First principles study on interfacial electronic structures in exchange-spring magnets

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Abstract. We study the magnetic properties of Nd\textsubscript{2}Fe\textsubscript{14}B/α-Fe multilayer systems, especially the exchange coupling between the two layers and the crystal field parameters $A_h^0(r^2)$ for the Nd ions located around the interfaces, based on first principles calculations. We find that the exchange coupling depends on the Miller indices of the crystallographic planes at the interface, and can be negative which favors antiparallel alignment of the magnetizations of the hard- and soft-magnet layers.

Exchange-spring magnets are nanocomposite materials that are composed of hard- and soft-magnetic phases that interact by magnetic exchange coupling\cite{1, 2, 3, 4}. These are promising systems for advanced permanent magnetic applications because they have been expected, based on micromagnetic simulations, to have a large energy product compared to conventional single-phase materials.

However, in practice, it is well known that such high values of the energy product have been hard to achieve in real materials. This would be due to the difficulty in controlling the nanostructure such as grain sizes of hard and soft crystallites, and crystallographic alignment of the hard grains. Moreover, there might exist much complicated factors in the mechanisms which dominates the coercivity and energy product of exchange-spring magnets, which have inevitably been neglected in micromagnetic simulations and should be described microscopically. Thus it is important to have detailed experimental and theoretical information on the electronic states around well-fabricated interfaces in exchange-spring magnets.

Exchange-spring multilayer thin films will have such well-fabricated interfacial structures, and thus will serve as a desirable model system for studying fundamental physical properties of exchange-spring magnets. Actually, Zhang \textit{et al.} have recently succeeded to fabricate the SmCo\textsubscript{5}/Fe multilayer film that approach the ideal exchange-spring magnets with aligned hard- and soft-layers \cite{5}. The largest $(BH)_{\text{max}}$ of the film has been reported as 32MGOe, which is larger than the theoretical limit for a SmCo\textsubscript{5} single phase bulk magnet, 28.8MGOe. This was the first example that exchange-spring magnets can exhibit larger $(BH)_{\text{max}}$ than the theoretical limit. We can naturally expect that, experimental realization of exchange-spring thin film magnets based on Nd\textsubscript{2}Fe\textsubscript{14}B is only a matter of time. Therefore, it is urgent to have detailed information on the electronic states around the interfaces in such multilayers based on Nd\textsubscript{2}Fe\textsubscript{14}B.

Motivated by these backgrounds, we theoretically study the magnetic properties of Nd\textsubscript{2}Fe\textsubscript{14}B/α-Fe multilayer systems, especially the crystal field parameters (CFPs) of Nd ions and the exchange coupling between hard- and soft-layers. Very recently, three of the present authors have shown that the CFPs $A_h^0(r^2)$ of Nd ions located around a (001) surface of crystalline Nd\textsubscript{2}Fe\textsubscript{14}B are negative, based on the
first principles calculations [6]. This implies that those Nd ions would be nucleation center of reversed magnetic domains, and that the coercivity of Nd$_2$Fe$_{14}$B-based exchange-spring magnets may also be affected by such Nd ions around interfaces. Thus in this paper, as a first step, we focus on the magnetic properties of the (a) Nd$_2$Fe$_{14}$B(001)/α-Fe(001) and (b) Nd$_2$Fe$_{14}$B(100)/α-Fe(110) multilayered systems, shown in Fig. 1. We note that the crystallographic planes at the interfaces of α-Fe in the cases (a) and (b) are chosen so as to realize commensurate interfacial structures with Nd$_2$Fe$_{14}$B (001) and (100) planes. Also we should note here that the lattice constants of Nd$_2$Fe$_{14}$B are set to experimental values of $a = b = 8.8\,$Å, $c = 12.19\,$Å, while those for α-Fe are slightly modified for commensurability of the interfacial structures: $a = b = 2.93\,$Å, $c = 2.83\,$Å for the Nd$_2$Fe$_{14}$B(001)/α-Fe(001) system, and $a = b = 2.85\,$Å, $c = 2.93\,$Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 89.1^{\circ}$ for the Nd$_2$Fe$_{14}$B(100)/α-Fe(110) system. We confirmed that α-Fe with lattice distortion assumed here also exhibit ferromagnetism even in the bulk system. Furthermore, the lattice distortion does not affect significantly the magnetic properties of α-Fe such as magnetic moments of each Fe.

