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Electronic structure, vibronic properties and enhanced magnetic anisotropy induced by tetragonal symmetry in ternary iron nitrides: A first-principles study

Z.R. Li, W.B. Mi*, H.L. Bai*

Tianjin Key laboratory of Low Dimensional Materials Physics and Preparation Technology, School of Science, Tianjin University, Tianjin 300354, China

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ABSTRACT

Electronic structure, vibronic properties and magnetic anisotropy energy of ternary iron nitrides M_x Fe_{4-x}N (x = 1, 3) with 3*d* transition metal *M* are systematically studied using first-principles calculations. Different substitution elements and sites result in different lattice structure and exchange coupling. We found that the magnetic anisotropy energy in *M*Fe₃N and M_3 FeN with tetragonal structure greatly improves, which is much larger than cubic Fe₄N. Enhanced magnetic anisotropy is closely related to the tetragonal structure transition, and this result will help to further understand the mechanism of low-temperature anisotropic magnetoresistance of Fe₄N. In consideration of the magnetism and stability, the implantation of Mn, Co, and Ni is more valuable in all of substitutions. MnFe₃N energetically favors the tetragonal structure and has a perpendicular magnetic anisotropy, while Mn₃FeN prefers to cubic structure and the total magnetic moment is enhanced. Co shows no strong preference for either lattice site but negative spin polarization appears, whereas Ni₃FeN clearly favors tetragonal structure and possesses perpendicular magnetic anisotropy. Our results lay the groundwork for developing the application of Fe₄N in spintronic devices and can stimulate further experimental research.

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1. Introduction

Iron nitride Fe₄N has been considered as a promising material in spintronic devices owing to its excellent properties such as high magnetization, high spin polarization, wear and corrosion resistance [1–5]. 3d transition metal nitrides (Co₄N and Ni₄N) share the same antiperovskite-like structure and similar magnetic and electronic properties with Fe₄N [6-8]. In order to improve the magnetism, the substitutions of 3d transition metal atoms for Fe in Fe₄N lattice have been extensively investigated [9–16]. Theoretical calculations show that MnFe₃N with Mn substitution on the cubic corner or face-center site displays ferromagnetic or antiferromagnetic coupling. MnFe₃N structure which Mn occupies cubic corner site exhibits an enhanced magnetization [9-11]. *M*Fe₃N (*M* = Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, and Os) compounds have good ductility and are prone to shearing [13-15]. Preferential occupancy sites of MFe_3N (M = Sc, Ti, V, Cr, Mn, Co, Ni, Cu, and Zn) were determined using the space group Pm-3m or P4/mmm [16]. Co₃FeN and Ni₃FeN with three Fe atoms substituted compounds have been fabricated experimentally and their anisotropic magnetoresistance (AMR)

* Corresponding authors. E-mail addresses: miwenbo@tju.edu.cn (W.B. Mi), baihaili@tju.edu.cn (H.L. Bai). were studied [17,18]. The marked increase of AMR at low temperature in the transition metal nitrides was attributed to the tetragonal crystal field [5,17–19].

In transition metal alloys, lowering lattice symmetry such as a tetragonal distortion will lead to the enhancement of magnetic anisotropy. A strong anisotropy enhancement has been reported in the tetragonally distorted $Fe_{1-x}Co_x$ alloys and Fe-Pd magnetic shape memory alloys [20-22]. Zhao et al. have also found that the magnetic anisotropy of tetragonal Fe₁₆N₂ can be greatly improved by substituting Fe with Co [23]. But so far, most people focus on the enhancement of magnetism and mechanical properties, few attentions to magnetic anisotropy and spin polarization of MFe₃N were paid. Magnetic anisotropy and spin polarization are key properties to determine materials performance as a ferromagnetic electrode in spintronic devices. From the application point of view, perpendicular magnetic anisotropy can decline energy switching the electrode's magnetization and spin polarization decides the sign and magnitude of the tunneling magnetic resistance in magnetic tunnel junction, which are very important in magnetic random access memories [24]. Therefore, inspired by the experimental and theoretical results, the substitution of 3dtransition metal in Fe₄N is expected to produce a tetragonal struc-







ture, and then we can investigate the change of magnetic anisotropy and spin polarization of these substitutions.

In this work, the systematic investigations on the substitution sites, lattice structure, magnetism, electronic structure, magnetic anisotropy energy and dynamic stability of M_x Fe_{4-x}N (x = 1, 3) compounds were conducted by the first-principles calculations. *M*Fe₃N with *M* (M = 3d transition metal) occupying the face-center site will bring tetragonal lattice structure and the magnetic anisotropy energy enhances by two orders of magnitude. We also study the lattice structure and magnetic properties of M_3 FeN as the concentration of *M* increases. If the tetragonal M_x Fe_{4-x}N could induce a high magnetic anisotropy and retain a high negative spin polarization, it will expand the practical application of Fe₄N in spintronic devices.

