

**ELECTRONIC PROPERTIES OF
TERNARY AND BINARY COMPOUNDS**

Thesis Submitted for the Award of the Degree of

Master of Science

BY

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CERTIFICATE

This is to certify that the project thesis entitled “**Electronic properties of ternary and binary compounds**” being submitted by Rutuparna Mohanty in partial fulfillment for the requirement of the one year project course (PH-592) of M.Sc. degree in Physics of National Institute of Technology, Rourkela has been carried out under my supervision. The result incorporated in the thesis has been reproduced by using **Quantum ESPRESSO** codes.

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(Rutuparna Mohanty)

ABSTRACT

The electronic properties of binary compounds and ternary chalcopyrite semiconductors are studied using density functional theory based first principle technique using LDA exchange co-relation function within Quantum ESPRESSO method. From band structure it is observed that chalcopyrites are direct band gap semiconductor and band gaps are also calculated. The anti-ferromagnetic properties is also studied in transition metal oxide using LDA+U exchange co-relation function within Quantum ESPRESSO method. Crystal Structure is studied using Xcrysden.

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1 Introduction

The effective potential in the Schroedinger's equation includes the external potential and the effects of the Coulomb interactions between the electrons, i.e., the exchange and correlation interactions. The exchange potential is due to the interaction described by Pauli's exclusion principle and the correlation potential is due to the effect of a given electron on the overall charge distribution. The exchange and correlation functional are of various types such as LDA, LSDA, GGA, meta GGA. LDA stands for local density approximation which implies that the exchange potential in each point in space depends only on (spin) density in that same point. GGA stands for generalized gradient approximation and is an addition to LDA part, by including terms that depend on derivatives of the density[1].

In LDA the value of $E_{xc}[n(r)]$ is approximated by the exchange co-relation energy of an electron in a homogeneous electron gas of same density $n(r)$. The most accurate data for $E_{xc}(n(r))$ is from Quantum Monte Carlo calculation[2]. The LDA is often surprisingly accurate and for systems with slowly varying charge density generally gives very good results. It has tendency to favor more homogeneous systems and weakly bonded systems. LDA works well in system consisting of sp bonds. LDA performs well in bulk group-IV

semiconductors but not clear ,how well it performs at surface of these material[3].

Despite the remarkable success of LDA,limitation means that care must be taken in application, for systems where the density varies slowly the LDA tends to perform very well. But in strongly co-related systems where an independent particle picture is break down,the LDA is very inaccurate.The transition metal oxides are all Mott insulator, but the LDA predicts that they are semiconductors but finds several to be metallic but in reality they are insulating at 0k [3]. The LDA finds the wrong ground states for titanium atom. It also does not account for vander waals bonding and gives a very poor description of hydrogen bonding[4].

The exchange potential arises mainly from exchange interaction, are nothing more than electrostatic interaction arising because charges of the same spin cost energy when they are close together and save energy when they are apart.In rare earths the 4f electrons are strongly localized and lie very close to the nucleus with little probability density extending significantly further than about a tenth of the inter-atomic spacing.In transition metals the 3d orbitals extend further from the nucleus. This means that the direct exchange interaction is unlikely to be very effective in above cases. So an

indirect exchange takes place in between two magnetic ions mediated by non magnetic ion. So an Hubbard term is added with LDA to study the properties of transition metal. The onsite coulomb interaction(double occupancy of a same site) in Hubbard model is known as Hubbard parameter U . If U is large each site of lattice remains singly occupied and it will try to visit its neighbor site for opposite spin. So the system is having anti-ferromagnetic nature and insulator[5].

Christoph Loschen et.al[6] mentioned that it is important to mention that just discussed observables are computed for ground state of Ce_2O_3 which found to be insulating and anti-ferromagnetic and which lies 25 mv. With respect to the electronic structure of Ce_2O_3 , the major effect of U_{eff} in the LDA+U approaches is to force the localization of 4f electron within the band gap. As a result this material becomes to be properly described as insulating instead of metallic as been described by other groups.

The mean field Hubbard correction popularly called $LDA + U$ or $XC + U$ is a semi empirical correction which tries to improve the deficiencies of the LDA functionals. Energy is lowered if states become fully occupied. If the energy levels move away from the fermi level i.e the band gap the Hubbard U improves on the deficiencies of the exchange-correlation energy. The NiO

crystal has too low band gap in LDA and one of the standard examples of how the LDA+U approximation can be used to improve the description of the electronic structure of solids[7]. By using LDA the band gap of NiO is very small compared to experimental value but using LDA+U it is nearly to experimental value[8].

