Current Status of Research and Development toward Permanent Magnets Free from Critical Elements

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The current status of R&D activities and major results are briefly reviewed, mainly focusing on work reported since about 2010. Developments in and perspectives on less-Dy and Dy-free Nd-(Dy)-Fe-B-type permanent magnets, search and discovery of new hard magnetic materials, progress in the basic understandings of coercivity in hard magnets, and perspectives on anisotropic nanocomposite permanent magnets are overviewed.

Key words: permanent magnets, critical elements, magnetic hardness, coercivity, rare earth-free, nanocomposite

1. Introduction

Permanent magnets are unquestionably one of the key materials required to realize high efficiency in energy conversion devices such as electric motors and generators. For these applications, the anisotropic sintered Nd-Dy-Fe-B-type permanent magnets are almost exclusively used. The predicted increase and the recent concerns about the criticality of Dy, however, resulted in worldwide reconsideration of the permanent magnet materials and their usage, which included search for new materials free from the critical elements, recycling of rare earths elements, alternative devices using less-critical materials such as hard ferrites, and so on. The research and development activities on new materials free from critical elements are now conducted in plural projects and consortiums in many nations1)

reinvestigation of variety of rare earth-free magnet materials such as MnAl and MnBi. However, if a benchmark is set on the current high-performance permanent magnet materials, one has to focus on hard magnetic materials that have magnetization large enough to compete with those top-grade commercial products.

The base compound used in current high-end permanent magnets is (Nd1-xDyx)2Fe14B in which up to about one third of rare earth elements is replaced by Dy, i.e., x ≤ 0.3. To be comparable to this compound, a material that may be accepted by the industry as a potential candidate should have spontaneous saturation magnetization (JS) of this compound, namely, JS ≥ 1.4 T. Furthermore, the candidates must have large enough positive uniaxial magnetocrystalline anisotropy

![Map of JS and K1 of various hard magnetic compounds and desirable range (unshaded area) of parameters at (a) room temperature and at (b) 573 K.](image)

**Fig. 1** Map of JS and K1 of various hard magnetic compounds and desirable range (unshaded area) of parameters at (a) room temperature and at (b) 573 K.
constant ($K_u$, which, for simplicity, is abbreviated to $K_1$ in the following) to overcome self-demagnetizing magnetostatic energy, which is proportional to magnetization as $(1/2)\mu_0^{-1}J_s^2$. The argument given above sets a relatively rigorous condition to the intrinsic magnetic properties for a magnetic material. If we adopt the widely accepted criterion that the intrinsic coercivity factor $x = \{μ_0K_u/(J_s^2)\}^{1/2}$, should be larger than one, our target area on the $J_s-K_1$ plane at room temperature becomes the un-shadowed region in Fig. 1a, where only a few rare earth-transition metal compounds can be found. The line marked as $x = 1.4$ represents a practical guide line based on experiences with existing hard magnetic compounds from which useful permanent magnet materials for modern motor applications have been developed. One of insights that can be obtained from this figure is that the main contribution of the partial replacement of Nd with Dy or Tb, which is widely used in order to realize high coercivity, is an enhancement of the magnetic hardness factor by reducing $J_s$ of the base compound. Since we are now forced to depart from such a conventional, easy, method, we have to find other ways to obtain high coercivity.

In this article, recent progresses of investigations toward critical-elements-free permanent magnets based on the potential candidates in the framework of the argument given above are reviewed. Since the intrinsic coercivity of a magnet is primarily governed by the microstructure of the materials, the main focus is set on microstructural engineering of the candidate materials. Another topical field covered in this article is the theoretical and empirical search for new members in the desired region in Fig. 1a.

2. Less-Dy- and Dy-free Nd-Fe-B permanent magnets

Anisotropic permanent magnets based on the Nd$_2$Fe$_{14}$B-type compound are the prevailing material with outstanding magnetic properties, as shown in Fig. 2, which is a performance map of various commercial permanent magnet materials described in manufacturer’s datasheets of transversely pressed grades for which higher performance than the axially pressed grades can be realized (only typical values are picked up for the purpose rather than making an exhaustive list). The current high-end materials are the Dy (or Tb) grain-boundary-diffusion (GBD)-processed grades in which the heavy rare earth elements are effectively enriched in outer shell layers of the crystal grains of the (Nd$_{1-x}$Dy$_x$)$_2$Fe$_{14}$B phase. The process was invented and reported as early as 2005$^3$ and quickly adopted in commercial magnets with various modifications$^4-6)$. A process to blend HRE-rich alloy powder prior to sintering to create the core/shell structure has also been proposed.$^7$ These are Dy-saving techniques by allocating Dy more densely in the Dy-enriched shell than interior of the grains, reducing the undesirable decrease in $J_s$ caused heavy rare earths (HRE which is Dy or Tb), the magnetic moment of which couples antiferromagnetically with those of Nd and Fe. In the case of so-called GBD-process, the process utilizes mass transfer from HRE-rich sources such as metallic HRE or HRE-containing compounds placed on surfaces of a bulk magnet to the interior of the bulk that has a lower HRE content. The typical grain-boundary diffusion processing temperatures are significantly lower than the sintering temperatures. A prolonged heat treatment causes formation of too thick HRE-rich shells to result in a reduction of magnetization and should be avoided. Thus, the GBD-processed magnets have a distribution of coercivity along the direction normal to the surface from which the HRE was provided. Such inhomogeneous distribution of coercivity can be useful in certain motor and generator designs in which the high coercivity regions are matched with high armature field regions in the magnetic circuit.$^9$ Composition and microstructure of the base material may be optimized to result in the designed magnetic properties after the grain-boundary diffusion treatment.

