Electronic structure and thermoelectric properties of the intermetallic compound Yb_2Ge

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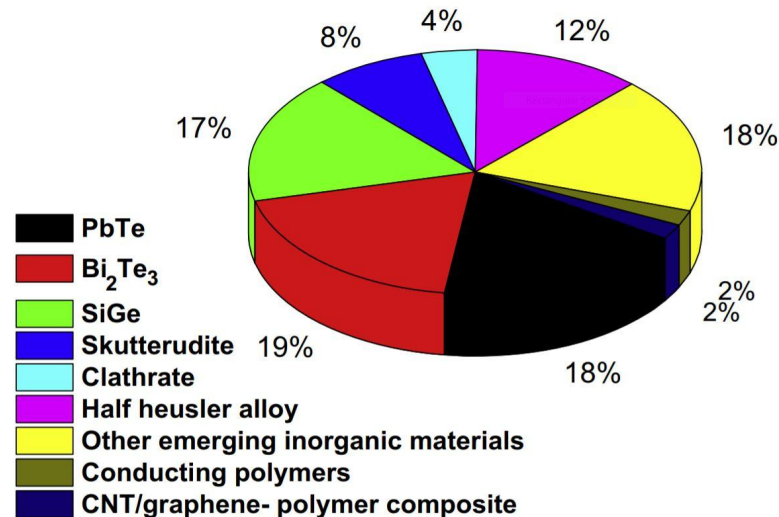Reg. No. 1713102072110

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Objective

- The global sustainable energy crisis opens up a major need to identify newer technologies and materials to obtain cleaner energy.
- Thermoelectric devices can scavenge heat from any source and covert any form of heat, including solar and waste heat into electricity.
- Solid state thermoelectric generators and Peltier coolers are found to be silent, reliable, and scalable.

In search for new materials

- An extensive literature survey was undertaken to find suitable thermoelectric materials that was previously not studied. The materials currently used are reported below.

Legend:
- PbTe
- Bi_2Te_3
- SiGe
- Skutterudite
- Clathrate
- Half heusler alloy
- Other emerging inorganic materials
- Conducting polymers
- CNT/graphene- polymer composite

Observations made from the literature survey

- A good thermoelectric possesses a high thermoelectric figure of merit (ZT).
- In order to maximize ZT, electrical conductivity (σ) should be very high while thermal conductivity (κ) must be kept low.

$$ZT = \frac{\sigma \alpha^2 T}{\kappa}$$

- Intermetallic compounds are found to have a low band gap if not any. Semiconducting intermetallics are suspected to be good contenders for use in a thermoelectric device.
- Thus Yb_2Ge, a previously unexplored semiconducting intermetallic is chosen for this study.

To find an optimal method of study

- It is given that the resources (in nature and otherwise) are limited. The need of the hour is to optimize maximum useful output with minimal wastage.
- Three approaches to find new properties of a given material:

Traditional experimental approach using characterizing tests.	Pro: Error-free if performed properly. Con: Expensive and wasteful.
Quantum mechanics based, Density Functional Theory (DFT) computations	Pro: Predicts to a good degree of accuracy. Con: Complicated algorithm involved.
Recent, Machine Learning (ML) based data-driven statistical approach.	Pro: Produces the best results optimally. Con: Requires bountiful data.

The problem in solving the Schrödinger Equation

- A system of M well defined atoms with N electrons to be described and studied.
- M nuclei are at positions $\mathbf{R_1}$, $\mathbf{R_2}$, …, $\mathbf{R_M}$ $\Rightarrow$ $E(\mathbf{R_1},..,\mathbf{R_M})$ is the energy.
- The wavefunction $\psi = \psi_1(\mathbf{r_1}).\psi_2(\mathbf{r_2})...\psi_N(\mathbf{r_N})$ $\Rightarrow$ Hartree Product.

$$\left[\frac{h^2}{2m} \sum_{i\,1}^{N} \nabla_i^2 + \sum_{i\,1}^{N} V(\mathbf{r}_i) + \sum_{i\,1}^{N} \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi$$

- In one molecule of CO_2, ψ has 66 dimensions (3 set of coordinates for 22 electrons)
- In molecule of Yb_2Ge, there are 172 electrons $\Rightarrow$ ψ has 516 dimensions!
- Here 12 molecules of Yb_2Ge were studied. $\Rightarrow$ ψ has 6192 dimensions!

A simple alternative. DFT.

- The wave function for any particular set of coordinates cannot be directly observed.
- The quantity that can (in principle) be measured is the probability that the N electrons are at a particular set of coordinates. This probability is equal to $|\psi_i(\mathbf{r})|^2$.
- A closely related quantity is the density of the electrons at a particular position in space, $n(\mathbf{r})$.
- This can be written in terms of the individual electron wave functions as:

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

- Note: The electron density depends only on 3 dimensions.
- Hence, (electron) Density Functional Theory is of extreme importance.

The "functional" in DFT

Hohenberg-Kohn Theorem:

Theorem 1: **The ground-state energy from Schrödinger equation is a unique functional of the electron density.**

Theorem 2: **The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.**

The Kohn - Sham equation - in terms of energy functional

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}]$$

$$E_{\text{known}}[\{\psi_i\}] = \frac{h^2}{m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(\mathbf{r}) n(\mathbf{r}) \, d^3r$$

$$+ \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} \quad \mathbf{r}'|} \, d^3r \, d^3r' + E_{\text{ion}}.$$

The Kohn - Sham equation in terms of potentials

$$\left[\frac{h^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} \quad \mathbf{r}'|} d^3 r'.$$

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

Algorithm to solve Kohn Sham equation

1. Define an initial, trial electron density, $n(\mathbf{r})$.

2. Solve the Kohn – Sham equations defined using the trial electron density to find the single-particle wave functions, $\psi_i(\mathbf{r})$.

3. Calculate the electron density defined by the Kohn –Sham single particle wave functions from step 2,

$$n_{KS}(\mathbf{r}) = 2 \, \Sigma \, \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}).$$

4. Compare the calculated electron density, $n_{KS}(\mathbf{r})$, with the electron density used in solving the Kohn –Sham equations, $n(\mathbf{r})$. If the two densities are the same, then this is the ground-state electron density, and it can be used to compute the total energy. If the two densities are different, then the trial electron density must be updated in some way. Once this is done, the process begins again from step 2.

    This iterative method leads to a **self consistent solution** for the Kohn Sham equation.

Self Consistent Field (SCF) calculation for Si

```
&CONTROL
    calculation = "scf"
    max_seconds =  8.64000e+04
    pseudo_dir =
"C:\Users\Rohith\.burai\.pseudopot"
    tprnfor     = .TRUE.
    tstress     = .TRUE.
/
&SYSTEM
    a           =  5.46873e+00
    degauss     =  1.00000e-02
    ecutrho     =  1.00000e+02
    ecutwfc     =  2.50000e+01
    ibrav       = 2
    nat         = 2
    ntyp        = 1
    occupations = "fixed"
    smearing    = "gaussian"
/
```

```
&ELECTRONS
    conv_thr        =  1.00000e-06
    electron_maxstep =  200
    mixing_beta     =  7.00000e-01
    startingpot     = "atomic"
    startingwfc     = "atomic+random"
/

K_POINTS {automatic}
 4  4  4  0 0 0

ATOMIC_SPECIES
Si     28.08550   Si.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Si     -4.101546   4.101546   4.101546
Si     -2.734364   2.734364   2.734364
```

Output for SCF calculation for Si

```
highest occupied level (ev):       6.0835

total energy              =      -15.85264031 Ry
Harris-Foulkes estimate   =      -15.85264035 Ry
estimated scf accuracy    <        0.00000009 Ry

The total energy is the sum of the following terms:

one-electron contribution =        4.78582276 Ry
hartree contribution      =        1.07820387 Ry
xc contribution           =       -4.81690833 Ry
ewald contribution        =      -16.89975862 Ry

convergence has been achieved in    5 iterations
```

