Solutions for excercise sheet 3

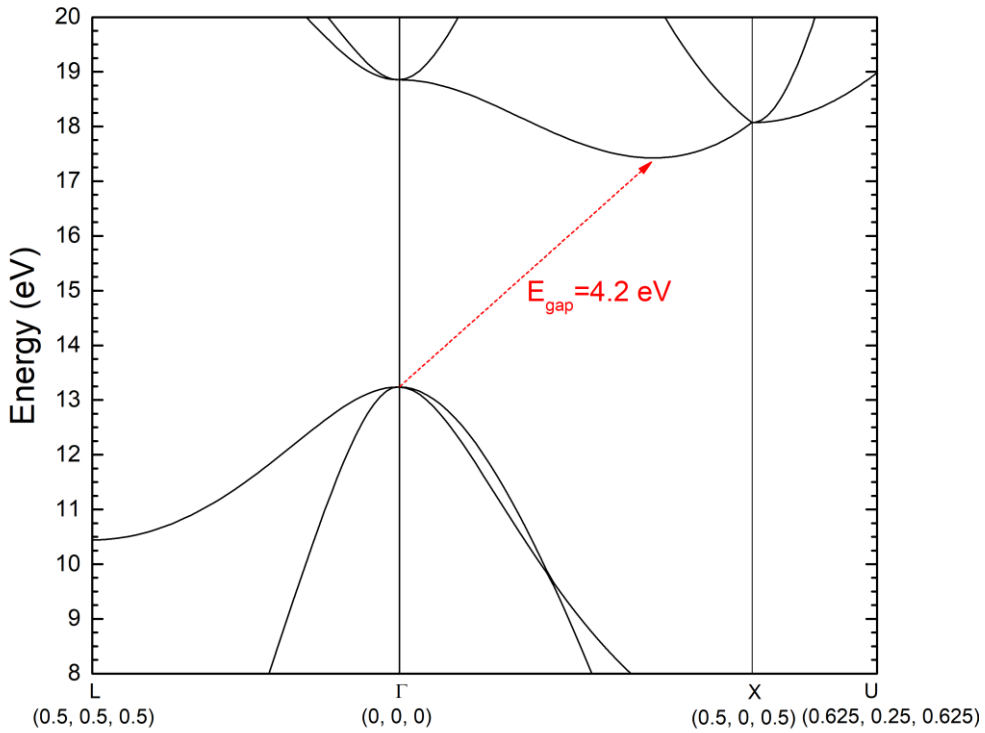
Exercise 1: Electronic bandstructure of diamond

In this exercise, we will look at the electronic band structure of diamond, both from the view of local density functional theory and hybrid functionals.

(a)

```
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  1   force =     0.00000000    0.00000000    0.00000000
     atom    2 type  1   force =     0.00000000    0.00000000    0.00000000

     Total force =     0.000000     Total SCF correction =     0.000000


     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.02
   0.00000017  -0.00000000  -0.00000000         0.02     -0.00     -0.00
  -0.00000000   0.00000017   0.00000000        -0.00      0.02      0.00
  -0.00000000   0.00000000   0.00000017        -0.00      0.00      0.02

     Message from routine bfgs:
     history already reset at previous step: stopping
     Message from routine volume:
     axis vectors are left-handed

     bfgs converged in   5 scf cycles and   2 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  2.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -24.0733728716 Ry
Begin final coordinates
     new unit-cell volume =     76.95573 a.u.^3 (    11.40366 Ang^3 )
     density =      3.49475 g/cm^3

CELL_PARAMETERS (alat=  1.88972599)
   0.000000000   1.786507378   1.786507378
   1.786507378   1.786507378   0.000000000
   1.786507378   0.000000000   1.786507378

ATOMIC_POSITIONS (crystal)
C       -0.000000000  -0.000000000   0.000000000
C        0.250000000   0.250000000   0.250000000
End final coordinates
```

