CHAPTER 3: COMPUTATIONAL TOOLS

3.1. The WIEN2K code

All the calculations presented in this work are performed using the WIEN2k software package developed by P. Blaha and K. Schwarz *et al.* [78] based on Full Potential Linearized Augmented Plane wave (FP-LAPW) method [79] for computation of the electronic structures of crystals (solids) within the Density Functional Theory (DFT). This method is one of the most accurate methods for estimation of the ground state properties of solids.

The main advantages of this package (code) are that it is an all-electron and full-potential method and performs investigation of properties which are sensitive to core electrons. Using this code, the simulation of a wide range of material's properties, such as structural, electronic, optical properties (elastic constants, NMR spectroscopy, X-Ray, XPS, EELS...) are also possible. Also a web interface is present which provides a clear guidance at each calculation levels.

The basis set used in the WIEN2k code is the Linearized Augmented Plane Wave (LAPW). In this method the lattice is divided into non-overlapping spheres (called an atomic or muffin tin (MT) sphere) surrounding each atomic site and an interstitial region. Therefore two different types of basis sets are chosen for expressing the single particle wave functions. Inside the MT region, the basis function is a product of radial function and spherical harmonics $Y_{lm}(r)$

i.e. $$\phi_{k_n} = \sum_{lm} [A_{lm,k_n} u_l(r, E_l) + B_{lm,k_n} \dot{u}_l(r, E_l)] Y_{lm}(\hat{r}) \qquad (3.1)$$

where $u_l(r, E_l)$ is the regular solution of the radial Schroedinger equation for energy E_l and the spherical part of the potential inside sphere t; $\dot{u}_l(r, E_l)$ is the energy derivative of u_l evaluated at the same energy E_l. A linear combination of

these two functions constitute the linearization of the radial functions; the coefficients A_{lm} and B_{lm} are functions of k_n determined by requiring that this basis matches each plane wave the corresponding basis function of the interstitial region; u_l and $\dot{u}_l$ are obtained by numerical integration of the radial Schroedinger equation on a radial mesh inside the sphere.

For the interstitial regions that are outside the MT sphere, the basis functions are expanded in plane waves.

i.e. $\phi_{k_n} = \dfrac{1}{\sqrt{\omega}} e^{ik_n \cdot r}$ (3.2)

where $k_n = k + K_n$; K_n are the reciprocal lattice vectors and k is the wave vector inside the first Brillouin zone. Each plane wave is augmented by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method.

$\psi_k = \sum_n c_n \phi_{k_n}$ (3.3)

And the coefficients c_n are determined by the Rayleigh-Ritz variational principal. The convergence of this basis set is controlled by a cut off parameter $R_{mt}K_{max}$=6-9, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest K vector in equation (3.3).

Two major parts are present in the program: the initialization, and the main self-consistent field (SCF) cycle. Many analytical tools like band structure, density of states, charge densities, volume optimization, optical properties etc are implemented.

In the initialisation part the nearest neighbours are calculated up to a specified distance and the atomic sphere radii. Overlapping spheres, coordination numbers and nearest neighbour distances are also checked. It is also checked whether the equivalent atoms are really crystallographically equivalent and then calculates the point and space groups for the given structure. The space group symmetry operation is generated. The point group of the individual atomic sites are determined and generated for the lattice harmonics and local rotation matrices. The symmetry operations and the point groupsymmetry of the atoms (to compare them with the "International Tables for X-Ray Crystallography") are then checked. The atomic valance densities are then generated. The k-mesh is generated in the Brillouin zone (BZ). Thus in the initialisation part an initial crystal density is obtained by superposition of atomic densities for the SCF cycle.

The second part i.e. SCF cycle consists of five steps:

1. LAPW0 which generates the potential from the density and construct the effective potential.

2. LAPW1 which calculates the valance band i.e. the eigenvalues and eigenvectors by solving the Kohn Sham equation of valance electrons.

3. LAPW2 which computes new valance densities from the eigenvectors.

4. LCORE which computes the potential and the charge density of the core electrons, and

5. LMIXER which mixes the electron densities of core, semi-core and valance states and generate new input density for the next iterations.

In all the calculations, the number of k-points used for the integration part for both zinc blende and rock salt structure of III-V and II-VI compound semiconductors is 8000 k-points with 20*20*20 k mesh which is reduced to 256 irreducible k-points inside the Brillion zone including five high symmetry points

W, L, Γ, X and K. Convergence of the basis set is obtained at $R_{MT}K_{max} = 9.0$ where K_{max} gives us the plane wave cut-off. The position of the of the first and second atom in ZB structure is taken to be (0,0,0) and (0.25,0.25,0.25) and in RS structure it is (0,0,0) and (0.5,0.5,0.5) respectively.

3.2. Elastic constant code: Cubic Elastic

The elastic constant calculations have been performed using the energy approach. In this method elastic constants were calculated by applying small strains to the unstrained lattice.

For a cubic system only three independent elastic constants namely C_{11}, C_{12} and C_{44} are present. Hence, a set of three sets of distortions are used to determine the three elastic constants. For determining the C_{11} and C_{12} we use two types of distortion D_1 and D_2

The first distortion is the orthorhombic distortion,

$$D_1 = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1-\delta & 0 \\ 0 & 0 & \dfrac{1}{(1-\delta)^2} \end{bmatrix} \tag{3.4}$$

which gives us the energy,

$$E(V,\delta) = E_0 + V_0 \left\{ (C_{11} - C_{12})\delta^2 + O(\delta^4) \right\} \tag{3.5}$$

The second distortion or strain is the volume cubic distortion,

$$D_2 = \begin{bmatrix} 1+\delta & 0 & 0 \\ \delta & 1+\delta & 0 \\ 0 & 0 & 1+\delta \end{bmatrix}$$

The volume is expanded giving the energy,

$$E(V,\delta) = E_0 + V_0\delta(\sigma_1 + \sigma_2 + \sigma_3) + V_0\left\{\frac{3}{2}(C_{11} + 2C_{12})\delta^2 + O(\delta^3)\right\} \tag{3.6}$$

The third distortion is the distortional monoclinic deformation which determines the C_{44},

$$D_3 = \begin{bmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & \dfrac{1}{(1+\delta^2)} \end{bmatrix}$$

which give us the energy,

$$E(V,\delta) = E_0 + V_0\left\{(2C_{44})\delta^2 + O(\delta^4)\right\} \tag{3.7}$$

The elastic constants are thus determined from the above three equations (3.5, 3.6, 3.7).

The elastic constants are calculated with the elastic package interfaced with WIEN2k as developed by Morteza Jamal [80]. The cubic elastic package is a set of programs and scripts that can calculate elastic tensor calculations for cubic phases (primitive, body-centred, or face centred) by using WIEN code. To run this program a valid cubic structure file should exist. This package generates WIEN input files simulating strained structures. It also generates scripts to make WIEN calculate these structures and analyse the results, plot them, and derive their elastic parameters.