Convergence plot of SCF for Si
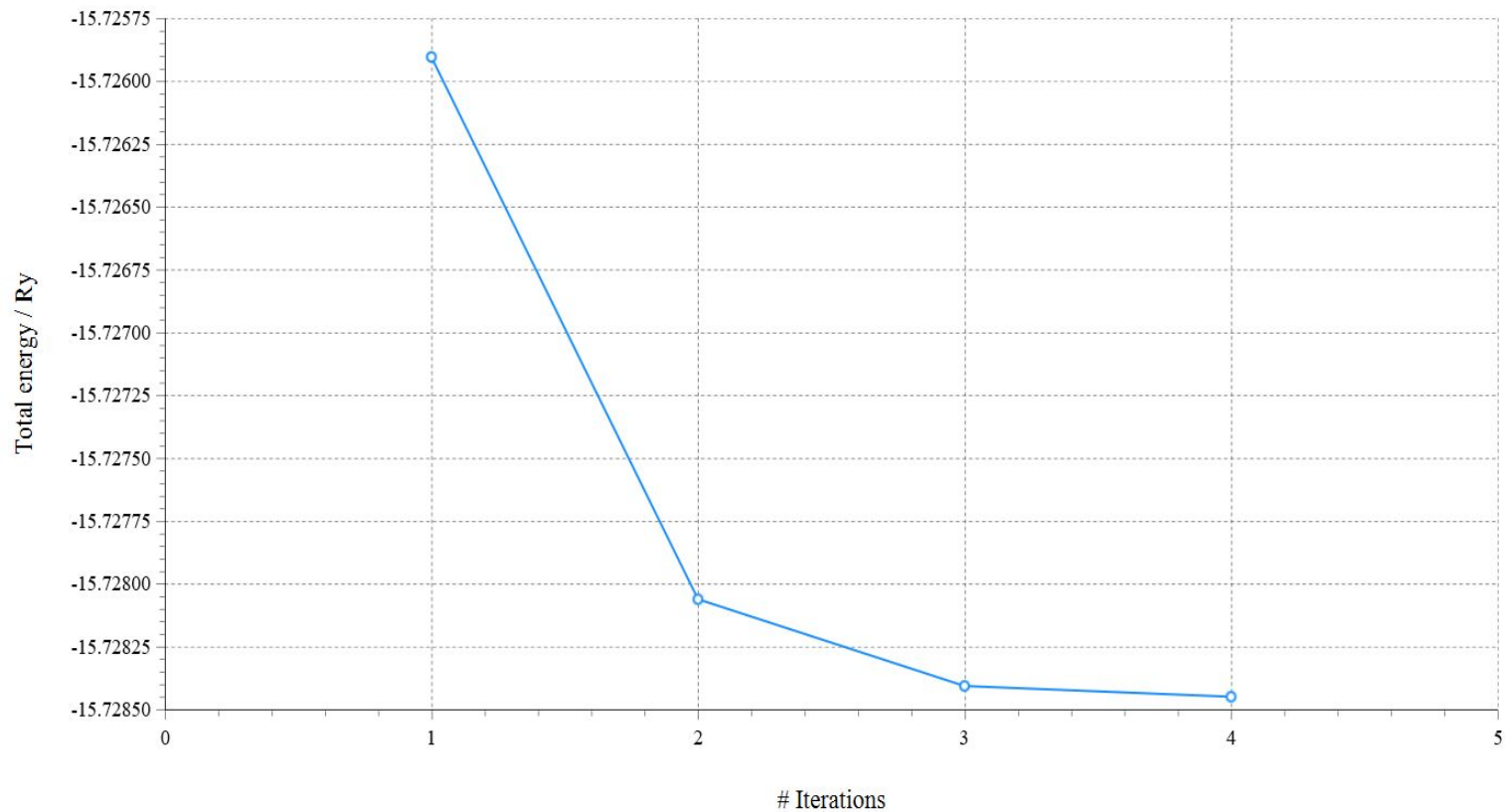
Optimization of lattice parameter

```sh
#!/bin/sh
rm -f si.eos.out si.etot_vs_alat
touch si.etot_vs_alat

for alat in 9.8 9.9 10.0 10.1 10.2 10.3 10.4
10.5 10.6 10.7 ; do

cat > si.eos.in << EOF
 &control
    Calculation = 'scf',
    prefix='silicon',
    pseudo_dir =
'C:\Users\Rohith\.burai\.pseudopot',
    outdir='C:\Users\Rohith\output'
 /
 &system
    ibrav=  2, celldm(1) =$alat, nat=  2,
ntyp= 1,
    ecutwfc = 20.0,
 /
```
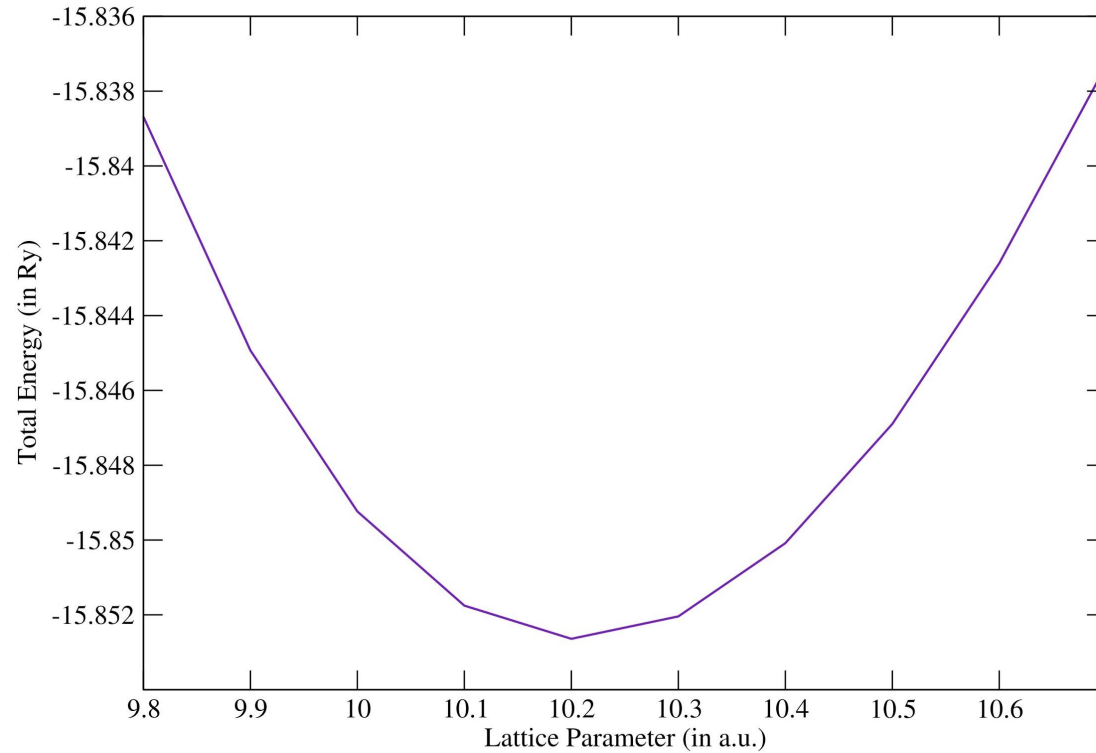
```sh
ATOMIC_SPECIES
 Si  28.086  Si.pz-vbc.UPF
ATOMIC_POSITIONS
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
   4 4 4 1 1 1
EOF
pw.x -in si.eos.in > si.eos.out
grep -e 'lattice parameter' -e !
si.eos.out | \
awk '/lattice/{alat=$(NF-1)}/!/{print
alat, $(NF-1)}'>> si.etot_vs_alat

done
```
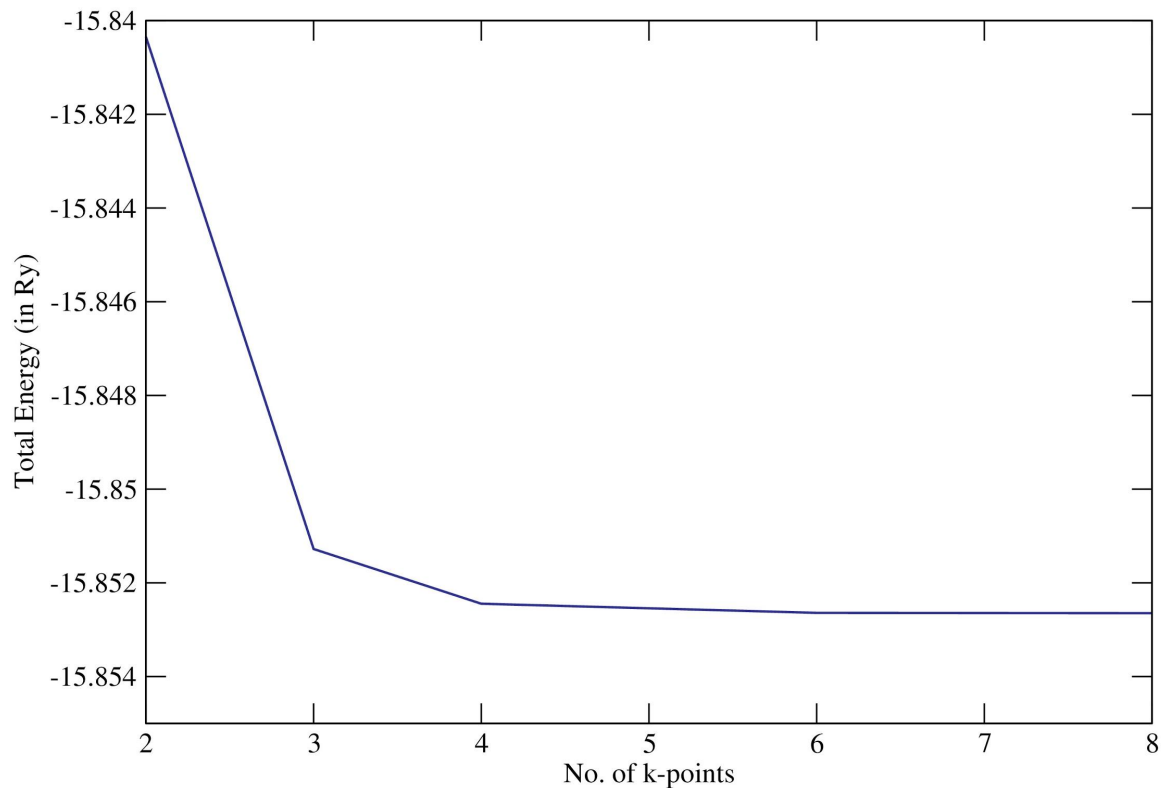
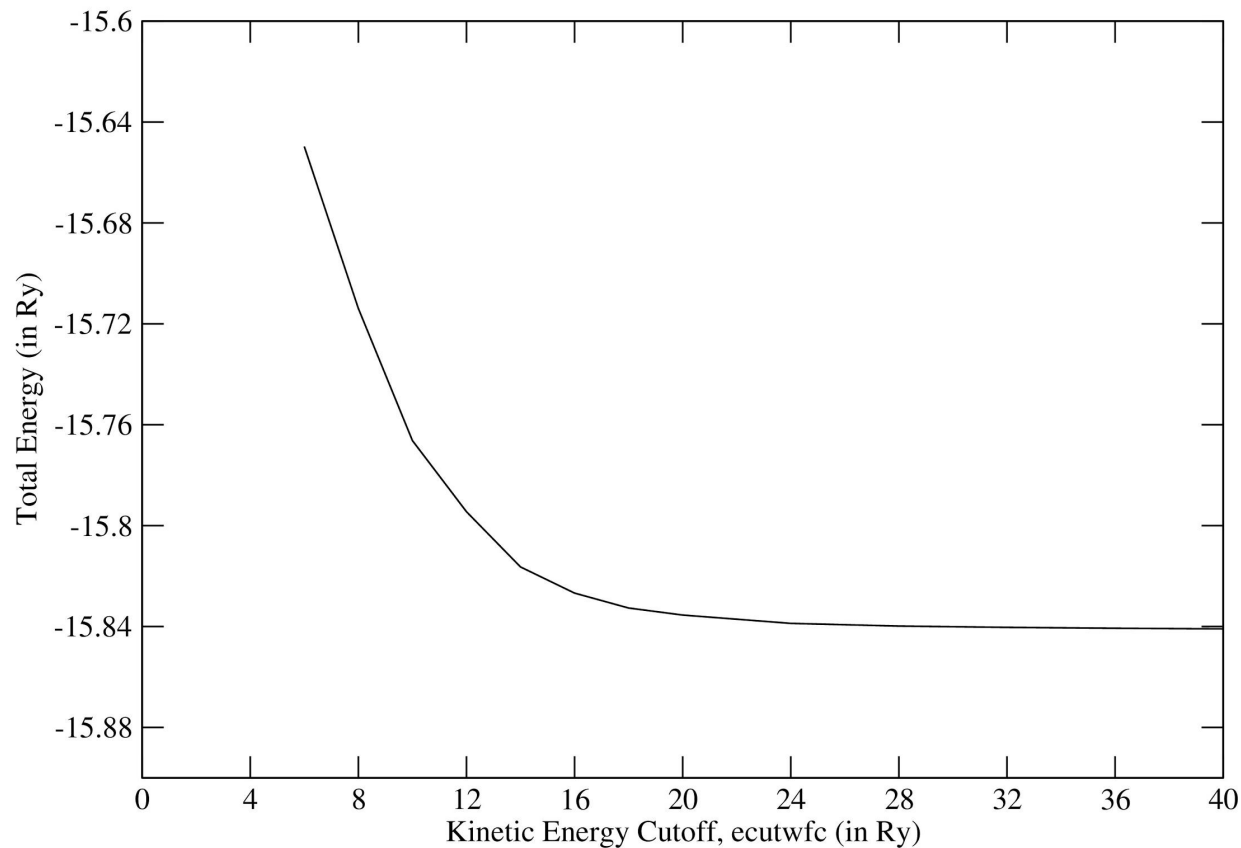# Optimization of lattice parameter

