Perspectives for high-performance permanent magnets: applications, coercivity, and new materials

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Abstract
High-performance permanent magnets are indispensable in the production of high-efficiency motors and generators and ultimately for sustaining the green earth. The central issue of modern permanent magnetism is to realize high coercivity near and above room temperature on marginally hard magnetic materials without relying upon the critical elements such as heavy rare earths by means of nanostructure engineering. Recent investigations based on advanced nanostructure analysis and large-scale first principles calculations have led to significant paradigm shifts in the understandings of coercivity mechanism in Nd–Fe–B permanent magnets, which includes the discovery of the ferromagnetism of the thin (2 nm) intergranular phase surrounding the Nd2Fe14B grains, the occurrence of negative (in-plane) magnetocrystalline anisotropy of Nd ions and some Fe atoms at the interface which degrades coercivity, and visualization of the stochastic behaviors of magnetization in the magnetization reversal process at high temperatures. A major change may occur also in the motor topologies, which is currently overwhelmed by the magnetic flux weakening interior permanent magnet motor type, to other types with variable flux permanent magnet type in some applications to open up a niche for new permanent magnet materials.

Keywords: permanent magnets, surface, interface, coercivity, critical elements

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1. Introduction

High-performance permanent magnets are one of the fundamental materials that support modern technologies in which electric energy is converted to motion, or vice versa, with the possibly highest efficiency. Examples of applications of the high-performance permanent magnets include disc drives
for information-storage devices, hybrid and electric vehicles (HEV and EV), electric bicycles, and transducers including loudspeakers [1, 2]. Among these, the markets of HEV and EV are growing at rapid rate to consume a large amount of the highest grade permanent magnets, and, wind power generators and other energy-generation or energy-storage devices are expected to be the near-future applications that also use a large volume of high-performance permanent magnets. The currently used interior permanent magnet (IPM) type topology of motors for the HEV, EV, and wind turbine applications inherently requires a high coercivity [3, 4]. The potential supply risks of the heavy rare earth elements such as Dy, which is currently used in order to realize the high coercivity of the magnets at their operation temperatures reaching approximately 200 °C for the case of HEV, has never disappeared [5]. Realization of high coercivity at high temperatures without using the heavy rare earth elements is, therefore, strongly required for a sustainable growth of these application markets and, ultimately, for sustaining the green earth.

To induce magnetic flux outside of the material, a permanent magnet needs to have a certain thickness along the direction of its magnetic flux lines. In other words, a permanent magnet is a ‘bulk’ polycrystalline material rather than a thin-film or a nanomaterial. However, the core properties of permanent magnets, namely the large residual magnetic polarization and the coercivity, are the manifestation of the quantum magnetic properties of electrons in the macroscopic scale as a result of strong coupling between nanoscale structural features and magnetic structures such as magnetic domain walls inside the material. The typical length scale relevant to the coercivity of a permanent magnet is the thickness (or width) of magnetic domain walls, the typical value of which is around 4 nm in rare earth magnets [6]. To generate a large coercivity, the related magnetic properties, namely, the magnetic exchange and anisotropy energies need to have sharp profiles in the size range between atomic scales to nanometers in the structural features which are found near interfaces of crystal grains in the polycrystalline hard magnetic materials.

It is only recent that electronic structures and relevant magnetic properties near interfaces of most important hard magnetic compounds containing the 4f elements such as Nd and Sm are discussed in terms of the first-principles calculations [7]. Furthermore, in spite that the operation of the motors and generators is at temperatures fairly above the room temperature, reaching about 200 °C in some automobile applications, understandings of the magnetic behaviors, especially demagnetizing behaviors at elevated temperatures are insufficient and remain to be one of the urgent and challenging issues that still await elemental progresses. However, the recent investigations have led to significant paradigm shifts in the understandings of coercivity mechanism in Nd–Fe–B permanent magnets, kindled by the discoveries of the ferromagnetism of the thin (2 nm) intergranular phase surrounding the Nd2Fe14B grains with three different methods [8–10], the occurrence of negative (in-plane) magnetocrystalline anisotropy of Nd ions and some Fe atoms at the interface which degrades coercivity [11–13], the characteristics of the temperature dependence of magnetocrystalline anisotropy of the rare earth ions in the compound [14–16], and by visualization of the stochastic behaviors of magnetization in the magnetization reversal process at high temperatures (shown in section 2). In this article, the current situations of solid state physics concerning the coercivity mechanism at elevated temperatures in Nd–Fe–B-type permanent magnets is overviewed and the future perspectives of development of new permanent magnets free from critical elements are discussed.