In this work, the electronic structures of the multilayer models are calculated with first-principles density functional calculations using a plane-wave basis set. We use the Vienna Ab-initio Simulation Package (VASP) [8, 9]. The ionic potentials are described by projector-augmented-wave (PAW) method and the exchange-correlation energy of the electrons is described within a generalized gradient approximation (GGA). We use the exchange-correlation functional determined by Ceperly and Alder and parameterized by Perdew and Zunger. The energy cutoff of 318.6 eV is used to generate a plane wave basis set. For the $k$-point integration, we use a $3 \times 3 \times 3$ mesh for the unit cell of a bulk Nd$_2$Fe$_{14}$B model and equivalent densities of mesh points for the multilayer models. The total energy convergence is less than 0.1meV per unit cell.

The CF parameter $A^0_2(r^2)$ of a Nd ion in the systems can be given as [10]

$$A^0_2(r^2) = \frac{1}{4} \int_{|R|<R_{MT}} dR \left(3 \cos^2 \theta - 1\right) \rho(R) \int_{r>R_{MT}} dr \left(\frac{r^2}{r^2}\right)^2 |R_A(r)|^2,$$

where $r_\leq \equiv \min(r,|R|)$, $r_\geq \equiv \max(r,|R|)$, and $\rho(R)$ is the valence charge density within the atomic sphere ($r < r_{AS}$) of the Nd ions of the system. The $R_A(r)$ describes the radial shape of the localized 4f charge density of the Nd ion. In the present study we used a self-interaction corrected (SIC) wave function from atomic calculations. This approach [11] was found to provide a 4f charge density being very close to that obtained from more rigorous SIC-DFT band-calculations [12].
Table 1. The magnetic moments in $\mu_B$ for the crystalline Nd$_2$Fe$_{14}$B obtained by the present calculations, APW+lo[6], and FP-LMTO methods[13].

|         | this work | APW+lo | FP-LMTO |
|---------|-----------|--------|---------|
| Fe(16k$_1$) | 2.18      | 2.27   | 2.22    |
| Fe(16k$_2$) | 2.28      | 2.38   | 2.28    |
| Fe(8j$_1$)  | 2.15      | 2.34   | 2.67    |
| Fe(8j$_2$)  | 2.65      | 2.73   | 2.16    |
| Fe(4e)      | 2.11      | 2.16   | 1.96    |
| Fe(4c)      | 2.41      | 2.47   | 2.43    |
| B(4g)       | -0.15     | -0.18  | -0.13   |
| interstitial| -         | -4.92  | -       |

Table 2. The CF parameters $A_2^0(r^2)$[K] of Nd ions obtained for the crystalline Nd$_2$Fe$_{14}$B.

|         | this work | APW+lo | FP-LMTO |
|---------|-----------|--------|---------|
| Nd(4f)  | 547       | 427    | 540     |
| Nd(4g)  | 320       | 464    | 323     |

First, let us briefly look at the results for the crystalline Nd$_2$Fe$_{14}$B. We show the magnetic moments obtained inside each of the atomic spheres in Table 1, and also show the crystal field parameters $A_2^0(r^2)$ for Nd ions in Table 2, in comparison with the previous works [6, 13] using the full potential linearized augmented plane wave plus local orbitals method (APW+lo) using WIEN2k [14] and by the full-potential linear-muffin-tin-orbital (FP-LMTO) method. The present results are in good agreement with both the APW+lo and the FP-LMTO results, especially with the latter. 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 we also note here that 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 Nd$_2$Fe$_{14}$B (001)/α-Fe (001) interface model, shown in Fig. 1 (a). Figure 2 shows the total electronic energy of the system for parallel and anti-parallel magnetization alignments between Nd$_2$Fe$_{14}$B and α-Fe layers, as functions of the interlayer distance $d_1$ shown in Fig. 1 (a). We can easily see that, in this case, the parallel alignment of the magnetizations is always favored in $2.0 \leq d_1 \leq 2.6$Å, and that $d_1$ is optimized at $d_1 \approx 2.2$Å for the parallel and $d_1 \approx 2.3$Å for the anti-parallel cases. The exchange coupling per unit area between the magnetizations of the two layers is estimated as $J \approx 0.06$ J/m² at $d_1 = 2.2$Å. The CFPs obtained for the Nd ions are shown in table 3(a). Since the $P4_2/mnm$ symmetry of the crystalline Nd$_2$Fe$_{14}$B is broken in this multilayer model, we have four Nd ions crystallographically inequivalent. We label them as Nd(f)-a and Nd(g)-a, located at the (001) interface, and Nd(f)-b and Nd(f)-b, inside. In contrast to the Nd$_2$Fe$_{14}$B (001) surface model[6] mentioned above, the CFPs $A_2^0(r^2)$ are all positive as shown in Table 3(b), that is, they are restored as in the bulk system. In the present multilayer system, there exist Fe ions in the α-Fe layer lie directly on the interfacial Nd ions. The valence electrons of the Nd ions couple with the 3d electrons of those Fe ions and thus slightly extend outward from the interfaces, then they form the crystal field which gives the uniaxial magnetic anisotropy perpendicular to the (001) interface of the Nd$_2$Fe$_{14}$B layer. We speculate that this is the reason for the restored CFPs of the Nd ions.

