Effects of alloying and strain on the magnetic properties of Fe\textsubscript{16}N\textsubscript{2}

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(Received 9 April 2013; published 8 July 2013)

The electronic structure and magnetic properties of pure and doped Fe\textsubscript{16}N\textsubscript{2} systems have been studied in the local-density (LDA) and quasiparticle self-consistent GW approximations. The GW magnetic moment of pure Fe\textsubscript{16}N\textsubscript{2} is somewhat larger compared to LDA but not anomalously large. The effects of doping on magnetic moment and exchange coupling were analyzed using the coherent potential approximation. Our lowest estimate of the Curie temperature in pure Fe\textsubscript{16}N\textsubscript{2} is significantly higher than the measured value, which we mainly attribute to the quality of available samples and the interpretation of experimental results. We found that different Fe sites contribute very differently to the magnetocrystalline anisotropy energy (MAE), which offers a way to increase the MAE by small site-specific doping of Co or Ti for Fe. The MAE also increases under tetragonal strain.

DOI: 10.1103/PhysRevB.88.024404 PACS number(s): 75.50.Ww, 75.50.Bb, 71.20.Be, 75.30.Cr

I. INTRODUCTION

Ordered nitrogen martensite α′′-Fe\textsubscript{16}N\textsubscript{2} was first synthesized in bulk form by quenching of the cubic nitrogen austenite γ-FeN with a subsequent annealing. 1 Quenching initially produces disordered α′-FeN, which then orders during low-temperature annealing to produce α′′-Fe\textsubscript{16}N\textsubscript{2}. The latter is a metastable phase with a distorted body-centered tetragonal structure, which decomposes into α-Fe and Fe\textsubscript{4}N near 500 K.

Interest in α′′-Fe\textsubscript{16}N\textsubscript{2} was revived much later when it was synthesized in thin film form and a very large value (∼3\textsubscript{M\textsubscript{B}}) for the average Fe magnetic moment was reported. 2 This result was not independently confirmed until twenty years later. 3 Owing to the rapid development of the magnetic recording technologies, this confirmation inspired numerous studies of thin-film samples. However, the existence of the “giant” Fe moment remains controversial as many researchers did not reproduce these findings, while others confirmed them. 4–6 The lack of consistent and reproducible experimental results may be attributed to the difficulties associated with the preparation of single-crystal Fe\textsubscript{16}N\textsubscript{2} and stabilization of nitrogen, as well as with the accurate measurement of the magnetization in multiphase Fe nitride samples. This issue has recently attracted additional interest due to the search for new permanent magnetic materials without rare-earth elements. 7 A new way to prepare single-phase Fe\textsubscript{16}N\textsubscript{2} powder was recently reported, along with evidence of high maximum energy product (B\textsubscript{H\textsubscript{max}}). 8

Most theoretical studies of the magnetization of α′′-Fe\textsubscript{16}N\textsubscript{2} were performed using the local density approximation, generalized gradient approximation (GGA), or LDA + U, though recently Sims et al. 9 applied a hybrid functional and the GW approximation to this material. In LDA or GGA the magnetic moment of Fe\textsubscript{16}N\textsubscript{2} is only slightly enhanced compared to elemental Fe. Lai et al. 10 included electronic correlations within LDA + U and found an enhanced magnetization M = 2.85\textsubscript{M\textsubscript{B}}/Fe. Wang et al. 11–13 identified a localized Fe state coexisting with the itinerant states in x-ray magnetic circular dichroism (XMCD) measurements. They introduced a specific charge transfer between different Fe sites and obtained a large M in LDA + U. However, the choice of the correlated orbitals and the associated value of the Hubbard U parameter is not well defined for metallic systems. For example, the on-site interaction parameters obtained by Sims et al. 9 using the constrained random phase approximation (RPA) differ substantially from those proposed by Wang et al. The quasiparticle self-consistent GW approximation (QSGW) 14,15 is more reliable and provides a more satisfactory way to determine the ground state density and magnetic moment. In the present paper we apply this method to Fe\textsubscript{16}N\textsubscript{2}.

Studies of exchange interaction, Curie temperature (T\textsubscript{C}), and MAE of Fe\textsubscript{16}N\textsubscript{2} met with additional difficulties. In particular, measurements of T\textsubscript{C} are hampered by the decomposition of the metastable Fe\textsubscript{16}N\textsubscript{2} into Fe\textsubscript{4}N and Fe, which was reported to occur above 200 °C, 9 in the 230–300 °C range, 2 or at 400 °C. 3 Sugita et al. 16 extrapolated their data to estimate T\textsubscript{C} at 540 °C. 9 Thermal stability of Fe\textsubscript{16}N\textsubscript{2} was reported to increase with addition of Co and Ti 16,17 (up to 700 °C in the Ti case). However, no experimental information is presently available about the T\textsubscript{C} of Co or Ti-doped Fe\textsubscript{16}N\textsubscript{2}, of any other Fe\textsubscript{16}N\textsubscript{2} samples stabilized at high temperatures. To the best of our knowledge, there have been no theoretical studies of the exchange interaction and Curie temperature in Fe\textsubscript{16}N\textsubscript{2}. Systematic studies of the effects of doping on M and T\textsubscript{C} in Fe\textsubscript{16}N\textsubscript{2} also appear to be lacking.

