The Effect of Al₂O₃ Oxygen Sub-Lattice on Femon₂ Phase Stability

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Abstract. All Magnetic phase transition in Iron Molybdate Nitride (FeMoN₂) has been studied within the framework of density-functional theory, using generalized gradient approximation (GGA) as exchange correlation functionals. In this study, we suppose that, under the application of pressure, a uni-axial out-of-plane structure optimization were done, where the in plane lattice parameters are fixed, within the pressure range of -50Kbar to 600Kbar. We found that the compound save the same structure (P6₃/mmc) with a volume collapses. The volume and magnetic moment of FeMoN₂ in its spin polarized case as well as none spin polarized case, have also been computed as ground state properties. The Magnetic moment of the FeMoN₂ undergoes an anomalous variation accompanied by volume collapse. This volume collapse is attributed to a large variation in the out-of-plane lattice parameter.

1. Introduction
These Ternary nitride materials that crystallize in layered structures are of great interest in scientific and technological development. They are expected to play a significant and growing role in future development [1]. Indeed, the ternary nitride materials combine the physical properties of ceramics and electronic properties of metals [2, 3]. However, high temperature nitride elaboration methods lead to limited success in the preparation of ternary nitrides due to their low decomposition temperature and the high bond energy of nitrogen N₂ (941.0 kJ / mol). FeMoN₂ is one of the layered nitrides, which is consisting of alternating MoN₆ prismatic layers and FeN₆ octahedral [4].

Panda et al. [5] have synthesized the FeMoN₂ hexagonal structure (P6₃/mmc) at 573K on NH₃ (g) flow for 6 hours. They reported that the values of the lattice parameters “a” and “c” are of about 2.843Å and 10.94Å, respectively. Recently, Enriquez et al. succeeded in the epitaxial growth of an hexagonal FeMoN₂ by a chemical solution deposition technique [6]. In this work the ternary nitride thin film (FeMoN₂) were grown on c-plane sapphire (Al₂O₃) substrate by a polymer assisted deposition (PAD) method, at a temperature of 923K and under NH₃ flow for 2 hours at an ambient pressure. They reported that the Fe site aligned itself with the oxygen sublattice in Al₂O₃. Therefore, the periodicity of oxygen sublattice of 2.88Å matches very good the in-plane lattice parameter "a ", while the out-of-plane lattice parameter "c" of FeMoN₂ takes the value of 10.47 Å. Paramagnetic nature of the ultrathin FeMoN₂ nitride film at room temperature and magnetic phase transition is
reported by Panda et al. [5] where a super paramagnetic to super-ferromagnetic ordering is occurred at lower temperatures [7] which is attributed to the presence of ferromagnetic impurities. In the present paper, we discuss the effect of the oxygen sublattice parameter of Al₂O₃ on the lattice parameters of FeMoN₂ structure and its magnetic orders in the different NM, FM, and AFM magnetic phases.

2. Computational details
First principle calculations have been performed in the framework of density functional theory (DFT) [8] using a Plane-Wave basis set and pseudopotentials as they coded in Quantum Espresso simulation package [9, 10]. Generalized gradient approximations (GGA) of Perdew-Burke-Ernzerhof (PBE) have been adopted for exchange and correlation potentials. It is worth to note that the ultrasoft pseudo potentials have been used in these calculations, which they were taken from BURAI package [11, 12], which is a GUI system for Quantum ESPRESSO code, and they used throughout the calculation. The valence states used for Fe, Mo and N are 3d⁶ 4s², 4d⁵ 5s¹ and 2s² 2p³, respectively. The k-space integration is performed using a division of 9 × 9 × 5 mesh within the full Brillouin zone. The total energy convergence criterion is fixed to 10⁻⁶ Ry in the self-consistent calculation and the volume optimization procedure. Table 1 shows the experimental structure parameters and atomic positions used in the calculations [5, 6].

The maximum of the kinetic energy for the plane waves, E cut (wfc), and charge density cutoff Ecutoff (rho) used in the calculations are chosen to the values of E cut (wfc)= 70 Ry and E cut (rho) = 637 Ry, respectively. The stability toward magnetism in each magnetic phase is given by comparing the spin polarized (SP) and the non spin-polarized (NSP) total energy values at theoretical equilibrium volume, the objective is to point out the possible magnetic instability for a fix ed lattice parameter that caused any magnetic phase transition.