* 1a.u. (Bohr unit) = 0.529Å, further, 1Ry = 13.6eV

Saturation of energy with respect to number of k points

Saturation of total energy with Kinetic Energy cutoff

Band Structure calculation for Si

```
&CONTROL
    calculation = "bands"
    max_seconds =  8.64000e+04
    pseudo_dir  = "C:\Users\Rohith\.burai\.pseudopot"
    tprnfor     = .TRUE.
    tstress     = .TRUE.
/

&SYSTEM
    a           =  5.46873e+00   degauss = 1.00000e-02
    ecutrho     =  1.00000e+02   ecutwfc = 2.50000e+01
    ibrav       = 2,   nat = 2,   ntyp = 1
    occupations = "fixed"
    nbnd        = 8      smearing    = "gaussian"
/

&ELECTRONS
    conv_thr        =  1.00000e-06
    electron_maxstep =  200
    mixing_beta     =  7.00000e-01
    startingpot     = "atomic"
    startingwfc     = "atomic+random"
```
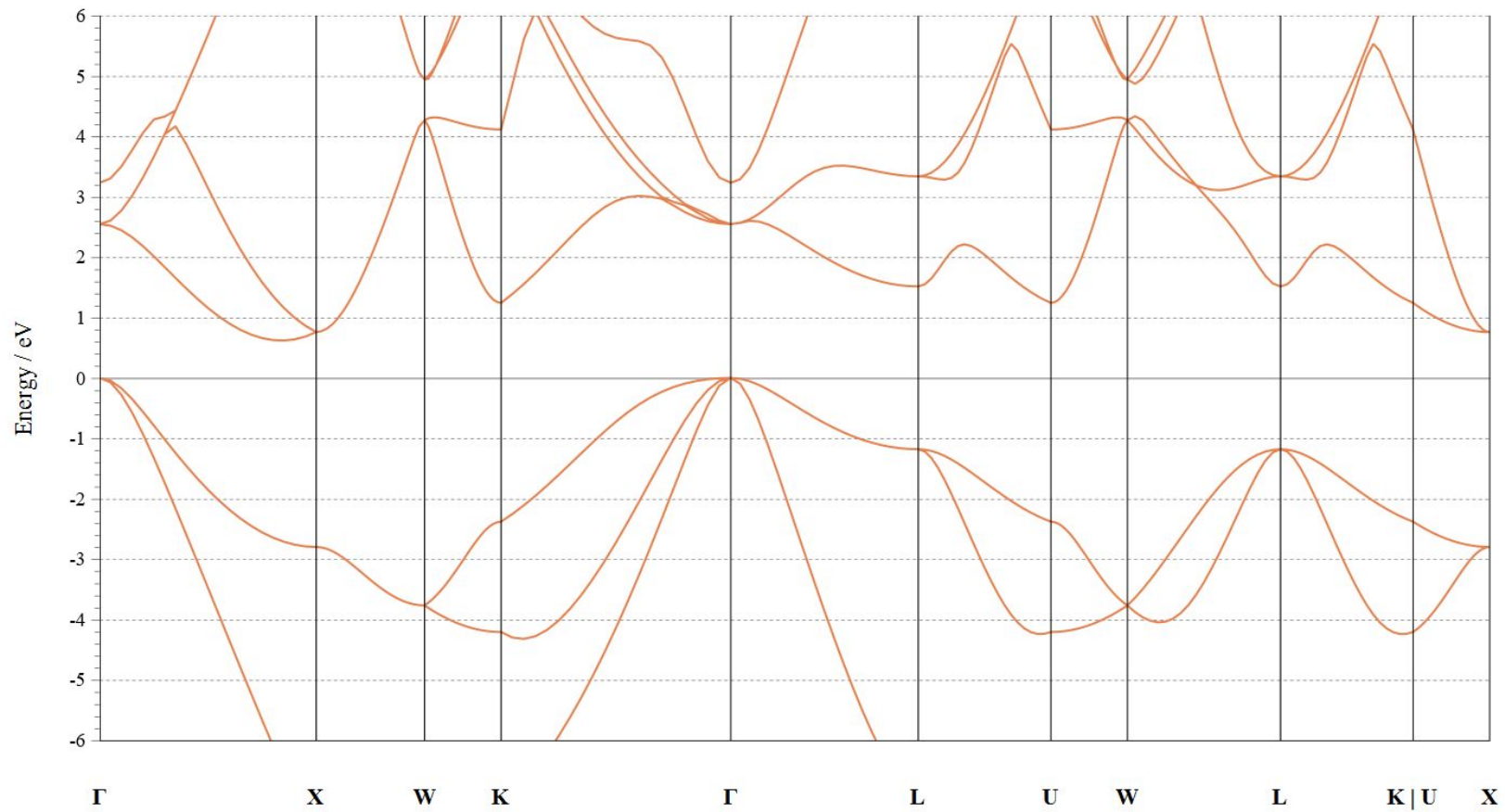
```
&BANDS
    lsym            = .FALSE.
    spin_component = 1
/
K_POINTS {tpiba_b}
12
gG      20
X       20
W       20
K       20
gG      20
L       20
U       20
W       20
L       20
K       0
U       20
X       0

ATOMIC_SPECIES
Si      28.08550   Si.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Si      -4.101546    4.101546    4.101546
Si      -2.734364    2.734364    2.734364
```
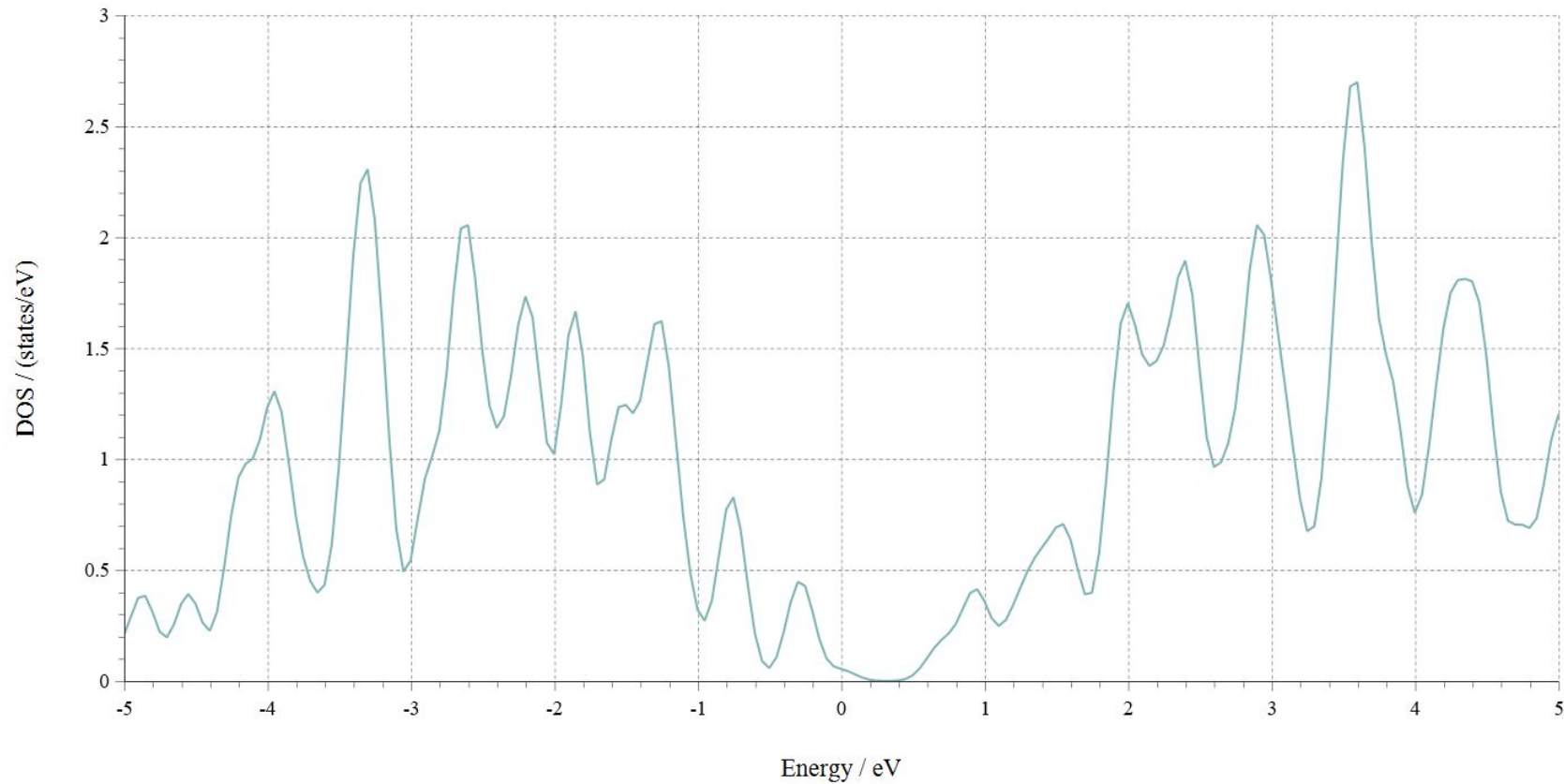
Band Structure for Si

Density of States for Si

Results and discussion for Si

- The valence bands stay well below the Fermi energy level as is expected from any material.