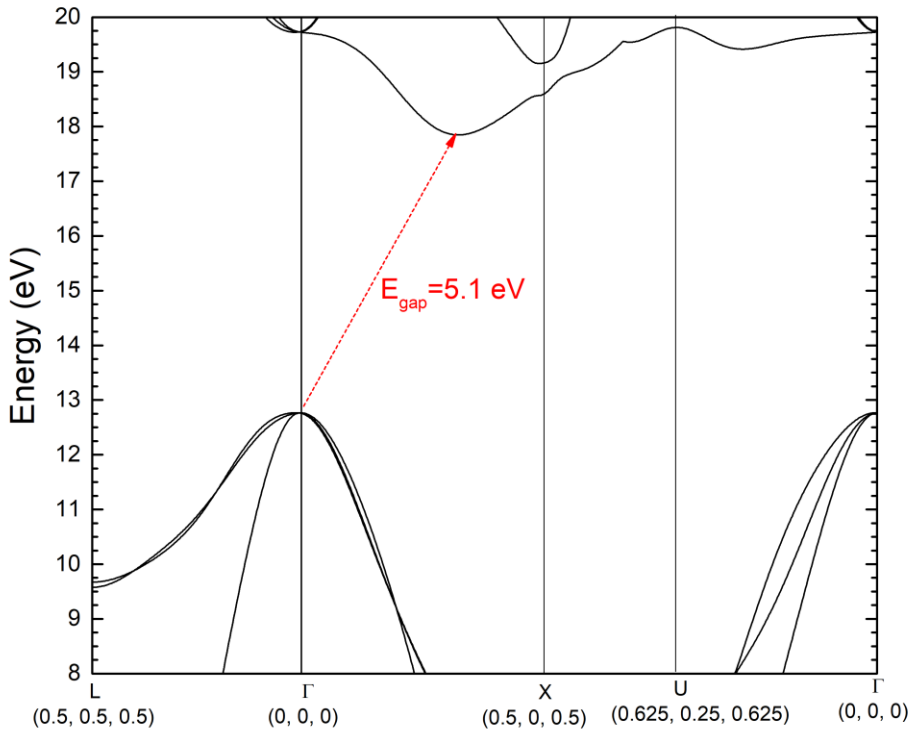
(b)



(c)

```
     highest occupied, lowest unoccupied level (ev):    12.7639   18.0404

!    total energy              =     -23.73530615 Ry
     Harris-Foulkes estimate   =     -23.73530615 Ry
     estimated scf accuracy    <          2.9E-11 Ry

     convergence has been achieved in   1 iterations

     Using ACE for calculation of exact exchange

!!   total energy              =     -23.73530615 Ry
     Harris-Foulkes estimate   =     -23.73530615 Ry
     est. exchange err (dexx)  =          2.8E-10 Ry
     - averaged Fock potential =       2.72848877 Ry
     + Fock energy (ACE)       =      -1.36424533 Ry

     EXX self-consistency reached
```

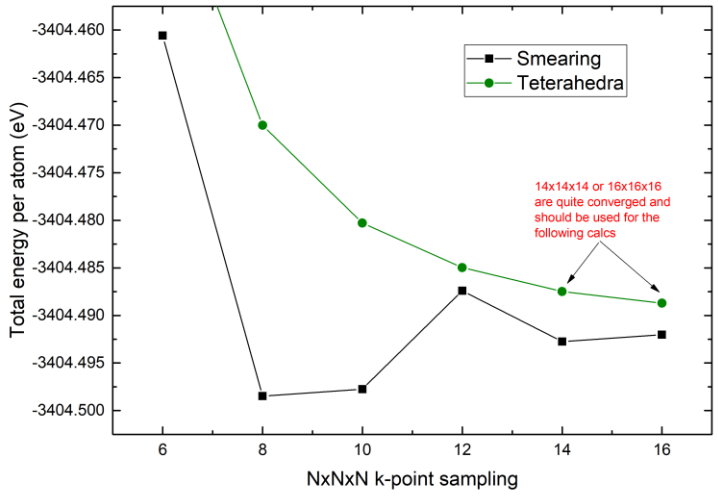
(d)



The use of the hybrid functional HSE largely improved the prediction of the electronic band gap of diamond (the experimental value is 5.4-5.5 eV), but one can see that the wannierization did not conserve the degeneracy of the conduction bands at the X point. We would have needed a denser k-point sampling in the wannierization procedure to properly capture this effect.

