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# Bridging atomistic magnetism and coercivity in Nd-Fe-B magnets

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ABSTRACT

Coercivity in rare-earth permanent magnets depends on the size and shape of magnetic grains. Recent experimental studies have revealed that, however, atomic scale structures around the grain-boundaries of magnets also play a crucial role to determine their coercivity. In this paper, we construct an effective spin model for the $Nd_2Fe_{14}B$ structure based on first-principles calculations to describe atomistic magnetization dynamics of the magnetic grains, incorporating the information of the electronic states of the system. We find that the Nd ions located on the surfaces of the grains may have planar magnetic anisotropy, and that they can cause coercivity reduction.



## 1. Introduction

Because of increasing demand for high performance hard magnets for applications like wind turbines or electric vehicles, intensive studies have been carried out to understand the coercivity mechanisms in rare-earth-based permanent magnets such as Nd-Fe-B. Those basic researches are not only necessary to improve the magnetic properties of Nd-Fe-B magnets, but also useful to develop novel magnetic materials suitable for permanent magnets.

Coercivity has often been discussed based on the phenomenological relation given as

$$H_c(T) = \alpha H_A(T) - N_{\text{eff}}\, M_S(T) - H_{\text{th}}(T) \quad (1)$$

in a standard notation, which was proposed by Kronmüller et al. a few decades ago [1]. The factor $\alpha$ in Eq. (1) accounts for the reduction in coercivity due to magnetic defects or misorientation in magnets, and also intergrain exchange couplings. The parameter $N_{\text{eff}}$ represents the effect of the local demagnetization field around corners of micron-scale grain structures. The thermal fluctuation effects on the coercivity is represented by the third term $H_{\text{th}}$ [2]. The last two terms in the right-hand side of Eq. (1) and the factor $\alpha$ ($<1$) represent the possible reduction mechanisms of coercivity over the micron scale.

Recently, however, a series of experimental studies have shown that *atomic scale* structures and elemental distributions around the grain boundaries of sintered Nd-Fe-B magnets significantly affect their coercivity [3-6]. This observation is quite intriguing, as it implies that atomic scale perturbations less than the magnetic coherence length may have an influence on macroscopic coercivity.

To reveal the coercivity reduction mechanisms due to the atomic scale structures, it is first necessary to obtain the information on the electronic states around the grain-boundaries of the systems. First-principles calculations may give the best description of the electronic states of various materials, and they have been quite successful in predicting and analyzing the properties of magnetic materials, for example, in the field of spintronics.

The authors and their coworkers have found by using first-principles calculations that the Nd ions exposed on the (001) surface not only lose their uniaxial local magnetic anisotropy but also exhibit planar anisotropy [7-9]. Here we call such Nd ions *anomalous* Nd. It has also been confirmed that this is the case even for Dy ions on the surface when Dy are substituted into the $Nd_2Fe_{14}B$ [8]. It is quite plausible that anomalous Nd/Dy ions exist even around the interfaces of $Nd_2Fe_{14}B$ particles in sintered Nd-Fe-B magnets. Thus these anomalous Nd/Dy can be a physical origin of the experimentally observed coercivity reduction [10].

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The next question we have to answer is how the coercivity of the particles can be affected by those anomalous Nd. Unfortunately, however, first-principles calculations provide only static description of the electronic ground states of materials. In contrast, the so-called micromagnetic simulation technique can describe magnetization reversal dynamics, but it usually contains less atomistic information around the grain-boundaries. Thus, our strategy is as follows: first, we construct a microscopic effective spin model for 2-14-1 systems based on first-principles calculations, and then carry out atomistic Landau-Lifshitz-Gilbert type calculations to figure out how atomistic magnetism around surfaces or interfaces can affect the coercivity of the granular particles.

In this paper, we provide a consistent description of a possible coercivity reduction mechanism due to atomistic origins around the surface or interfaces of granular particles of the rare-earth based permanent magnets. This paper is organized as follows. In Section 2, we describe the procedure of constructing the effective spin model for a $Nd_2Fe_{14}B$ particle based on first-principles calculations. In Section 3, we briefly review the recent progress of the electronic state calculations around the surface or interfaces of the particles. Then we discuss how the magnetic anisotropy constant $K_1$ and $K_2$, and also the coercivity of the particle are affected by the surface effects. The summary and future problems are presented in Section 4.

## 2. An effective spin model for $Nd_2Fe_{14}B$

### 2.1. Magnetocrystalline anisotropy and first-principles calculations

The standard way of evaluating magnetocrystalline anisotropy energy in first-principles calculations is to compute the energy difference as a function of the direction cosines of the magnetization. When this procedure is applied to rare-earth based magnetic materials, one has to treat explicitly the 4f electrons that play a central role in the anisotropy. Modern first-principles calculations, however, still have problems to treat 4f electrons, and some corrections such as LDA + $U$ or self-interaction correction are needed. Moreover, this procedure gives only $T = 0$ results, although our interest is mostly in the temperature dependences of the magnetic properties of rare-earth based magnets.