1.1 Density Functional Theory

Density functional theory (DFT) is a quantum mechanical modeling used to study the electronic structure of many body system. The properties of many electrons system can be determined by using functionals (function of another function). In DFT the functional is the spatially dependent electron density. In DFT, for periodic system, if we can find the electronic states then we can calculate thermal, optical and magnetic properties of solids, equations of state, electron density distributions and cohesive energies.

Hohenberg and Kohn tried to formulate the DFT as an exact theory for the many body systems[10]. The formulation applies to any system of interacting particles in an external potential $V_{ext}(r)$, including any problem of electrons and fixed nuclei, where the Hamiltonian is given by[9],

$$\hat{H} = -\frac{\hbar^2}{2m_e} + \sum_i \nabla_{i^2} + \sum_i V_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{(\hat{r}_i - \hat{r}_j)}$$

DFT is based upon two Hohenberg-Kohn theorem as given below.

- Theorem I: For any system of interacting particles in an external potential $V_{ext}(r)$, the potential $V_{ext}(r)$ is uniquely determined, except for a constant, by the ground state particle density $n_0(r)$ [10].
- Theorem II: A universal functional for the energy $E[n]$ in terms of the density $n(r)$ can be defined, valid for any external potential $V_{ext}(r)$. For any particular $V_{ext}(r)$, exact ground state energy of the system is the global minimum value of this functional, and the density $n(r)$ that minimizes the functional is the exact ground state density $n_0(r)$ [10].

Hohenberg-Kohn theorem shows that it is possible to use the ground state density to calculate properties of the system. But it doesn't provide a way of finding the ground state energy.

But Kohn-Sham equations provided that route. To derive these equations the ground state energy is considered as the functional of charge density. Kohn-Sham derived a set of single particle Schroedinger equations given by[9],

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r)$$

where,

ϵ_i : Kohn-Sham eigenvalues.

$\psi_i(r)$: Kohn-Sham single particle orbitals.

The effective potential is given by[11],

$$V_{eff}(r) = V_{ext}(r) + V_{Hartree}(r) + V_{xc}(r)$$

$V_{ext}(r)$ tells about the electron-ion interaction[9]. $V_{Hartree}(r)$ represents the Hartree potential, i.e., the classical electrostatic interaction. And $V_{xc}(r)$ is the exchange-correlation potential.

$V_{Hartree}(r)$ and $V_{xc}(r)$ are given by,

$$V_{Hartree}(r) = \int \frac{n(r')}{|r - r'|} dr'$$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$$

E_{xc} is the exchange-correlation energy. $V_{xc}(r)$ takes care of the many body effect.

Approximation for the E_{xc} : [9]

1. LDA (Local Density Approximation)

$$E_{xc}^{LDA}[n] = \int d^3r n(r) \epsilon_{xc}^{HEG}(n) \quad (\text{HEG-Homogeneous Electron Gas})$$

2. LSDA (Local Spin Density Approximation)

$$E_{xc}^{LDA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(r) \epsilon_{xc}^{HEG}(n_{\uparrow}, n_{\downarrow})$$

3. GGA (Generalized Gradient Approximation)

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(r) \epsilon_{xc}^{GGA}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) \quad [9]$$

4. MGGA (Metal generalized gradient approximation)

$$E_{xc}^{MGGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(r) \epsilon_{xc}^{MGGA}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \nabla^2 n_{\uparrow}, \nabla^2 n_{\downarrow}, \nabla_{\uparrow}, \nabla_{\downarrow})$$

