Research articles

Electronic, magnetic properties and phase diagrams of system with Fe$_4$N compound: An *ab initio* calculations and Monte Carlo study

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ABSTRACT

Self-consistent *ab initio* calculations, based on Density Functional Theory (DFT) approach and using Full potential Linear Augmented Plane Wave (FLAPW) method, are performed to investigate the electronic and magnetic properties of the Fe$_4$N compound. Polarized spin and spin-orbit coupling are included in calculations within the framework of the ferromagnetic state between Fe(I) and Fe(II) in Fe$_4$N compound. We have used the obtained data from *abinitio* calculations as an input in Monte Carlo simulation to calculate the magnetic properties of this compounds such as the ground state phase diagrams, total and partial magnetization of Fe(I) and Fe(II) as well as the transition temperatures are computed. The variation of magnetization with the crystal field are also studied. The magnetic hysteresis cycle of the same Fe$_4$N compound are determined for different values of temperatures and crystal field values. The two-step hysteresis loop are evidenced, which is typical for Fe$_4$N structure. The ferromagnetic and super-paramagnetic phase is observed as well.

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1. Introduction

The iron nitride compounds have attracted considerable attention due to its excellent magnetic properties such as low coercivity, good mechanical properties, corrosion resistance [1–5], large saturation magnetization [6,7], and chemical stability [8]. The stability of the iron nitride Fe$_4$N concerning its magnetic properties has made it a promising candidate in technological applications. Otherwise, the Fe–N binary systems have been one of the main subjects of the recent research because of their technological importance [9,10]. The structure parameters, electronic and magnetic properties as well as hyperfine interaction parameters of Iron nitride Fe$_4$N have been investigated [11]. The theoretical investigations of the electronic structure of bulk Fe$_4$N were performed using linearized augmented plane wave [12,13]. Also, First-principles calculations were employed to study the structural and magnetic properties of fully relaxed cubic Fe$_4$N(0 0 1) surfaces with both Fe$_2$- and Fe$_2$N-termination [5]. Experimentally, the (1 0 0) face of magnetic Fe$_4$N shows two different structures, which are studied here with scanning tunnelling microscope and low energy ion scattering as the main tools [14] and Mössbauer resonance studies on Mn-substituted Fe$_4$N show that manganese occupies statistically both iron sites in the lattice [15].

The experimental lattice parameter is 3.793 Å; and the magnetic moment for iron atoms at Fe(I) and Fe(II) sites are (2.98 and 2.01 μ_B [16]) and (2.84 and 2.25 μ_B [17]), respectively.

The *ab initio* studies of the magnetic moment variations, of both iron sites in the of Fe$_4$N structure, versus pressure are reported [9]. For that study, they used full-potential linearized augmented plane wave method including the Perdew–Burke–Ernzerh of functional as well as generalized gradient approximation to describe the exchange-correlation potential. Also, the magnetic properties of Fe$_4$N(0 0 1) with (Fe, N) and (Fe, Fe) surfaces have been investigated by using the full-potential linearized augmented plane wave method [18].

In addition, forFe$_4$N compounds, several experimental studies [6,19,20] as well as theoretical investigations involving the mean-field dynamic equations, Hubbard-Stoner approximation and Monte Carlo calculation were reported [21–24].The kinetics of the mixed spin-1 and spin-3/2 Ising model in Fe$_4$N compound is investigated using mean-field approach [25]. The outline of this work is as follows: The *ab initio* calculations, the model and its formulations will be discussed in Sections 2 and 3, respectively. The Monte Carlo simulations is presented in Section 4 whereas results and discussions are given in Section 5. The paper ends with a brief conclusion in Section 6.

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2. *Ab initio* calculations

We used the Full Augmented Plane Wave (FLAPW) method [9] which performs DFT calculations with the generalized gradient approximation (GGA). The Kohn-Sham equation and energy functional were evaluated consistently. For this doing, the space was divided into the interstitial and the non-overlapping muffin-tin spheres centered on the atomic sites. The basis function inside each atomic sphere consisted in linear expansion of the radial solution of a spherically potential multiplied by spherical harmonics. In the interstitial region, the wave function was taken as an expansion of plane waves and no shape approximation for the potential was introduced in this region consistently with the full potential method. The core electrons were described by atomic wave functions solved relativistically using the current spherical part. Spin polarized potential as well as the ferromagnetic state are considered. The atomic muffin-tin (MT) spheres, supposed not to overlap with each other, are taken as 1.64 and 1.85 a.u for N and Fe atoms, respectively. The gap energy, which defines the separation of the valence and core state, was chosen equal to -6.0 Ry. The largest reciprocal vector G in the charge Fourier expansion, G_{max}, was equal to 12 and the cut-off energy corresponding to the product of the muffin-tin radius and the maximum reciprocal space vector, RMT. K_{max}, was equal to 7. Inside the atomics spheres, the potential and charge density are expanded in crystal harmonics up to l_{max} = 6. Calculations are performed with 27 inequivalent k-points in the irreducible Brillouin zone. Such a value is large enough to ensure the magnetic moment. The convergence criterion was chosen to be the total energy and set at 10^{-4} eV. We used the lattice parameters reported in reference [10].