3. Results and Discussions
In order to discuss the controversial experimental results obtained for FeMoN₂ compound, we have calculated the variation of the total energy versus the pressure along the c-axis by keeping in-plane lattice parameters “a” fixed in the none magnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) magnetic orders. For each calculated structure, the atomic positions are relaxed.

In Fig. 1 the variation of the total energy of FeMoN₂ with the volume corresponding to a given out-of-plane “c” lattice parameter is plotted for the three magnetic orders. From this figure, it is clear that the AFM phase is the most stable one while the NM magnetic phase is the less stable magnetic phase.

| Atom | Wyckoff | x  | y  | z  |
|------|---------|----|----|----|
| Fe   | 2(a)    | 0  | 0  | 0  |
| Mo   | 2(b)    | 0  | 0  | 1/4|
| N    | 4(f)    | 1/3| 2/3| 0.37|

Table 1. The crystal structure and Wyckoff positions of FeMoN₂ (P6₃/mmc) used to initialize the DFT calculations. The z position of Nitrogen atom is adopted from that of the nitrogen position in MnMoN₂ compound [13], because to the best of our knowledge, there is no reported results for the atomic positions of FeMoN₂.
Table 2. Equilibrium volumes, magnetic moments, and total energy of the
ground state calculations for the three NM, FM, and AFM phases. The total
energy of NM phase is chosen as reference energy.

|                   | NM   | FM   | AFM  | Exp. |
|-------------------|------|------|------|------|
| Volume (Å³)       | 73.68| 77.92| 77.97| 73.16(a), 76.57(b) |
| Mag. mom (µB/Fe atom) | -    | 3.05 | 3.04 | -    |
| E_{TOT} (mRy)     | 0.00 | -65.4| 72.3 | -    |

(a): Ref [6]
(b): Ref [5]

The equilibrium volume of NM phase of FeMoN2 unit cell is lower than that of magnetic phases,
while the FM and AFM phases have a very close equilibrium volumes. To get more insight about
the ground states properties, we do a final total energy calculation at the equilibrium volumes for each
phase. The results are summarized in Table 2.

As already noted in Fig. 1 where we represent the experimental volumes as a vertical lines, the
present results show that the non-magnetic equilibrium volumes are close to the results reported
by Enriquez et al. [6], while the equilibrium volume of the two magnetic phases are close to that
of Panda et al. [5]. On the other hand, the NM phase is found to be stable under the high pressure
condition, where the magnetic moments of both AFM and FM magnetic phases vanishes for small
volumes. From the obtained pressure and volume data, the pressures versus volumes are plotted
in figure 2(a). The curve of the NM phase is monotonically decreasing with increasing pressure, while
those of the magnetic states undergo anomalies. Indeed, we can clearly notice that near the
equilibrium pressure there is a change in the slope of the curve up to the pressure of close 30 Kbar,
followed by another change in the interval 30 Kbar to 300 Kbar. At high pressures, greater than
300Kbar, all magnetic phases are degenerated by losing their magnetic moments.
The computed ground state volumes for FeMoN₂ in its NM phase and AFM phase are in a good agreement with the experimental results [5, 6], whereas the calculated magnetic moment for FeMoN₂ in its two magnetic phases decreased suddenly by about 1µB /Fe accompanying a collapse in the volume at pressure value of 30 Kbar, as shown in figure 2(b). This volume collapse corresponds to a large variation in the out-of-plane "c" lattice parameter. The reduction of the magnetic moment continues monotonically until they vanish at the pressure value of 300 Kbar.

4. Conclusion
The present study computes the magnetic phase transition in FeMoN₂ from antiferromagnetic to non magnetic phase at high pressure. Our main supposition is to fixed the in-plane lattice parameters to that of the oxygen periodic arrangement in Al₂O₃, where this is achieved by the [1100] orientation of FeMoN₂ aligns with the [2110] direction of the Al₂O₃ substrate (Underline a number, a minus sign), and let the out-of-plane lattice parameter "c" and internal atomic positions to be relaxed to the self consistent convergence. The obtained results are in good agreement and very supported by the experimental results.
5. References

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