Sepehri-Amin et al. investigated chemical composition profiles of elements in relatively deep portion, i.e. 0.4 mm from the surface, of a Dy-diffused sintered magnet using three-dimensional atom-probe tomography (3DAP) and found that Dy diffuses in the Nd$_2$Fe$_{14}$B phase from the grain boundary until the concentration gradient disappears within the Dy-enrich shell region and that there is no enrichment of Dy in the intergranular phase, which did show thickening as a result of rejection of Nd from the Dy-enriched shell.$^{10}$ Seelam et al. investigated the formation mechanism of the Dy-enriched shell structure which frequently showed faceting of the core/shell boundary when
metallic Dy is diffused from the surface of the magnet\textsuperscript{10}. It was concluded that partial melting of the Nd\textsubscript{2}Fe\textsubscript{14}B phase at the processing temperature due to the supply of excess rare earth elements leads to the formation of faceted Nd\textsubscript{2}Fe\textsubscript{14}B cores. The solidification of the Dy enriched liquid results in the formation of (Nd\textsubscript{1-x}Dy\textsubscript{x})\textsubscript{2}Fe\textsubscript{14}B shells with coherent core–shell interface and relatively flat concentration profile of Dy within the shell. This mechanism is similar to that proposed previously by Oono et al. for formation of a core/shell structure in sintered Nd–Fe–B magnets after grain-boundary diffusion of Dy–Ni–Al alloys\textsuperscript{11}. These investigations suggest that the enhancement of coercivity is a result of enhanced magnetic hardness in the HRE-enriched shell as was proposed earlier by Nakamura et al. basing on an observation that the change in coercivity ($\Delta H_c$) caused by the diffusion process using various rare earth elements was roughly proportional to the difference in anisotropy fields of R\textsubscript{2}Fe\textsubscript{14}B compounds ($\Delta(2K/JS)$) where R stands for the rare earth elements used in the experiment\textsuperscript{12}. Retrieving data from Ref. 12, this can be shown graphically as in Fig. 3, which depicts the dependence of the change of $H_c$ per mass % of diffused rare earth element R ($\Delta H_c/\Delta w$) on difference in anisotropy field, $\Delta H_a=\Delta(2K/JS)$, of the R\textsubscript{2}Fe\textsubscript{14}B compound from that of Nd\textsubscript{2}Fe\textsubscript{14}B. For magnetic HRE (Gd, Tb, Dy, Ho, Er, Tm), a linear fit of data cross the $\Delta H_a$ axis with a positive intercept, which may suggest that there is additional effect of enhanced magnetic hardness due to reduction of magnetization in the shell.

For further improvement of coercivity without introducing Dy or Tb, one needs to rely on microstructural engineering. One of conventional yet empirically most effective approaches is to reduce the grain size. While grain size reduction has been known to be one of effective ways to improve coercivity of various kinds of permanent magnets, it is only recent that elucidation of its origin was given basing on micromagnetic simulations\textsuperscript{13, 14}. According to these analyses, the grain size dependency of coercivity arises, at least partly, as a result of the grain size–dependence of the magnitude of magnetic dipole fields which are created by reversed magnetization of low-coercivity grains near collective defects such as surfaces of the magnet.