3. Theory and model

The magnetic properties of mixed spins $\sigma_{Fe(I)}$ = 1 and $S_{F(II)}$ = 3/2 ferrimagnetic Ising system as depicted in Fig. 1. The Hamiltonian of the system with a ferrimagnetic spin-3/2 and 1/2 configuration including the nearest neighbors interactions, external magnetic field and the crystal field is given as:
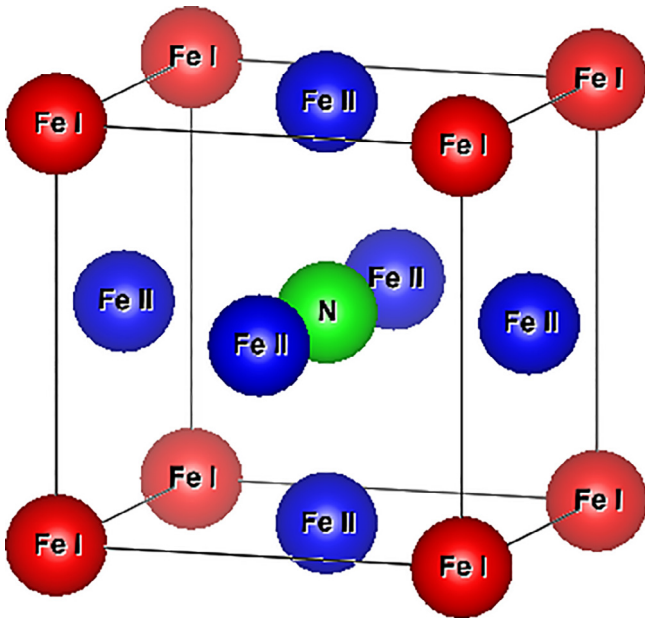

Fig. 1. Crystal structure of Fe$_4$N.

$$H = -J\sum_{\langle i,j \rangle}\sigma_i S_j - \Delta\left(\sum_i \sigma_i^2 + \sum_j S_j^2\right) - h\left(\sum_i \sigma_i + \sum_j S_j\right) \quad (1)$$

where $\langle i,j \rangle$ stand for the first nearest neighbor sites (i and j). Δ represent the crystal field and h is the external magnetic field. The J is the exchange interactions between the site(σ) and site(S) such as given in Fig. 1. The spin moment of $\sigma_{Fe(I)}$ = $\pm 1;0$ and $S_{F(II)}$ = $\pm 3/2$; $\pm 1/2$. In full text $\sigma = \sigma_{Fe(I)}$ and $S = S_{Fe(II)}$.

4. Monte Carlo simulations

The magnetic properties of mixed spins $\sigma_{Fe(I)}$ = 1 and $S_{F(II)}$ = 3/2 of Ising model with Fe$_4$N compound is assumed to reside in the unit cells and the system consists of the total number of spins N = $N_{Fe(I)} + N_{Fe(II)}$ where $N_{Fe(I)}$ = 125 and $N_{Fe(II)}$ = 375. We have applied a standard sampling method to simulate the Hamiltonian given by Eq. (1). The cyclic boundary conditions on the system were imposed and were generated by sequentially traversing the lattice and making single-spin flip attempts. The flips are accepted or rejected according to a heat-bath algorithm under the Metropolis approximation. Our data were generated with 10^5 Monte Carlo steps per spin, discarding the first 10^4 Monte Carlo simulations. Starting from different initial conditions, we performed the average of each parameter and estimate the Monte Carlo simulations, averaging over several initial conditions. Our program calculates namely the following parameters:

The magnetizations of each atom of iron $\sigma_{Fe(I)}$ and $S_{F(II)}$ in Fe$_4$N structure are given by:

$$M_\sigma = \langle \frac{1}{N_{\sigma_{Fe(I)}}}\sum_i \sigma_{i_{Fe(I)}} \rangle \quad (2)$$

$$M_S = \langle \frac{1}{N_{S_{Fe(II)}}}\sum_i S_{i_{Fe(II)}} \rangle \quad (3)$$

The total magnetization of two irons I and II is given by:

$$M_{tot} = \frac{N_{\sigma_{Fe(I)}}M_\sigma + N_{S_{Fe(II)}}M_S}{N_{\sigma_{Fe(I)}} + N_{S_{Fe(II)}}} \quad (4)$$

The internal energy E per site,

$$E = \frac{1}{N_{\sigma_{Fe(I)}} + N_{S_{Fe(II)}}}\langle H \rangle \quad (5)$$

The magnetic susceptibilities of iron $\sigma_{Fe(I)}$ and $S_{F(II)}$ in Fe$_4$N compound are given by:

$$\chi_\sigma = \beta\left(\langle M_\sigma^2 \rangle - \langle M_\sigma \rangle^2\right) \quad (6)$$

$$\chi_S = \beta\left(\langle M_S^2 \rangle - \langle M_S \rangle^2\right) \quad (7)$$

where $\beta = \frac{1}{k_B T}$, T denotes the absolute temperature and k_B is the Boltzmann's constant.

The total magnetic susceptibility of the mixed system is:

$$\chi_{tot} = \frac{N_{\sigma_{Fe(I)}}\chi_\sigma + N_{S_{Fe(II)}}\chi_S}{N_{\sigma_{Fe(I)}} + N_{S_{Fe(I)}}} \quad (8)$$

5. Results and discussion

Firstly, the lattice parameter is estimated theoretically from the minimisation of the energy versus the cell volume using Flapw calculations. As seen, in Fig. 2, the obtained energy minimum takes place in vicinity of a volume corresponding to lattice parameter a estimated to a = 7.1725 a.u. (0.37943 nm). This value is in good