Here we see how these results would be changed in the Nd$_2$Fe$_{14}$B (100)/α-Fe (110) model, shown in Fig. 1 (b). Figure 3 shows the total electronic energies for parallel and anti-parallel magnetization alignments between Nd$_2$Fe$_{14}$B and α-Fe layers, as functions of the interlayer distance $d_1$ shown in Fig. 1 (b). We can easily see that, in this case, the parallel alignment of the magnetizations is always favored in $2.0 \leq d_1 \leq 2.6$Å, and that $d_1$ is optimized at $d_1 \approx 2.2$Å for the parallel and $d_1 \approx 2.3$Å for the anti-parallel cases. The exchange coupling per unit area between the magnetizations of the two layers is estimated as $J \approx 0.06$ J/m² at $d_1 = 2.2$Å. The CFPs obtained for the Nd ions are shown in table 3(a). Since the $P4_2/mnm$ symmetry of the crystalline Nd$_2$Fe$_{14}$B is broken in this multilayer model, we have four Nd ions crystallographically inequivalent. We label them as Nd(f)-a and Nd(g)-a, located at the (001) interface, and Nd(f)-b and Nd(f)-b, inside. In contrast to the Nd$_2$Fe$_{14}$B (001) surface model[6] mentioned above, the CFPs $A_2^0(r^2)$ are all positive as shown in Table 3(b), that is, they are restored as in the bulk system. In the present multilayer system, there exist Fe ions in the α-Fe layer lie directly on the interfacial Nd ions. The valence electrons of the Nd ions couple with the 3d electrons of those Fe ions and thus slightly extend outward from the interfaces, then they form the crystal field which gives the uniaxial magnetic anisotropy perpendicular to the (001) interface of the Nd$_2$Fe$_{14}$B layer. We speculate that this is the reason for the restored CFPs of the Nd ions.

Here we see how these results would be changed in the Nd$_2$Fe$_{14}$B (100)/α-Fe (110) model, shown in Fig. 1 (b). Figure 3 shows the total electronic energies for parallel and anti-parallel magnetization alignments between Nd$_2$Fe$_{14}$B and α-Fe layers, as functions of the interlayer distance $d_1$ shown in Fig. 1 (b). We can easily see that, in this case, the parallel alignment of the magnetizations is always favored in $2.0 \leq d_1 \leq 2.6$Å, and that $d_1$ is optimized at $d_1 \approx 2.2$Å for the parallel and $d_1 \approx 2.3$Å for the anti-parallel cases. The exchange coupling per unit area between the magnetizations of the two layers is estimated as $J \approx 0.06$ J/m² at $d_1 = 2.2$Å. The CFPs obtained for the Nd ions are shown in table 3(a). Since the $P4_2/mnm$ symmetry of the crystalline Nd$_2$Fe$_{14}$B is broken in this multilayer model, we have four Nd ions crystallographically inequivalent. We label them as Nd(f)-a and Nd(g)-a, located at the (001) interface, and Nd(f)-b and Nd(f)-b, inside. In contrast to the Nd$_2$Fe$_{14}$B (001) surface model[6] mentioned above, the CFPs $A_2^0(r^2)$ are all positive as shown in Table 3(b), that is, they are restored as in the bulk system. In the present multilayer system, there exist Fe ions in the α-Fe layer lie directly on the interfacial Nd ions. The valence electrons of the Nd ions couple with the 3d electrons of those Fe ions and thus slightly extend outward from the interfaces, then they form the crystal field which gives the uniaxial magnetic anisotropy perpendicular to the (001) interface of the Nd$_2$Fe$_{14}$B layer. We speculate that this is the reason for the restored CFPs of the Nd ions.
Figure 2. The total electronic energy of the system for parallel (△) and anti-parallel (▼) magnetization alignments between Nd$_2$Fe$_{14}$B and α-Fe layers.