As for the MAE, only a few experimental values were reported, and they are varied and inconclusive. For example, Sugita et al. 3 obtained an in-plane MAE, while Takahashi 18 found a large uniaxial MAE. The only available theoretical calculations of MAE used an empirical tight binding (TB) approximation. 19 In this paper we study the magnetization, Curie temperature, and magnetocrystalline anisotropy energy of pure and doped Fe\textsubscript{16}N\textsubscript{2} using several well-tested electronic structure techniques and suggest possible routes for improving its properties for permanent magnet applications.
II. COMPUTATIONAL METHODS

Most LDA, GGA, and QSGW calculations were performed using a full-potential generalization of the standard linear muffin-tin orbital (LMTO) basis set. This scheme employs generalized Hankel functions as the envelope functions. Calculations of MAE were also performed using the recently-developed mixed-basis full-potential method, which employs a combination of augmented plane waves and generalized muffin-tin orbitals to represent the wave functions. The results of a traditional non-self-consistent application of the GW approximation depend on the noninteracting Hamiltonian generating the self-energy. This issue can be particularly problematic for metals. In contrast, the QSGW method does not suffer from this limitation: It is more reliable than the standard GW. This method gives quasiparticle energies, spin moments, dielectric functions, and a host of other properties in good agreement with experiments for a wide range of materials, including correlated ones such as NiO. The details of QSGW implementation and applications can be found elsewhere.

The pair exchange parameters were obtained using two linear response approaches:

(i) Static linear-response approach implemented within the atomic sphere approximation (ASA) to the Green’s function (GF) LMTO method. In addition to making a spherical approximation for the potential, this method makes the long-wave approximation (LWA), so that the pair exchange parameter is proportional to the corresponding spin susceptibility $\chi_{ij}$. The exchange parameters $A_{ij}$ obtained in this method are related to the parameters of the classical Heisenberg model

$$ H = - \sum_{ij} J_{ij} S_i \cdot S_j, \quad (1) $$

by the following renormalization for ferromagnetic (FM) and antiferromagnetic (AFM) cases:

$$ J_{ij} = \frac{A_{ij}}{S_i S_j} = \frac{4 A_{ij}}{m_i m_j} \begin{cases} 4 A_{ij} / m_i m_j & \text{FM} \\ -4 A_{ij} / m_i m_j & \text{AFM} \end{cases} \quad (2) $$

where $m_i$ is the magnetic moment on site $i$. With this renormalization all results obtained for the Heisenberg model Eq. (1) can be used directly. Thus, parameters $A_{ij}$ always stabilize (destabilize) the given magnetic configuration and can be treated as stability parameters. Curie temperature in the spin classical mean field approximation (MFA) is simply $T_C = 2/3 \sum_{ij} A_{ij}$.

(ii) Dynamical linear response approach with the bare susceptibility $\chi(q,\omega)$ calculated in the full product basis set representation using the LDA or QSGW electronic structure. The results are then projected onto the functions representing local spin densities on each magnetic site, which gives a matrix $\chi_{ij}(q,\omega)$ in basis site indices. This projection corresponds to the rigid spin approximation. The inversion of this matrix with a subsequent Fourier transform provides the real-space representation of the inverse susceptibility representing the effective pair exchange parameters:

$$ J_{ij} = \lim_{\omega \to 0} \frac{1}{\Omega_2} \int dq \left[ \chi(q,\omega) \right]^{-1} e^{iqR_{ij}}. \quad (3) $$

$T_C$ is calculated both in the MFA and the RPA-Tiablikov approximations. The actual $T_C$ may usually be expected to lie between the results of these two approximations.

To address the effects of doping, we used our implementation of the coherent potential approximation (CPA) within the TB-LMTO code, which follows the formulation of Turek et al. and Kudrnovský et al. A coherently interactor matrix $\Omega_i$ is introduced for each basis site $i$ treated within CPA. At self-consistency $g_{ii} = (P_i - \Omega_i)^{-1}$, where $P_i$ is the coherent potential matrix for site $i$, and $g_{ii}$ is the on-site block of the average auxiliary LMTO GF matrix $g = (P - \Omega)^{-1}$. This on-site block is extracted from the Brillouin zone integral of $g(k)$. The conditionally averaged GF at site $i$ occupied by component $a$ is $g_{a}^{ii} = (P_a - \Omega)^{-1}$, and the CPA self-consistency condition can be written as $g_{ii} = \sum_a c_a^i g_{a}^{ii}$; here $c_a^i$ is the concentration of component $a$ at site $i$. Using this equation, at the beginning of each iteration the stored matrices $\Omega_i$ are used to obtain an initial approximation to $P_i$. In turn, $P_i$ is used in the calculation of $g_{ii}$ by a Brillouin zone integral. The next approximation for $\Omega_i$ is obtained from $\Omega_i = P_i - g_{ii}$. These output matrices are then linearly mixed with the input $\Omega_i$ matrices at the end of the iteration.