2 Computational details

2.1 Local Density Approximation:

In LDA the functional depends only upon the density at the co-ordinates, where functional is evaluated. This approximation is used to find Eigenfunction and Eigenvalues of the Hamiltonian. It is commonly used along with plane wave basis. LDA is meant a functional whose functional derivative with respect to density at that point only. It is an approximation to the exchange part which depends upon the value of electron density at each point. This approximation is derived from the homogeneous electron gas model (like Jellium model). We are taking electrons of negative charge around that positive charges are there. So to lower the interactions between electrons we are considering exchange term. The exchange functional can also be expressed as the energy of

interaction between the electron density and the Fermi coulomb hole charge distribution. Local Density Approximation is a efficient method for large molecules and solids. The expression for energy and potential is given below [9]

$$E_{xc}(n) = \int E_{xc}[n](\hat{r})d^3r$$

where E_{xc} =exchange-correlation energy per electron

$$E_{xc}[n] = E_{xc}(n(\hat{r}))$$

LDA Exchange correlation potential

$$V_{xc}(r) = \frac{\delta E_{xc}(r)}{\delta n}$$

2.2 LDA+U:

This approximation is the improved form of LDA. In case of transition metals or rare earth metals ions (strongly co-related system),the LDA can not be be successful approximation. By applying LDA to transition metal compound ,it will provide metallic electronic structure with partially d band which is wrong. There are several approaches to improve LDA taking the strongly co-related electron-electron interaction. The Hamiltonian of LDA for above case can be improved by using the calculated self energy in a consistent procedure. The orbital dependent potential taking LDA+U approximation gives upper

and lower Hubbard bands with difference of coulomb parameter U . LDA+U approximation shows that the information obtained by this are not sensitive to particular form of localized orbitals. LDA+U theory is Hartee Fock theory for localized states (orbital of rare earth metal). By using the Hubbard U term ,a correction term to Hamiltonian of LDA ,there is large increase in the number of electronic structure calculations.Hubbard parameter term U which is relating the single particle potential to the magnetic order parameter. For impurity system,High Tc superconductors ,Mott insulators ,transition metal ,the LDA +U approach is surprisingly accurate. Delocalized s,p electron can be described by using a independent one electron potential e,g LDA but for localized d and f electron instead of averaged coulomb energy we are using Hubbard like term. So first subtracting the correct formula from LDA total energy and then adding the Hubbard term[12].

$$E_{original} = UN \frac{(N-1)}{2}$$

$$E = E_{LDA} - UN \frac{(N-1)}{2} + \frac{1}{2}U \sum_{i \neq j} n_i n_j$$

An extra U term added to potential is in the form of-

$$V_i(r) = V_{LDA}(r) + U\left(\frac{1}{2} - n_i\right)$$

where $n_i(r)$ is the charge density of a particular ith orbital.

2.3 Quantum Espresso

It is a computational technique for first principle calculation of periodic as well as disordered systems. It is mainly based on DFT theory (electron-ion interaction), plane wave and pseudopotentials (electron-electron interaction). It calculates the ground state energy and Kohn Sham orbital for both insulators and metals and various type of structural optimizations. Quantum espresso can be used to study metals, semiconductors as well as insulators. Three main components of method are PWSCF (Plane wave self consistent field), CP (Car Parinello), FPMD (First principle molecular dynamics).

PWSCF

It is a method to calculate the phonon dispersions for complex materials,i.e., to study the stability of crystal. The electronic structures can be calculated by expanding the wavefunctions into planewaves.

CP (Car Parinello)

It is a code for calculating molecular dynamics using ultrasoft pseudopotentials and for studying the structure of disordered materials. It can also be used for minimization of electronic energy functional to self consistency[13].

Pseudopotential

It is a modified effective potential term instead of coulombic potential term in Schroedinger equation for core electrons. There are two types of Pseudopotentials, i.e, ultrasoft pseudopotential and Norm conserving pseudopotential. The information about the type of exchange co-relational functional and type of pseudopotential can be found from the name of pseudopotential[11]. Plane wave formalism usually performed in combination with pseudopotential because a large number of plane waves are required to expand wavefunctions which is an obstacle to increase the computational efficiency. In pseudopotential, the Kohn Sham's radial equation is considered. It contains the contribution from valence electrons.

Exchange Co-relation potential

Need to diagonalize a matrix by iterative method. The no of eigenvalue computed for metals depends on valence electron.

2.4 Xcrysden

XCrySDen is a molecular and crystalline-structure visualization program, but its main function is as a property analyzer program. It can run on most UNIX platforms, without any special hardware or software requirements. Special efforts were made to allow for appropriate display of 3D isosurfaces and 2D contours. XCrySDen is also a graphical user interface for the CRYSTAL. It can perform real-time operations such as rotation and translation. A specialized periodic-structure visualization program must also possess additional specific features such as displaying the crystal cages (lattices) in direct and reciprocal space, and displaying the Wigner Seitz cell (direct space) and the first Brillouin zone (reciprocal space). Beside measuring the distances, angles, and dihedral, a measurement of crystal planes is almost mandatory[14].