- A very narrow band gap of about 0.7672 eV is obtained from the data. This less when compared to the experimental value of 1.14 eV. This is explained by the fact that DFT tends to underestimate the band gap. Physically, this discrepancy arises because the true, exact Kohn-Sham exchange-correlation functional depends on the total electron number and changes as the total electron count passes through each integer; This is generally referred to as the derivative discontinuity.

- The band gap for Si is an indirect band gap. This means that an electron in the valence band of Si jumps to the conduction band only by a change in quasi momentum (k point). This is referred to as phonon assisted transition.

- The density of states for Si shows a gap, roughly about 0.6 eV near the Fermi energy level. This value is in accordance with the known experimental value.

- The various peaks in the density of states indicate that a majority of electrons have an energy level corresponding to these states.

SCF Calculation for Al

```
&CONTROL
    calculation = "scf"
    max_seconds =  8.64000e+04
    pseudo_dir =
"C:\Users\Rohith\.burai\.pseudopot"
/

&SYSTEM
    a           =  4.03893e+00
    degauss     =  1.00000e-02
    ecutrho     =  1.00000e+02
    ecutwfc     =  2.50000e+01
    ibrav       = 2
    nat         = 1
    ntyp        = 1
    occupations = "smearing"
    smearing    = "marzari-vanderbilt"
/
```

```
&ELECTRONS
    conv_thr          =  1.00000e-06
    electron_maxstep  =  200
    mixing_beta       =  7.00000e-01
    startingpot       = "atomic"
    startingwfc       = "atomic+random"
/

K_POINTS {automatic}
 5  5  5  0 0 0

ATOMIC_SPECIES
Al    26.98154  Al.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Al      0.000000  0.000000  0.000000
```

Output for SCF calculation of Al

```
the Fermi energy is      8.3579 ev

    total energy              =       -4.13607255 Ry
    Harris-Foulkes estimate   =       -4.13607216 Ry
    estimated scf accuracy    <        0.00000031 Ry

    The total energy is the sum of the following terms:

    one-electron contribution =        2.87010978 Ry
    hartree contribution      =        0.00787481 Ry
    xc contribution           =       -1.60733226 Ry
    ewald contribution        =       -5.40634301 Ry
    smearing contrib. (-TS)   =       -0.00038186 Ry

    convergence has been achieved in   3 iterations
```
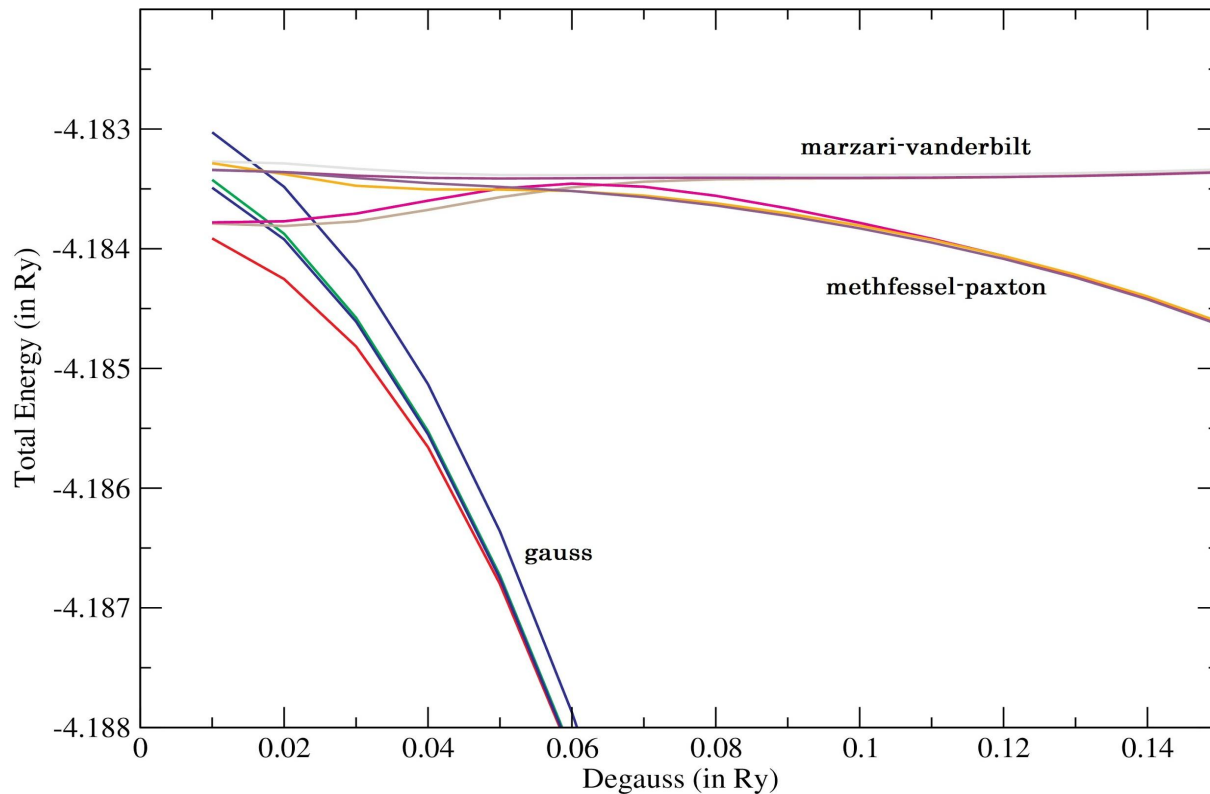
Variation of Total Energy with smearing for Al

