CompMatPhys Project Report 2020-21 Team-5: AB-initio Simulation of the Bulk Modulus of $\gamma' Fe_4N$ using Quantum Espresso*

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Convergence testing of the basis set size parameter, ecutwfc, density cutoff parameter, ecutrho and K Points for $\gamma' Fe_4N$ using Quantum Espresso has been carried out. The bulk modulus of $\gamma' Fe_4N$ has been obtained using the Murnaghan equation of state by simulating the variation of energy as a function of volume of a single unit cell. It is seen that a value of ecutwfc=100, ecutrho=700 and K points [7 7 7] leads to converged values of the total energy and pressure. bulk modulus of 243.6 GPa has been obtained and the equilibrium volume of $\gamma' Fe_4N$ is shown to be 52.23 Å^3 corresponding to a lattice parameter of 3.738 Å.

I. INTRODUCTION

The status of the four tasks of the project for the Computational Materials Physics Course [CompMatPhys] conducted online by Prof. Stefaan Cottier, University of Ghent, Belgium during the Academic Year 2020-21 are as follows:

1. Convergence testing for K mesh, ecutwfc and ecutrho.
2. Energy and Pressure variation as a function of volume of unit cell of $\gamma' Fe_4N$. Obtained the minimum volume at equilibrium and the bulk modulus.
3. Constructed a cif file of the low symmetry structure at 10 GPa as reported in Cheng's paper [1]. This yeilds a 10 atom unit cell. Setup the inputs for vc-relax at pressures 410 kbar to -400 kbar in steps of 100 kbar, but did not have the computational power to run the vc-relax on a 10 atom unit cell.
4. Attempted a phonon calculation of $\gamma' Fe_4N$ with compromised parameters of ecutwfc and ecutrho and K points so that some output comes from a laptop.

Details of the simulations and the results are provided in the subsequent sections.

II. METHOD

The ab-initio code Quantum Espresso [QE] was used to study the convergence of the total energy and pressure of a unit cell of $\gamma' Fe_4N$ for values of the K Points and the wavelength and density cutoff and using the PBE functional. Spin polarized calculations assuming magnetization in a general direction were carried out.

In order to estimate the bulk modulus, the volume of $\gamma' Fe_4N$ was reduced by 16% so as to obtain a maximum pressure around 40 GPa. This was then increased in steps of 2% till an expansion of 10% was achieved. The Energy as a function of volume was used to fit the Murnaghan Equation of State using the ew.x code shipped as a Quantum Espresso utility, from which the bulk modulus was obtained.

III. RESULTS

A. Convergence Testing

The results of the convergence testing for the K Points is presented in Table.I. Conclusion at the end of kpoints convergence testing is $7\times7\times7$ is a good choice of K points based on the convergence of Hydrostatic Pressure.

TABLE I. Convergence testing for K mesh. $ecutwfc = 71$&$ecutrho = 496$ was fixed based on the pseudopotential file recommendations

K-Points	Pressure (k-bar)	time (hh:mm:ss)
$1\times1\times1$	-129.00	00:02:25
$3\times3\times3$	-129.00	00:05:20
$5\times5\times5$	-133.32	00:10:59
$6\times6\times6$	-131.77	00:18:39
$7\times7\times7$	-131.09	00:18:07
$8\times8\times8$	-131.53	00:28:46
$9\times9\times9$	-131.98	00:31:31
$10\times10\times10$	-131.58	00:40:24

The results of the convergence testing for the basis set size is presented in Table.II. Conclusion at the end of wave function cutoff convergence testing is that $ecutwfc = 100$ is a good choice for obtaining a converged hydrostatic pressure.

The results of the convergence testing for the ratio of basis set size to the density cutoff is presented in Table.III. Conclusion at the end of the ratio of ecutrho to ecutwfc convergence testing is that $ecutrho/ecutwfc = 5$ is a good choice for obtaining a converged hydrostatic pressure. I guess the simulation time does not depend much on this ratio despite the possibility that some other processes were running when the ratio was 3.