Exercise 2: Electronic bandstructure and DOS of iron

(a)

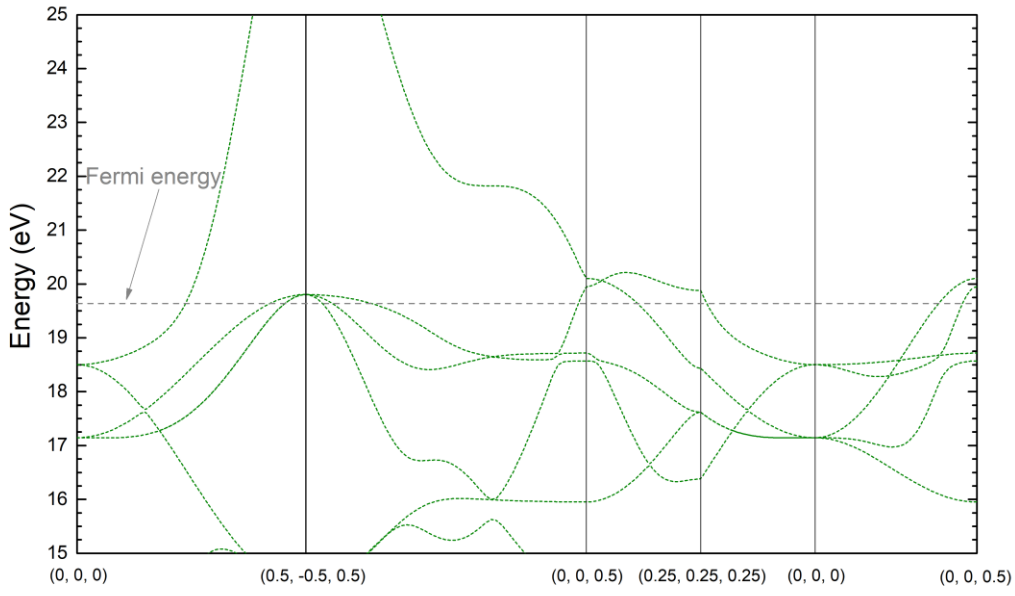


In the first step, as always, do a convergence test for the k-point sampling that should be used

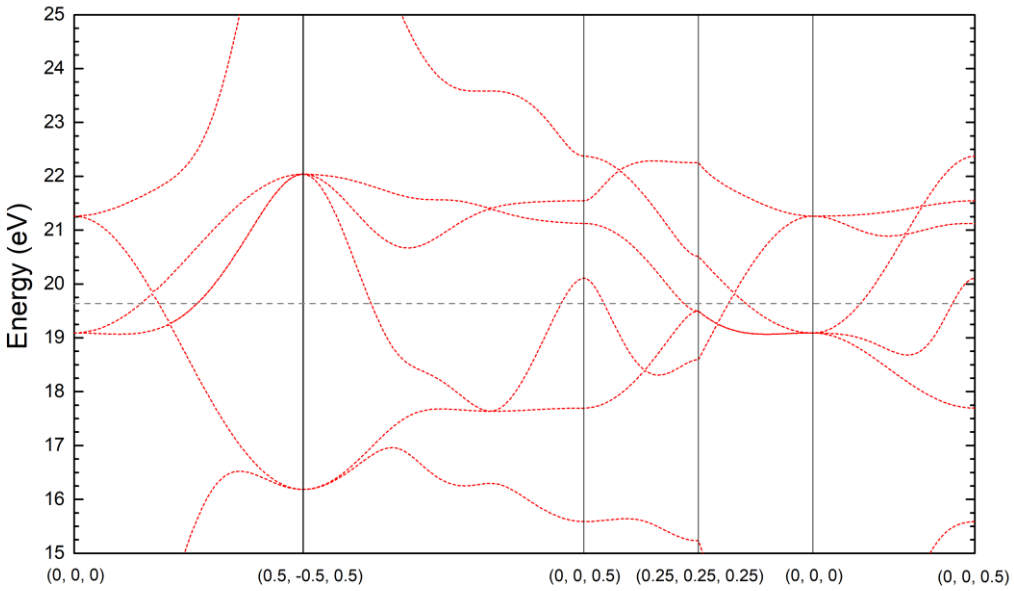
(b)

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.05
-0.00000031   0.00000000   0.00000000         -0.05      0.00      0.00
 0.00000000  -0.00000031  -0.00000000          0.00     -0.05     -0.00
 0.00000000  -0.00000000  -0.00000031          0.00     -0.00     -0.05


     bfgs converged in   3 scf cycles and   2 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  1.0E-01kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -250.3340306861 Ry
Begin final coordinates
     new unit-cell volume =     72.97004 a.u.^3 (    10.81304 Ang^3 )
     density =      8.57601 g/cm^3

CELL_PARAMETERS (angstrom)
   1.393037034   1.393037034   1.393037034
   1.393037034  -1.393037034   1.393037034
   1.393037034   1.393037034  -1.393037034