Band structure calculation for Al
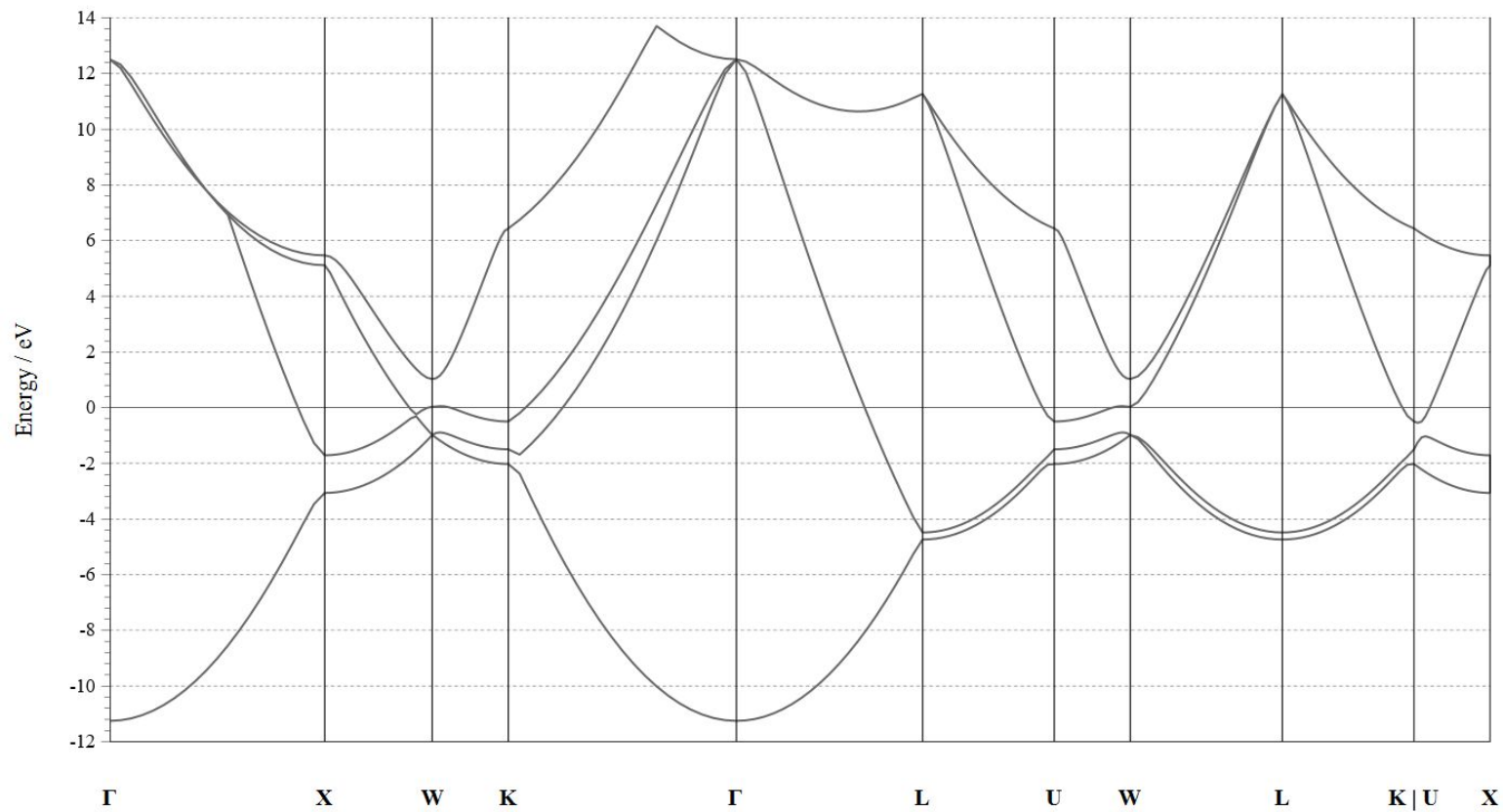
```
&CONTROL
    calculation = "bands"
    max_seconds =  8.64000e+04
    pseudo_dir  = "C:\Users\Rohith\.burai\.pseudopot"
/
&SYSTEM
    a           =  4.03893e+00
    degauss     =  1.00000e-02
    ecutrho     =  1.00000e+02
    ecutwfc     =  2.50000e+01
    ibrav       = 2
    nat         = 1
    nbnd        = 4
    ntyp        = 1
    occupations = "smearing"
    smearing    = "marzari-vanderbilt"
/
&ELECTRONS
    conv_thr        =  1.00000e-06
    electron_maxstep = 200
    mixing_beta     =  7.00000e-01
    startingpot     = "atomic"
    startingwfc     = "atomic+random"
/
```

```
&BANDS
    lsym            = .FALSE.
    spin_component = 1
/
K_POINTS {tpiba_b}
12
gG      20
X       20
W       20
K       20
gG      20
L       20
U       20
W       20
L       20
K       0
U       20
X       0

ATOMIC_SPECIES
Al    26.98154  Al.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Al     0.000000   0.000000   0.000000
```
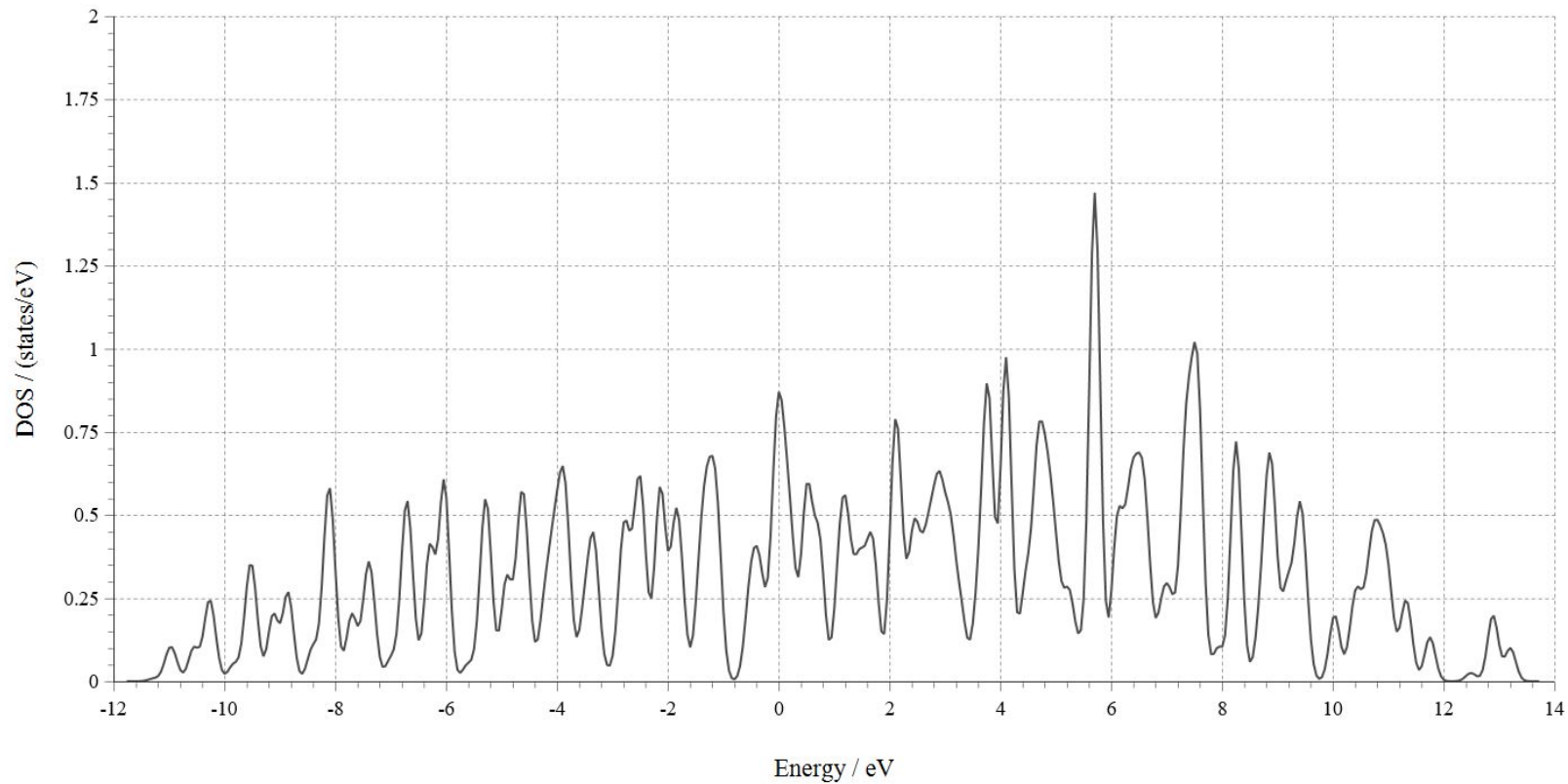
Band structure for Al

Density of states for Al

Results and discussion for Al

- The valence bands and conduction bands criss cross and overlap, which is a characteristic of any metal.

- This, and further the narrow peaks, imply a very a high electrical conductivity that is expected of metals.

- The peak at the Fermi level in the dos for Al shows the high density of states corresponding to this energy.

SCF calculation for NaCl

```
&CONTROL
    calculation = "scf"
    max_seconds =  8.64000e+04
    pseudo_dir =
"C:\Users\Rohith\.burai\.pseudopot"
    tprnfor     = .TRUE.
    tstress     = .TRUE.
/

&SYSTEM
    a           =  5.69169e+00
    degauss     =  1.00000e-02
    ecutrho     =  2.25000e+02
    ecutwfc     =  2.50000e+01
    ibrav       = 2
    nat         = 2
    ntyp        = 2
    occupations = "fixed"
    smearing    = "gaussian"
/
```

```
&ELECTRONS
    conv_thr        =  1.00000e-06
    electron_maxstep = 200
    mixing_beta     =  7.00000e-01
    startingpot     = "atomic"
    startingwfc     = "atomic+random"
/

K_POINTS {automatic}
 4  4  4  0 0 0

ATOMIC_SPECIES
Na      22.98977   Na.pbe-sp-van_ak.UPF
Cl      35.45270   Cl.pbe-n-van.UPF

ATOMIC_POSITIONS {angstrom}
Na       0.000000   0.000000   0.000000
Cl      -2.845847   2.845847   2.845847
```

Output for SCF of NaCl

```
highest occupied level (ev):     0.7662

     total energy              =     -128.42131163 Ry
     Harris-Foulkes estimate   =     -128.42131173 Ry
     estimated scf accuracy    <        0.00000069 Ry

     The total energy is the sum of the following terms:

     one-electron contribution =      -84.14509700 Ry
     hartree contribution      =       46.68154838 Ry
     xc contribution           =      -22.77661215 Ry
     ewald contribution        =      -68.18115086 Ry

     convergence has been achieved in    5 iterations
```