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TABLE II. Convergence testing for basis set size

ecutwfc	ecutrho	Pressure (k-bar)	time (hh:mm:ss)
35	245	-6058.76	00:05:17
80	560	-120.35	00:17:39
70	490	-130.81	00:14:29
90	630	-100.20	00:22:12
100	700	-93.6	00:27:44
110	770	-95.33	00:32:49
120	840	-97.07	00:39:51
130	910	-96.53	00:42.43
140	980	-94.47	00:47:50
170	1190	-92.93	01:12:10

TABLE III. Convergence testing for ecutwfc vs ecutrho ratio

ecutwfc	ecutrho	Pressure (k-bar)	time (hh:mm:ss)
100	300	-92.27	00:31:16
100	500	-93.43	00:25:14
100	900	-93.22	00:39:19

At the end of the convergence tests it is interesting to note that there seems to be a tensile hydrostatic pressure $\simeq 93\ k-bar$ implying that the unit cell size chosen is larger than it ought to be. The next step of geometric optimization will address this issue.

B. Geometry Optimization

Using the value for $K\_POINTS = 7{\times}7{\times}7$, $ecutwfc = 100$ and $ecutrho = 700$ the volume of the unit cell is varied by ten percent on either side of the value in the cif file in which the lattice constant, $a = 3.79$ Åand the corresponding volume is 54.44 Å^3. The volume is changed in steps of two percent, resulting in a total of 14 simulations to find the energy variation with volume.

TABLE IV. Energy variation with unit cell volume

a (Å)	Cell Volume (Å^3)	Pressure (k-bar)	Energy (Ry)
3.5760	45.730	440.35	-1345.29296716
3.6042	46.818	343.32	-1345.31252098
3.6319	47.907	256.94	-1345.32747968
3.6592	48.996	181.24	-1345.33839912
3.6861	50.085	112.67	-1345.34571306
3.7126	51.174	51.99	-1345.34981380
3.7388	52.262	-2.95	-1345.35105377
3.7646	53.351	-51.41	-1345.34973748
3.7900	54.440	-93.16	-1345.34614741
3.8151	55.529	-131.84	-1345.34053694
3.8399	56.618	-166.50	-1345.33311526
3.8643	57.706	-195.66	-1345.32412033
3.8885	58.795	-222.45	-1345.31365766
3.9123	59.884	-246.59	-1345.30197645

The ev.x tool shipped with Quantum Espresso was used to fit the Energy vs Volume data. It yeilded an Equilibrium volume $V_0 = 52.23$ Å^3, corresponding to a lattice parameter, $a = 3.738$ Åand a bulk modulus,$\kappa = 243.6\ GPa$. Fig.1 shows the variation of energy with volume and Fig.2 shows the variation of Pressure with volume for $\gamma' - Fe_4N$ from the ab-initio simulations.

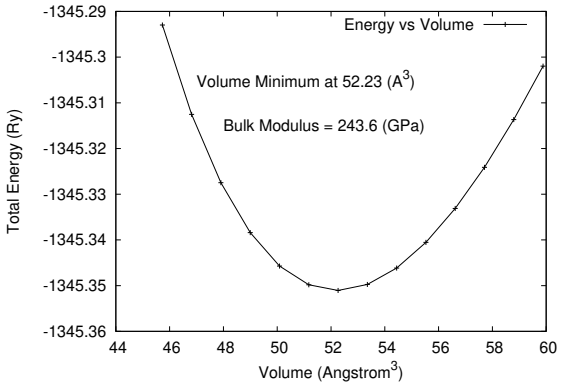

FIG. 1. Variation of the total energy of $\gamma^{prime} Fe_4N$ crystal as a function of volume

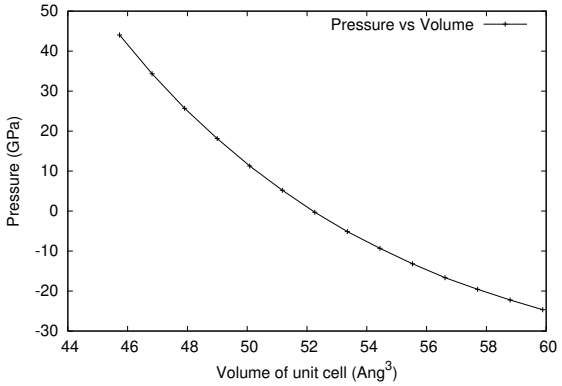

FIG. 2. Variation of the Pressure of $\gamma' Fe_4N$ crystal as a function of volume