3 Results and Analysis

3.1 ZnS (Zinc Blend Structure)

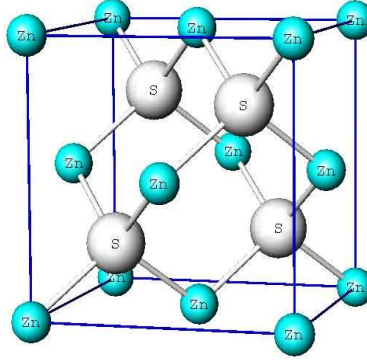


Figure 1: Unit cell of ZnS

The cubic zinc sulphide structure results when Zn atoms are placed on one fcc lattice and atoms on the other fcc lattice as shown figure. The conventional cell is a cube. The coordinates of the Zn atoms are $000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$: the coordinates of the S atoms are $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}$. The lattice is fcc. There are four molecules of ZnS per conventional cell. About each atom there are four equally distant atoms of the opposite kind arranged at the corners of a regular tetrahedron[15]. The electronic property of ZnS is studied. From figure 2, it is found that the kinetic energy cut-off is 25 Ry. Band gap is found to be 1.9 eV [Figure 3]. ZnS is a direct band gap semiconductor. From charge density plot shown in figure 5, it is observed that ZnS undergoes ionic bonding.

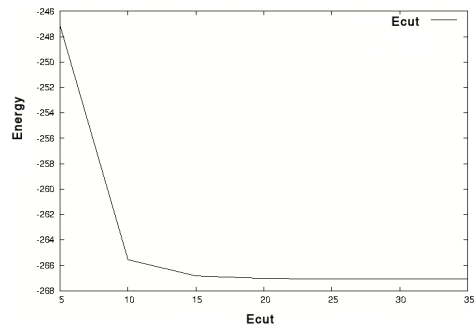


Figure 2: E vs Ecut-off graph

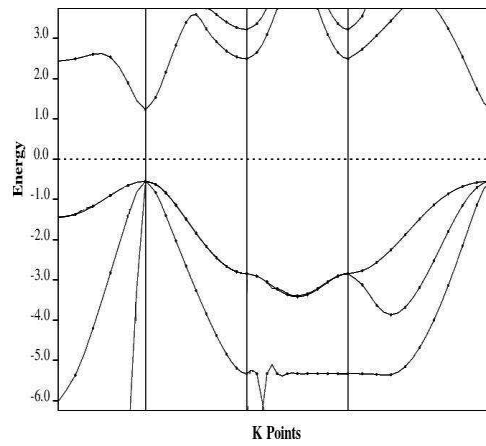


Figure 3: Band structure of ZnS

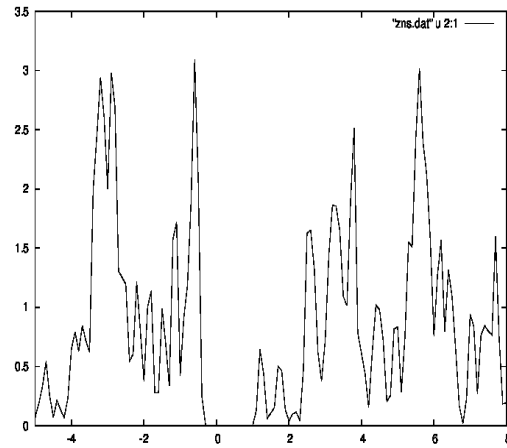


Figure 4: Density of state of ZnS

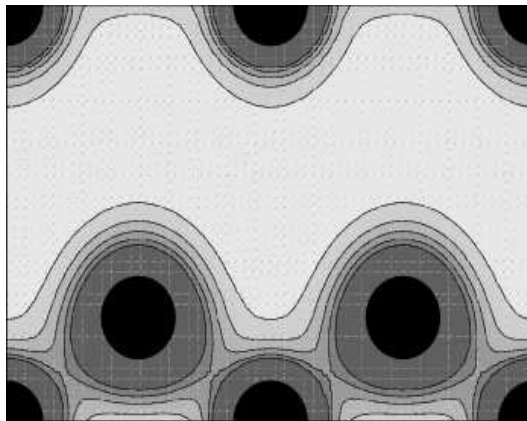


Figure 5: Charge density plot of ZnS

3.2 Chalcopyrite type Semiconductor

Chalcopyrite type of semiconductors are ternary compounds. The structure of chalcopyrite is modified and extended structure of zinc blende structure. This structure is considered as the doubling of zinc blende unit cell so that