![Fig. 3](image-url)

**Fig. 3** Dependence of change in $H_c$ per mass % of diffused rare earth element R ($\Delta H_c/\Delta w$) on difference in anisotropy field, $\Delta H_a=\Delta(2K/JS)$, of the R\textsubscript{2}Fe\textsubscript{14}B compound from that of Nd\textsubscript{2}Fe\textsubscript{14}B. Solid line is a linear fit for all rare earth elements, while the dashed line is only for magnetic HRE elements. Data were taken from Ref. 12.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>fcc-NdO\textsubscript{4}</td>
</tr>
<tr>
<td>B</td>
<td>cubic-Nd\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>C</td>
<td>α-Nd</td>
</tr>
<tr>
<td>D</td>
<td>Nd\textsubscript{1.5}Fe\textsubscript{3}B\textsubscript{4}</td>
</tr>
<tr>
<td>E</td>
<td>fcc-NdO\textsubscript{4}</td>
</tr>
<tr>
<td>F</td>
<td>fcc-NdO\textsubscript{4}</td>
</tr>
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</table>

The empirical approach to obtain high coercivity by reducing the grain size has been pursued in Nd–Fe–B magnets including various processes. For sintered Nd–Fe–B, finely pulverized powders of sub-micrometer size obtained by jet-milling using He gas, with which much higher velocity than N\textsubscript{2} gas for milling process was used to produce magnets with average grain size of 1 μm\textsuperscript{15}. To produce grain size in the vicinity of the single domain critical size, which is about 200 nm, the hydrogenation/disproportionation/desorption/recombination (HDDR) process\textsuperscript{16, 17} or rapid-solidification followed by hot-deformation process (abbreviated as hot-deformation process in the following)\textsuperscript{18, 19} were adopted. Fig. 4 shows the current status of coercivity values achieved in various Nd–Fe–B magnets with various grain sizes collected from the literature\textsuperscript{19-22}. Although the HRE elements are excluded from the materials shown in this figure, small amounts of Pr and a few non-magnetic additional elements such as Al, Cu, Ga, Ag, etc. are alloyed in these magnets. Nevertheless, the linear dependence of coercivity on logarithm of grain size is observed for sintered Nd–Fe–B for which the coercivity keeps increasing with decreasing grain size down to about one micrometer. For HDDR and hot-deformed magnets, the coercivity falls short of expected values extrapolated from the sintered magnet regime. The open symbols in Fig. 4 are for those specimens produced by applying the grain boundary diffusion (GBD) process using
low-melting-temperature eutectic alloys of magnetic light rare earth elements (Pr and Nd) with X = Al, Cu, Ag, Nd-Cu, etc. The GBD process with Nd-X was first used on HDDR-processed Nd–Fe–B powders to increase coercivity without using heavy rare earth elements\textsuperscript{16,17} and recently it is used most effectively on the hot-deformed Nd–Fe–B, in which superior alignment of the easy axis of grains can be achieved, to obtain magnetic properties comparable to those of the high-performance sintered Nd–Dy–Fe–B\textsuperscript{18}. One of shortcomings of this process is a decrease in remanence due to infiltration of a large volume fraction of the non-magnetic alloys. Recently, Akiya et al. produced Dy-free specimens that showed magnetic properties comparable to sintered Nd–Fe–B containing about 4 mass % Dy by applying a constraint during the GBD heat-treatment process to avoid undesirable extreme uptake of the infiltrant\textsuperscript{19}. The infiltration process is also applicable on thin-film specimens and very high coercivity values around 2.4 MA/m have been achieved in HRE-free specimens\textsuperscript{23}.

Behind these recent developments of grain boundary engineering of the intergranular grain boundary region exist the renewed understandings of structure and magnetic properties of the grain boundary phases. Sintered Nd–Fe–B-type magnets have a structure which is schematically shown in Fig. 5. The intergranular thin layer is an amorphous phase constituted of Fe (and Co if the magnet contains Co) which amounts about 70 atomic percent and Nd (and Pr in some commercial magnets) with trace of B and Cu\textsuperscript{24}. It does not contain any significant amount of oxygen. The Nd-rich region which appears in junction areas of the main phase is composed of metallic Nd and various oxide phases\textsuperscript{25–28}. There is also a B-rich phase, NdFe\textsubscript{4}B\textsubscript{4}. These sub-phases in sintered Nd–Fe–B are listed in Table 1.

The magnetic property of the intergranular phase was recently determined by several techniques, namely, the electron holography\textsuperscript{29}, spin-polarization analysis in scanning electron microscopy\textsuperscript{30}, and soft X-ray magnetic circular dichroism\textsuperscript{31}, and was proven to be ferromagnetic with a smaller magnetization and a lower magnetic ordering temperature than the main phase Nd\textsubscript{2}Fe\textsubscript{14}B. Values for the magnetic moment of the intergranular phase ($J_{s,\text{GB}}$) measured with these methods are listed in Table 2. The temperature dependence of the Fe XMCD and estimated magnetic moment of Fe are shown in Fig. 6\textsuperscript{31}.

**Fig. 4** Current status of coercivity values achieved in various HRE-free Nd–Fe–B magnets with various average grain sizes.

**Fig. 5** Schematic of typical microstructure for sintered Nd–Fe–B permanent magnets in which Nd-rich regions, Nd and NdO\textsubscript{x}, are mixtures of different sub-phase.