We found that the mixing coefficient of 0.4 for $\Omega_i$ works well in most cases. For fastest overall convergence, we found that it is usually desirable to iterate CPA iterations until the $\Omega_i$ matrices are converged to a small tolerance, and only then perform the charge iteration. The convergence of $\Omega$ is done separately for each point on the complex contour to the same tolerance. With this procedure, fairly aggressive Broyden mixing can be used for LMTO charge moments. CPA convergence at each charge iteration usually takes 10–50 iterations depending on the imaginary part of the energy and the selected tolerance. At the beginning of the calculation, the $\Omega_i$ matrices are set to zero; afterwards they are stored and reused for subsequent iterations. In order to avoid unphysical symmetry-breaking CPA solutions (which otherwise often appear), the coherent potentials and the $k$-integrated average auxiliary GF are explicitly symmetrized using the full space group of the crystal. As a result, the use of CPA does not impose any restrictions on the symmetry of the crystal. Calculations reported here were performed without using charge screening corrections for the Madelung potentials and total energy.

The effective exchange coupling in CPA is calculated as

$$ A_0 (c) = c A_X (c) + (1 - c) A_Y (c), \quad (4) $$

where the component-specific $A_0(c)$ are obtained using the conditionally averaged GF and the formalism of Ref. 31.

For MAE calculations the self-consistent solutions are found including spin-orbit coupling (SOC) terms of order $1/c^2$. The MAE is defined below as $K = E_{100} - E_{001}$, where $E_{001}$ and $E_{100}$ are the total energies for the magnetization oriented along the [001] and [100] directions, respectively. Positive (negative) $K$ corresponds to uniaxial (planar) anisotropy. We used a $24 \times 24 \times 24$ k-point mesh for MAE calculations to ensure sufficient convergence; MAE changed by less than 2% when a denser $32 \times 32 \times 32$ mesh was employed. All calculations
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except QSGW were performed with both LDA and GGA exchange-correlation potentials for comparison.

III. RESULTS AND DISCUSSION

The crystal structure of Fe16N2 is body-center-tetragonal (bct) with space group I4/mmm(140). It may be viewed as a distorted 2 × 2 × 2 bct-Fe superlattice with c/a = 1.1. Crystal structure of Fe16N2 was first identified by Jack. Here we use lattice constants a = b = 5.72 Å c = 6.29 Å and atomic position parameters zFe = 0.3125 and xN = 0.25 from Jack’s work as the experimental structure (Fig. 1).

We also relaxed the structure by minimizing the total energy in LDA and obtained zFe = 0.293 and xN = 0.242, nearly identical to that obtained by Sawada et al. The primitive cell contains one N and eight Fe atoms divided into three groups indicated by Wyckoff sites: two 4e, four 8h, and two 4d sites (correspondingly first, second, and third neighbors to N).

A. Magnetic moments and electronic structure

Table I shows the atomic spin moment mi at the three Fe sites and magnetization M (orbital magnetic moment is small, hereafter we only include spin magnetization in M). Within the LDA, M = 2.38μB/Fe was obtained, in good agreement with previously reported calculations. The enhancement relative to elemental bcc-Fe has been attributed to the size effect. QSGW gives M = 2.59μB/Fe, about 9% larger than LDA. While it is known that GW enhances spin moments relative to LDA, to ensure the genuineness of this enhancement of moment, we also carried out the QSGW calculation of bcc-Fe and found that QSGW enhance the LDA magnetic moment in elemental Fe by only ~2% (2.20→2.24μB).

B. Exchange coupling and Curie temperature

The Heisenberg model parameters Jij using LDA-ASA in the LWA, FP-LDA, and FP-QSGW are plotted in Fig. 3 and tabulated in Table II. The two LDA results are quite similar, confirming that the ASA and the LWA form a reasonable approximation. QSGW shows some differences, particularly reducing those interactions which are AFM.

The structure of Jij is much more complicated in Fe16N2 than in elemental bcc-Fe. The vectors connecting the nearest 8h–4e or 8h–4d sites are nearly along the [111] direction;
the magnetic interactions between them are generally large. In comparison, the largest interaction is also between the nearest sites connected by vectors along the [111] direction in bcc-Fe. $J_{ij}$ between $8h-4e$ sites is very anisotropic due to the distortion of the lattice around N atom. Similar anisotropy was also found for the in-plane couplings on the $8h$ lattice. Interestingly, a large coupling ($J_{ij} = 23.75$ meV in the FP-LDA calculation) occurs between two $4e$ atoms along [001]. This pair has been squeezed together by neighboring N atoms. Since exchange coupling is sensitive to the distance between those two sites, we also examined this exchange parameter for the experimental atom coordinates, for which the bond length of the $4e-4e$ pair shrinks from 2.60 to 2.36 Å, and found that this $J_{ij}$ increases from 23.75 to 36.55 meV, indicating significant exchange-striction effect. The second nearest $4e-4e$ coupling (two Fe atoms with a N atom between them along the (110) direction) is 14.2 meV in FP and 4.18 meV in ASA. The relatively large disagreement may be a consequence of the shape approximation used in ASA, considering the presence of N atom and strong lattice distortion around this pair of atoms.