C. Low Symmetry Structure studies

Created a cif file of the low symmetry structure at 10 GPa from Table.2 of Cheng's paper [1] with the space group p2/m as suggested in the paper. The cif file is as follows:

```
data_default
loop__symmetry_space_group_name_H-M   'P 2 / m'
_cell_angle_alpha                     90
_cell_angle_beta                      90
_cell_angle_gamma                     90
_cell_length_a                        5.24780
_cell_length_b                        3.71980
_cell_length_c                        5.24780
```

```
_cell_volume                    102.440
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
loop_
_symmetry_equiv_pos_as_xyz
x,y,z
-x,y,-z
-x,-y,-z
x,-y,z
loop_
Fe 0.5      0.5      0.0
Fe 0.7294   0.0      0.7293
Fe 0.76405  0.0      0.23587
Fe 0.0      0.5      0.0
Fe 0.0      0.5      0.5
Fe 0.5      0.5      0.5
N  0.74894  0.5      0.74893
```

The resulting structure is shown in Fig.3.

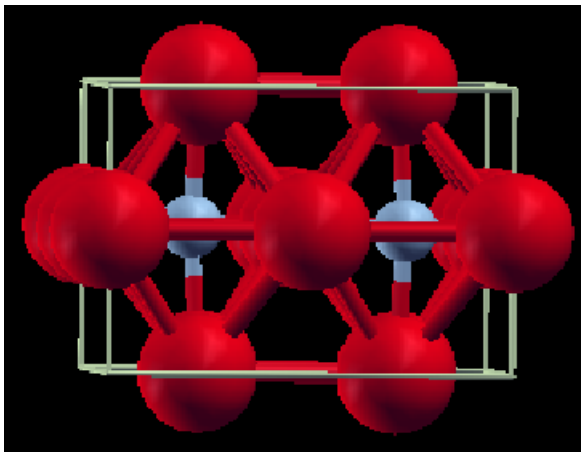

FIG. 3. Low symmetry Fe4N Unit cell at 10 GPa with space group P2/m

D. Phonon Calculations

Carried out a phonon calculation of $\gamma' Fe_4N$ at 10 GPa with compromised parameters for ecutwfc (=70) and ecutrho (496) and K vector (obtained from the bilbao crystallographic server) q values

```
K_POINTS {crystal_b}
10
  0.0  0.0  0.0  1 !GM
  0.5  0.5  0.5  1 !R
  0.5  0.5  0.0  1 !M
  0.0  0.5  0.0  1 !X
  0.75 0.75 0.75 1 !LD
  0.0  0.75 0.0  1 !DT
  0.5  0.5  0.75 1 !T
  0.75 0.5  0.0  1 !Z
  0.75 0.75 0.25 1 !C
  0.75 0.25 0.5  1 !GP
```

so that we get an idea of the resulting frequencies. The lowest frequency would correspond to the softest mode of vibration was the idea since $\omega = \sqrt{k/m}$. The lowest frequency obtained is 1.377231 THz. This however did not shed any light on the corresponding direction of vibration and possible structural transition under stresses.

IV. CONCLUSIONS

It is seen that $7 \times 7 \times 7$ is a good choice of K points, $ecutwfc = 100$ is a good choice for the basis set and a ratio of $ecutrho/ecutwfc = 5$ is a good choice for obtaining a converged total energy and hydrostatic pressure in $\gamma' Fe_4N$. It is shown that $\gamma' Fe_4N$ has an Equilibrium volume $V_0 = 52.23$ Å^3, corresponding to a lattice parameter, $a = 3.738$ Åand a bulk modulus, $\kappa = 243.6\ GPa$. The low symmetry structure with space group P2/m as described in Cheng's paper [Cheng] was constructed. Phonon frequencies of $\gamma' Fe_4N$ at 10 GPa were obtained using compromised parameters to study the work-flow. The full project, unfortunately could not be completed and we hope to do that post the deadline for submission.

[CompMatPhys] ttp://compmatphys.epotentia.com/

[QE] . Giannozzi et al., J.Phys.:Condens.Matter 21, 395502 (2009) http://dx.doi.org/10.1088/0953-8984/21/39/395502; P. Giannozzi et al., J.Phys.:Condens.Matter 29, 465901 (2017) http://iopscience.iop.org/article/10.1088/1361-648X/aa8f79

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