ATOMIC_POSITIONS (crystal)
Fe       0.000000000   0.000000000   0.000000000
End final coordinates
```

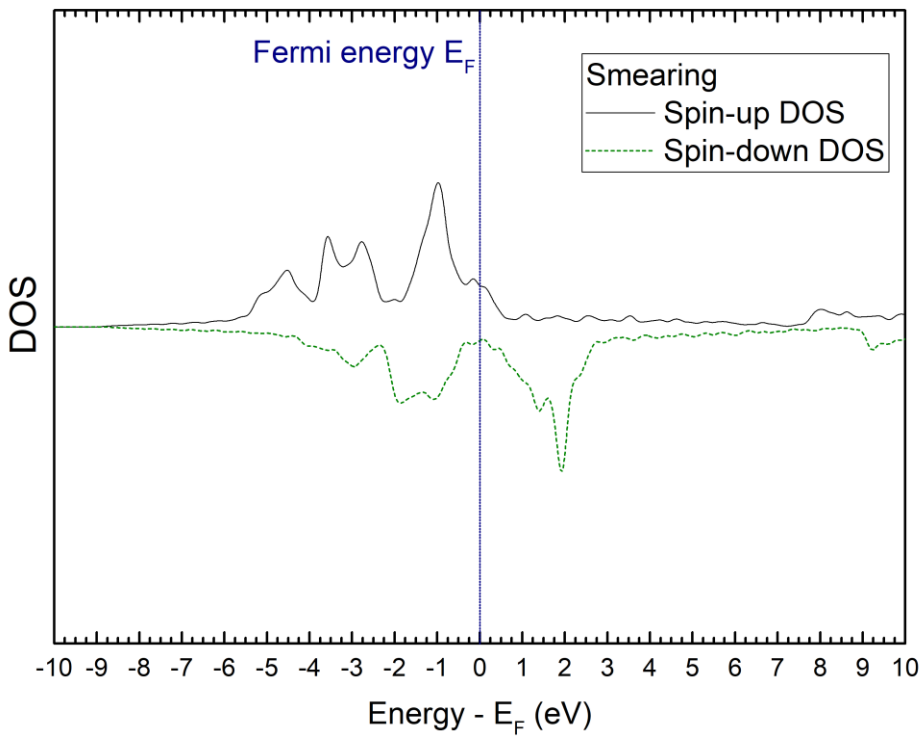
(c) Spin-up bands



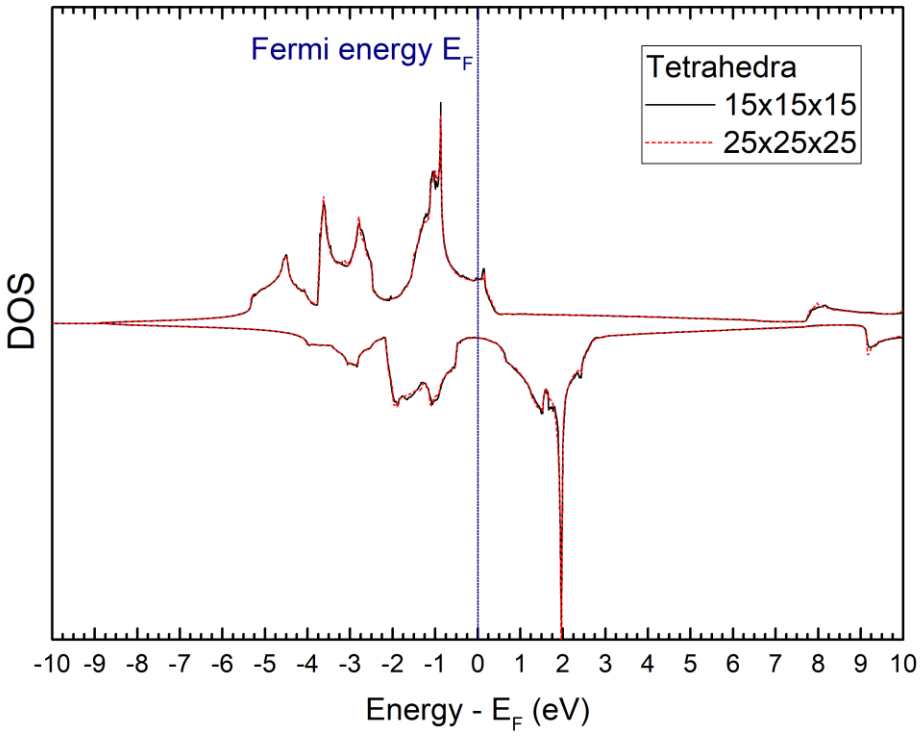
Spin-down bands



(d)

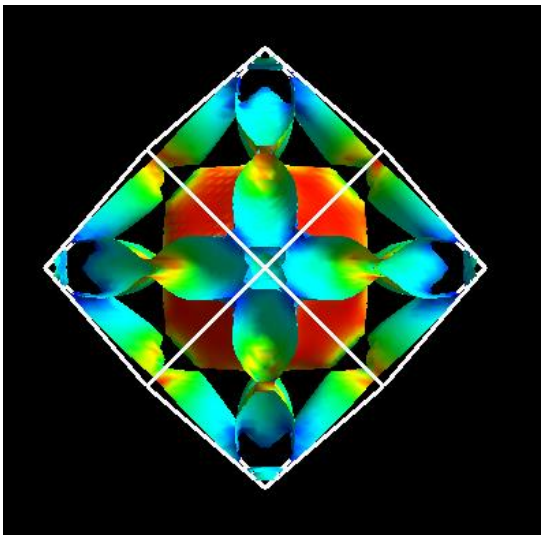


(e)

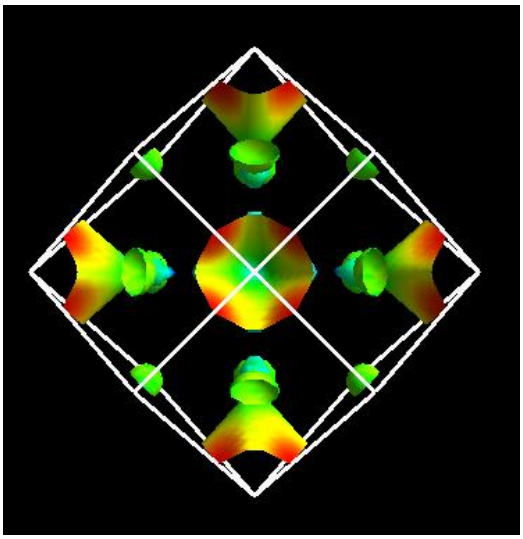


(f)

Spin-up Fermi surface