one is 90° rotated with respect to other. In this type of structure the C axis is doubled, i.e., doubling takes place in Z direction, $C = 2a$. The A and B cations lie on the corners and face of the unit cell and the C anions lie inside the unit cell. Each cation is tetrahedrally co-ordinated by four anions. Sum of valence electrons in the unit cell is 8, so it also obeys the octate rule. Bravais lattice is body centered tetragonal[16]. Chalcopyrite type of

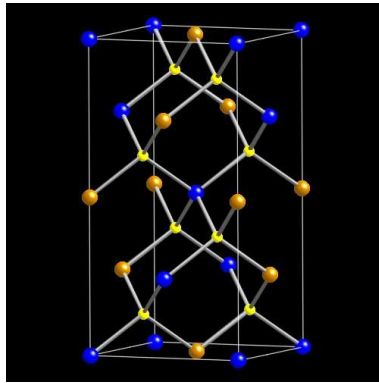
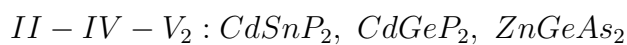
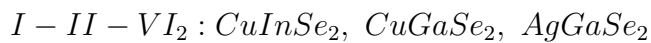


Figure 6: Unit cell of Chalcopyrite

semiconductors are of two types: $I - III - VI_2$ type and $II - IV - V_2$ type. These two types can be given by the general formula ABC_2 (A = Li, Na, Cu, Ag; B = Al, Ga, In; C = S, Se). The material is known as a low temperature phase because a perfect chalcopyrite phase can be obtained at $T=0k$.

The example of chalcopyrite type semiconductors are:



In our global country the energy supplied to customer has its origin in fossil and nuclear power plants. Now the chalcopyrite type material which are used as absorber layer in thin film solar cells, is showing excellent optical properties and having high efficiency. It is also used in detectors, polycrystalline solar cells, light emitting diode, dilute magnetic semiconductors (DMS) and spintronics application, optoelectronic devices[16].

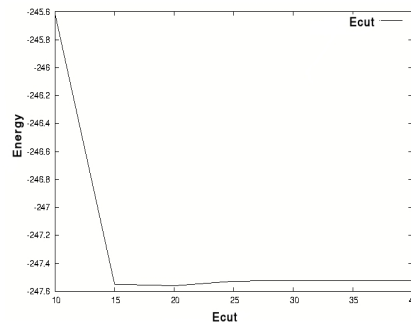
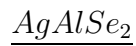


Figure 7: E vs Ecut-off graph of $AgAlSe_2$

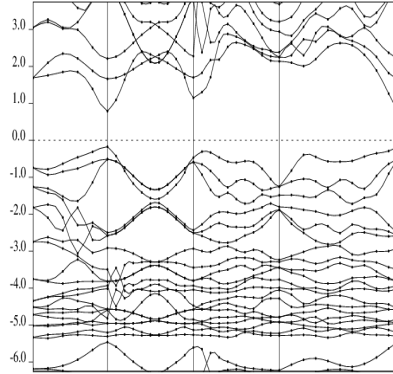


Figure 8: Band structure of $AgAlSe_2$

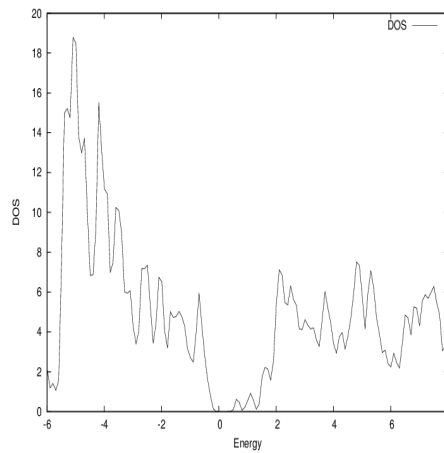


Figure 9: Density of state of $AgAlSe_2$

Electronic properties of $AgAlSe_2$ is studied using LDA as exchange correlation function. From figure-7 the kinetic energy cut-off is calculated to be 30 Ry. From figure-8 Band gap is found to be 0.94 eV and having direct band gap.

