# Magnetism of Tetragonal Distorted α-Mn: Ab Initio Density Functional Study

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## 1. Introduction

Manganese is known to be the most complex metallic element and have four allotropic modifications exhibiting a complex phase diagram [1]. From the various experimental results, α-Mn, which is the stable phase below 1000 K, orders in noncollinear antiferromagnetic (AFM) structure [2]. The 29 atoms per primitive unit cell (58 atoms per cubic cell) are distributed over four crystallographically inequivalent sites with complex crystal structure. α-Mn undergoes a paramagnetic to AFM phase transition at the Néel temperature of $T_N$ = 95 K. β-Mn is stable in the temperature range from 1000 to 1368 K and its crystalline structure is simple cubic structure with two types (in Wyckoff positions of 8c and 12d) of atomic sites per unit cell containing 20 atoms. In the temperature interval between 1368 K and the melting point of 1517 K, there exist other phases of fcc γ-Mn and bcc δ-Mn.

The related to this study, D. Hobbs et al. [3] reported extensively structural and magnetic properties of α-Mn by using ab initio calculations. They considered noncollinear antiferromagnetism, but the calculated equilibrium magnetic structure is still collinear AFM. The α-Mn formed by strongly magnetic (MnI, MnII) and weakly magnetic (MnIII) or even nearly nonmagnetic (MnIV) atoms for AFM state. Thanks to development of technology it can be possible to synthesize artificial materials. It would be an quite interesting question how the magnetism change with tetragonal distortion.

## 2. Computational Method

In calculation, we employed the Vienna ab initio simulation package (VASP) [4, 5], in which the projector augmented wave (PAW) pseudopotentials have been constructed by considering the all-electrons effect. The calculations were spin-polarized and the exchange and correlation contributions to the total energy were obtained using generalized gradient approximation of Perdew et al. [6] Structural relaxations have been performed using the exact Hellmann-Feynman forces acting on the atoms. Brillouin-zone integrations were performed using an 4x4x4 Monkhorst-Pack grid with a plane-wave cutoff energy of 250 eV was used.

## 3. Results and Discussion

First, in order to determine the equilibrium atomic volume, we calculated total energies as a function of the atomic volume for the ferromagnetic (FM), AFM, and paramagnetic (PM) states. The lowest energies are 11.23 Å³/atom for AFM states which consistent with D. Hobbs et al. results [3]. Subsequently, we calculated the total energies and magnetic moments as functions of

the tetragonal distortion ($c/a$ ratio) in range from 0.7 to 1.3, assuming that an atomic volume is conserved as the equilibrium one (11.23 $\text{Å}^3$/atom) of the cubic. The results are plotted in Fig. 1.

It is interesting that even though the magnetic ground state of α-Mn is AFM [3], the total energy differences are decreased with the tetragonal distortion. Eventually, FM states are more stable than AFM states at big distortions such as c/a = 0.7 and 1.3. The calculated total energy differences are quit small, 0.42 and 0.16 meV/atom for $c/a$ = 0.7 and 1.3, respectively. At $c/a$ ratio of 0.7, the calculated magnetic moments are 2.52(3.05), -0.91(2.63), 0.64/0.17(-0.58), 0.17, and -0.14/-0.05(0.21) $\mu_B$ for the MnI, MnII, MnIIIa/MnIIIb, and MnIVa/MnIVb in FM state, respectively. Numbers in parentheses represent at $c/a$ = 1.0. In the tetragonal distortion, it is well known that we observed splitting of site III and IV into two group [2, 3]. The tetragonal distortion leads reduced magnetic moments.

## 4. Summary

We have investigated the structural and magnetic properties of α-Mn, with the VASP code. At significantly distorted($c/a$ = 0.7 and 1.3), it was found for α-Mn to be energetically more stable in FM states, compared to AFM. The magnitude of calculated magnetic moments are decreased with the tetragonal distortion.