The calculated magnetic interactions between different types of atoms have very different spatial dependence and correspondent asymptotic behavior. To demonstrate it explicitly on Fig. 3(d) we show $J_{ij}$ scaled with $(R_{ij}/a)^2$. With this renormalization $J_{ij}$ between atoms on $4e$ positions (smaller moments) are approximately constant in this range of distances (long-ranged interaction), while $J_{ij}$ between Fe atoms on $4d$ sites (with the largest moments) decay much faster (short-ranged interaction), corresponding to more localized moment behavior. Such very different asymptotic behavior suggests that these localized and delocalized interactions correspond to Fermi surface shapes with different dimensionalities.

$T_C$ is calculated from the exchange parameters and tabulated in Table II. RPA values are about 30% smaller than the MFA ones. Typically experimental values fall between the MFA and RPA results, with the RPA being closer to the experiment in normal three dimensional systems. In the present case, however, the reported extrapolated experimental estimate...
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| $|R_{ij}|/a$ | direction | ASA | FP | GW |
|------------|-----------|-----|----|----|
| 4e–4e      | 0.454     | 0   | 0  | −0.455 | 19.37 | 23.75 | 16.75 |
|            | 0.645     | 0   | 0  | 0.645  | 4.18  | 14.20 | 3.76  |
|            | 0.713     | −0.5| −0.5| 0.095  | 3.24  | 2.33  | 1.88  |
|            | 0.895     | −0.5| −0.5| −0.550 | −1.92 | −2.91 | −1.44 |
| 8h–8h      | 0.483     | 0   | −0.484| 0   | 2.00  | −2.55 | 1.69  |
|            | 0.516     | 0   | 0.516 | 0.49  | 1.49  | 1.37  | 4.84  |
|            | 0.550     | 0.016| 0.016| 0.550 | 5.74  | 4.60  | 4.67  |
|            | 0.684     | −0.484| −0.484| 0   | 7.00  | 11.07 | 11.80 |
|            | 0.707     | 0.516| −0.484| 0   | 0.20  | −0.68 | 0.13  |
|            | 0.730     | 0.516| 0.516 | 0.39  | −0.01 | −2.50 |
| 4d–4d      | 0.550     | 0   | 0   | 0.550 | 2.76  | 1.54  | 3.67  |
|            | 0.707     | −0.5| 0.5  | 1.15  | 1.44  | 0.78  |
|            | 0.895     | −0.5| −0.5| −0.550 | −2.37 | −4.49 | −1.90 |
| 4e–8h      | 0.430     | −0.258| −0.258| −0.227 | 20.55 | 20.00 | 14.08 |
|            | 0.470     | 0.242| 0.242 | 0.323 | 4.20  | 5.88  | 5.88  |
| 8h–4d      | 0.448     | 0.258| −0.242| 0.275 | 15.73 | 22.30 | 16.18 |
|            | 0.827     | −0.242| −0.742| −0.275 | 0.58  | 0.60  | 0.64  |
| 4d–4e      | 0.502     | −0.5| 0   | 0.048 | 1.56  | 1.85  | 4.72  |
|            | 0.708     | 0   | −0.5| −0.502 | 0.49  | −0.23 | −0.21 |

$T_C = 810$ K is smaller than both the MFA and RPA values, and smaller than the one in bcc-Fe.24 This is rather unusual. In bcc-Fe, we estimate $T_C$ to be $\sim 1300$ K and $\sim 900$ K in the MFA and RPA, respectively, which bracket the experimental value of 1023 K (as is typical). Contrary to experiment, our calculated $T_C$ for Fe$_{16}$N$_2$ is higher than for bcc Fe in all our estimations. Such disagreement between theory and experiment is much larger in Fe$_{16}$N$_2$ than other Fe-rich phases. The disagreement may originate from approximations to the theory (absence of spin quantum effects, temperature dependence of exchange, among others) that uniquely affect Fe$_{16}$N$_2$, or alternatively from the experimental interpretation of the measured $T_C$. We cannot completely discount the former possibility, but for this local-moment system, it is unlikely that the most serious errors originate in density functional theory that generate exchange parameters. For instance, parameters generated from QSGW also do not improve agreement with the experiment; indeed this increases the discrepancy. On the other hand, as noted in the introduction Fe$_{16}$N$_2$ decomposes with increasing $T$; moreover, there is a transition to the (nonmagnetic) $\gamma$ phase at 1185 K. Since the measured $M(T)$ is not a measurement of the single-phase material, it is still unknown what is the experimental value for the $T_C$ in a single-phase Fe$_{16}$N$_2$. Unfortunately, disentangling the structural and magnetic degrees of freedom is very difficult, experimentally. Finally, if $M$ increases in Fe$_{16}$N$_2$, as is observed and predicted, $T_C$ should increase. Thus we conclude that $T_C$ in high quality samples of pure Fe$_{16}$N$_2$ is probably larger than what has been reported so far, and larger than in pure bcc-Fe.