CuGaS₂

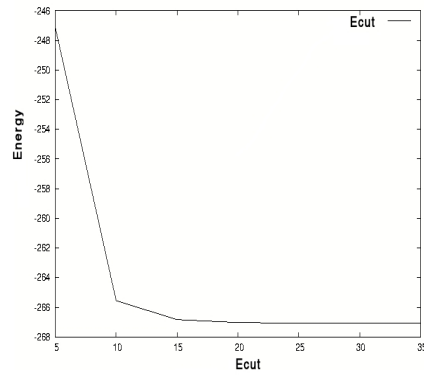


Figure 10: E vs Eut-off graph of *CuGaS₂*

Electronic properties of *CuGaS₂* is studied and figure 10 the kinetic energy cut-off is calculated to be 25 Ry. From figure 11 band gap is found to be 0.81 eV and also observed that this is a direct band gap semiconductor.

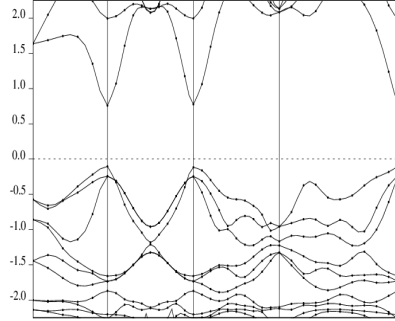


Figure 11: Band structure of $CuGaS_2$

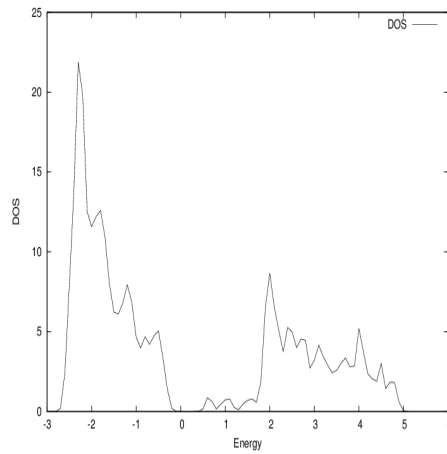


Figure 12: Density of state of $CuGaS_2$

3.3 NiO(transition metal oxide)

Electronic properties of NiO is studied both using LDA and LDA+U as exchange correlation function. From plot[13],[14] it is observed to be showing anti ferromagnetic nature. In magnetic properties the Hubbard energy, absolute magnetization and total magnetization is calculated .

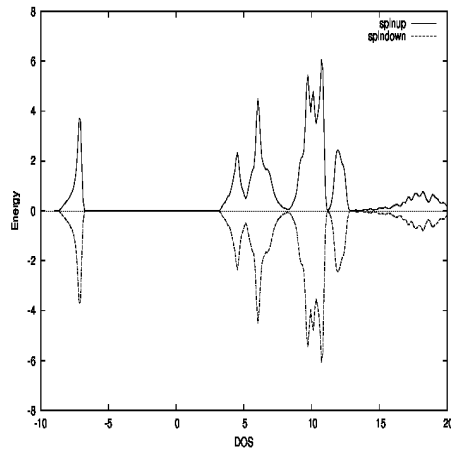


Figure 13: Density of state of NiO using LDA

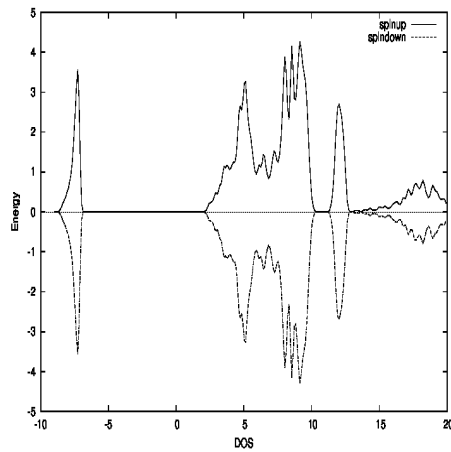


Figure 14: Density of state of NiO using LDA+U

3.4 Cobalt Oxide(CoO)

In Electronic properties study of CoO from Figure 15,16 it is observed to be showing ferromagnetic nature. Magnetic properties is studied.