## 5. References

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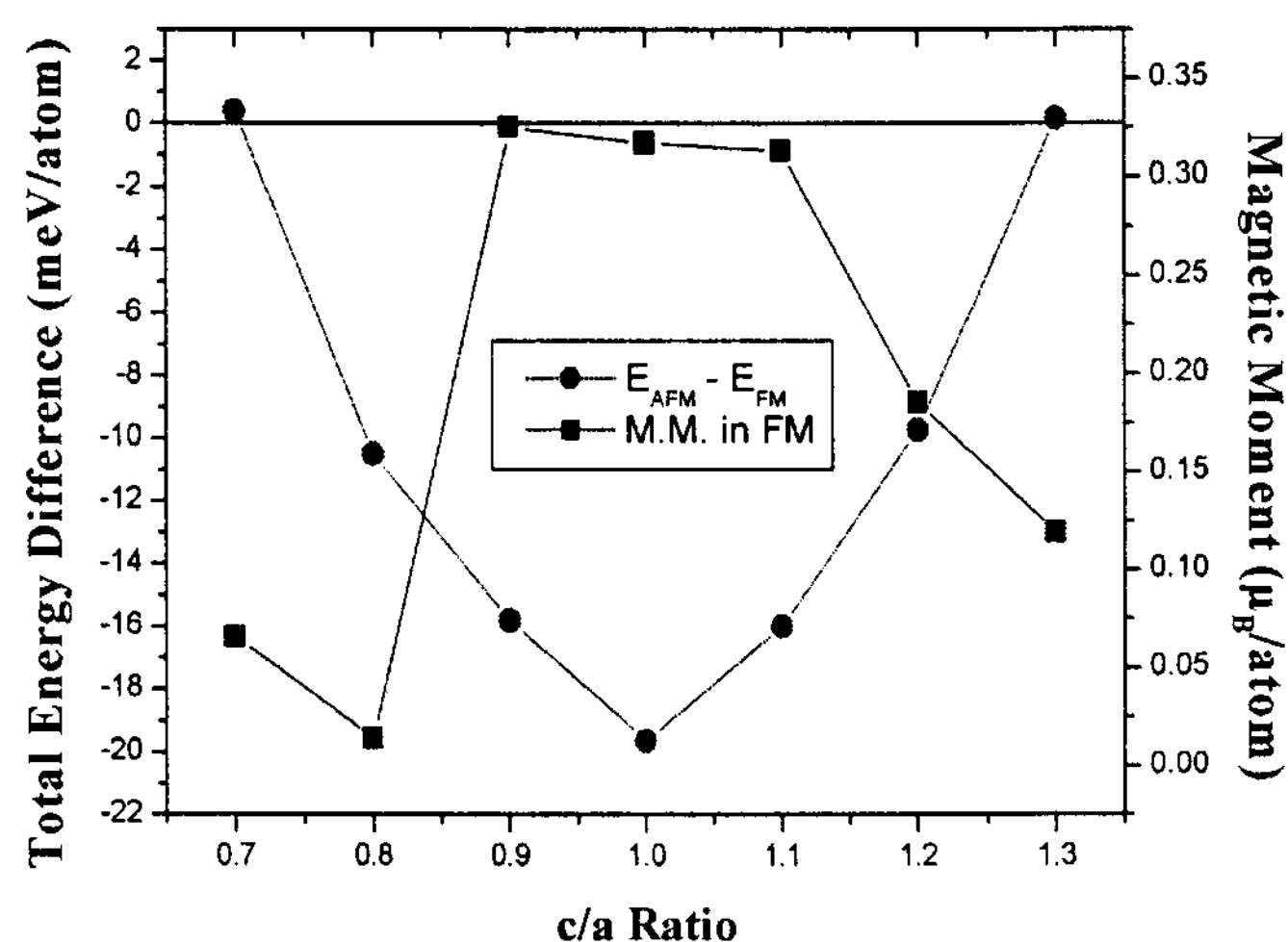
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Fig. 1. Total energy difference and magnetic moment of a-Mn. Red circles and blue squares represent total energy difference and magnetic moment in FM state, respectively.