2. Nanoscopic origins of coercivity of bulk permanent magnets

In traditional description of ferromagnetic materials in the framework of the continuum picture, magnetization within the exchange length, \( l_\text{ex} = \sqrt{\frac{\alpha K}{A}} \), where \( \alpha \) is the exchange stiffness and \( K \) is the magnetocrystalline anisotropy constant, may be represented approximately with a single macro spin. The thickness (or width) of magnetic domain walls is given by \( \pi l_\text{ex} \). These are the most important size scales in the microstructural engineering of permanent magnets, and with \( A = 6.6 \, \text{pJ m}^{-1} \) [17] and \( K = 4.3 \, \text{MJ m}^{-3} \) [18] for NdFeB at room temperature, \( l_\text{ex} = 1.2 \, \text{nm} \). In contrast, structural characteristic lengths such as grain sizes in real permanent magnets are of the order of microns [19], being several orders magnitude larger than \( l_\text{ex} \) and magnetization of a permanent magnet may reverse its direction by means of both nucleation of irreversible magnetic domains and displacement of magnetic domain walls. Therefore, local magnetic properties with the size scale of nanometers play the key role in the microstructure-magnetic properties interplay in permanent magnets as figure 1 illustrates. The central extrinsic property that characterize a permanent magnet is the intrinsic coercivity which is defined as the magnitude of applied magnetic field that demagnetizes a permanent magnet to zero polarization from the fully magnetized state. Having the intrinsic coercivity greater than a half of the saturation magnetic flux density at the operation temperature is required for permanent magnets to avoid any demagnetization because the optimal operation point to minimize the volume of the permanent magnet is set at the maximal \( BH \) product, which occurs at around \( H = (1/2)B_c \) in normal device configurations where \( H \) is the magnetic field and \( B_c \) is the remanence.

The intrinsic coercivity \( (H_\text{c}) \) of permanent magnets can be related to the intrinsic magnetic properties of the main hard magnetic phase, namely the magnetic anisotropy field \( H_A = 2K/\mu_0 M_S \) and the saturation magnetization \( M_S \), in the following very simple form [20]

\[
H_\text{c} = \alpha H_A - N_{\text{eff}} M_S \tag{1}
\]

where \( \alpha \) and \( N_{\text{eff}} \) are phenomenological parameters which can be empirically determined by analyzing temperature dependence of \( H_\text{c}, H_A, \) and \( M_S \) assuming that the microstructure of the material does not change with temperature.
Theoretical analysis of the relation between the parameters $\alpha$ and $N_{\text{eff}}$ and the magnetic inhomogeneity of nm sizes has been given by several groups in terms of micromagnetic theory by assuming model profiles of the anisotropy constant $K$ and the exchange stiffness $A$ as a function of position. Kronmüller et al assumed analytical smooth function for $K$ which has a minimum at the center of 2D magnetic inhomogeneity [20] and Sakuma assumed a stepwise change of $K$ and $A$ for a magnetically soft 2D inhomogeneity sandwiched between two hard magnetic regions [21], for instance. An important implication of these theoretical investigations was that the critical field for nucleation of a reversed magnetic domain at the inhomogeneity is always larger than the critical field for a pinned domain wall to break away from the same inhomogeneity. This means that once reversed domain nucleates, the identical inhomogeneity cannot stop the domain wall propagations, letting the whole magnet reverses its magnetization. However, if there exist a magnetically soft spot where magnetization reversal takes place under a much smaller field, the coercivity of the magnet may be determined by pinning field at the stronger inhomogeneity. Generally, the surfaces of a bulk magnet contain various defects as a consequence of mechanical and/or chemical treatments in the finishing processes of production. In such cases, the coercivity may be regarded as pinning-controlled at the interior inhomogeneity.

