Convergence and Bulk Modulus of γ-Fe_4N

Team 8, Collective of Authors

***Abstract*—The instabilities to symmetry breaking distortions of the γ-Fe_4N compound under large pressures make it a good testing ground for ab-initio calculations. In this study, we compare the results from previous work with results obtained using the Quantum Espresso DFT code. We start by determination of the correct settings for the converged calculation. Then we evaluate the parameters of the equation of state of the material. Finally, we discuss other possible calculations.**

I. Introduction & Methodology

This project replicates some of the results of the previously published paper [1]. In the γ-Fe_4N material, nitrogen is located at the cubic body centre, while iron atoms are located at the face centres and corners of the cubic conventional unit cell. The space group of the material is $Pn\bar{m}a$, with space group index 221. Details of the crystal are displayed in Fig. **??**. The unit cell parameter is given in [1] as 3.795 Å. The properties of this material are evaluated using the Quantum Espresso code [2, 3, 4], which is a DFT code using a plane wave basis. We used the internal database of ultrasoft pseudopotentials for the modelling of atomic potentials [5], in the scalar relativistic approximation.

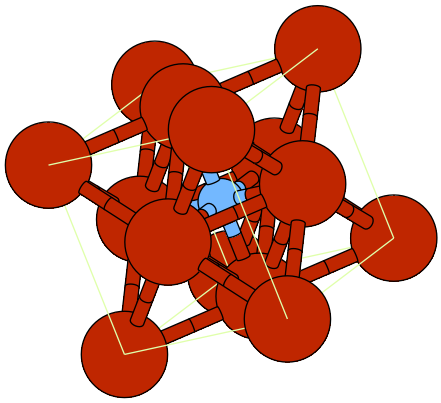

Fig. 1. Geometry of the crystal of γ-Fe_4N. The Wyckoff positions of the atoms are $1b$ for nitrogen, and $1a$ and $3c$ for the iron. The nitrogen is effectively a body-centered interstitial in the face centered cubic system.

II. Convergence Study

In order to determine the necessary minimal basis size, we carried out a convergence study. As a criterion for the convergence, we chose the mechanical stress in the material, as determined by the Quantum Espresso (from now on QE) code. Besides the basis size, which is influenced by the energy cut-off value for both the wavefunction and electron density basis sets, a density of the points chosen in the reciprocal space (so called k-point density) plays an important role, as many parameters of the material are evaluated by integrals over the reciprocal space. Hence, three distinct values were changed and the resulting difference in the mechanical isotropic stress was noted. The results are summarized in the tables below. The internal pseudopotential files include some estimates on the needed wavefunction and density energy cutoff values. Hence, we started by investigating the convergence in the k-point density (see Table I).

Number of k-points (side length)	Pressure [kbar]
3	-258.92
5	-234.38
7	-230.34
9	-233.78
11	-233.80
13	-234.62
15	-233.91

TABLE I
The convergence of the isotropic mechanical pressure, as function of the k-point density. The wavefunction cutoff energy was chosen to be the recommended value for the given pseudopotentials, which was 50 Ry. For the density cutoff energy, 250 Ry was chosen.

The grid in reciprocal space is always cubical, with a side of given number of k-point. The following calculation determines the necessary energy cutoff needed for a precise calculation. The larger the energy cutoff value, the more plane waves are included in the basis of the wavefunction (see Table II). Finally, the dependence on the ratio of the wavefunction and density energy cutoff is determined (see Table III). After these studies, one final, very high accuracy calculation was done, with k-point grid of 15x15x15, wavefunction energy cutoff of 200 Ry and density / wavefunction ratio of 5. The resultant mechanical pressure was -41.88 kbar, so for precision of about 1 kbar, the lower settings are sufficient. The settings used in the following calculations were k-point grid of 9x9x9, energy cutoff for wavefunction of 130 Ry, and density / wavefunction ratio of 6.

