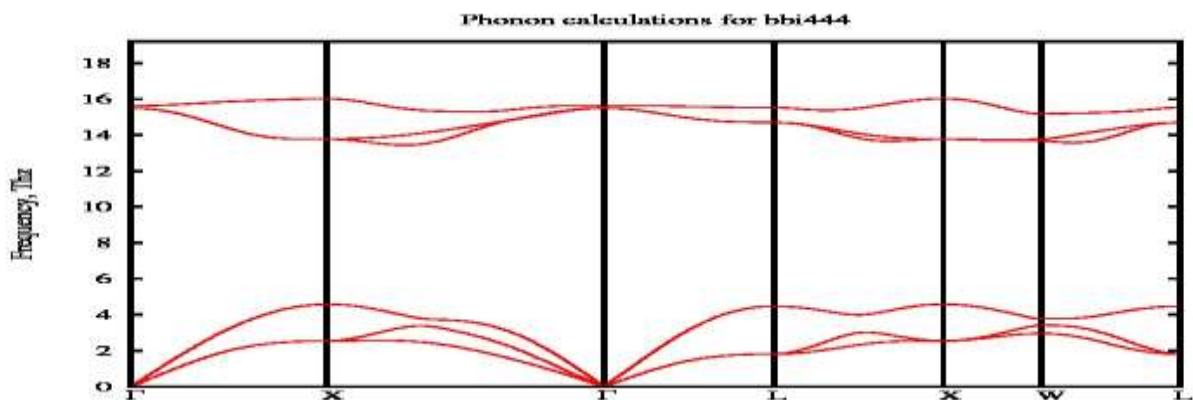


Fig 4.7a (ii) Phonon Dispersion relation of Boron-Bismuth (GGA)

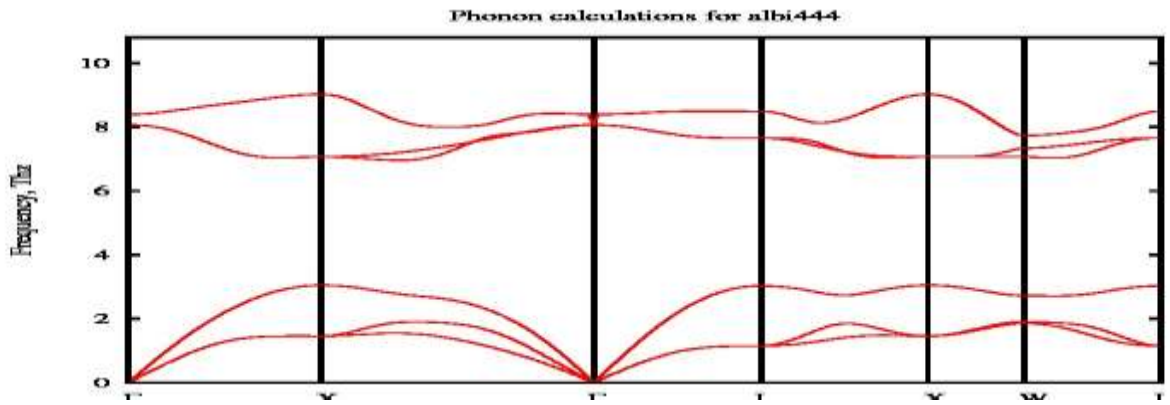


Fig 4.7b (i) Phonon Dispersion relation of Aluminium-Bismuth (GGA)