**Table 2.** Magnetic moment of intergranular phase measured with different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>$J_{s,\text{GB}}$ (T)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron holography</td>
<td>1</td>
<td>29</td>
</tr>
<tr>
<td>Spin-SEM</td>
<td>0.41 to 0.48</td>
<td>30</td>
</tr>
<tr>
<td>Soft X-ray MCD</td>
<td>$\mu(\text{Fe})<em>{\text{GB}} \approx 1.3 \mu</em>\text{B}$</td>
<td>31</td>
</tr>
</tbody>
</table>

**Fig. 6** Dependence of Fe XMCD and estimated magnetic moment of Fe on temperature (reused from Ref. 31 with permission).
Since the domain wall width is larger than the typical thickness and decrease in exchange stiffness, $A$, and $K_1$ order to increase the pinning force, an increase in the ferromagnetic inhomogeneity that can pin domain-walls, suggest that the intergranular phase may act as a thin of the fcc-NdO$_x$ phase by Chen et al. revealed that this out that the depth of a defected layer (which appeared possible atomic structures of the interfaces and pointed in contact with the Nd$_2$Fe$_{14}$B grains in sintered Nd-Fe-B and that it has a preferable effect on coercivity$^{32-34}$. Recent first-principles calculations of formation energy of the fcc-NdO$_x$ phase by Chen et al. revealed that this phase can be stable within relatively large concentration range of oxygen ($0 < x < 0.5$) as a compound of the ZnS-type structure with a large amount of oxygen vacancy$^{35,36}$. It was also pointed out that the calculated lattice constant of the fcc-NdO$_x$ phase varies over a wide range of about seven percent with a variation of oxygen content, suggesting that the phase is forgiving to reduce strain energy when it forms epitaxially on Nd$_2$Fe$_{14}$B grains. Hrkac et al. used solid state molecular dynamics simulation to investigate possible atomic structures of the interfaces and pointed out that the depth of a defected layer (which appeared to be amorphous) near the surface of Nd$_2$Fe$_{14}$B sensitively depends on orientation and lattice structures of the adjacent sub-phases$^{19,37}$. For simple orientation relations, precise large-scale calculations of atomic positions near Nd$_2$Fe$_{14}$B/NdO$_x$ interfaces are recently performed using super computers$^{38}$. In the case when an oxygen-rich oxide (Nd$_2$O$_3$) is in contact with Nd$_2$Fe$_{14}$B main phase, the simulation showed that atomic displacements were restricted only in the first layer of the fcc-NdO$_x$ (Fig. 7) and that the oxygen atoms prefer to locate close to Nd ions. These oxygen atoms may cause a significantly altered electronic distribution of valence electrons (5d) which may result in a reverse of the sign of principal crystal electric field (CEF) parameter $A_0^\alpha$ of Nd ions in Nd$_2$Fe$_{14}$B$^{39}$. Such changes, even taking place in atomic scales, may result in a significant reduction of nucleation field of reversed magnetic domains when the changes occur on the surface of the hard magnetic phase$^{40}$.

The thermodynamic origin of the various oxide formations in the Nd-Fe-B-type permanent magnets is still a subject of further investigations. Even the Nd-O phase diagram distributed currently$^{41}$ has serious disagreements with recent experimental findings and need to be reassessed$^{42}$. The situation becomes more complicated in the real magnets with simultaneously microalloyed additives such as Al, Co, Ga, and Cu, which may affect thermodynamic events forming other compounds in the Nd-rich regions. Typically, Cu has been pointed out to play a key role by relocating itself during a post-sintering heat treatment, leading to the formation of the Nd-rich intergranular phase ("Nd-Cu-rich" in Fig. 5)$^{40}$. Although it seems that Cu (and Al and Ga as well) affects interfacial energy of Nd$_2$Fe$_{14}$B/Nd-rich boundaries, entire mechanism is not clear yet. Besides this interfacial energy issue, there exists interplay among free energies of relevant phases such as NdO$_x$. Detailed investigations on equilibria including interfacial phases are important for further grain boundary engineering of industrial grades of Nd-Fe-B-type permanent magnets in order to realize HRE-free high coercivity materials.