Let us now discuss the influence on $T_C$ when other atoms substitute for Fe or N. The CPA is an elegant, single-site ab initio approach to study substitutional alloys. We have implemented the CPA, including a MFA estimate for $T_C$, within the ASA. As we have seen by comparing exchange interactions in the ASA to those without this approximation, the ASA does not seem to be a serious approximation to the LDA in this material.

Figure 4 shows the $M$ and and the normalized effective exchange (or MFA estimation of $T_C$ in units of pure Fe$_{16}$N$_2$)

\[ \frac{M}{\mu_B/\text{Atom}} \]

\[ x \]

\[ \frac{\text{Normalized exchange}}{\text{Co, Mn, B, C, P, Al, Al}} \]

\[ 0.0 \]

\[ 0.1 \]

\[ 0.2 \]

\[ 0.3 \]

\[ 0.4 \]

\[ 0.5 \]

\[ 0.6 \]

\[ 0.7 \]

\[ 0.8 \]

\[ 0.9 \]

\[ 1.0 \]

\[ x \]

\[ 0.0 \]

\[ 0.1 \]

\[ 0.2 \]

\[ 0.3 \]

\[ 0.4 \]

\[ 0.5 \]

\[ 0.6 \]

\[ 0.7 \]

\[ 0.8 \]

\[ 0.9 \]

\[ 1.0 \]

\[ x \]

\[ 0.0 \]

\[ 0.1 \]

\[ 0.2 \]

\[ 0.3 \]

\[ 0.4 \]

\[ 0.5 \]

\[ 0.6 \]

\[ 0.7 \]

\[ 0.8 \]

\[ 0.9 \]

\[ 1.0 \]

\[ x \]

\[ 0.0 \]

\[ 0.1 \]

\[ 0.2 \]

\[ 0.3 \]

\[ 0.4 \]

\[ 0.5 \]

\[ 0.6 \]

\[ 0.7 \]

\[ 0.8 \]

\[ 0.9 \]

\[ 1.0 \]

\[ x \]

\[ 0.0 \]

\[ 0.1 \]

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\[ 0.9 \]

\[ 1.0 \]

\[ x \]

\[ 0.0 \]

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\[ 0.9 \]

\[ 1.0 \]

\[ x \]

\[ 0.0 \]

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\[ 0.5 \]

\[ 0.6 \]

\[ 0.7 \]

\[ 0.8 \]

\[ 0.9 \]

\[ 1.0 \]

FIG. 4. (Color online) Spin magnetization $M$ (a) and normalized exchange $J_{ij}/J_0(\text{Fe}_{16}\text{N}_2)$ (with respect to pure $\text{Fe}_{16}\text{N}_2$) (b) as functions of doping concentration in $\text{Fe}_{16}\text{N}_2$. The concentration $x$ of doping element $T$ is defined as $(\text{Fe}_{1-x}\text{~T}_x)\text{~N}_2$ with Fe site doping ($T = \text{Co, Mn}$); and $\text{Fe}_{16}(\text{~N}_1-x\text{~T}_x)\text{~N}_2$ with N site doping ($T = \text{B, C, P, and Al}$).
TABLE III. Component-resolved atomic spin moments $m_i$ (the atomic spin moment of substitutional component are given in parentheses), magnetization $M$, and exchanges $J_0$ in Co- and Mn-doped Fe$_{16}$N$_2$ calculated within ASA-GF.

| Substituent | $x$ | $4e$ | $8h$ | $4d$ | $M(\mu_B/\text{atom})$ | $J_0(\text{meV})$ |
|-------------|-----|------|------|------|------------------------|------------------|
| Co          |     | 0.00 | 2.10 (1.44) | 2.41 (1.68) | 2.99 (2.11) | 2.47 | 12.95 (11.37) |
|             |     | 0.10 | 2.09 (1.34) | 2.43 (1.64) | 3.01 (2.09) | 2.40 | 11.97 (9.62)  |
|             |     | 0.20 | 2.08 (1.27) | 2.45 (1.62) | 3.02 (2.08) | 2.32 | 11.24 (8.47)  |
| Mn          |     | 0.00 | 2.10 (1.88) | 2.41 (2.25) | 2.99 (3.23) | 2.47 | 12.96 (7.05)  |
|             |     | 0.10 | 2.07 (1.75) | 2.35 (2.04) | 2.96 (3.03) | 2.40 | 12.03 (5.64)  |
|             |     | 0.20 | 2.06 (1.64) | 2.30 (1.85) | 2.93 (2.90) | 2.32 | 11.15 (4.41)  |

FIG. 5. (Color online) Densities of state of substitutional component in random alloy (Fe$_{1-x}$Co$_x$)$_{16}$N$_2$ (a) and (Fe$_{1-x}$Mn$_x$)$_{16}$N$_2$ (b).

with doping by different elements. Both Co and Mn doping cause $T_C$ to decrease. On the other hand, with N site being doped with B, C, P, or Al elements, $T_C$ and $M$ change slightly and the Fermi surface character is barely affected.

