DFT study of $\gamma' - Fe_4N$ at different pressures

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1 Introduction and computational settings: convergence testing

In this project we aim to verify the results obtained from [1] for the crystal $\gamma^{'}-Fe_4N$ using DFT calculations to verify how the symmetry is broken under pressure.
The work is divided in 4 parts: a convergence test, a geometry optimization procedure and two soft mode analysis. At first we run some calculations to verify the optimal settings in order to study the crystal. We have valued several convergence testings both with our local machine and the help of the supercomputer Jean Zay in France.
At first we have converged the value of the energy-cutoff for the wave functions and the density using a big k-mesh (20x20x20) and then run several calculations to find the optimal compromise between efficiency and precision. We used the hydrostatic pressure as a physical reference to be converged since it is the most sensible to the variations of our DFT settings. We deduced that an energy cut-off for the wave functions between 120/150 Ry and a factor x5 for the cut-off density with a k-mesh of 11x11x11 is the best option for the calculation of the crystal with P3m symmetry under a pressure within the range between 0GPa and 10GPa, all the calculations were done with spin-polarization.
Lastly, we have also confronted our results between two different occupations methods: 'smearing' and 'tetrahedra'. At the end we opted for the smearing one since the value of the more significant physical quantities were the same but with a quicker computational time.

2 Energy per Volume curve of the iron nitrite

Having found the optimal settings for our calculations we proceed with the study of the energy per volume graph of our crystal. Considering the iron nitrite with the P3m crystal structure it is possible to vary the value of the lattice parameter in order to explore a wide region of pressures and energies. We are mostly interested in finding the minimum of the E(V) graph and the value of the lattice parameter for which we obtain a pressure of 10GPa and 30GPa. In order to do so we extract the values of the total energies from QE and use the program ev.x to fit our data withing the Birch-Murnaghan equation of state. In this way, with 2 different calculations we explored a wide region of a (lattice parameter) ($3.500 < a < 4.100$) with special focus on the values near the pressures of interest. We are confident to say that the pressure of 10GPa is reached for $3.780 < a < 3.790$ and of 30GPa for $3.760 < a < 3.776$. In the figure down below we report the Energy-volume graph.

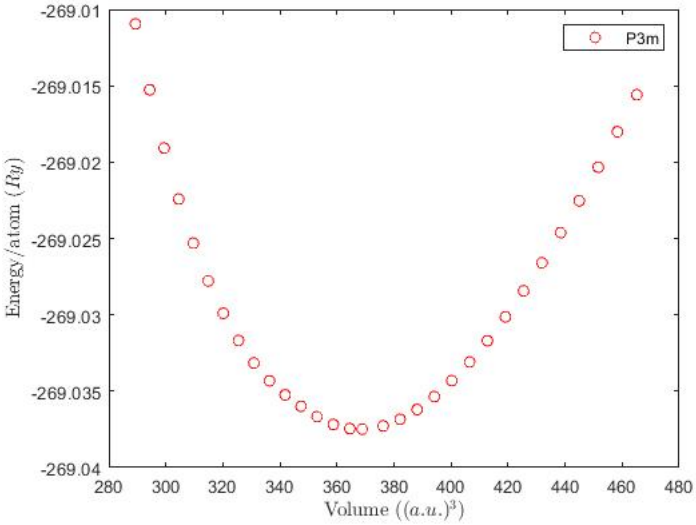

Figure 1: E(V) graph of the crystal with P3m symmetry

3 Phonon modes and instability

The graph in Fig. 2 has been inspired by the presence of an M-instability in the phonon spectrum of $\gamma' - Fe4N$. This instability is evident since in the M-point the spectrum present negative frequencies which ultimately lead to an instability at this given pressure, resulting in a transition to a less symmetric structure. The negative frequencies are called "soft-mode". For a pressure of 10GPa the new less symmetric structure has been reported in the work of *Cheng et al*, we pass from the P3m to the P2m symmetry group. We have found the optimal lattice parameter for this new structure and performed a vc-relaxation for this specific unit-cell. We observed that there was only a slightly difference between the structure given in the paper and the one we have found with the relaxation.

	vc-relax	**Reference**
a	5.24517344	5.24311965
c	3.71641536	3.71648243
a/c	1.41135286	1.41077477
Energy (Ry)	-2690.35968	-2690.35905

It is indeed possible to see that at a pressure of $100kbar$ and $300kbar$ the P2m crystal structure is favourite. It would be easier to see it with an Energy-Pressure graph and we are going to report that one in the slides.