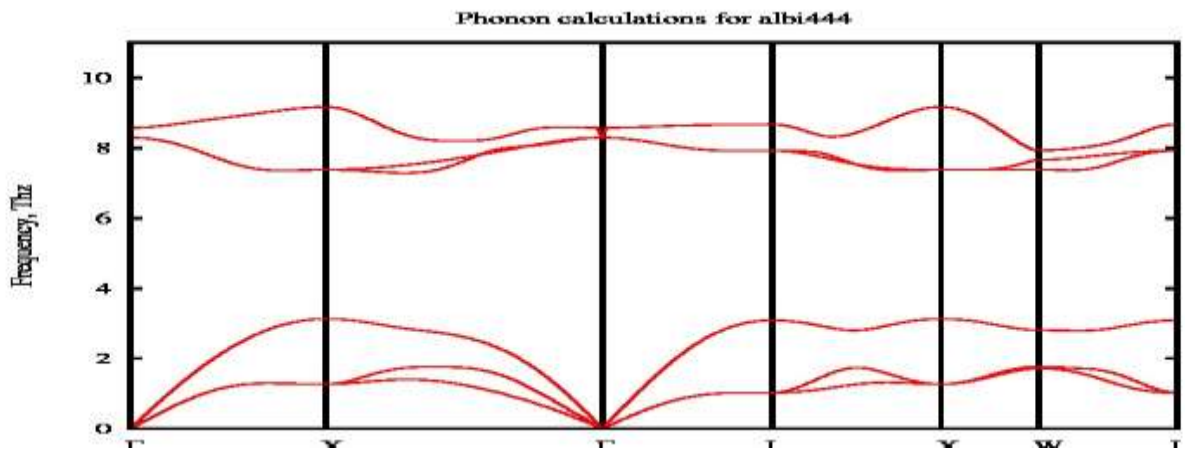


Fig 4.7b (ii) Phonon Dispersion relation of Aluminium-Bismuth (GGA)

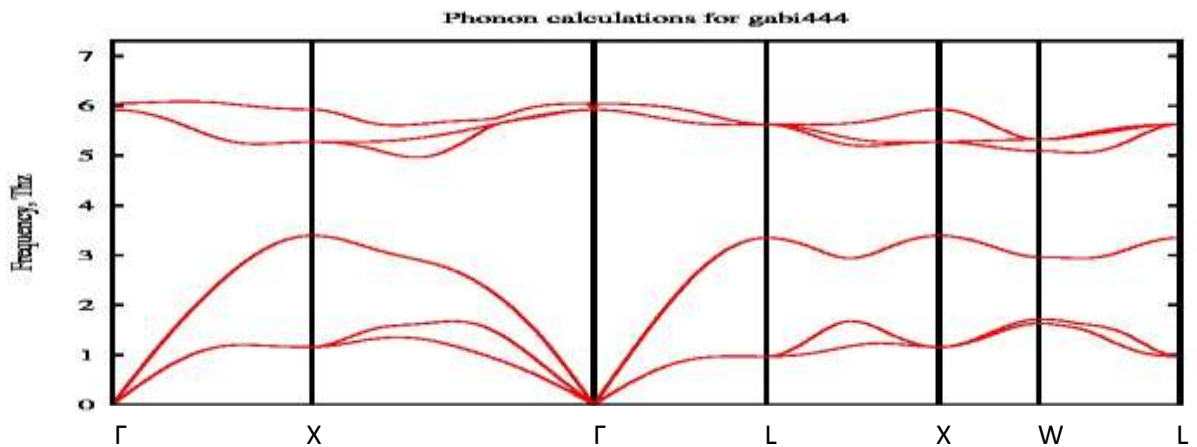


Fig 4.7c (i) Phonon Dispersion relation of Gallium-Bismuth (LDA)