As shown in Fig. 4, Co or Mn-doped Fe$_{16}$N$_2$ decrease moment and exchange coupling. We neglected the possible site preference effect in this calculation, and doped all three Fe sites with equal probability. Table III shows the magnetic moment and $J_0$ parameters of Fe and substitutional components on all three different Fe sites. It indicates an opportunity to increase the Fe moments on Co doping and slightly increase with Co doping. With Co doping, carried out the FP calculation of Fe$_7$CoN, with one out of eight Fe atoms being replaced by a Co atom and confirmed that the magnetization decreases, especially when Co replaces the Fe on the 4e site. This is consistent with the CPA results. Mn substituents have larger magnetic moments than Co substituents. However, Mn doping decreases moments on Fe sites. Overall, the dependence of the total magnetic moments on substituent concentration are almost exactly the same with Co and Mn doping. Another interesting observation is that magnetic moments of both substituents decrease with increasing of doping concentration. This can be explained by the partial density of states shown in Fig. 5. The magnetic moment of Co slightly decreases with increasing of doping concentration. As shown in Fig. 5, the unoccupied DOS peak right above the Fermi energy ($E_F$) in the minority spin channel moves toward it. More electrons fill in the minority channel and decrease the magnetic moment as doping increases. With Mn doping, on the other hand, the peak in the majority channel right below $E_F$ becomes less pronounced. It shifts toward $E_F$ and decreases the magnetic moment of Mn component. For the Fe component DOS, there is no peak structure near the $E_F$, and magnetic moment is much less sensitive to the substitutional concentration.

C. Magnetic anisotropy

Values of MAE from previous works are summarized in Table IV. Results of present works are shown in Table V. All calculations are carried out within LDA unless GGA is specified. For the pure Fe$_{16}$N$_2$, both experimental and optimized structures are investigated. Note that doping and SOC lower the symmetry, and the degeneracy of $l$ varied.

Within LDA, a uniaxial magnetic anisotropy $K = 144 \times 10^5$ erg/cm$^3$ was obtained with experimental atomic coordinates. Structural optimization gives a smaller MAE with $K = 103 \times 10^5$ erg/cm$^3$. GGA gives smaller MAE than LDA. It is usually nontrivial to analyze the origin or site dependence of magnetic anisotropy. Below we define the atomic magnetic

TABLE IV. Previous works on magnetic anisotropy in Fe$_{16}$N$_2$.

| Method      | $K$ (10^5 erg/cm$^3$) | Easy axis | Ref. |
|-------------|-----------------------|-----------|------|
| Exp.        | Sugita et al. 4.8     | [001]     | 3    |
|             | Takahashi et al. 200   | [001]     | 18   |
|             | Takahashi et al. 97    | [001]     | 19   |
|             | Kita et al. 44        | [001]     | 36   |
|             | Ji et al. 100         | [001]     | 37   |
|             | Uchida et al. 140     | [001]     | 19   |

aValue of $(K_1 + K_2)$.

bMeasured in partial-ordering Fe$_{16}$N$_2$; author claimed MAE should be much higher for the single-phase sample.

cTight binding approximation.
TABLE V. The MAE $K$, on-site orbital magnetic moment $l$, and the AMAE $\Delta$ with different spin quantization axis direction in pure, Co-doped, and Ti-doped Fe$_{16}$N$_2$. Spin quantization axis direction $e$ are along [001], [100], and [110] directions, respectively. With the spin along [100] and [110], $\Delta$ and $K$ values (with respect to [001] direction) directions are given. To estimate $\Delta$, $\xi_i = 50,70$ meV had been used for Fe and Co atoms, respectively.