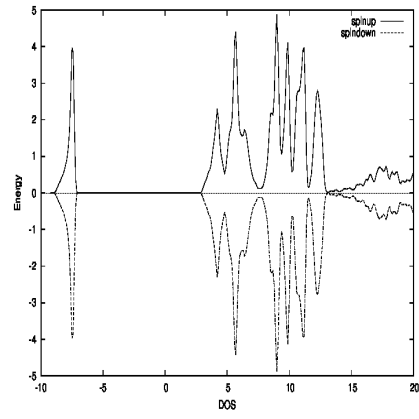


Figure 15: Density of state of CoO using LDA

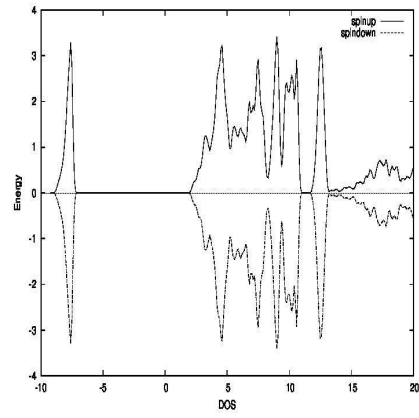


Figure 16: Density of state of CoO using LDA+U

3.5 Structure of ZnS using Xcrysden

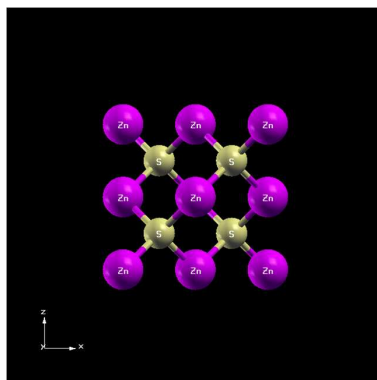


Figure 17: unit cell of ZnS

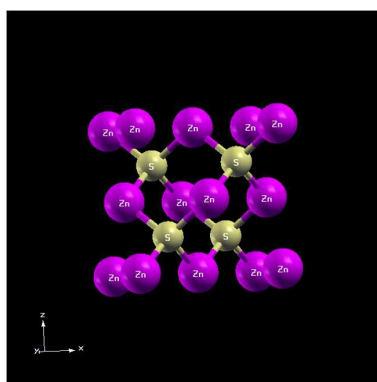


Figure 18: unit cell of ZnS in different angle of view

3.6 Structure of Chalcopyrite using Xcrystden

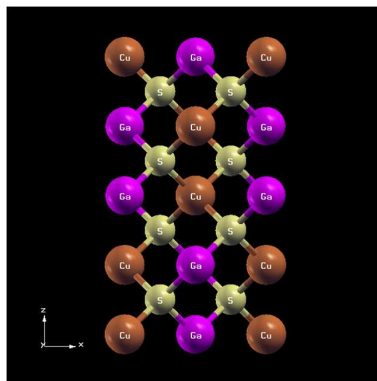


Figure 19: unit cell of $CuGaS_2$ structure

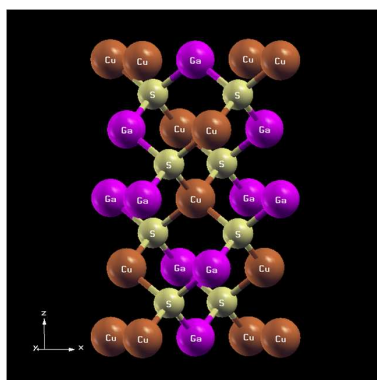


Figure 20: unit cell of $CuGaSe_2$ with different angle of view

4 Conclusion

Installation of Quantum espresso and Xcrysden. In Quantum espresso electronic properties of ZnS, $AgAlSe_2$, $CuGaS_2$ are studied using LDA exchange co-relation function. Band structure, Band gap, cut-off and total density of states are calculated. Electronic properties of transition metal oxides such as NiO, CoO are studied by LDA+U exchange co-relation function. Spin up and spin down density of states are observed for NiO, CoO system which shows anti ferromagnetic behavior. In Xcrysden Crystal Structure is generated both for zinc blende and chalcopyrite.

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