First-principles calculation of crystal field parameters of Dy ions substituted for Nd in Nd-Fe-B magnets

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Abstract. We study the electronic structures of crystalline Nd₂Fe₁₄B, Dy₂Fe₁₄B and Dy-doped Nd-Fe-B, and estimate the crystal field parameter \( A_0^2(r^2) \) of the rare earth ions of these systems based on the first principles calculations. We find that the crystal field of the Dy ions is appreciably insensitive to its crystallographic location than that of Nd ions.

1. Introduction

Nd-Fe-B sintered magnets have had few high-temperature applications because of their relatively low Curie temperature despite their excellent room temperature properties. Addition of Dy to the Nd-Fe-B magnets is known to increase the coercivity of the Nd₂Fe₁₄B hard phase. In particular, the Dy substitution has a significant beneficial effect on the thermal stability of the magnetic properties. It has been believed, from a phenomenological viewpoint, that this is due to the higher value of the anisotropy field \( H_a \) of Dy₂Fe₁₄B than that of Nd₂Fe₁₄B. However, the microscopic study for this mechanism has not been reported. Moreover, nowadays, technology that can increase the coercivity of Dy-free Nd-Fe-B sintered magnets is strongly desired. Thus it is important to reveal the role of the substituted Dy ions, and to give a guiding principle for improving the coercivity of Dy-free Nd-Fe-B sintered magnets.

Thus in this paper, as a first step, we theoretically study the electronic structures, the magnetic moments and the crystal field (CF) parameters of Nd and Dy ions in Dy-doped crystalline Nd₂Fe₁₄B, by using a first principles method based on density functional theory. Needless to say, in general, there would exist much complicated factors in the mechanisms which dominates the coercivity of rare-earth (RE) permanent magnets. However, we believe that it is useful to estimate the local magnetic anisotropy of the substituted Dy ions.

Figure 1 shows the crystal structure of Nd₂Fe₁₄B (space group \( P4_2/mnm \)). There are two crystallographically inequivalent Nd sites, denoted as f and g, in this structure as shown in Fig. 1. Here, for simplicity, we focus on the following two extreme cases: (i) Dy is substituted for all of the Nd at the f-sites of the system, which is denoted here by DyNdFe₁₄B, and (ii) for all of the Nd at g-sites, denoted by NdDyFe₁₄B.
Figure 1. The unit cell of (RE)$_2$Fe$_{14}$B. Nd and Dy ions are located at RE f- or g-sites.

2. Computational details

The magnetic anisotropy energy of RE ions is described by the Hamiltonian consisting of spin-orbit interaction, magnetic exchange, and crystal field interactions. The crystal field interaction energy depends on the orientation of 4f magnetic moment, because a rotation of magnetic moment leads to a rotation of the 4f aspherical charge cloud due to strong spin-orbit interaction. Thus the 4f anisotropic magnetic energy depends on the crystal field energy described by the standard model Hamiltonian \( H = \sum_{L,M} \Theta_{L} A_{LM}^{M} \langle r^{L} \rangle \hat{O}_{L}^{M} \), (1)

where \( \hat{O}_{L}^{M} \) are the Stevens operator equivalents, and \( \Theta_{L} \) are the reduced matrix elements [2].

Following Diviš et al. [3, 4], the CF parameters \( A_{LM}^{M} \langle r^{L} \rangle \) originating from the aspherical part of the total single particle DFT potential in the crystal can be obtained from

\[
A_{LM}^{M} \langle r^{L} \rangle = a_{LM} \left( \int_{0}^{R_{MT}} dr r^{2} |R_{4f}(r)|^{2} V_{LM}^{M} + \int_{R_{MT}}^{\infty} dr r^{2} |R_{4f}(r)|^{2} W_{LM}^{M} \right),
\]

(2)

with

\[
\langle r^{L} \rangle = \int_{0}^{R_{MT}} dr r^{L-1} |R_{4f}(r)|^{2},
\]

(3)

where \( V_{LM}^{M}(r) \) and \( W_{LM}^{M}(r) \) are the components of the total (Coulomb and exchange-correlation) potential inside the atomic sphere of the rare-earth ions with the muffin-tin sphere radius \( R_{MT} \), and its continuation in the interstitial region, respectively. The \( R_{4f}(r) \) is the radial part of the 4f-orbital wave function. The conversion factors \( a_{LM} \) show the relation between the symmetrized spherical harmonics and the real tesseral harmonics which transfers in the same way as the tensor operators \( O_{LM}^{M} \). In particular, \( a_{20} = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \).