Spin-down Fermi surface



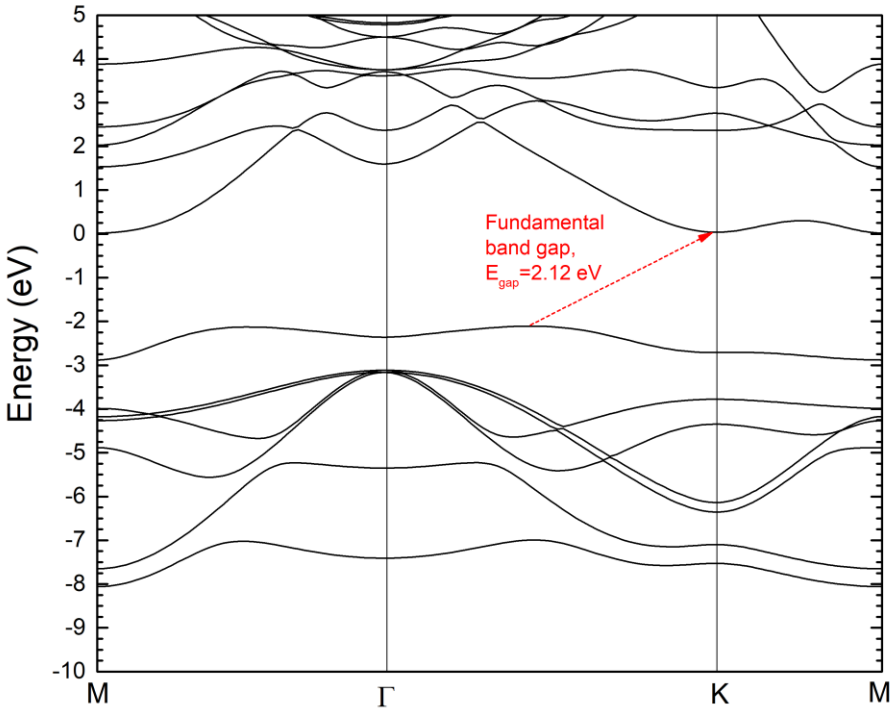
Exercise 3: Electronic structure of monolayer Al_2S_2

Here, we will have a look at the electronic properties of Al_2S_2, a novel two-dimensional semiconductor material with a hexagonal structure and four atoms per unit cell.

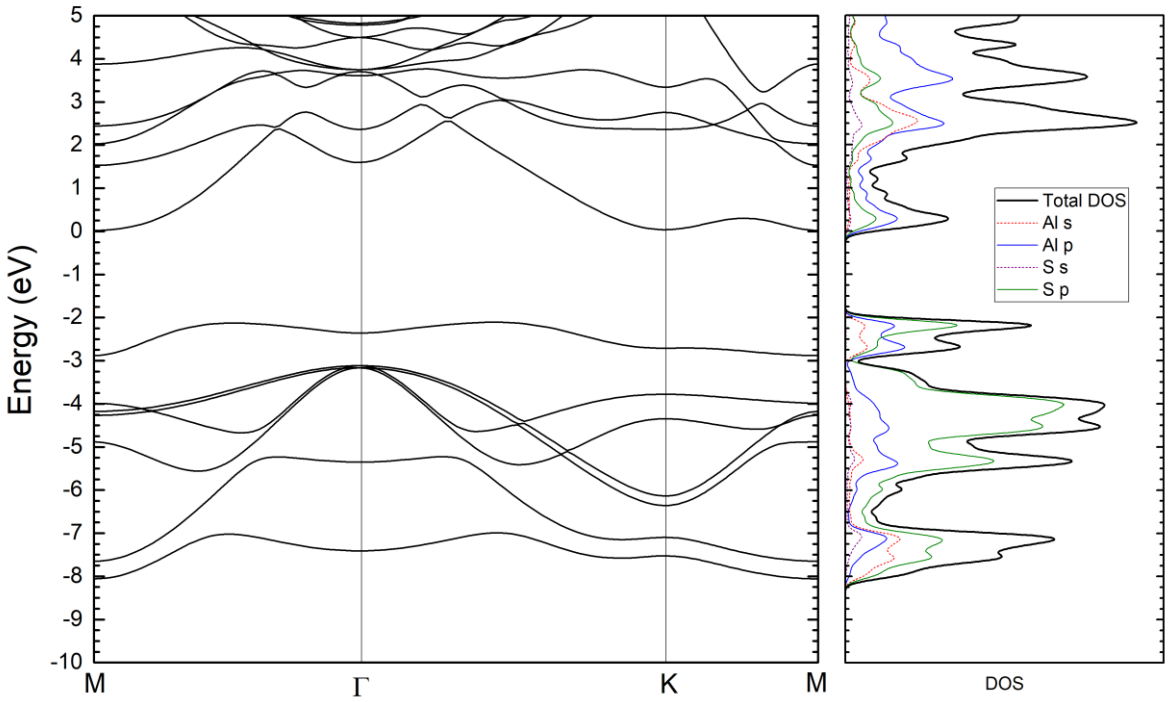
(a)