Band structure calculation for NaCl

```
&CONTROL
    calculation = "scf"
    max_seconds =  8.64000e+04
    pseudo_dir  =
"C:\Users\Rohith\.burai\.pseudopot"
    tprnfor     = .TRUE.
    tstress     = .TRUE.
/

&SYSTEM
    a           =  5.69169e+00
    degauss     =  1.00000e-02
    ecutrho     =  2.25000e+02
    ecutwfc     =  2.50000e+01
    ibrav       = 2
    nat         = 2
    ntyp        = 2
    occupations = "fixed"
    smearing    = "gaussian"
/
```

```
&BANDS
    lsym           = .FALSE.
    spin_component = 1
/
K_POINTS {tpiba_b}
12
gG     20
X      20
W      20
K      20
gG     20
L      20
U      20
W      20
L      20
K      0
U      20
X      0

ATOMIC_SPECIES
Na     22.98977   Na.pbe-sp-van_ak.UPF
Cl     35.45270   Cl.pbe-n-van.UPF

ATOMIC_POSITIONS {angstrom}
Na      0.000000   0.000000   0.000000
Cl     -2.845847   2.845847   2.845847
```
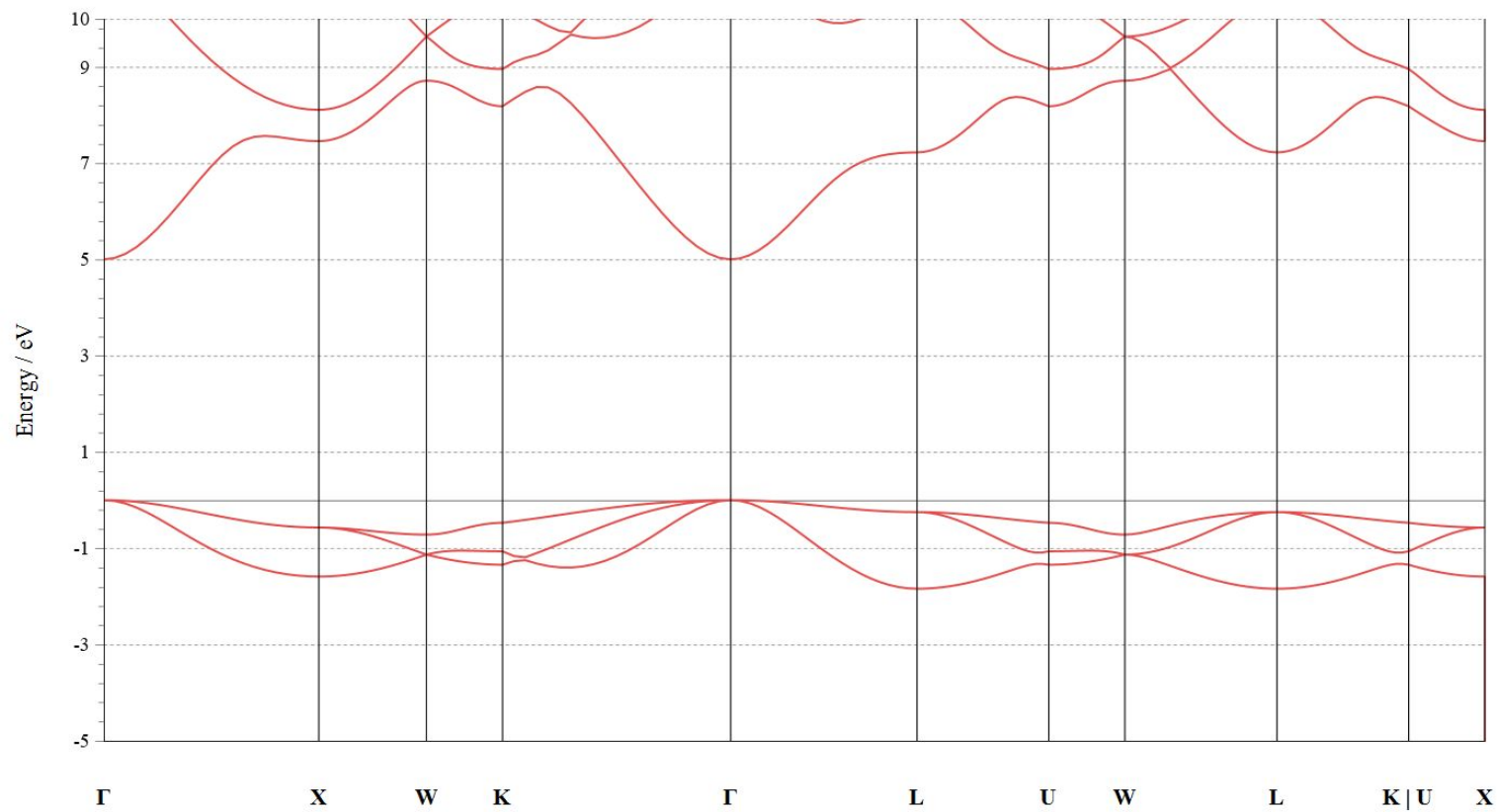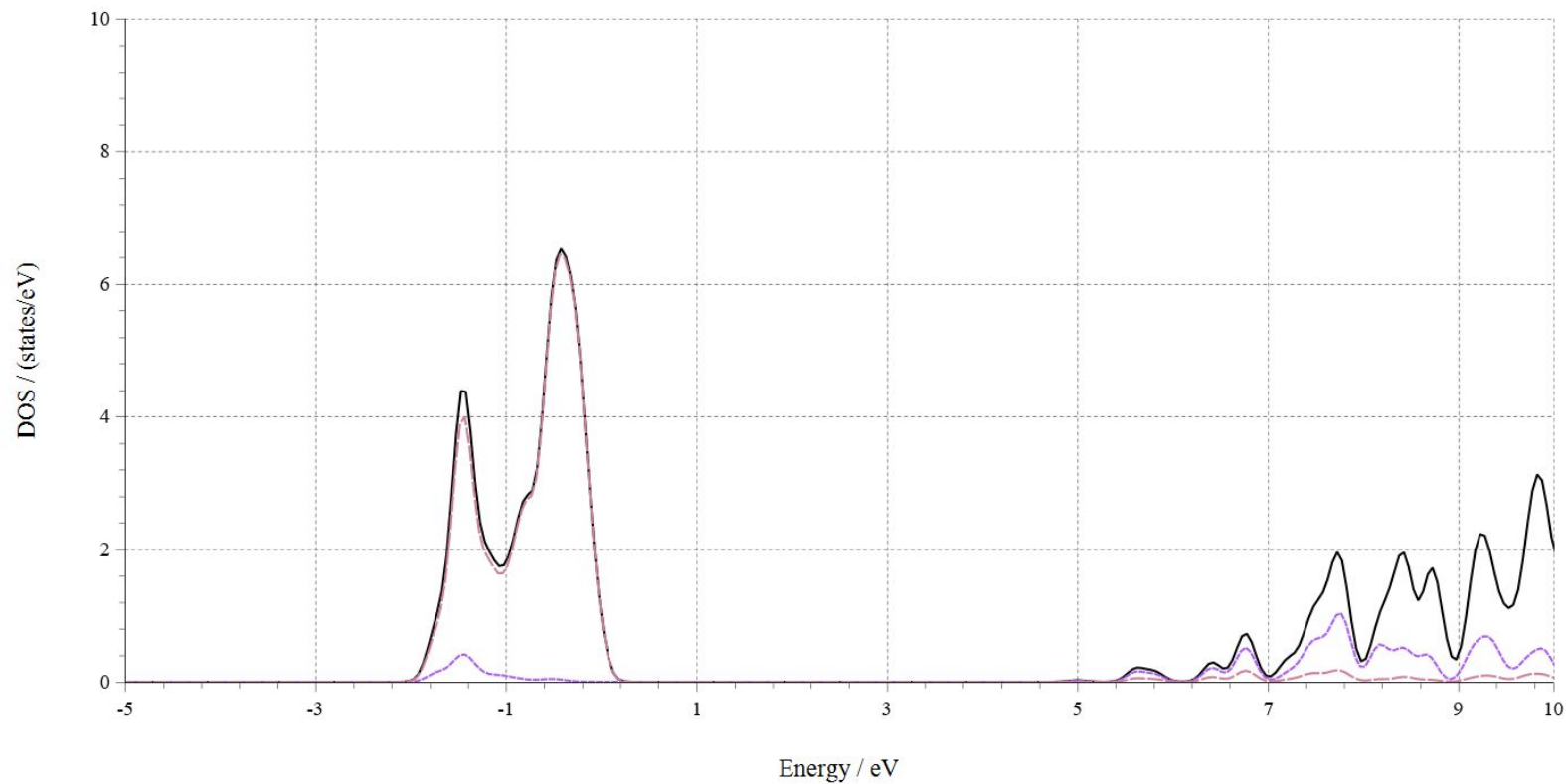
Band structure for NaCl

Density of states for NaCl

Results and discussion for NaCl

- The valence bands and conduction bands have a wide band gap in between them which is a characteristic of an insulator

- This implies a very low electrical conductivity that is expected of insulators.

- There are no peaks at Fermi energy level which is in good agreement with experimental results.

Computations on Yb$_2$Ge

- The binary compounds with general formula M$_2$X (M = Ca, Sr, Ba, Eu, Yb) (X = Si, Ge, Sn, Pb) have been extensively studied in the literature.

- Except Yb$_2$Sn, which crystallizes with the Ni$_2$In structure, and Yb$_2$Si, whose existence is still doubtful, all the other known compounds belong to the Pb$_2$Cl type, including the intermetallic compound of choice, Yb$_2$Ge.

- Yb$_2$Ge crystallizes in the orthorhombic lattice in space group number 62, much alike Pb$_2$Cl, with lattice parameters:

  a = 4.818 Å

  b = 7.461 Å

  c = 8.954 Å

  $\alpha = \beta = \gamma = 90°$
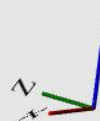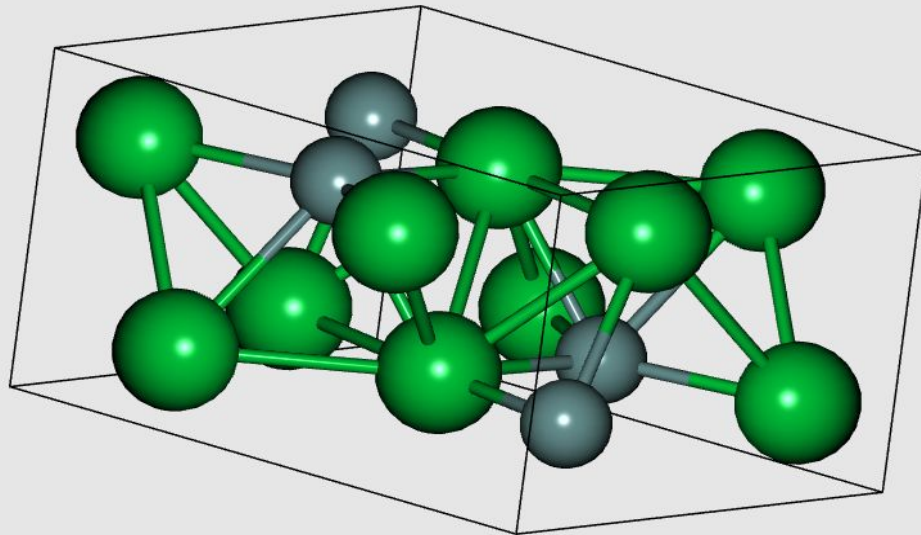
SCF calculation for Yb₂Ge

```
&CONTROL
    calculation = "scf"
    max_seconds  =  8.64000e+04
    pseudo_dir   = "C:\Users\Rohith\.burai\.pseudopot"
/

&SYSTEM
    a                          =  4.81773e+00
    b                          =  7.46135e+00
    c                          =  8.95411e+00
    degauss                    =  1.00000e-02
    ecutrho                    =  3.54905e+02
    ecutwfc                    =  3.94339e+01
    ibrav                      =  8
    nat                        =  12
    nspin                      =  2
    ntyp                       =  2
    occupations                =  "smearing"
    smearing                   =  "gaussian"
    starting_magnetization(1)  =  2.00000e-01
    starting_magnetization(2)  =  0.00000e+00
/
```

```
&ELECTRONS
    conv_thr          =  1.00000e-06
    electron_maxstep  =  200
    mixing_beta       =  4.00000e-01
    startingpot       =  "atomic"
    startingwfc       =  "atomic+random"
/

K_POINTS {automatic}
 8 4 2  0 0 0

ATOMIC_SPECIES
Yb    173.04000  Yb.pbe-spn-rrkjus_psl.1.0.0.UPF
Ge     72.61000  Ge.pbe-n-rrkjus_psl.1.0.0.UPF

ATOMIC_POSITIONS {angstrom}
Yb      3.613297   6.293768    0.680539
Yb      1.204432   1.167582    8.273569
Yb      3.613297   2.563093    3.796515
Yb      1.204432   4.898257    5.157593
Yb      1.204432   3.875224    1.620129
Yb      3.613297   3.586126    7.333979
Yb      1.204432   0.144549    2.856925
Yb      3.613297   7.316801    6.097184
Ge      1.204432   5.606369    8.029122
Ge      3.613297   1.854981    0.924986
Ge      1.204432   1.875694    5.402040
Ge      3.613297   5.585656    3.552068
```