### 3. Discovering new hard magnetic materials

Number of new hard magnetic materials discovered after Nd$_2$Fe$_{14}$B in the desired magnetic parameters as shown in Fig. 1 have been very limited, with Sm$_2$Fe$_{17}$N$_3$ and NdFe$_{12-x}$M$_x$N with $M =$ Mo, Ti, V being the only members. All of these compounds are inferior to Nd$_2$Fe$_{14}$B in terms of saturation magnetization at and near room temperature. Recent investigations aiming at development of non-rare-earth permanent magnets include revisits to previously known 3d-transition metal alloys and compounds such as Alnico, MnAl, MnBi, L$_{10}$FeNi, tet-FeCo, and $\alpha'$-Fe$_{16}$N$_{22}$ $^{2}$ One of goals of research activities with such materials is to develop permanent magnets operative at high temperatures (such as 180 °C) with intermediate properties between hard ferrites and Nd-Dy-Fe-B by improving compounds.
Mn-Sn-Co-N alloys have been discovered\(^{47-49}\). Among these alloys, Mn\(_{82.5}\)Sn\(_{10}\)Co\(_{7.5}\) alloy showed a low \(J_S\) of 26 mT but a large \(H_c\) of 1270 kA/m. The high coercivity was attributed to a phase separation and formation of a two-phase microstructure during a two-step heat treatment in \(N_2\) at 900 °C followed by at 500 °C. The fine two-phase microstructure was composed of a permavskite-type \(Mn_3N\)-like phase and \(\delta\)-\(Mn\) phase.

Although experimental possibilities may not have been exhausted, these compounds are not ready for the industrial development for permanent magnet materials. The search for totally novel hard magnetic materials still need to be continued.

Quite recently, Hirayama et al. synthesized \(\text{NdFe}_{12}\) and its interstitially-modified compound, \(\text{NdFe}_{12}N\), as epitaxial films on \(W\)-buffered \(MgO\) substrate\(^{50}\). The possibility of realizing large values for \(J_S\) and \(K_1\) in \(\text{NdFe}_{12}N\) had been theoretically predicted by Miyake et al. prior to the synthesis\(^{51}\). The compound has the \(\text{ThMn}_{12}\)-type tetragonal structure and has \(J_S\) and \(K_1\) values at room temperature of 1.66±0.08 T and 5.3 MJ/m\(^3\), respectively. These values exceed those of \(\text{Nd}_2\text{Fe}_{14}B\), namely, 1.61 T and 4.9 MJ/m\(^3\). The Curie temperature of \(\text{NdFe}_{12}N\) was estimated to be about 550 °C, which is much higher than 316K of \(\text{Nd}_2\text{Fe}_{14}B\). The \(\text{NdFe}_{12}\) compound, into which nitrogen atoms are to be interstitially diffused, could be grown to a thickness of 350 nm, suggesting that the compound is not unstable but is metastable. The location of \(\text{NdFe}_{12}N\) on the \(J_S-K_1\) map is shown in Fig. 1 for room temperature (Fig. 1a) and 200 °C (Fig. 1b). Although \(\text{NdFe}_{12}N\) decomposes above about 600 °C, suggesting that conventional thermal processes cannot be applied on this compound to fully densify powders or to develop heat treatment processes for development of coercivity, the excellent magnetic properties at high temperatures are strongly attractive. Finally, it should be mentioned that the \(\text{ThMn}_{12}\)-type \(\text{R-Fe}\) compound is a member of homologous compounds \(\text{R}_{m-n}\text{T}_{5m+2n}\) where \(T\) stands for 3d-transition metals\(^{52}\). These compounds are generated by systematic replacement of \(R\) atoms with a dumb-bell \(T\)-pairs in the \(\text{CaCu}_5\)-type \(RT\) compound (Table 3). With \(m=2\) and \(n=1\), the \(\text{ThMn}_{12}\)-type compounds are generated, but for \(T=\text{Fe}\), pure \(\text{Fe}_{12}\) compounds does not form without substituting a part of Fe with stabilizing elements such as Ti and Mo in conventional solidification processes including rapid quenching or mechanical alloying process followed by isothermal heat treatments. The finding that the \(\text{NdFe}_{12}\) is a metastable compound suggests that this compound may be grown further once a seed crystal is formed. The Nd content in \(\text{NdFe}_{12}N\) is only about 17 mass % in contrast to \(ca\., 27\) mass % in \(\text{Nd}_2\text{Fe}_{14}B\). Further investigations aiming at utilization of this compound as bulk hard magnetic materials are of great importance.

### Table 3. Structural types of homologous compounds \(\text{R}_{m-n}\text{T}_{5m+2n}\), where \(T\) stands for 3d-transition metals.

