



Relations of electronic energies and magnetic moments of tetra-3d metal (Mn, Fe, Co and Ni) nitrides calculated using a plane-wave basis method

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ABSTRACT

Geometrical optimization of tetra-3d metal nitrides (Mn_4N , Fe_4N , Co_4N , and Ni_4N) has been performed and the relations of their energies (E) and their total magnetic moments (M) are obtained by plane-wave-basis density-functional calculations without any assumption of specific spin arrangement. The E vs. M relations obtained for Fe_4N and Mn_4N have a bimodal character. The ground state of Fe_4N is a high-spin state, which would correspond to the ferromagnetic character, while that of Mn_4N is a low-spin state, which would correspond to the observed ferrimagnetic character. Lattice constants and total magnetic moments of these tetra-3d metal nitrides are almost accurately predicted. From the spin-polarized densities of states curves, Co_4N would have the largest spin polarization ratio of 0.88, which suggests Co_4N can be a candidate material for ferromagnetic electrodes for spin-injection.

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1. Introduction

There has been a renewed interest in iron-based nitrides, especially in Fe_4N , for ferromagnetic electrodes for spin-injection toward highly efficient spin-electronic devices [1]. Vast number of studies [2–4] have been devoted so far in order to understand the higher magnetic moment of Fe_4N than pure Fe. The calculated total magnetic moments per formula unit lie between 9.34 and 9.67 μ_B [3], which is close to 8.86 μ_B , the value of magnetic measurements [5].

Fe_4N crystallizes in a simple-cubic antiperovskite structure with the space group $P_{m\bar{3}m}$. Fe atoms are arranged in the face-centered-cubic (fcc) structure and N atoms occupy the body center positions of the Fe fcc cells. The insertion of N atoms leads to two inequivalent crystallographic Fe sites, the corner Fe (Fe^c) and the face-center Fe (Fe^f). Though this structure is common for neighboring tetra-3d metal nitrides, Mn_4N , Co_4N and Ni_4N , theoretical and experimental studies on these nitrides are relatively scarce with the exception of the ferrimagnetic Mn_4N . How the magnetic characters of these tetra-nitrides are dependent on the number of 3d-electrons has not been extensively studied. This situation has motivated the present work; that is, the aim of the present work is to clarify how the number of 3d-electrons will have affect the magnetic behaviors.

It is well-known that the distance between atoms has a vital effect on the magnetic properties through the exchange

interaction. We tried to perform geometrical optimization so as to avoid possible inherent errors caused by the approximation, and then, the magnetic moments were calculated using optimized parameters instead of observed ones.

It should be noted here that most of the previous calculations on magnetic properties have been performed using a spherical wave expansion of wavefunctions (an atomic sphere approximation; ASA) or the linearized muffin tin orbital (LMTO) method. However, these calculations are based on a localized basis set and are not favorable for optimization because (1) correction using “empty sphere” to overcome the difficult in treating the interstitial region of ‘open’ structure is problematic if the atoms move as in the case of geometrical optimization and (2) Pulay correction in the calculation of Hellmann–Feynmann force in the optimization process is also problematic when localized basis sets are used. Therefore, we did not adopt these methods. Instead, we adopted a plane-wave-basis calculation, since this is favorable for performing geometrical optimization calculation.

No specific spin arrangement was assumed beforehand such as ferromagnetic, ferrimagnetic, or pure antiferromagnetic coupling between Me^c and Me^f sites, which was not the case for the previous calculation of Mn_4N [6]. One may consider that there is still room for dispute on whether the present plane-wave method can treat properly non-collinear spin arrangement such as an antiferromagnetic triangular lattice or not. Since we could not obtain spatial spin-distribution of the system, we cannot say anything unambiguously about this anxiety at present. Therefore, the description of ‘no specific spin arrangement was assumed’ here might be limited to the cases where non-collinear arrangements are not allowed.

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2. Calculation methods

We used a code of CASTEP (CAMbride Serial Total Energy Package) [7], a first-principle pseudopotential method based on DFT, for describing the electron–electron interaction, a pseudopotential description of the electron–core interaction, and a plane-wave expansion of the wavefunctions, developed by Payne et al. As for the method of approximation to the exchange–correlation term of the DFT, the local spin density approximation with the generalized gradient correction [8] was used. The pseudopotential used is the ultrasoft pseudopotential generated by the scheme of Vanderbilt [9] with the non-linear correction [10,11] implemented to treat the local spin density dependence of the exchange and correlation energy. Wavefunctions were expanded by plane-waves, the number of plane-wave-expansion of which is characterized by a cutoff energy, E_{cutoff} . The adopted E_{cutoff} is 400 eV. As for the k -points sampling for the total energy calculation, the Monkhorst–Packe scheme [12] with the mesh parameter of $10 \times 10 \times 10$ was used, which corresponded to the spacing of 0.3 nm^{-1} in the reciprocal space and produced 500 k -points from the irreducible part of the Brillouin zone.