Output for 4 formula units of Yb$_2$Ge

```
the Fermi energy is      7.8740 ev
     total energy             =     -958.58898970 Ry
     Harris-Foulkes estimate  =     -958.58897673 Ry
     estimated scf accuracy   <         0.00000090 Ry

     The total energy is the sum of the following terms:

     one-electron contribution =    -164.36564411 Ry
     hartree contribution       =     107.21792866 Ry
     xc contribution            =    -482.10797422 Ry
     ewald contribution         =    -419.33043802 Ry
     smearing contrib. (-TS)    =      -0.00286201 Ry

     total magnetization        =       0.03 Bohr mag/cell
     absolute magnetization     =       0.08 Bohr mag/cell

     convergence has been achieved in   8 iterations
```

Band structure calculation for Yb$_2$Ge

```
&CONTROL
    calculation = "bands"
    max_seconds =  8.64000e+04
    pseudo_dir  = "C:\Users\Rohith\.burai\.pseudopot"
/

&SYSTEM
    a                        =  4.81773e+00
    b                        =  7.46135e+00
    c                        =  8.95411e+00
    degauss                  =  1.00000e-02
    ecutrho                  =  3.54905e+02
    ecutwfc                  =  3.94339e+01
    ibrav                    = 8
    nat                      = 12
    nbnd                     = 144
    nspin                    = 2
    ntyp                     = 2
    occupations              = "smearing"
    smearing                 = "gaussian"
    starting_magnetization(1) =  2.00000e-01
    starting_magnetization(2) =  0.00000e+00
/
```
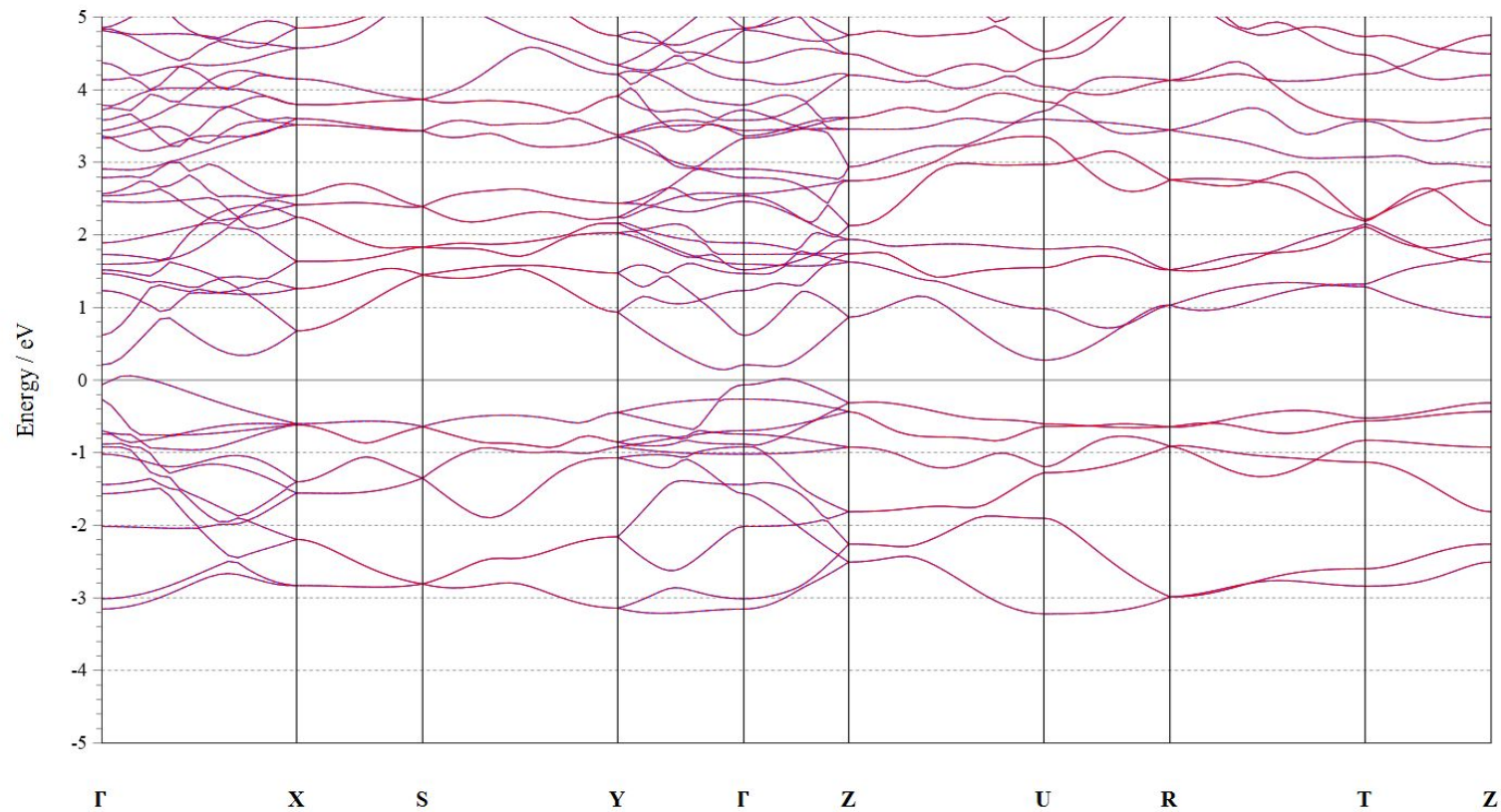
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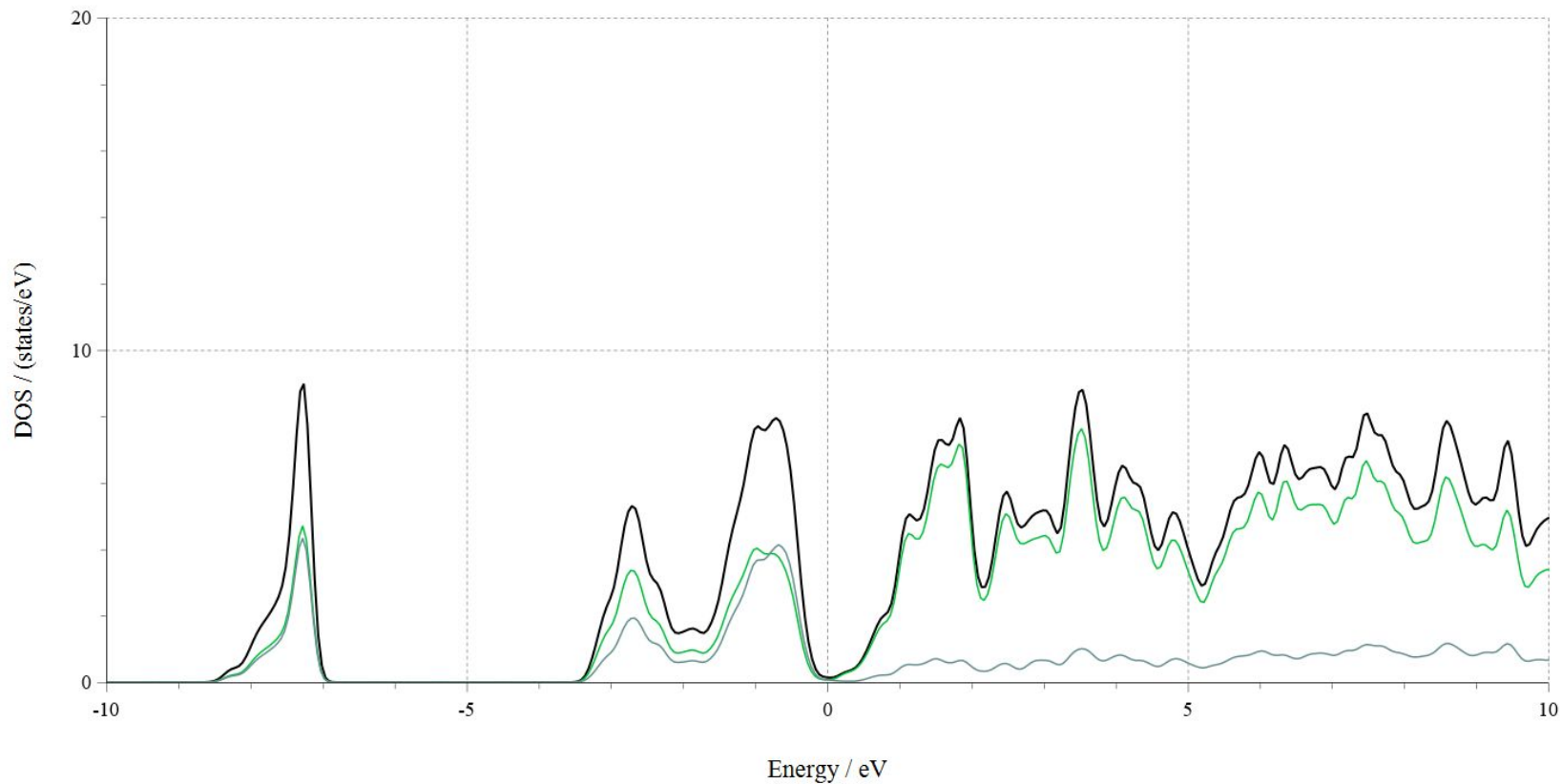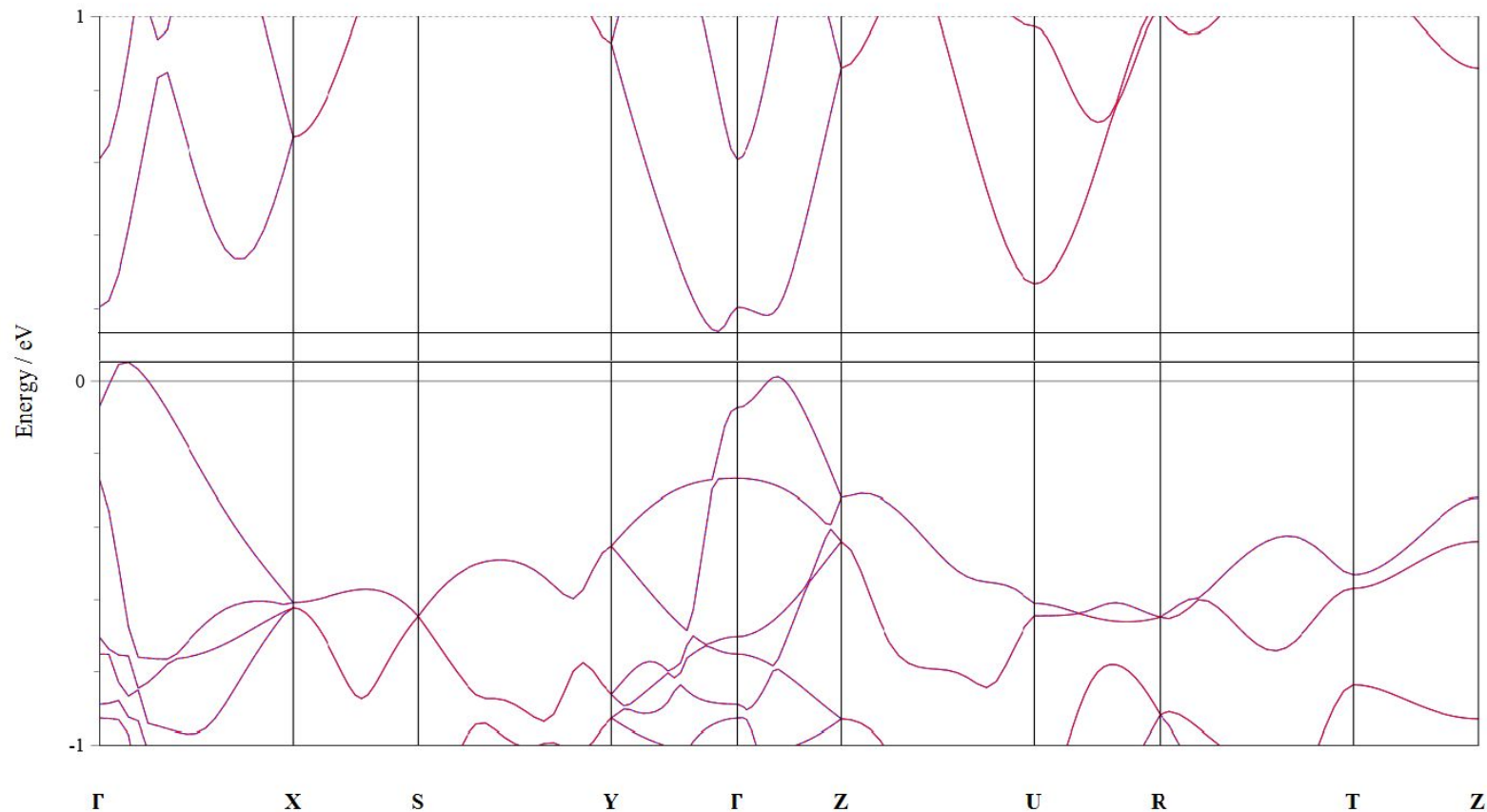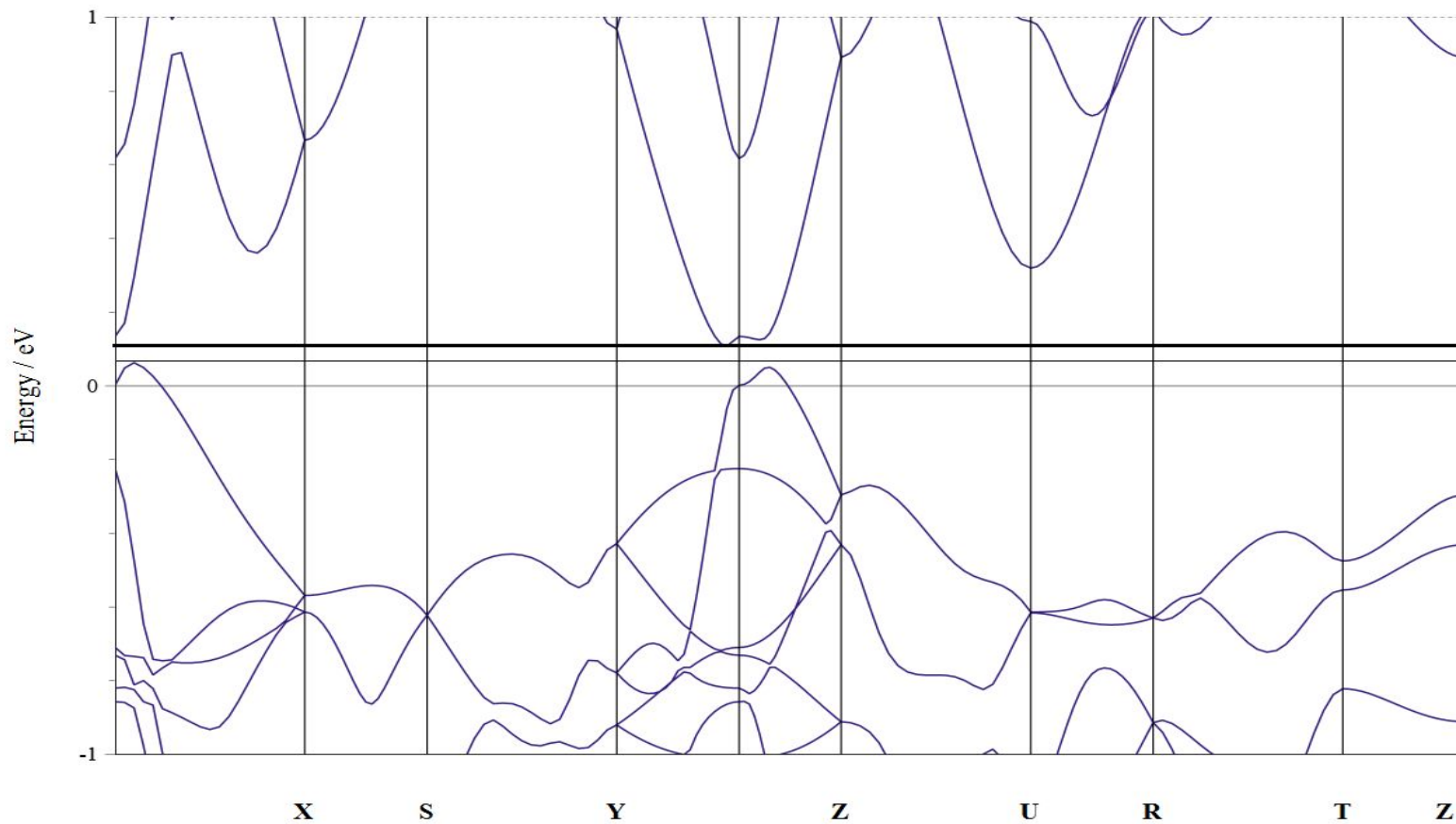
Band Structure for Yb$_2$Ge

Density of states for Yb$_2$Ge

A closer look at band structure calculated using GGA

Improved band structure using GGA+U

Results and discussion

The following observations are made with respect to the molecule Yb_2Ge based on the data computed above.

