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Competing ferromagnetic and anti-ferromagnetic interactions in iron nitride ζ-Fe_2N

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ABSTRACT

The paper discusses the magnetic state of zeta phase of iron nitride viz. ζ-Fe_2N on the basis of spin polarized first principles electronic structure calculations together with a review of already published data. Results of our first principles study suggest that the ground state of ζ-Fe_2N is ferromagnetic (FM) with a magnetic moment of $1.528\mu_B$ on the Fe site. The FM ground state is lower than the anti-ferromagnetic (AFM) state by 8.44 meV and non-magnetic (NM) state by 191 meV per formula unit. These results are important in view of reports which claim that ζ-Fe_2N undergoes an AFM transition below 10 K and others which do not observe any magnetic transition up to 4.2 K. We argue that the experimental results of AFM transition below 10 K are inconclusive and we propose the presence of competing FM and AFM superexchange interactions between Fe sites mediated by nitrogen atoms, which are consistent with Goodenough-Kanamori-Anderson rules. We find that the anti-ferromagnetically coupled Fe sites are outnumbered by ferromagnetically coupled Fe sites leading to a stable FM ground state. A Stoner analysis of the results also supports our claim of a FM ground state.

1. Introduction

Nitriding is a process used for surface hardening of austenitic steel which improves the corrosion and wear resistance of its surface [1]. It involves passing a gaseous mixture of ammonia and hydrogen on Fe surface, which produces a number of iron compounds, of the type Fe_xN, depending upon the temperature and nitrogen chemical potential at the surface of iron. Most of these iron nitride phases are unstable at ambient temperatures and pressures but the high kinetic barrier of the $N + N \rightarrow N_2$ reaction prevents their decomposition at temperatures below 400 °C [2]. Hence, nitrified steel at ambient temperatures and pressures could contain phases of the type Fe_4N, Fe_2N etc. on its surface which would greatly affect its properties and concomitant applicability. Very recently, $Fe_{16}N_2$ was in news as strongest known magnet yet and as a candidate for magnetic motors [3]. This together with search for materials with potential magnetic properties has brought iron nitrides to the attention of materials research community.

Magnetic state of Fe_2N, both experimentally and theoretically, has been a topic of debate since the beginning of its investigation. The experimental measurements by Bridelle [4] suggested feeble FM magnetization in ζ-Fe_2N at 78 K. The magnetic and Mössbauer measurements by Mekata et al. [5] agree with Bridelle and a Curie temperature of 4 K was assigned, while a later report by Bainbridge et al. [6] based on Mössbauer spectra did not observe any magnetic splitting in the material down to 4.2 K. Thus, they reported a paramagnetic (PM) state of Fe atoms in the material. Subsequent experimental works on the material have only added to the controversy, as findings by Hinomura et al. [7] and Kano et al. [8] have suggested that the material is AFM with a Néel temperature in the range of about 9–11 K. One of the major hurdles to experimental investigation of ζ phase can be traced back to its strict stoichiometric composition of Fe_2N and its structural similarity to ϵ phase which is non-stoichiometric with a composition $Fe_{2-3}N$.

Theoretical first principles calculations have also been inconsistent regarding the magnetic state of ζ-Fe_2N, with different publications reporting conflicting results. Matar and Mohn [9] report a FM state that is more stable than an unpolarized state by 175 meV per formula unit and magnetic moment per Fe atom of $1.47\mu_B$. Their Density of States (DOS) curves show a metallic state and itinerant ferromagnetism. Additionally, an analysis on the basis of Slater-Pauling-Friedel plot predicts that ζ-Fe_2N should behave like a strong ferromagnet. The work of Eck and coworkers [10], shows a metallic phase with 1.5 unpaired electrons per Fe atom. They report that the phase is PM. Further work of Sifkovits et al. [11], reports a magnetic moment of $1.43\mu_B$ per iron atom. The DOS

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reported shows a metallic state with Fermi Level (E_F) lying in Fe band. They do not claim PM or FM state for ζ-Fe_2N. Thereafter, comprehensive investigations of electronic structure of several phases of Fe_2N and Fe_2C were studied in a recently published work by Fang and co-workers [12]. The work dealt with understanding relative stability, bonding character and Fermi level properties of several possible structures of Fe_2N and Fe_2C. Out of the several Fe_2N structures possible, relative enthalpy of formation is observed to be highest for ζ-Fe_2N structure and is likely to be the most probable structural phase formed on the surface of nitrided steel. Fang's works yield a magnetic moment of $1.56\mu_B$ per iron atom. They claim that the structure is FM. More recently, calculations by Chen et al. [13], yield 1.38 unpaired electrons per Fe. They claim that the structure is PM and the DOS curve shows a metallic state. The results of Chen are intriguing considering they obtain a magnetic moment for Fe based on spin polarized calculation and that estimates of Stoner parameter are not reported by them.

Considering immense potential magnetic applications for iron nitrides and the lack of a clear understanding, both experimentally and theoretically, with regards to their magnetic state, we undertake detailed investigations into the magnetic state of ζ-Fe_2N structure. The next section describes the crystal structure and methodology employed while Section 3 discusses results of electronic structure calculations. In Section 4 we discuss magnetism in this structure and Section 5 concludes the work.