To obtain \( V_{LM}^{M}(r) \) and \( W_{LM}^{M}(r) \), we use the full-potential linearized augmented plane wave plus local orbitals method (APW+lo) implemented in the WIEN2k code [5]. The Kohn-Sham equations are solved within the generalized-gradient approximation (GGA). At this stage, however, we neglect the term \( W_{LM}^{M}(r) \) because the radial wave function \( R_{4f}(r) \) quickly decays around \( r \geq R_{MT} \), as described below. For the Brillouin zone integration, a modified tetrahedron method with 12 \( k \) points in the irreducible wedge was used in constructing the charge density in each self-consistency step. The number of the basis functions is 7183, including 848 local
orbitals. Throughout the present calculation, we take $R_{MT} = 2.8, 2.02, 1.8$ a.u. for RE, Fe, B ions, respectively.

To simulate localized $4f$ states in the (RE)$_2$Fe$_{14}$B systems, we switch off the hybridization between $4f$ and valence states, and treat the RE $4f$ states in the spherical part of the potential as atomic-like core states (the so-called open-core treatment). Here, $R_{4f}(r)$ is obtained by performing separate atomic calculations of the electronic structure of an isolated RE atom. In these calculations the correction for the self-interaction (SIC) was included, which leads to better approximation for the single electron densities. This approach [6] was found to provide a $4f$ charge density being very close to that obtained from more rigorous SIC-DFT band calculations [1]. We obtain $\langle r^2 \rangle = 1.02a_0$ for the Nd $4f$-density and $\langle r^2 \rangle = 0.727a_0$ for Dy, where $a_0$ is the Bohr radius.

We should note here that the lattice constants of Nd$_2$Fe$_{14}$B and Dy$_2$Fe$_{14}$B are set to the experimental values of $a = b = 8.80\text{Å}$ and $c = 12.19\text{Å}$ [7], and $a = b = 8.76\text{Å}$ and $c = 11.99\text{Å}$ [8], respectively. We also use these values for the DyNdFe$_{14}$B and the NdDyFe$_{14}$B systems.

### 3. Results and discussion

We show the magnetic moments obtained inside each of the atomic spheres in Table 1, in comparison with the previous works for Nd$_2$Fe$_{14}$B using the LDA+$U$ method [12] and by the full-potential linear-muffin-tin-orbital (FP-LMTO) method [13]. We can see that, for Nd$_2$Fe$_{14}$B, the present results obtained by the open-core treatment are in good agreement with both the LDA+$U$ and the FP-LMTO results, especially with the former. We also find that the systems including Dy, that is, Dy$_2$Fe$_{14}$B, DyNdFe$_{14}$B and NdDyFe$_{14}$B have quite similar but slightly smaller magnetic moments to those of Nd$_2$Fe$_{14}$B. As noted above, these results for the Dy-doped systems are obtained using the lattice constants for the crystalline Nd$_2$Fe$_{14}$B. We find that the magnetic moment of each Fe ion in DyNdFe$_{14}$B and NdDyFe$_{14}$B shrinks down about 1 percent if we use the lattice constants for the crystalline Dy$_2$Fe$_{14}$B, which are smaller than those for Nd$_2$Fe$_{14}$B. This can be understood from the well-known property of ferromagnets, that is, ferromagnetism favors narrower band structure. We should also note here that, in the present calculations, all magnetic moments are aligned parallel to the crystallographic $c$-axis, while the magnetic moments undergo the well-known spin-reorientation into non-collinear structure at very low temperatures in real Nd$_2$Fe$_{14}$B compounds. Thus the present results should be interpreted as extrapolated ones from the situation above the reorientation temperature to $T = 0$.

Next, we show the results for the CF parameter $A_0^2\langle r^2 \rangle$ of Nd and Dy ions in these systems. Here we show the results in Table 2 in the same manner as in Table 1. It should be noted

| (this work) | Nd$_2$Fe$_{14}$B (LDA+$U$) | Dy$_2$Fe$_{14}$B | DyNdFe$_{14}$B | NdDyFe$_{14}$B |
|------------|-----------------------------|-----------------|-----------------|----------------|
| Fe(16k$_1$) | 2.29                        | 2.27            | 2.22            | 2.27           |
| Fe(16k$_2$) | 2.38                        | 2.38            | 2.28            | 2.36           |
| Fe(8j$_1$)  | 2.31                        | 2.34            | 2.67            | 2.30           |
| Fe(8j$_2$)  | 2.74                        | 2.73            | 2.16            | 2.73           |
| Fe(4c)      | 2.16                        | 2.16            | 1.96            | 2.15           |
| Fe(4c)      | 2.47                        | 2.47            | 2.43            | 2.43           |
| B(4g)       | -0.17                       | -0.18           | -0.13           | -0.16          |
| interstitial| -5.42                       | -4.92           | -               | -5.00          |
|            |                             |                 |                 | -5.35          |
Table 2. The crystal field parameters $A_2^0(r^2)$ obtained by the present calculations, LDA+$U$[12], and FP-LMTO methods[13].