```
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  1   force =     0.00000000   -0.00000000    0.00000052
     atom    2 type  1   force =    -0.00000000    0.00000000   -0.00000052
     atom    3 type  2   force =    -0.00000000    0.00000000   -0.00000770
     atom    4 type  2   force =     0.00000000    0.00000000    0.00000770

     Total force =     0.000011     Total SCF correction =     0.000000


     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.01
  -0.00000001   0.00000000   0.00000000         -0.00      0.00      0.00
   0.00000000  -0.00000001   0.00000000          0.00     -0.00      0.00
   0.00000000   0.00000000  -0.00000010          0.00      0.00     -0.01


     bfgs converged in  14 scf cycles and  13 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  2.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -53.5290000247 Ry
Begin final coordinates
     new unit-cell volume =   1464.50858 a.u.^3 (   217.01778 Ang^3 )
     density =      0.90289 g/cm^3

CELL_PARAMETERS (angstrom)
   3.065476381  -1.769853614   0.000000000
   0.000000000   3.539707227   0.000000000
   0.000000000   0.000000000  20.000000000

ATOMIC_POSITIONS (crystal)
Al       0.000000000   0.000000000   0.564926176
Al       0.000000000   0.000000000  -0.564926176
S        0.333333333  -0.333333333   0.619059234
S        0.333333333  -0.333333333  -0.619059234
End final coordinates
```

(b)


Energy (eV)
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
M
Γ
K
M
Fundamental
band gap,
E_gap=2.12 eV

(c)


Energy (eV)
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
M
Γ
K
M
Total DOS
Al s
Al p
S s
S p
DOS