Proposal for coercivity mechanism in rare-earth magnets based on comparison between experiments on model-interface samples and ab-initio calculations

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There are high needs of developing higher coercivity Nd-Fe-B magnets without using heavy rare elements. In our project research, our final goal is to obtain a guiding principle to create supreme-performance permanent magnets beyond that of the current Nd-Fe-B magnet, by making full use of the nanoscale structure control to create the model-interface samples, which simulate the intergranular structure of sintered Nd-Fe-B magnets. We investigate the magnetic properties of these model-interface samples and compare the experimental results with the ab-initio calculations.

We briefly describe the results of our project research below and propose a hypothesis for the coercivity mechanism dominated in sintered Nd-Fe-B magnets.

(1) Effect of Nd and La coating on the coercivity of highly-oriented $Nd_2Fe_{14}B$ thin films

Highly oriented $Nd_2Fe_{14}B$ thin films were fabricated on the single-crystal substrates, with the *c*-axis of the tetragonal $Nd_2Fe_{14}B$ cell perpendicular to the film plane. As the average grain size was decreased from 300 nm to 50 nm, the coercivity H_c increased linearly from 7 kOe to 17 kOe, as shown by the black circles in Fig. 1. We then coated these films with the Nd overlayer and annealed, which led to the systematic enhancement of the coercivity [1] as shown by the red circles in the Fig. 1. Similar behavior was observed for the La-coated $Nd_2Fe_{14}B$ films [2] as shown by the cross symbols in Fig.1. Detailed microstructure investigation on these samples have shown us that there exist the oxide phases of Nd or La at the interface with the $Nd_2Fe_{14}B$ phase in both of the two model systems. In the sintered Nd-Fe-B magnets, we recognized so far that an existence of the excess Nd in the vicinity of the main $Nd_2Fe_{14}B$ phase was crucial for the higher coercivity based on the morphology change of the Nd-rich phase after low-temperature annealing [3]. However, the results shown in Fig. 1 strongly suggest that it is not the Nd nor the La but the O atom, that is important for the coercivity enhancement. We then performed recently the atomic-scale investigation of the interface structure in the La-coated $Nd_2Fe_{14}B$ films before (H_c~10 kOe) and after (H_c~15 kOe) annealing. The STEM-EDS elemental analysis revealed that the content of La, Nd, and Fe was unchanged by the annealing, and showed that the only difference caused by the annealing was the O content in the LaO_x layer, which increased from 15 to 35 at.% [4]. These results therefore suggest that the magnetocrystalline anisotropy of the Nd atoms which would be reduced at the surface of $Nd_2Fe_{14}B$ has then recovered by a presence of O, leading to a remarkable enhancement of the coercivity. This discovery is in consistent with the recent theoretical calculation reported by Toga et al.[5].

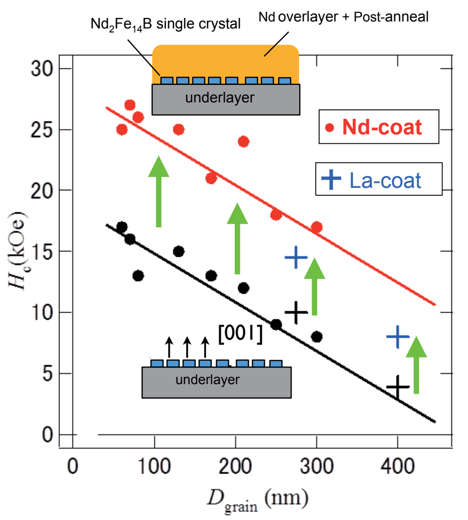

Fig. 1 Coercivity of Nd- and La-coated $Nd_2Fe_{14}B$ films after post annealing, together with that for the uncoated $Nd_2Fe_{14}B$ films, as a a function of averaged grain size along the lateral direction.

(2) Orientation-dependent exchange coupling between $Nd_2Fe_{14}B$ and α-Fe interfaces

An idea of exchange-coupled hard/soft nanocomposite magnets is the promising candidate [6] to fabricate superior-performance magnets exceeding the theoretical limit of the energy-product value in the Nd-Fe-B magnet. In the case of $Nd_2Fe_{14}B/\alpha$-Fe system, reported $(BH)_{max}$ values are still much lower because of the difficulty in controlling the size and alignment of the hard-phase grains. Moreover, the exchange coupling between the hard and soft magnetic phases is the important factor in dominating the magnetic properties of the nanocomposite magnet. Being motivated by the stimulating theoretical prediction [7], a model sample with an interface of the $Nd_2Fe_{14}B(100)$ plane and the α-Fe were fabricated in order to evaluate the exchange-coupling constant J_{ex} between these two ferromagnetic phases. By measuring the ferromagnetic resonance fields and the Kerr loops, the exchange-coupling constant J_{ex} was confirmed to be negative [8] with the value of $J_{ex} = -6.5\times10^{-4}$ J·m^{-2} at the $Nd_2Fe_{14}B(100)/\alpha$-Fe interface, in striking contrast to the positive J_{ex} value for the $Nd_2Fe_{14}B(001)/\alpha$-Fe interface [9, 10]. Figure 2 shows the field-induced moment reversal behavior of the Fe magnetic moment, which is the direct evidence of the antiparallel coupling at zero field, i. e. the negative J_{ex}.

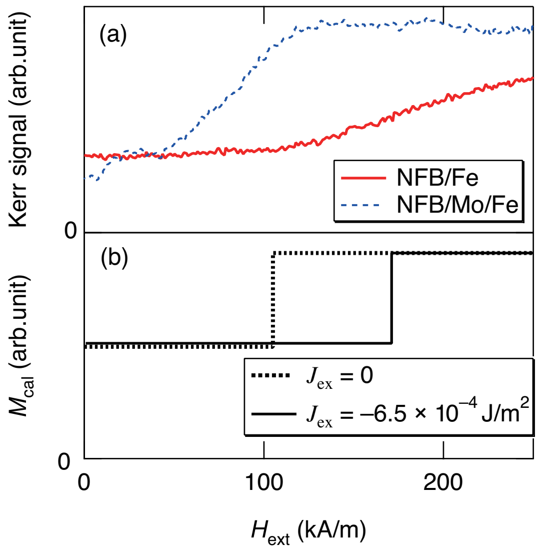

Fig. 2 (a) Local magnetization curves measured by longitudinal MOKE in $Nd_2Fe_{14}B(100)/\alpha$-Fe and $Nd_2Fe_{14}B(100)/Mo/\alpha$-Fe samples, in comparison with (b) the calculated magnetization curves with and without negative exchange coupling. Field-induced spin-flip transition indicates the antiparallel exchange coupling at the interface in the $Nd_2Fe_{14}B(100)/\alpha$-Fe sample.

Other topics to be introduced in the presentation are as follows.

(3) Surface state and spin switching in millimeter-sized single crystals of $R_2Fe_{14}B$ (R=Nd and Tb)

(4) Creation of orientation-controlled $Nd_2Fe_{14}B/\alpha$-Fe nano-composite magnets

We finally propose a hypothesis that an existence of not only the O but also Fe or Cu at the interface is essential [5, 11] for the recovery of the magnetocrystalline anisotropy of the R atoms which would have been reduced being at the outermost surface of the $R_2Fe_{14}B$ grains owing to a breaking of the periodic symmetry. This scenario would be applicable to other rare-earth-containing permanent magnets, provided that a nucleation of reversed domains is the dominant process for the coercivity. This work was supported by the Collaborative Research Based on Industrial Demand, from Japan Science and Technology Agency (JST).

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