| e     | $\mu_N$ | $10^3 \text{meV}$ | $l(10^{-1} \mu_B)$ | $\Delta$ |
|-------|---------|-------------------|-------------------|---------|
|       |         |                   | 4e               | 8h      | 4d    |       |
|       |         |                   |      |       |       |       |
| Exp.  | 001     | 116               | 144             | 54      | 45    | 71    |
|       | 100     | 116               | 144             | 35      | 49    | 64    |
|       | 110     | 116               | 144             | 36      | 58.39 | 64    |
| Exp.  | 001     |                   | 52              | 44      | 68    |
|       |         |                   | 36              | 48      | 61    | 110   |
| GGA   | 100     | 105               | 131             | 36      | 57.39 | 61    |
|       | 110     | 105               | 131             | 36      | 57.39 | 61    |
| Theo. | 001     |                   | 62              | 46      | 67    |
|       |         |                   | 39              | 50      | 63    | 137   |
|       | 100     | 84                | 103             | 39      | 58.41 | 63    |
|       | 110     | 84                | 103             | 39      | 58.41 | 63    |
| Theo. | 001     |                   | 56              | 43      | 62    |
|       |         |                   | 38              | 47      | 58    |
| GGA   | 100     | 52                | 65              | 38      | 55.40 | 58    |
|       | 110     | 52                | 65              | 38      | 55.40 | 58    |
| Fe$_7$CoN | 001  |                   | 91              | 72      | 47    | 76    |
| (4e)$^c$ | 100 | 165               | 206             | 49$^d$  | 30    | 61.64 | 337   |
|       | 110     | 165               | 206             | 49$^d$  | 30    | 61.64 | 336   |
|       |         |                   | 63              | 69$^d$  | 41.44 | 70    |
| (8h)  | 100     | 42                | 52              | 36      | 77$^d$ 46.50.47 | 67    | 123   |
|       | 110     | 16                | 20              | 40      | 90$^d$ 38.38.56 | 67    | 81    |
|       |         |                   | 63              | 51      | 120$^d$ 81 |
| (4d)  | 100     | 138               | 171             | 33.38   | 52    | 106$^d$ 70 | 271   |
|       | 110     | 138               | 171             | 36      | 62.42  | 106$^d$ 70 | 271   |
| Fe$_7$TiN | 001  |                   | 11$^d$ 63      | 40      | 69    |
| (4e)$^c$ | 100 | 127               | 158             | 10$^d$ 27 | 46    | 65.65 | 62    |
|       | 110     | 127               | 158             | 10$^d$ 27 | 55.38 | 65    | 62    |
|       |         |                   | 55              | 14$^d$ 48.48.41 | 69    |
| (8h)  | 100     | 57                | 71              | 38      | 13$^d$ 48.50.50 | 65    | 122   |
|       | 110     | 43                | 53              | 35      | 13$^d$ 41.41.62 | 68    | 83    |
|       |         |                   | 60              | 40      | 14$^d$ 69 |
| (4d)  | 100     | 102               | 127             | 38.38   | 45    | 13$^d$ 67 | 83    |
|       | 110     | 103               | 128             | 38      | 52.38  | 13$^d$ 67 | 83    |

$anisotropy energy (AMAE) \Delta_i as half of the difference of the SOC energies along different magnetic field directions, that is in turn defined by the corresponding anisotropy of orbital magnetic moments:

$$\sum \Delta_i(\theta = 90^\circ) = \sum \xi_i m_i (l_i^{(01)} - l_i^{(10)}) / 4, \quad (5)$$

where $\xi_i$ is a SOC parameter, while $m_i$ and $l_i$ are atomic spin and orbital magnetic moments correspondingly. The sum of $\Delta_i$ can be compared with the total MAE $K$ obtained using the total energies. This approach takes into account the SOC anisotropy and its renormalization by crystal field effects. We further assume that the spin moment has very weak anisotropy and the main change in $\xi \mathbf{L} \cdot \mathbf{S}$ product comes from the change of orbital magnetic moment (see also Ref. 39). This is the case for Fe$_{16}$N$_2$ (see Table V). For the pure Fe$_{16}$N$_2$, when the spin quantization axis rotates from [100] to [001], $l$ decreases on 8h sites, but increases on 4d and 4e. While $l$ depends on site, the total $l$ increases during this rotation, which agrees with the predicted uniaxial character of MAE. When the spin quantization axis points along [110], SOC lowers the symmetry, and splits the four equivalent 8h sites into two pairs with $l$ increasing on one pair and decreasing on the other.

As shown in Fig. 6, there is a strong correlation between $K$ and $\Delta$ (with respect to magnetic field along [001] direction, and atomic value $\xi_i = 50$ meV is used for all three different Fe sites for simplicity), where $i$ indicates all atomic sites. Obviously, the atomic 8h sites make negative contributions to the desired uniaxial MAE, while 4e and 4d sites make positive contributions. Thus, one may hope that doping on 8h site, thus eliminating negative (in-plane) contribution to MAE, may improve the uniaxial MAE.
FIG. 6. (Color online) AMAE on 4e, 8h, 4d Fe sites (Δ) and their average value (Δ̄) and the LDA total energy relative to the ground state (E_LDA) as functions of spin quantization axis rotation.