The magnetocrystalline anisotropy of the rare earth permanent magnet compounds owes its origin to electrostatic energy of localized 4f electrons in the electric fields created mainly by onsite valence electrons at the rare earth sites [22]. Consequently, local environments around the rare earth ions at the interfaces can be strongly affected by nearest neighbor atomic arrangements at the interface. Figure 2 illustrates the layered structure of atomic arrangements in the Nd$_2$Fe$_{14}$B crystal structure (figure 2(a)), the pancake-shaped 4f orbitals of an Nd ion sitting in an aspherical distribution of valence electrons which has larger density along the principal axis of symmetry of the Nd$_2$Fe$_{14}$B lattice (figure 2(b)), and a hypothetical situation at a surface or an interface with a sub-phase containing oxygen in which the Nd valence electrons moved toward the oxygen atom for bonding (figure 2(c)). Clarification of coercivity mechanism requires information of atomic scale profiles of the magnetic properties near the surface or interface.

Magnetocrystalline anisotropy of rare earth ions in a crystal can be calculated using the crystal field theory for well localized 4f ions in which the anisotropic energy is described by crystal electric field (CEF) Hamiltonian,

$$H_{\text{CEF}} = \sum_{l,m} \Theta_l A^m_l \langle i^l \rangle \hat{O}^m_l$$

(2)

where $J$ is the total angular momentum number, $\Theta_l$ is Stevens parameter, $A^m_l$ is crystal field parameter, and $\hat{O}^m_l$ is the Stevens operator [23]. The CEF energy is assumed to be smaller than the exchange energy $2(g_J - 1)J \cdot \mathbf{H}_\text{ex}$ in this theory (where $J$ denotes the total angular momentum). For a simplified discussion in this section, it is sufficient to note that the main contribution from CEF to magnetocrystalline anisotropy constant in the ground state (0K) is written as

![Figure 1. Magnetic characteristic lengths and illustration of typical microstructures in permanent magnets (anisotropic Nd–Fe–B magnets).](image)
In metals and intermetallic compounds of rare earths, the intra-atomic valence electron contributions to the electric field gradient at the rare earth site is the most important ones [24]. The crystal field parameters may be calculated if single-electron potential due to the valence electrons at the rare earth site is obtained by first-principles calculations using the density functional theory (DFT) and local density approximations (LDA). Once the potential for the rare earth ion \( V(r) \) is obtained, the intra-atomic contribution to crystal field parameters \( A^m_l \) within a muffin-tin radius \( R_{MT} \) are obtained by the following equation,

\[
K_1 = -3J(J - \frac{1}{2})\Theta_2 A^3_l \langle r^2 \rangle.
\]

To examine effects of the local profiles of magnetocrystalline anisotropy near surfaces and interfaces on coercivity, the first-principles calculations of crystal field parameters for Nd ions near surfaces of Nd\(_2\)Fe\(_{14}\)B were carried out by Moriya et al [11] and by Tanaka et al [30] and the \( A^3_l \langle r^2 \rangle \) parameter at the Nd sites exposed to vacuum on the (001) surface was shown to become negative. Although the \( A^3_l \langle r^2 \rangle \) parameters at the Nd sites in the atomic layer next to the surface layer were maintained to be positive, the overall average of the \( A^3_l \langle r^2 \rangle \) parameters in the first two layers containing Nd ions became negative as a consequence. This means that the magnetocrystalline anisotropy of Nd ions in the surface layers with about 0.6 nm is intrinsically negative when there is nothing to cover the surface. Mitsumata et al showed that such negative contribution from the surface layer could result in a significant decrease in the critical magnetic field of magnetic reversal by a simplified atomistic micromagnetic simulation [12]. The most important point is that the crystal field parameters can be strongly different at the rare earth sites on surfaces or interfaces depending on the intra-atomic distribution of the valence electrons within the Wigner–Seitz cell and can make significant impacts on the critical fields and, consequently, on the magnetization reversal process. Because the molecular filed interactions and the electric field interactions are of the same magnitude, when a rare earth ion in the surface atomic layer has a negative anisotropy, it will rotate by a larger angle under a demagnetizing magnetic field and exert additional torque to rotate atomic moments in the underneath atomic layers in comparison to the case of positive magnetocrystalline anisotropy, resulting in a substantial decrease in the intrinsic coercivity. This effect of the surface/interface magnetic moments with negative magnetocrystalline anisotropy is surprisingly stronger than that expected from the averaged magnetocrystalline anisotropy energy within the exchange length \( (\sqrt{\pi/\xi}) \).

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interface anisotropy may not be correctly reproduced in the finite element micromagnetic simulations if the local magnetic properties are merely averaged numerically. Further investigations are required in order to establish a reasonable way to identify micromagnetic parameters to be used for surface/interface cells in the finite element micromagnetic simulations based on the continuum picture of micromagnetics.