<table>
<thead>
<tr>
<th>Formula</th>
<th>(m)</th>
<th>(n)</th>
<th>Structure type</th>
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<tbody>
<tr>
<td>(\text{RT}_5)</td>
<td>1</td>
<td>0</td>
<td>(\text{CaCu}_5)</td>
</tr>
<tr>
<td>(\text{R}<em>2\text{T}</em>{17})</td>
<td>3</td>
<td>1</td>
<td>(\text{Th}<em>2\text{Zn}</em>{17}) (\text{Th}<em>2\text{Ni}</em>{17})</td>
</tr>
<tr>
<td>(\text{R}<em>3\text{T}</em>{29})</td>
<td>5</td>
<td>2</td>
<td>(\text{Nd}<em>3(\text{Fe}</em>{12}\text{Ti})_{29})</td>
</tr>
<tr>
<td>(\text{RT}_{12})</td>
<td>2</td>
<td>1</td>
<td>(\text{ThMn}_{12})</td>
</tr>
</tbody>
</table>

### 4. Progresses in the basic understandings of coercivity in hard magnets

Coercivity is the central issue of development of permanent magnet materials free from critical elements. The recent progress in both multi-scale and multi-aspect structural and magnetic analysis and computational assessment of atomic magnetic properties such as site-resolved magnetocrystalline anisotropy energy have enabled construction of atomistic view of local properties of defects such as interfaces and grain boundaries in which the magnetization reversal or domain wall unpinning may take place. However, actual calculation of such magnetization process in atomistic picture is difficult because a meaningful calculation requires length scale that encompasses a few times of the exchange length \((A/K_1)^{1/2}\) which is typically about 1 nm in hard magnetic materials. This means that a few thousand of atoms are...
Atomistic calculations using the Landou-Lifshitz-Gilbert (LLG) equations may be possible in principle but require enormous computational resources. On the other hand, finite element simulations using the LLG equations are required to be performed with the cell size equivalent with the exchange length, resulting in also a huge number of cells to deal with real microstructure. To link these regimes, the atomic spin system needs to be reduced to a simplified system without losing any decisive intrinsic characteristics of the original system so that the calculation over several nanometers scale can be performed. This is called coarse graining and the methodology for it is still on the early stage of development.

Although the methodology to build the link has not been fully established, large scale finite-element method (FEM) LLG simulations with nm cell sizes have been performed using super computers such as "K" of RIKEN. Fujisaki et al. demonstrated the necessity of using such fine cell sizes smaller than the domain wall width in order to correctly describe domain wall motion in Nd₂Fe₁₄B-based multi grain structures magnetically coupled with a ferromagnetic intergranular phase to attack the long-standing problem of the dependence of coercivity on degree of c-axis alignment⁵³, which has never been explained satisfactorily using micromagnetic simulations. The phenomenon is characterized by a general tendency that coercivity sharply decreases with increasing the degree of alignment, indicating that the coercivity mechanism involves domain wall unpinning⁵⁴, and for this reason, can be regarded as a challenging test case for multi-phase, large-scale LLG simulations. Although the simulation did not perfectly reproduce the actual texture-dependency of coercivity in sintered magnets for higher grain alignment, it suggested that enhancement of stray fields due to thinner width of grain boundary phase affects the coercivity of a multigrain object, resulting in a decrease in coercivity with increasing texture (Fig. 9).

On the experimental side of investigations, new approaches using novel probes are currently proposed and have proven their effectiveness. Neutron beam is an ideal tool to analyze magnetic structure of bulk magnetic materials as a whole because of its high transmission ability. Particularly, the small angle scattering analysis is suitable to obtain averaged information of structural and magnetic structures in the length scales ranging from 1 nm to a few hundred nm. The small angle neutron scattering (SANS) experiments have been performed on fine-grained Nd–Fe–B permanent magnets with the Pr–Cu or Nd–Cu grain boundary infiltration treatment and have led to a conclusion that the magnetic reversal takes place within a specific size comparable with the average grain size in the Pr/Nd-Cu-filtrated specimen while in specimens without the infiltration treatment magnetic reversal takes place within a larger region engulfing many grains, suggesting that the infiltration indeed contributed to magnetic isolation of grains in the reversal process⁵⁵–⁵⁶. Ono et al. performed neutron Brillouin scattering measurement on polycrystalline Nd₂Fe₁₄B specimen and obtained the exchange stiffness constant A of 6.6 ± 0.3 pJ/m in a good agreement with a previous measurement on single crystal specimen on Nd₂Fe₁₄(B)⁵⁷.

![Fig. 9 Dependence of coercivity on degree of alignment for multigrain model constituting 27 cubic Nd₂Fe₁₄B grains of 50nm edges and ferromagnetic intergranular phase with various thicknesses, calculated using LLG simulation with a cell size smaller than the exchange length (1.7 nm in Nd₂Fe₁₄B phase) and parallel computation with 500-1000 CPUs (©2014IEEE. Reprinted with permission from Ref. 54).](image)

X-ray magnetic circular dichroism (XMCD) using X-ray nanobeam is a powerful tool to investigate local magnetic properties element-specifically⁵⁸. Hard X-ray nanobeams are available in major synchrotron light facilities and X-ray transmission microscopy (STXM) is an established technology. Ohtori et al. analyzed the dipolar energy in magnetization reversal process in 60 nm-thick anisotropic nanocrystalline Nd-Fe-B by visualizing magnetic dipolar interaction with STXM and calculated the energy density of the dipole interactions in the specimens after applying different demagnetizing fields⁵⁹. This technique, if combined with detailed microstructural observations, may become an interesting tool for semi-quantitative investigations of magnetic interactions among grains. A soft X-ray nano-beam line has been constructed recently in SPring-8 and is expected to provide useful information from various sub-phases in permanent magnets utilizing its surface sensitivity and element selectivity⁶⁰.