Thus we here estimate the magnetocrystalline anisotropy via crystal field theory based on first-principles calculations [11]. In this approach, we first calculate the crystal field coefficients $A_l^m$ for Nd ions in the $Nd_2Fe_{14}B$ structure, and then construct a crystal field Hamiltonian

$$\mathcal{H}_{\rm CEF} = \sum_{l,m} \Theta_l A_l^m \langle r^l \rangle \hat{O}_l^m, \tag{2}$$

where $\hat{O}_l^m$ are the Stevens *operator equivalents*, and $\Theta_l$ are the reduced matrix elements [12,13]. Here we can describe the localized 4f contribution to the magnetocrystalline energy based on the standard model Hamiltonian [14]

$$\hat{\mathcal{H}}_{\rm eff}^J(\theta,\phi) = \hat{\mathcal{H}}_{\rm CEF}^J + 2(g_J - 1)\hat{\boldsymbol{J}}\cdot\boldsymbol{H}_m(\theta,\phi) \tag{3}$$

where $g_J$ is Landé $g$-factor, $\hat{\boldsymbol{J}}$ is lowest $J$ multiplet, $\boldsymbol{H}_m$ is the Fe molecular field acting on the spin component of $4f$ electron in Nd ions.

Following the previous works by P. Novák [15] and M. Diviš [16,17], the crystal field coefficients $A_l^m\langle r^l\rangle$ are given as

$$A_l^m \langle r^l \rangle = a_{lm} \int_0^{R_{\rm MT}} dr r^2 |R_{4f}(r)|^2 V_l^m(r) \tag{4}$$

with

$$\langle r^l \rangle = \int_0^{R_{\rm MT}} dr r^{l+2} |R_{4f}(r)|^2, \tag{5}$$

where $V_l^m(r)$ is the components of the total Coulomb potential of a rare-earth ion within an atomic sphere of radius $R_{\rm MT}$. The $R_{4f}(r)$ describes the radial shape of the localized 4f charge density of the rare-earth ions. It is worth noting here that we can obtain the function $V_l^m(r)$ directly by using first-principles calculations. Also, to simulate localized 4f electronic states in the system, we use the so-called open-core method in which we switch off the hybridization between 4f and valence 5d and 6p states, and treat the 4f states in the spherical part of the potential as atomic-like core states [15]. Thus the function $R_{4f}(r)$ in Eq. (4) can be obtained by performing separate atomic calculations of the electronic structure of an isolated rare-earth atom. The details of the calculations are given in refs. [15-17].

We should note here that there is some uncertainty of the crystal field parameters in connection with their dependence on the radius of atomic sphere $R_{\rm MT}$. While the radial density of the 4f electrons decreases fast as the distance from the nuclei increases, the potential decrease is slower. Indeed, it has been reported that the radial integration in Eq. (4) should be taken for fairly large value of $R_{\rm MT}$ to obtain quantitatively reliable results [14]. One of the authors (P.N.) and his coworkers have recently proposed a new method to calculate the crystal field parameters without such uncertainty in principle [18]. We have adopted this method to $Nd_2Fe_{14}B$ [19], and have confirmed that the open-core method fortunately gives satisfactory results for the present purpose when we take $R_{\rm MT} = 3.2$ a.u. for each Nd ion. Thus, we here use the open-core method for reducing computational time.

The crystal field parameters for the crystalline $Nd_2Fe_{14}B$ obtained here by using the WIEN2k code [20] are shown in Table 1. Here the lattice constants of the primitive cell are set to the experimental values of $a = b = 8.80$ Å and $c = 12.19$ Å [21]. Throughout this paper, we take $R_{MT} = 3.2, 2.09, 1.85$ a.u. for Nd, Fe, B ions, respectively. We also obtain $\langle r^2\rangle = 1.02a_0$ for the Nd $4f$-density, where $a_0$ is the Bohr radius. The computational detail is given in ref. [9].

### 2.2. Constructing an effective spin model

Next, we construct an effective spin model for the $Nd_2Fe_{14}B$ structure based on the information obtained in the Section 2.1. The idea of the effective spin model is quite simple, and not very new. The model is just a Heisenberg-type model that consists of 64 classical spins for each unit cell. There are several model parameters to be determined: the magnetic moments on each Fe or Nd ion, the magnetocrystalline energy of Nd ion and also Fe sublattice, and the exchange couplings between Fe-Fe and Nd-Fe ions. We note here that, in principle, all these parameters can be estimated by using first-principles calculations; for example, the site-resolved magnetocrystalline anisotropy of the Fe-sublattice is reported by Miura et al. [22].

Within these model parameters, let us first look at the magnetocrystalline anisotropy energy of Nd ions based on the effective Hamiltonian $\mathcal{H}_{\rm eff}^J$ given in Eq. (3). When we take $|\boldsymbol{H}_m| \to \infty$, the Hilbert space for this Hamiltonian is restricted only within $|J, M = -J\rangle$, resulting in the energy expectation value

$$\begin{aligned} E^{\rm Nd}(\theta,\phi) &= \langle J, M = -J|\hat{\mathcal{H}}_{\rm eff}^J(\theta,\phi)|J, M = -J\rangle \\ &= K_1\sin^2\theta + [K_2\sin^4\theta + K_3\cos 4\phi]\sin^4\theta \\ &\quad + [K_4 + K_5\cos 4\phi]\sin^6\theta, \end{aligned} \tag{6}$$

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