2. Calculation details

The first-principles calculations of M_x Fe_{4-x}N are carried out based on density functional theory and the projector augmented wave method as implemented in the Vienna Ab Initio Simulation Package (VASP) code [25]. The generalized-gradient-approxima tion proposed by Perdew, Burke, and Ernzerhof for the exchangecorrelation energy is used [26-28]. The cutoff energy of planewave basis set is set to 500 eV. Unit cells containing five atoms are studied on a mesh of $13 \times 13 \times 13$ Monkhorst-Pack k-point grid. The space group of M_x Fe_{4-x}N is set as cubic Pm-3m of Fe₄N initially. The energy convergence criterion of the calculation is 5 \times 10^{-6} eV/atom. The cell geometry and atom positions are optimized until the forces are less than 1×10^{-3} eV/Å. The ground states of M_x Fe_{4-x}N are obtained by comparing the total energy of ferromagnetic or antiferromagnetic states. The phonon calculations are performed by the PHONOPY code based on density-functional perturbation theory with $2 \times 2 \times 2$ supercells (40 atoms) for M_x -Fe_{4-x}N [29]. The magnetic anisotropy energy (MAE) is determined from the force theorem, as the difference of the eigenvalues sums for the two magnetization directions when the spin-orbit coupling is included [30]. In transition metal systems, the MAE appears only at second and higher orders of the perturbation expansion over the spin-orbit coupling imposing stringent requirements for the computational accuracy. In order to get the reliable result, we improve the accuracy of the calculation as much as possible. A much denser $21 \times 21 \times 21$ Γ -centered *k*-point grid (9261 *k* points) in the Brillouin zone is used in the MAE calculations. The MAE is obtained by performing a fully self-consistent calculation for the collinear case and in the second step, freezing the potential charge density for different orientations of the magnetization direction and then taking the energy differences $\Delta E = E^{[001]} - E^{[100]}$, where $E^{[001]}$ and $\vec{E}^{(1\,0\,0]}$ are the energies with the magnetization in the [0 0 1] and [1 0 0] directions [20].

3. Results and discussion

The lattice structures and various occupying positions of M_x -Fe_{4-x}N are illustrated in Fig. 1. Fig. 1(b) and (c) show the two types of models for *M*Fe₃N and M_3 FeN. The Fe atom in the cubic-corner FeI site (c) or face-center FeIIB site (f) is substituted by one 3*d* metal atom to form *M*^cFe₃N or *M*^fFe₃N. In M_3 Fe^cN, all the facecenter sites are occupied by *M* atoms, while *M* atoms in M_3 Fe^fN locate at cubic-corner site and face-center FeIIA sites. The space group transforms from cubic *Pm*-3*m* to tetragonal *P*4/*mmm* for *M*^f-Fe₃N and M_3 Fe^fN, but preserves cubic *Pm*-3*m* for *M*^cFe₃N and M_3 -Fe^cN. The shape anisotropy in the tetragonal lattice structure will strengthen the MAE (discussed below).

To compare the electronic structure and magnetic properties of MFe_3N relative with Fe_4N , we first give the reference of Fe_4N . The



Fig. 1. The unit cell of M_x Fe_{4-x}N with *M* occupying the different positions of Fe₄N. (a) Fe₄N, (b) *M*Fe₃N, *M*^cFe₃N represent *M* occupying the Fel (cubic corner) site, *M*^fFe₃N represents *M* occupying the FellB (face-center) site, (c) M_3 FeN, M_3 Fe^fN represent *M* occupying the Fel and FellA sites while Fe occupying the FellB site, M_3 Fe^cN represents *M* occupying the FellA and FellB sites while Fe occupying the Fel site.

calculated lattice constant *a* = 3.793 Å of Fe₄N is close to the experimental value of 3.791 Å [31]. The total magnetic moment is 9.915 μ_B , which is in good agreement with the previous reported results [10,12,14,15,32]. The above calculated results show that our calculations are reasonable.

The lattice constants and magnetic moments of M^{c} Fe₃N are shown in Fig. 2(a) and (b). $M^{c}Fe_{3}N$ has a cubic Pm-3m structure and lattice constants reveal an oscillatory behavior. It is found that the Ti, V, Cr, Zn substitution gives rise to an antiferromagnetic alignment with Fe atom while other 3d metal substitutions bring a ferromagnetic coupling, which is consistent with the earlier theoretical results [10,16]. Generally, due to the magnetovolume effect, a larger volume gives a larger moment. So a larger magnetic moment of Cr ($-3.356 \mu_B$) and Mn ($3.599 \mu_B$) compared to Fe₄N arises. Particularly, the lattice constant of Sc^cFe₃N increases to 3.803 Å, in contrast to the zero moment, which may be attributed to the relative large Sc atom size and very small magnetic moment of Sc. A larger moment of Cr and Mn than Fe results in an enhancement of total magnetic moment (10.512 μ_B) of Mn^cFe₃N over Fe₄N, but a lower total moment of Cr^cFe₃N due to the antiferromagnetic coupling of Cr with Fe.

The substitution on FeIIB site gives a structure transition for M^{f} -Fe₃N. The FeIIB-site substitution of Fe₄N makes the space group lower to P4/mmm and the lattice structure changes from cubic to tetragonal. Fig. 2(c) shows the c/a ratio of M^{f} Fe₃N. We note that c/a ratios are slightly less than 1.0 when substituting elements are in the vicinity of Fe, which can be ascribed to the similar atom radius. The substitution of M atoms with a relatively larger atom radius gives rise to a c/a value larger than 1.0. It can be shown that there is a close correlation between the lattice constant and the atom radii of M atoms, which is similar to the experimental results [33]. These results manifest that the substituted transition metal atoms at FeIIB site make c axis varies, which lead to a structure transition.

Fig. 2(d) gives the magnetic moment of each atom and total magnetic moment in M^{f} Fe₃N. The curve of total magnetic moment is similar to that of *M* atoms. Meanwhile, the substituted atoms in

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