At temperatures at and above room temperature, thermal activation process in the magnetization reversal cannot be neglected. Givord et al argued that the coercivity is governed by a passage-expansion process [31], which is a stochastic process in which a part of the domain walls breaks into the hard magnetic grain from a small region which can be regarded as the activation volume (figure 3). The expression of coercivity may be modified as

$$H_C = \alpha H_a - N_{eff}M_S - \frac{25k_B T}{\mu_0 M_S v},$$

(7)

where $v$ is the activation volume which is related to magnetic viscosity $S_v$ in

$$v = k_B T/(\mu_0 M_S/S_v).$$

(8)

Investigations of the magnetic viscosity measurements in Nd–Fe–B permanent magnets have shown that the diameter of the activation volume is only a few times of the domain wall thickness [32]. With $v = 300 \text{nm}^3$ and $M_S = 1.28 \text{MA m}^{-1}$ for Nd$_2$Fe$_{14}$B, the magnitude of the third term in equation (7) at 300K is about 200 kA m$^{-1}$ and increases with temperature, becoming a significant portion in equation (7). Therefore, the local magnetic properties and their special profiles play the key role in the thermal activation process of magnetization reversal.

The magnetization reversal behavior at elevated temperatures can be described and the impact of the local micromagnetic profiles can be discussed by micromagnetic simulations using the Landau–Lifshitz–Gilbert (LLG) equation. The effects of temperature are usually taken into account by using temperature-dependent anisotropy field and saturation magnetization. However, the impact of thermal activation is not included in such simulations. If the energy landscape in the course of magnetization reversal can be obtained from the LLG simulations, it is possible to estimate the dependence of the energy barrier as a function of applied magnetic field and define coercivity as a magnitude of magnetic field at which the energy barrier is overcome by the thermal energy $25 k_B T$.

Bance et al recently demonstrated that this can be performed on a small particle with a composite structure [33]. Another approach to deal with the thermal activation in the magnetization process is to add a randomly fluctuating field to the magnetic field in the LLG equation;

$$\frac{dM_i}{dt} = -\gamma M_i \times (H_i^{\text{eff}} + \xi_i) - \frac{\alpha_i}{(1 + \alpha_i^2)} M_i \times [M_i \times (H_i^{\text{eff}} + \xi_i)],$$

(9)

where $M_i$ is atomic magnetic moment at the $i$th site, $H_i^{\text{eff}}$ and $\xi_i$ are, respectively, the effective magnetic field and the white Gaussian noise at the $i$th site, $\alpha_i$ is the damping factor and $\gamma$ is the gyromagnetic ratio. $H_i^{\text{eff}}$ is derived from the total magnetic energy as the derivative with respect to $M_i$ as

$$H_i^{\text{eff}} = -\frac{\partial}{\partial M_i} H(M_i, \ldots, M_N, t).$$

(10)

The condition to be fulfilled in specifying the amplitude of $\xi_i$ and $\alpha_i$ at each site with site-dependent magnetization $M_i$ in magnetically inhomogeneous system such as in the rare earth permanent magnet compounds composed of at least two (namely, rare earth and transition metal) sub-lattices has been discussed by Nishino and Miyashita [34].

The total magnetic energy contains the exchange energy, the magnetocrystalline anisotropy energy, the magnetostatic energy arising from the external field, and the dipole field interactions. The recent progresses of the first-principles calculations methods have enabled estimation of atomic pair exchange parameters $J_{ij}$ and magnetocrystalline

![Figure 3](image-url)
Figure 4. Snapshots of magnetization reversal in a single crystal Nd$_2$Fe$_{14}$B particle of the size of $10 \times 10 \times 4$ supercell at 400 K under a magnetic field of $3.6 \text{ MA}\text{m}^{-1}$ with time proceeds from (a) to (f) visualized by means of stochastic LLG simulation. Red (dark gray) and blue (light gray) arrows are atomic magnetic moments pointing in the upper hemisphere and the lower hemisphere, respectively.