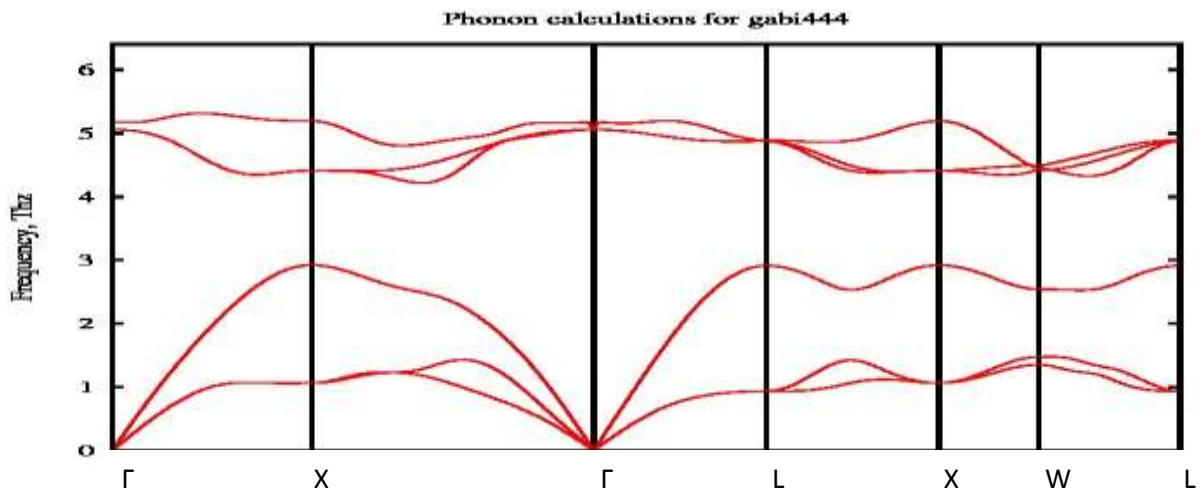


Fig 4.7c (ii) Phonon Dispersion relation of Gallium-Bismuth (GGA)

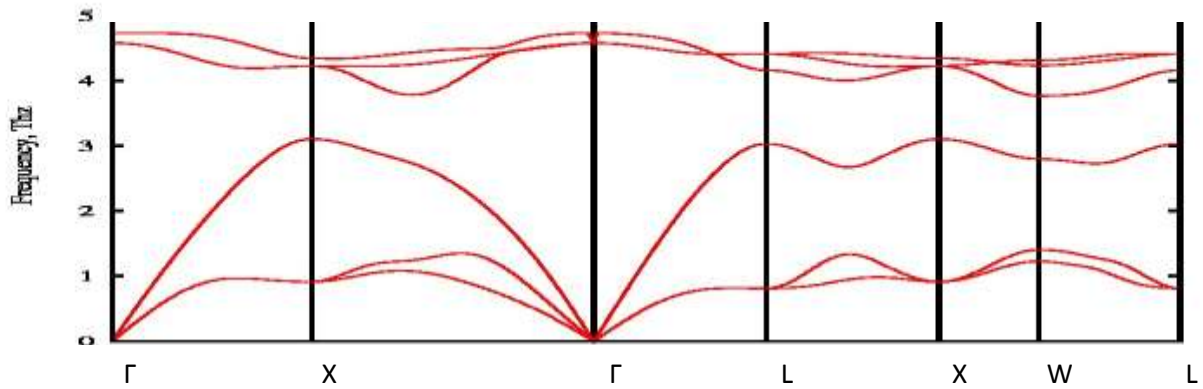


Fig 4.7d (i) Phonon Dispersion relation of Indium-Bismuth (LDA)

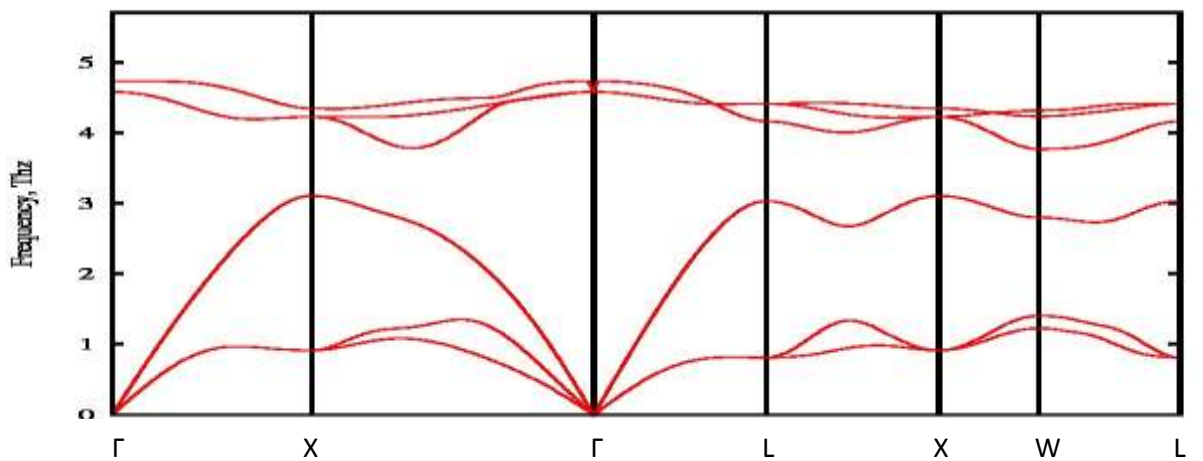


Fig 4.7d (ii) Phonon Dispersion relation of Indium-Bismuth (GGA)

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