- The valence bands and conduction bands do not overlap. They possess a small band gap of the order of 0.1eV. The band gap formed is direct.

- The band-gap calculation is complicated by the self-interaction error which arises in the occupied states in standard DFT. If one considers the "true" band structure, then semi-local DFT (using GGA or LDA) has a spurious self-interaction in the occupied states, which over-delocalizes them and forces them to take a higher energy, thus reducing the band-gap.

Results and discussion

- A method to correct the self-interaction in DFT for localised atomic-like states (e.g. for d and f-block elements) is to introduce a modest Hubbard U term and do a DFT+U calculation. The Hubbard U introduces a potential which favours localising the states to which it is applied, thus re-localising them (compared to standard Kohn-Sham DFT) and lowering their energy.

- Thus the computation was performed once in GGA yielding a band gap of 0.1eV. Further the computation was performed again in GGA+U, which yielded a more accurate band gap of 0.045eV.

- Since the band gap is low and since the conduction band minimum is dispersed, Yb_2Ge has a relatively high electrical conductivity, which makes it suitable for use as a thermoelectric.

Conclusions, learning outcomes and scope for further research

- The need for better thermoelectric materials and the required properties were investigated.
- The theoretical backgrounds for DFT was studied.
- Calculations were performed using Quantum ESPRESSO and the results were plotted and studied.
- Further work include the study of charge density and the study on the orbitals that cause the particular peaks and valleys in the density of states.
- The phonon properties that give insight into the thermal conductivity is to be studied.
- Once a large amount of good DFT data is generated Machine Learning algorithms can be written to optimize further.

Thank you for patiently listening and assessing this project work.

~ Rohith Krishna