Anisotropy at each site in the fairly large unit cells of the rare earth permanent magnet compounds such as Nd$_2$Fe$_{14}$B which contains 68 atoms and their supercells [16]. Investigation of the stochastic magnetization reversal processes in Nd$_2$Fe$_{14}$B-based permanent magnets at elevated temperatures are currently in progress using the atomistic and stochastic LLG simulation on the exact structure model of Nd$_2$Fe$_{14}$B with atomic exchange parameters, magnetocrystalline anisotropy, and magnetic moments obtained by the first-principles calculations. Figure 4 shows a sequence of snapshots of magnetization reversal in a single crystal Nd$_2$Fe$_{14}$B particle of the size of $10 \times 10 \times 4$ supercell at 400 K under a magnetic field of $3.6 \text{ MA}\text{m}^{-1}$ ($\mu_0H = 4$ T). An inhomogeneous magnetization state and formation of a nucleus of a reversed magnetic domain are clearly seen in spite of the fact that the size of the crystal is smaller than the coherent rotation critical size defined in the continuum model of micromagnetics. The time frame here is in the sub-nanosecond (ns) regime. The corners of the crystal are weak points because of reduced numbers of neighboring atoms which should cause larger fluctuations of atomic moments. The activation of magnetization reversal seems to be triggered by accidental formation of a small region in which a large number of the magnetic moments are flipped, followed by a collective expansion of the revered region.

The practical time regime for measurement of coercivity of permanent magnets is in the range from 1 s to about 100 s, which is out of the reach in the present stochastic LLG approach because of the limited computation speed. In classical theory of time-dependent magnetization process, the coercivity of a system with energy barrier $E_0$ and the critical field $H_0$ of magnetization reversal in the absence of thermal activation process, the time dependence of coercivity is described by

$$H_c(t) = H_0 \left[1 - \left(\frac{E_0}{T} \ln\left(\frac{f_0 t}{E_0} \ln 2\right)\right)^{1/n}\right].$$  \hspace{1cm} (11)

where $f_0$ is the characteristic frequency of the magnetization ($\approx 10^{11} \text{ s}^{-1}$) provided that the energy barrier $E_0$ has magnetic-field dependency of the form

$$E_0(H) = E_0(1 - H/H_0)^n,$$  \hspace{1cm} (12)

with the power index $n$ which depends on the magnetization reversal mode [35]. The typical values of $E_0/k_B$ and $H_0$ for anisotropic Nd$_2$Fe$_{14}$B-based permanent magnets are, respectively, in the range of $4-6 \times 10^4$ K and $0.2-0.35$ $H_A$ at room temperature empirically, as was shown by Givord et al for sintered magnets [32] and by Okamoto et al for hot-deformed magnets [36]. The atomistic LLG simulations with the thermally fluctuating noise field can be used in investigation of the effects of magnetic inhomogeneity in atomic scales on magnetization reversal behaviors under demagnetizing magnetic fields close to $H_0$. The information obtained from such investigations is expected to envision thermally activated magnetization reversal processes under smaller magnetic fields to explain coercivity observed in the longer time regime of 1 s orders (namely, $\ln(f_0 t) = 25$ for $t = 1 \text{ s}$).

3. Current status and perspectives of Dy-free Nd–Fe–B anisotropic permanent magnets

The discovery that the grain boundary intergranular phase in Nd–Fe–B anisotropic permanent magnets is ferromagnetic was triggered by the findings that the intergranular phase between adjacent Nd$_2$Fe$_{14}$B grains with thickness of a few nm contained more than about 80 atomic percent Fe and Co according to atomic resolution analyses of chemical compositions across the grain boundary regions using 3D atom probe tomography (3DAPT) [37, 38]. The discovery led to development of a grain boundary engineering process in which low melting-temperature light-rare earth-rich eutectic alloys such as Nd$_{70}$Cu$_{30}$ are infiltrated along grain boundaries after fabrication of anisotropic, fine-grained, polycrystalline permanent magnet blocks or coarse polycrystalline granules to modify...
the composition of the intergranular grain boundary phase selectively [39–41].

The fine grain sizes in the sub-micrometer region are believed to be beneficial to generate a large coercivity because the effective demagnetization field originating from magnetically reversed surface grains decreases with the average grain size. Anisotropic Nd–Fe–B magnets with such fine grain sizes can be fabricated by means of hydrogenation–disproportionation–desorption–recombination (HDDR) process [42] or rapid solidification-hot-deformation process [43] without going through preparation of sub-micron fine particles. Figure 5 illustrates the procedure of the grain boundary engineering for the case using the hot-deformed Nd–Fe–B permanent magnet blocks with the typical grain size of 500 nm along the transverse direction perpendicular to the easy direction of magnetization as the starting material.