Crystallographic parameters and the total magnetic moments of compounds are determined by the total energy minimization algorithm using the Broyden–Fletcher–Goldfarb–Shannon optimization procedure under the constraint condition of the space group. The convergence of the optimization mode is controlled by four criteria, namely, the energy change between two steps, the root-mean-square (rms) residual force on movable atoms, the rms displacement of atoms during the geometrical optimization process, and the rms residual bulk stress must be smaller than 1 meV, 10^{-10} N , 10^{-4} nm , and $\pm 0.3 \text{ GPa}$, respectively.

However, choice of initial parameters to find the state with minimum energy has been found to be very problematic. When all the parameters are simultaneously varied, the conversion process in the optimization procedure is sometime unstable and finally attains different states depending on the assumed initial parameters. This was found to have a close relation to the ‘bistability’ of the system, as stated later.

Therefore, we were obliged to perform optimization calculations using several initial conditions and selected the really stable state by choosing the state that had the minimum energy. In concrete, the calculations have been first performed by the ‘fixed-spin-moment procedure’, which finds the ground state of an electron’s system under a constraint that the total magnetic moment of the system is fixed to several assumed values. After obtaining the relation of energies (E) and assumed total magnetic moments (M) of the system, we restarted a full-optimization calculation with simultaneous relaxation of lattice parameters and the total magnetic moment using the state of the local energy minimum in the obtained E vs. M relation as an initial condition of the present full optimization.

3. Results and discussion

At first, we show the results on the total magnetic moment, M , dependence of the energy, E , of Fe_4N in Fig. 1. Though we anticipated a simple relation such as a quadratic one between M and E , the results show a bimodal property. In this figure, closed circles show the results by a fixed-spin-moment procedure. The result shown by an open circle (lattice parameter, $a=0.376 \text{ nm}$, $M=9.55 \mu_{\text{B}}$, and $E=-3745.54 \text{ eV}$) was obtained by a full optimization.

Optimization processes converged well to this state, being irrespective of which states shown by closed circles are selected as an initial condition. This convergent process is expressed

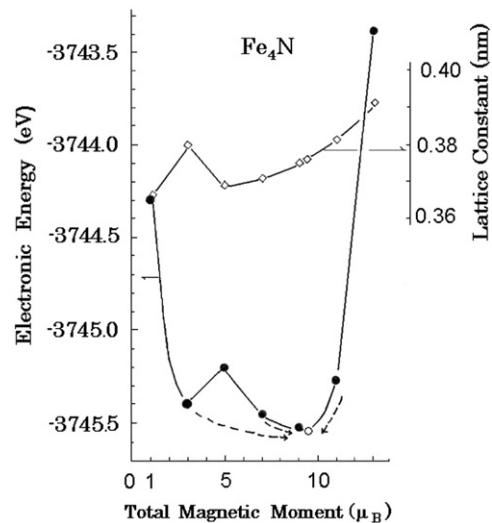


Fig. 1. Total magnetic moment dependence of the energy of Fe_4N . In this and succeeding figures, closed circles show the results obtained by a fixed-spin-moment procedure. An open circle shows the result obtained by simultaneous relaxations of the lattice constant and spin of the total system. Optimized lattice constants for each magnetic moment are also given by open squares. Dashed arrows symbolize the convergence of that optimization process irrespective of which states shown by closed circles are selected as an initial condition.

symbolically by dashed arrows in Fig. 1. Thus, the state with the minimum energy could be rigorously predicted in this case. However, this is not the case in Mn_4N as described later. The predicted magnetic moment of $9.55 \mu_{\text{B}}/\text{cell}$ is close to the previous results of calculations referred above [3].

The lattice constants of optimized structure under several assumed magnetic moments are also presented by open squares in Fig. 1. Increase in the magnetic moment is generally accompanied by the increase in the lattice constant, which is usually observed as magnetovolume effect in ferromagnetic alloys. The predicted lattice constant at the energy minimum, 0.376 nm , is close to the observed value of 0.3796 nm [13] and the present calculation was found to give a relatively reliable prediction.

However, it should be noted that there is another energy-minimum near the point of ($M=3 \mu_{\text{B}}/\text{cell}$). Though the corresponding state has not been experimentally confirmed, this must be a metastable state with a ferrimagnetic character since this behavior resembles the case of fcc-Fe where a high-spin phase and low-spin phase appear at several selected cell volumes [14]. This ferrimagnetic state has a relatively large lattice constant, compared to the neighboring states of $M=1$ and $M=5 \mu_{\text{B}}/\text{cell}$. This is apparently contrary to the general tendency between M and lattice constants stated above. This can be understood if the magnitude of atomic moments on each atom would remain large and antiparallel alignment of localized moments gives birth to the small total magnetic moment of the system just as in the case of antiferromagnetic Ni–Mn alloy. For binary solid solution of 3d transition metal alloys, the relation between the lattice constant and the magnetic moment is expressed as $a(x)=a_A(1-x)+a_Bx+C <|\mu| >$, where x is the atomic fraction, a_A , a_B , and C are parameters, $<|\mu| >$ is the average magnitude of atomic magnetic moments but not the total magnetic moment of the system [15]. This behavior seems partly to support the localized spin model of metals and alloys, though itinerant spin models are usually appropriate for the explanation of magnetism of metals and alloys. It may be interesting that the present calculations are essentially based on

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