2. Methodology

ζ-Fe_2N has an orthorhombic unit cell, with space group Pbcn (#60), where the Fe and N atoms occupy 8d and 4c crystallographic positions respectively (see Table 1). The structure may be considered as a distorted HCP lattice of Fe atoms with N atoms occupying octahedral sites. A nitrogen atom is bonded to 6 Fe atoms, with 2 atoms each at a distance of 1.87 Å, 1.92 Å and 1.96 Å, giving rise to slightly tetragonally distorted octahedra. In view of discussion on magnetic state in later sections, we note from Fig. 1, a Fe atom is at the vertex of three tetrahedra and is hence bonded to three N-atoms and has fifteen nearest neighbor Fe atoms. Out of these fifteen Fe–Fe nearest neighbor pairs, three pairs have Fe–N–Fe bond angle of $\sim 180^\circ$ while the remaining 12 pairs have a Fe–N–Fe bond angle of $\sim 90^\circ$. [1] For example in Fig. 1, consider the atom Fe3: It has three 180° neighbors (namely Fe3–N3–Fe2, Fe3–N4–Fe7, Fe3–N2–Fe2) and twelve 90° neighbors (i.e. the rest of the Fe atoms in the three octahedra).

All electronic structure calculations were performed by using the density functional theory codes implemented in Vienna ab initio simulation package (VASP) [14]. The Projector Augmented Wave (PAW) method was employed and exchange correlation interactions were treated by means of Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA). The PAW potentials were constructed for valence configurations: Fe($4s^1 3d^7$) and N($2s^2 2p^3$). The electron occupations were smeared with a gaussian distribution function with a smearing width of 1 meV. The geometry optimization were performed with a converged Monkhorst Pack grid of $(9 \times 9 \times 9)$ k-points till the residual forces were less than 0.01 eVÅ^{-1} and tolerances of 10^{-5} eV was chosen for self-consistency loops. The plane waves were incorporated till a high energy cut-off of 400 eV. The DOS calculations were performed using tetrahedron method with Blöchl corrections.

For benchmarking the results of Fe_2N, first principles calculations have also been performed on bcc-Fe using a dense mesh of $21 \times 21 \times 21$ k-points with other convergence and tolerance values kept similar to the Fe_2N ones. The converged lattice constant and magnetic moment per atom were 2.832 Å and $2.186\mu_B$, which are in excellent agreement with previously reported [15] values of 2.82Å and $2.18\mu_B$.

Crystal Overlap Hamilton Population (COHP) analysis was done using the LOBSTER [16] package. Bader charge analysis was done using the algorithm implemented by Henkelman [17] research group. All crystal structure and charge density images were rendered using VESTA [18] software package.

[1] The $\sim 180^\circ$ angles are actually, 177.15, 177.14 and 177.15 degrees while the $\sim 90^\circ$ ones are 87.8, 90, 86.1, 91, 87.8, 92.02, 89.9, 90.1, 91.06, 91.77, 89.96, 92.04 degrees. The 90° and 180° pairs have an average Fe-Fe distance of 2.709 Å and 3.83 Å respectively.

Table 1
Charges and magnetic moments on ions obtained by Bader analysis.

Atom	Wyckoff Site	Charge (e)	Magnetic moment (μ_B)
Fe	8d (0.251, 0.128, 0.008)	+0.834	1.528
N	4c (0, 0.864, 0.25)	−1.668	−0.06

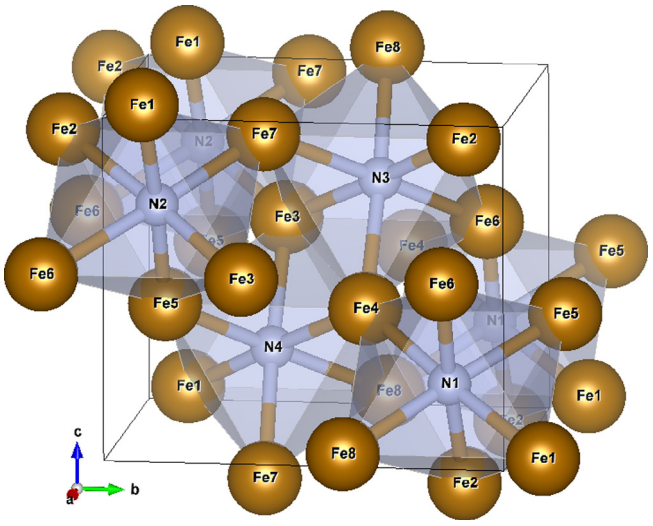

Fig. 1. Orthorhombic unit cell of ζ-Fe_2N. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

3. Results

Unit cell volume relaxations were done and the converged lattice parameters (a = 4.3466 Å, b = 5.4682 Å, c = 4.7436 Å) obtained via spin polarized calculations are close to previously reported experimental values by Rechenbach and Jacobs [19] (a = 4.437 Å, b = 5.541 Å, c = 4.843 Å) and computational work done by Fang et al. [12] (a = 4.3406 Å, b = 5.4480 Å, c = 4.7544 Å).

Total energy calculations show that the FM ground state is more stable than the NM state and AFM state by 191 meV and 8.44 meV per formula unit respectively. All results reported henceforth pertain to the FM state.

The charges on ions were computed using Bader charge analysis and are tabulated in Table 1 which clearly shows a charge transfer of $0.8e^-$ occurring from Fe to N. This implies that 2 Fe lose their 4s electrons to 2p state of N. This charge transfer should cause the Fe 4s band to lie in the conduction band with the N 2p band partially filled and hybridizing with the 3d band of Fe.

Our charge transfer results are in agreement with Fang et al.'s report of 0.62 e^-/Fe atom being transferred to the more electronegative N atom but are contrary to the nitrogen donor model proposed by Bainbridge et al. [6]. According to it, 3 N atoms surrounding each Fe donate 1.5 electrons and thus predicts a Fe