As discussed in the previous section, theoretical estimation of local magnetic properties in atomistic scale near the interface region in realistic multi-phase hard magnetic materials is important. However, since hard magnetic rare-earth-transition metal compounds have large unit cells with a large number of atoms,
first-principles theoretical investigations of magnetic properties require large computational resources, in general. Torbatian et al. investigated strain effects on the magnetic anisotropy energy (MAE) and the magnetic moment of Y$_2$Fe$_{14}$B, which has the same crystal structure as Nd$_2$Fe$_{14}$B but without 4f-electron contributions, on the basis of density functional theory$^{61}$. These authors explained that couplings between the occupied (unoccupied) d$_{x^2-y^2}$ component and the unoccupied (occupied) d$_{xy}$ component, respectively, close to the Fermi energy are the most significant origin of the MAE enhancement upon compression in Y$_2$Fe$_{14}$B. Changes in the local density of states (LDOS) result in enhancement of $K_1$ upon compression (Fig. 10). Calculations of magnetic properties of itinerant 3d electrons in YCo$_5$ have been attacked by Matsumoto et al. on the basis of a combination of DFT and relativistic version of the disordered local-moment (DLM) approximation to give the qualitative agreement with the experimental data$^{62}$. The authors showed that calculated magnetic anisotropy energy plotted as the function of the valence electron number has strong oscillation and has a peak at 54 per formula unit, which is the case for YCo$_5$, and argued that the high-temperature MAE may be enhanced by letting the electronic states below the peak of MAE be thermally populated by doping holes.

**Fig. 10** Dependence of MAE of Y$_2$Fe$_{14}$B on strain (at 0K) (Reused from Ref. 61 with permission).

Except for high temperatures (above c.a., 200°C), the rare earth contribution is the major part of MAE in rare earth permanent magnets. In classical treatment, the temperature dependence of MAE in rare earth-3d-transition metal intermetallic compounds have been treated using the single ion anisotropy model, in which localized 4f magnetic moments (which are proportional to the total angular momentum of the 4f orbitals) of rare earth ions are magnetically polarized with molecular fields and are situated in electric field gradients (EFG)$^{63}$. With the understandings that EFG is dominated by intra-atomic valence 5d electrons contributions$^{64}$, $^{65}$, attempts to estimate the EFG with the first-principles calculations have been undertaken and applied to theoretical model surfaces of Nd$_2$Fe$_{14}$B$^{66}$. Yoshioka et al.$^{68}$, $^{69}$ improved the calculation to eliminate dependence of EFG parameters on the muffin-tin radius by adopting recently developed first-principles approach, which is based on Wannier functions$^{70}$. The temperature dependence of MAE of rare earth atoms in a tetragonal compound may be precisely estimated if the crystal electric field (CEF) parameters $A_{mn}$ up to the sixth order are given. The set of $A_{mn}$ up to the sixth order was calculated for each R$_2$Fe$_{14}$B compound recently but it is on the way toward more accurate calculation using the Wannier functions. The current calculations of $A_{mn}$ are still a non-finite temperature calculation. Finite temperature calculations of CEF parameters and 3d-electron MAE are subjects for future investigations.

Coercivity in real bulk magnets consisting of a huge number of grains cannot be described by oversimplified pictures such as genuine nucleation or domain wall pinning events. Now, information of local structure and magnetic properties near interfaces where magnetic reversal nucleates and/or pinned can be obtained in some selected cases$^{71}$. Recent developments of atomistic micromagnetic simulation techniques and finite-elements large-scale simulations over several hundred nm scales, combined with the advanced analytical technologies, the very complicated problem of coercivity may be quantitatively attacked. At present, however, the effects of lattice distortions due to thermal vibrations (phonons), which might be augmented near collective structural defects such as grain boundaries or interfaces, are totally neglected. The solid state molecular dynamics may be one of powerful tools, but it is not clear how to estimate the effects in the time frame of magnetization reversal events. These are challenging issues in both experimental and theoretical magnetism.

### 5. Nanocomposite permanent magnets

Isotropic nanocomposite permanent magnets have been developed with various combinations of constituent phases and a review on them was given elsewhere$^{72}$. The isotropic nanocomposites based on Nd-Fe-B alloys can be industrially manufactured by means of rapid solidification and subsequent heat treatment processes. After pulverizing, they can be utilized as the hard magnetic particulate component of polymer-bonded magnets. In contrast, anisotropic permanent magnets are still subjects of ongoing studies, proving their difficulty to be mastered.