III. Elastic Behaviour of the Material

The elastic behaviour of the material was studied to the extent of determination of parameters in Birch-Murnaghan equation of state [6]. The parameters were fitted using an procedure included in the QE code. The data for the fit were generated by relaxation of the unit cell parameters

Wavefunction energy cutoff [Ry]	Pressure [kbar]
50	-233.78
70	-80.19
90	-48.82
110	-44.29
130	-44.73
150	-41.48
170	-42.04

TABLE II
THE CONVERGENCE OF THE ISOTROPIC MECHANICAL PRESSURE, AS FUNCTION OF THE WAVEFUNCTION ENERGY CUTOFF. IT CAN BE SEEN THAT THE CHANGES IN THE MECHANICAL PRESSURE ARE SIGNIFICANTLY HIGHER THAN IN THE CASE OF k-POINTS, POINTING THAT THE INITIAL GUESS FOR BASIS SIZE WAS HIGHLY INSUFFICIENT. THE GRID OF k-POINTS IS CONSTANT IN THIS SERIES OF CALCULATIONS, WITH 9X9X9 GRID. THE RATIO OF WAVEFUNCTION AND DENSITY ENERGY CUTOFF VALUE IS ALSO KEPT CONSTANT, AT 5.

Wavefunction / Density Energy Cutoff Ratio	Pressure [kbar]
3	-42.10
4	-42.29
5	-42.04
6	-42.35
7	-42.34
8	-42.29
9	-42.49
10	-42.08
11	-42.25
12	-42.37

TABLE III
THE CONVERGENCE OF THE ISOTROPIC MECHANICAL PRESSURE, AS FUNCTION OF THE WAVEFUNCTION ENERGY CUTOFF. IT CAN BE SEEN THAT THE CHANGES IN THE MECHANICAL PRESSURE ARE SIGNIFICANTLY HIGHER THAN IN THE CASE OF k-POINTS, POINTING THAT THE INITIAL GUESS FOR BASIS SIZE WAS HIGHLY INSUFFICIENT. THE GRID OF k-POINTS IS CONSTANT IN THIS SERIES OF CALCULATIONS, WITH 9X9X9 GRID. THE RATIO OF WAVEFUNCTION AND DENSITY ENERGY CUTOFF VALUE IS ALSO KEPT CONSTANT, AT 5.

towards a given isotropic mechanical stress value. The fitting is summarised in Fig. 2

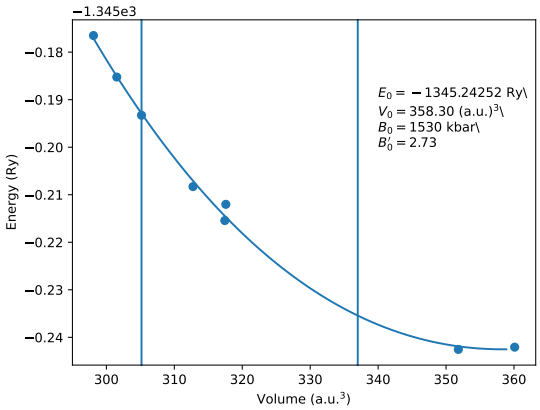

Fig. 2. The fit to the Birch-Murnaghan equation of state. The bulk modulus of the material in the linear approximation is one of the paramaters, and stands at $B_0 = 1530$ kbar. The lines represent the thresholds, where the pressure in the material exceeds 30 GPa and 10 GPa (from the left, respectively). These are the pressures, where the structural changes occur, according to [1]. The change in the volume of the unit cell at these thresholds is in the order of percents, which is quite significant.

IV. DISCUSSION & OVERVIEW

We planned on determining the instability criteria for the M-instability as mentioned in [1], but unfortunately we ran short on time. The calculations for the extended unit cell with lower symmetry were quite expensive, and we did not manage to effectively distribute the workload among the team. However, at least some values were generated as a result of this project, and a good understanding of procedures needed for a calculation of elastic properties was acquired by the participants.

V. ACKNOWLEDGEMENTS

Part of the calculations was done with the support from the project "e-Infrastruktura CZ" (e-INFRA LM2018140) provided within the program Projects of Large Research, Development and Innovations Infrastructures.

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