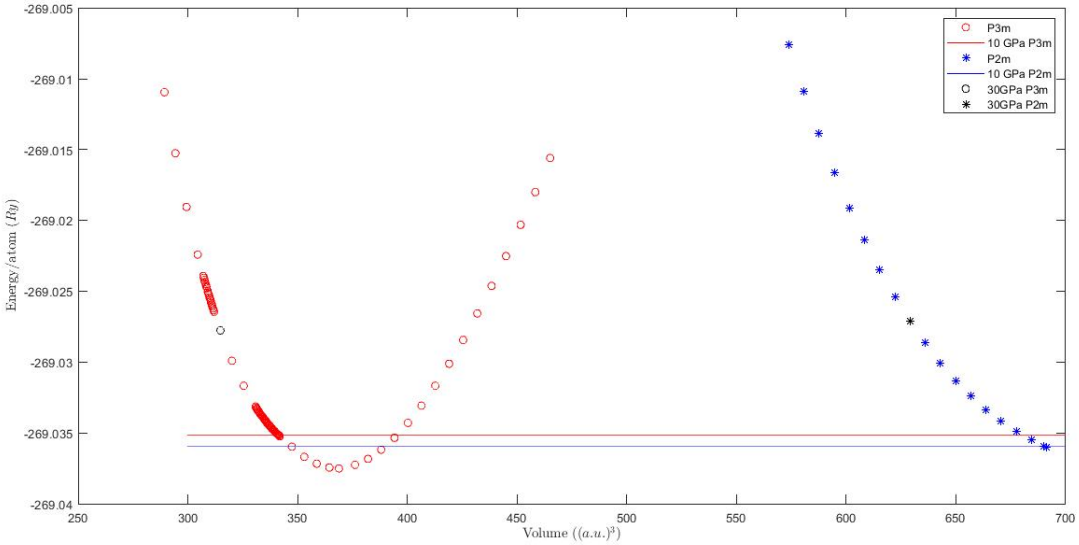

Figure 2: E(V) graph of the two symmetry structures studied. Note that around a pressure of 100kbar the P2m symmetry structure is more stable. Points in black indicate the volume at 300kbar pressure, once again the P2m symmetry is more stable.

At the very end we have also analyzed a new soft-mode, the X-instability of the crystal at around 30GPa. We have used the program ISODISTORT to evaluate the displaced structures corresponding to the X k-vector displacement. In this way, we have determined that along the possible modes the x5+p1 is the most stable one around that pressure and optimized his unit-cell with that pressure. After the displacement the crystal assume a "CmCm" crystal structure.
We report in Fig. 3 the E(V) graph for our 3 structures, both at 30GPa and 10GPa the CmCm symmetry is the most stable one.

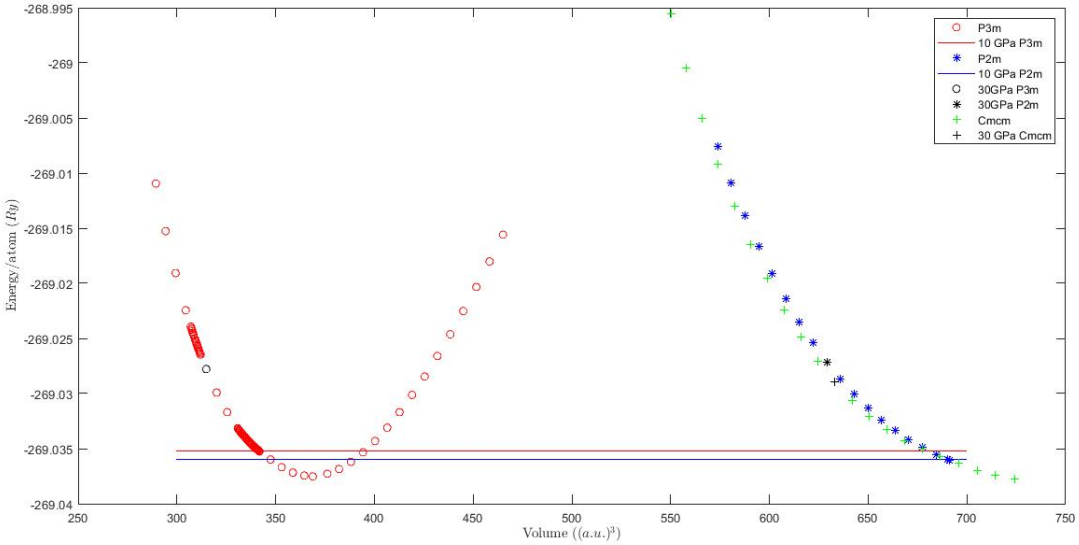

Figure 3: E(V) graph of the three symmetry structures studied. Note that around a pressure of 100kbar and 300kbar the CmCm symmetry structure is more stable. Points in black indicate the volume at 300kbar pressure, once again the P2m symmetry is more stable.

References

[1] Tai-min Cheng, Guo-liang Yu , Yong Su , Lin Zhu and Lin Li "Spontaneous magnetization-induced phonons stability in $\gamma^{'} - Fe_4N$ crystalline alloys and high-pressure new phase", Journal of Magnetism and Magnetic Materials 451 (2018) 87–95