Table 3. The CF parameters $A^0_{ij}(r^2)$ [K] of Nd ions obtained for the (a) Nd$_2$Fe$_{14}$B (001)/α-Fe (001) and (b) Nd$_2$Fe$_{14}$B (100)/α-Fe (110) models.

|                | (a) Nd$_2$Fe$_{14}$B (001)/α-Fe (001) | (b) Nd$_2$Fe$_{14}$B (100)/α-Fe (110) |
|----------------|--------------------------------------|--------------------------------------|
| Nd(4f)-a       | 491 - 976                            | Nd(4f)-c                            |
| Nd(4g)-a       | 309 - 1403                           | 639 - 695                           |
| Nd(4f)-b       | 538                                  | Nd(4g)-c                            |
| Nd(4g)-b       | 253                                  | 31 - 98                             |
|                |                                      | Nd(4f)-d                            |
|                |                                      | 623 - 464                           |
|                |                                      | Nd(4g)-d                            |
|                |                                      | 221 - 224                           |

alignments as functions of the interlayer distance $d_2$, in the same manner as in Fig. 2. At this time, the anti-parallel alignment is stabilized around the minimum of the total energy, $1.6 \leq d_2 \leq 2.0$[Å]. The exchange coupling per unit area between the magnetizations of the two layers is estimated as $J = 0.013$ J/m$^2$ at $d_2 = 1.8$Å. The CFPs obtained for the Nd ions are shown in table 3(b). Here we label the Nd ions in this model as Nd(f)-c and Nd(g)-c, located around the (100) interface, and Nd(f)-d and Nd(f)-d, inside. In this case, the CFPs are all positive. We would note here that, we have confirmed very recently [15] that they are also all positive even if the Nd ions are located around the (100) surfaces of the crystalline Nd$_2$Fe$_{14}$B using the WIEN2k code.

An existence of such anti-parallel coupling between the hard- and soft-layers, which might have been realized partially in random dispersed geometry such as melt-spun ribbons of exchange-spring magnets, would have given rise to a negative contribution to the magnetic properties, especially to the maximum energy product. We believe that the present results, that is, the exchange coupling between the hard- and soft-phases depends on the Miller indices of the interfacial planes, can be checked by experimental study on well-fabricated Nd$_2$Fe$_{14}$B (100)/Fe multilayer systems.

In our calculation, so far, the structural relaxation around the interfaces has not been taken into account. We have actually tried such relaxation calculations for our models and have seen that they support the present results. Needless to say, there would exist much complicated structures around the grain boundaries of real samples of exchange-spring magnets, or even around the interfaces of exchange-spring multilayer thin films, while the number of atoms nowadays available in first principles calculations are far from sufficient to reproduce such realistic structures. In fact, even if we fully optimize the local structures of the present models, they would still be simple mimics of the real systems. However, the first aim of this paper is to point out that the anti-parallel coupling between hard- and soft-layers in exchange-spring magnets can be realized, and thus we believe that the modes should not necessarily be
Figure 3. The total electronic energy of the system for parallel (△) and anti-parallel (▼) magnetization alignments between Nd$_2$Fe$_{14}$B and α-Fe layers.

well-realistic for this aim.

In summary, we have theoretically investigated the magnetic properties of the Nd$_2$Fe$_{14}$B/α-Fe multilayer models which can be fundamental systems to reveal the important factors in the mechanisms which dominates the coercivity and energy product of exchange-spring magnets. On the basis of first principles calculations, we predict that the exchange coupling between the two layers of the models depends on the Miller indices of the interfacial planes, and can be negative.

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