Although being a rough argument, it may be acceptable to assume that magnetization behaves in nearly coherent manner in length scales encompassing a few composite nano-grains in strongly exchange-coupled composite. In such a case, the overall magnetic hardness will fall in the vicinity of the value calculated using the volume-averaged values of $JS$ and $K_1$ of the terminal compounds, which moves in the direction of arrows shown in Fig. 11 as examples for
the nanocomposite to prevent propagation of magnetization reversal throughout the entire composite.

The anisotropic nanocomposite permanent magnet specimens with impressive properties have been demonstrated only in well-designed multi-layered films of SmCo5/Fe-Co73) and Nd2Fe14B/Fe-Co74) at room temperature in which the crystallographic orientations and interfaces of constituent phases are well controlled. Magnetic properties of thin-film nanocomposite permanent magnets thus achieved are shown in Table 4.73-78) Provision of internal structure in the hard magnetic layers to generate coercivity was indispensable in these experiments. Building up approach toward bulk anisotropic nanocomposite permanent magnets from nanoparticles of SmCo5 and Fe has been investigated but still is in a phase of struggling with serious deterioration of coercivity upon densification79, 80). Aiming at novel materials with magnetic properties filling the gap between hard ferrites and rare earth magnets at high temperatures, some researchers consider MnBi as a hard magnetic component of a nanocomposite81).

Nanocomposite permanent magnets are challenging targets in hard magnetism. They are very complicated systems of a large fraction of interfaces of constituent phases that have various orientations and characteristics. Even in simple models such as Nd2Fe14B/Fe, the sign of the exchange coupling in simple combinations can be both positive and negative depending on orientation, as suggested by Toga et al.82) The magnetic properties of the defected region near interfaces cannot be easily computed theoretically or measured experimentally. Moreover, in the case when the adjacent phases tend to form equilibrium third intermediate phase, the interface region would be a complicated one. In this sense, the nanocomposite permanent magnet is a challenging test case for theoretical hard magnetism.

6. Summary

The current status of research and developments toward permanent magnets free from critical elements has been briefly reviewed in this article by omitting previous developments before c.a., 2010 for which other

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>( B_r ) (T)</th>
<th>( H_{cJ} ) (kA/m)</th>
<th>( (BH)_{\text{max}} ) (kJ/m(^3))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Fe/ Nd2Fe14B</td>
<td>SiO2/NdFeB/Fe/NdFeB/Cr</td>
<td>1.2</td>
<td>380</td>
<td>N/A</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Ti/Fe(NdFeB/Fe)/Ti</td>
<td>0.75</td>
<td>240</td>
<td>43</td>
<td>76</td>
</tr>
<tr>
<td>Co/Sm-Co</td>
<td>MgO/Cr/[Sm-Co(45nm)/Co(30nm)](_{10})/Cr</td>
<td>N/A</td>
<td>500</td>
<td>N/A</td>
<td>77</td>
</tr>
<tr>
<td>( \alpha )-Fe/SmFe12</td>
<td>(25vol.% ( \alpha )-Fe)/(75 vol. % SmFe12)</td>
<td>1.3</td>
<td>240</td>
<td>151</td>
<td>78</td>
</tr>
<tr>
<td>Fe/SmCo5</td>
<td>Fe(211)[01-1]/SmCo5(10-10)[0001]</td>
<td>1.7</td>
<td>400</td>
<td>400</td>
<td>73</td>
</tr>
<tr>
<td>Fe17Co33/Nd:Fe14B</td>
<td>Ta/[Nd-Fe-B/Nd/Ta/Fe 67 Co 33 /Ta] ( \infty ) /Nd-Fe-B/Nd/Ta</td>
<td>1.61</td>
<td>110</td>
<td>486</td>
<td>74</td>
</tr>
</tbody>
</table>
excellent review articles are available[85-89]. There exists tremendous difficulty in realizing new permanent magnets to replace todays best grade Nd-Dy-Fe-B permanent magnets. Dy-free Nd-Fe-B anisotropic magnets are under development along the grain size refinement and grain boundary engineering, and further understanding of coercivity mechanism and thermodynamic properties governing the formation of microstructures are essential. Fundamental understanding of magnetism near interfaces and grain boundaries are expected to serve in progresses in such understandings, for which systematic research involving wide range of expertise and discipline are highly desirable.

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References


43) T. Abe, private communication (in preparation for publication).

44) H. Tsuchiura, private communication (in preparation for publication).

45) E. Constantines, JOM 64, 752 (2012)


47) T. Abe, private communication


49) T. Kojima, M. Ogawa, M. Mizuguchi, M. Kotsugi, T.