Since Co and Ti doping had been reported to stabilize the Fe_{16}N_{2} phase, it seems logical to study the prediction above using these dopants. We replace one out of eight Fe atoms in the primitive cell with a Co or Ti atom and relax the atomic positions within LDA and then study the anisotropy. If we replace one of four 8h atoms with a Co atom, we find that the Co atom has a larger $l$ than any other Fe sites, however, it does not eliminate the negative contribution from 8h sites. Instead, it makes $K$ smaller. Also $l$ and then $K$ along the [100] and [110] directions become more anisotropic. Surprisingly, however, with a Co atom on 4e or 8h sites, the $l$ difference between out-of-plane and in-plane cases becomes even larger on 4e and 4d sites and smaller on 8h sites. In other words, it makes the positive contribution from 4e and 4d sites stronger and the negative contribution from 8h sites smaller. As a result, calculated MAE is doubled ($K = 206 \times 10^5$ erg/cm$^3$) within LDA with doped Co being on the 4e site. A similar effect had been found with Ti doping. $K$ increases when Ti is substituted on the 4e and 4d sites and decreases when substituted on 8h. Unlike the Co doping, magnetic orbital moments of Ti atom are small and barely change with spin rotation. Generally, for the same structure, $K$ is always strongly correlated with $Δ$. The larger $Δ$ is, the larger $K$ is along that specific spin quantization direction. However, this correlation may no longer hold true with different structures. For example, in Fe$_{7}$TiN, $Δ$ is the largest with Ti doped on 8h site, however $K$ is much smaller than those with Ti doped on 4e and 4d sites.

Tetragonality is another factor which may affect the anisotropy in a significant way. Let us compare Fe$_{16}$N$_{2}$ with bct-Fe, where even for $c/a = 1.1$ (the $c/a$ ratio for Fe$_{16}$N$_{2}$) MAE is still rather tiny. In Fig. 7 the calculated MAE in Fe$_{16}$N$_{2}$ is shown as a function of $c/a$ in Fe$_{16}$N$_{2}$. This dependence is much stronger than in bct-Fe and we assume that MAE mostly originates from distortion of Fe sublattice around the N atom and the Fe-N hybridization. Experimentally, the large tetragonality can be obtained in films, where it can be tuned by the nitrogen concentration. However, according to our results above, doping bulk Fe$_{16}$N$_{2}$ in a way that increases $c/a$ may lead to MAE increase. The MAE and AMAE are well correlated as shown in Fig. 7. Within this $c/a$ range, the spin magnetization varies within 2%; it is not likely to be responsible for the MAE increase. On the other hand the anisotropy of orbital moment strongly correlates with MAE and is probably responsible for its enhancement as tetragonality increases. Orbital magnetic moments can be measured more precisely, so new XMCD types of experiments for this system are desirable.

IV. CONCLUSION

In this study of intrinsic magnetic properties of Fe$_{16}$N$_{2}$, our LDA results for magnetization agree with previously reported values while QSGW increases magnetization by 9%. This enhancement is largely due to on-site exchange splitting between the $d$ minority and majority states—an effect seen in many other magnetic systems such as NiO and MnAs. In Fe$_{16}$N$_{2}$ in particular, we find no evidence of localized states or correlations not already found in Fe. Taking together all of those factors we expect that the QSGW prediction for $M$ is not far from what should be observed in the ideal Fe$_{16}$N$_{2}$ compound. We find no evidence of charge transfer between different Fe sites as proposed elsewhere. Thus, the theoretical magnetization predicted for Fe$_{16}$N$_{2}$ does not exceed the maximum on the Slater-Pauling curve ($\sim 2.5\mu_B$) and is smaller than the corresponding maximum of magnetization observed in Fe-Co alloys, which may still be considered as a record holder among $d$ atomic magnets.

LDA calculations predict $T_C$ significantly larger than the experimental value; the QSGW result is even larger. We assume that Fe$_{16}$N$_{2}$ will have a higher $T_C$ if one can find
a way to stabilize it. Effects of doping by various elements on $M$ and $T_C$ were studied in the LMTO-CPA approximation. Various dopants affect $M$ and $T_C$ differently; but unfortunately no dopants we considered enhanced $M$ or $T_C$.

A uniaxial magnetocrystalline anisotropy $K = 103 \times 10^5$ erg/cm$^3$ was calculated in the LDA with the theoretically optimized crystal structure. $K$ is strongly correlated with the atomic magnetic anisotropy energy due to spin-orbit coupling only. We found it can be increased by increasing $e/a$ or by adding a small amount of Co or Ti atoms on 4e or 4d sites.

Fe$_{16}$N$_2$ is one of the more promising candidates for permanent magnets that do not contain rare-earth elements. We believe that there is room for improvement and we studied several possible routes to obtain better properties. A further investigation on increasing the thermal stability and/or changing crystal structure tetragonality is desired.

ACKNOWLEDGMENTS

This work was supported by the US Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), under its Vehicle Technologies Program, through the Ames Laboratory. Ames Laboratory is operated by Iowa State University under contract DE-AC02-07CH11358. K.D.B. acknowledges support from NSF through Grant Nos. DMR-1005642, EPS-1010674 (Nebraska EPSCoR), and DMR-0820521 (Nebraska MRSEC).

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