| rare-earth site | Nd$_2$Fe$_{14}$B (LDA+$U$) | Dy$_2$Fe$_{14}$B | DyNdFe$_{14}$B | NdDyFe$_{14}$B |
|-----------------|---------------------------|-----------------|-----------------|-----------------|
| f               | 552                       | 507 (Dy)        | 556 (Dy)        | 507 (Nd)        |
| g               | 790                       | 604 (Dy)        | 604 (Dy)        | 736 (Nd)        |

Here again that the Dy-doped systems are obtained using the lattice constants for Nd$_2$Fe$_{14}$B. For Nd$_2$Fe$_{14}$B, we find that our result is in good agreement with the previous studies for the f-site, but not for the g-site. The possible reasons of such significant discrepancy are mainly the difference of the adopted theoretical schemes, such as the open-core method used here, the LDA+$U$ method and the LMTO method. In particular, it is known that the self-interaction of 4f-electrons can be only partially corrected within the LDA+$U$ method.

Here let us look at the results for the systems containing Dy. We find that, in Dy$_2$Fe$_{14}$B, the difference between the value of $A_2^0(r^2)$ for the f- and g-site is rather smaller than in Nd$_2$Fe$_{14}$B. This implies that the CF of Dy is less affected by crystallographic location than that of Nd. The variation of $A_2^0(r^2)$ from the pure systems, such as Nd$_2$Fe$_{14}$B and Dy$_2$Fe$_{14}$B, is 6.8 percent less for Nd(g) in DyNdFe$_{14}$B and 8.2 percent less for Nd(f) in NdDyFe$_{14}$B, while 0.3 percent more for Dy(g) in NdDyFe$_{14}$B and 3.5 percent more for Dy(f) in DyNdFe$_{14}$B. Moreover, this tendency is more marked when we use the lattice constants for the crystalline Dy$_2$Fe$_{14}$B. Indeed, we obtain the 16.8 percent less for Nd(f) and 5.0 percent more for Dy(g) in NdDyFe$_{14}$B with the smaller lattice constants. Thus, indeed, the crystal field of Dy is appreciably more insensitive to its surroundings than that of Nd. We speculate that this is due to the more localized 4f-electronic density $|R_{4f}(r)|^2$ of Dy than that of Nd. Recently, three of the present authors have pointed out that Nd ions located around a (001) surface of Nd$_2$Fe$_{14}$B exhibits $A_2^0(r^2) < 0$, which implies local, in-plane magnetic anisotropy [12]. Also, we have confirmed quite recently that such Nd ions with negative $A_2^0(r^2)$ can be nucleation sites of magnetization reversal of the whole system by using micromagnetic simulation technique [14]. Thus it is interesting to study the CF parameter of Dy substituted for the surface Nd, and to reveal whether it can be negative or not.

4. Summary
In summary, we have estimated the crystal field parameter $A_2^0(r^2)$ of Nd and Dy ions in crystalline Nd$_2$Fe$_{14}$B, Dy$_2$Fe$_{14}$B, and Dy-doped Nd-Fe-B systems. We found that the crystal field of the Dy ions is appreciably more insensitive to their surrounding than that of Nd ions.

Acknowledgments
A part of numerical computations in this work was carried out at the Yukawa Institute Computer Facility, and also at Cyberscience Center, Tohoku University. Some parts of this work are the results of the research supported by Rare Metal Substitute Materials Development of technology for reducing dysprosium usage in a rare-earth magnet, from METI, Japan. The work of M. D. is a part of the research program MSM 0021620834 financed by the Ministry of Education of the Czech Republic and was also supported by the Grant Agency of Czech Republic (Project 202/09/1027). Also this work is partly supported by Grant-in-Aid for Scientific Research (C) and also by Next Generation Supercomputing Project, Nanoscience Program, from the Ministry of Education, Culture, Sports, Science and Technology of Japan.
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