Microscopic investigations have shown that the thickness and chemical compositions of the intergranular boundary phases in both sintered Nd–Fe–B and hot-deformed Nd–Fe–B magnets are strongly dependent on orientation of the grain boundary [38, 44–46]. The thickness and Nd concentration of the boundary phase increases on the (001) surfaces of the Nd₃Fe₁₄B grains whereas they are still rich in Fe and Co on the surfaces perpendicular to (001) after infiltration of the R-rich low melting-point alloy [47, 48]. The Nd content in the grain boundary phase on the (001) surface increases to typically 80% which is sufficient to make the phase paramagnetic at and above room temperature [49]. Therefore, the present situation is that the intergranular grain boundary phase on the (001) surface side of Nd₃Fe₁₄B grains are paramagnetic but those on the side approximately perpendicular to (001) are still ferromagnetic, although the pinning force has been improved (figure 5(b)).

The currently reported magnetic properties of Dy-free Nd–Fe–B anisotropic permanent magnets prepared by the GBD process [41, 50, 51] are plotted in figure 6 on a map of remanence versus coercivity extracted from available technical data sheets provided by Japanese magnet producers. Also included are magnetic properties of recently developed Nd–Fe–B-type sintered magnets with a slightly Nd-enriched and Ga-added composition in which all sub-phases are reported to become non-ferromagnetic [52, 53]. It can be seen that further improvements of magnetic properties, especially the remanence \( B_r \) are required for the Dy-free Nd–Fe–B to be fully compatible with the commercial sintered magnets. This may be achieved if the desired microstructure with all the grains being surrounded by paramagnetic grain boundary phase without creating large non-ferromagnetic spaces that cause local stray fields acting as demagnetizing force is realized (figure 5(c)). It should be noted that the reduced effective demagnetizing field (the \( N_{eff}M_S \) term in equation (1)) which is realized in the fine-grained magnets reduces (i.e. improves) the temperature dependence of coercivity. The current target value for coercivity at room temperature is 2 MA m⁻¹ as required to safely operate the magnet at 160 °C for the sub-micron fine-grained Nd–Fe–B anisotropic magnets. Since the coercivity of the currently developed Dy-free Nd–Fe–B magnets seems to have arrived at the target level, reduction of the R-rich grain boundary phases without decreasing coercivity is desired.

A hint to move toward the desired direction was provided from micromagnetic simulations by Fujisaki et al [54] which suggested that there was practically no difference in coercivity
values no matter whether grains are exchange coupled or decoupled along the direction parallel to the easy axis if the exchange stiffness reduces to zero in the intergranular grain boundary phase along the side grain boundaries. In any case, it is regarded that further control of the magnetism of the intergranular grain boundary phase is the key to further improve the coercivity of anisotropic Nd–Fe–B permanent magnets, for which an in-depth research of thermodynamic properties of Nd–Fe–B-based multi-component systems involving interface energy is required.

4. Hard magnetic Fe-rich light-rare earth compounds

The currently known Fe-rich light-rare earth hard magnetic compounds that have larger Fe fractions than Nd$_2$Fe$_{14}$B belong to the derivatives of the RT$_5$ compound in which R atoms in RT$_5$ with the CaCu$_5$-type structure are replaced by pairs of T atoms called ‘dumbbells’ [55, 56]. Figure 7(a) illustrates the relations among crystallographic major axes of these compounds. R$_2$Fe$_{17}$ compounds with either the Th$_2$Ni$_{17}$ or the Th$_2$Zn$_{17}$ structure have low Curie temperatures only slightly above room temperature [57]. By introducing interstitial atoms such as N and C, however, the Curie temperature significantly increases and become practically usable hard magnetic compounds [58]. Sm$_2$Fe$_{17}$N$_3$ is the best known compound among this family and it is used commercially as a hard magnetic component in resin-bonded permanent magnets in a form of fine powder [59]. The interstitially modified Sm$_2$Fe$_{17}$N$_3$ is metastable up to about 600 °C and decomposes at higher temperatures. Further replacement of the R atoms with the dumbbell T atoms leads to relatively stable RT$_{10}$ compounds with hexagonal symmetry [55, 60] and finally to the ThMn$_{12}$-type tetragonal compounds (figure 7(b)) in which a half of dumbbells pairs of T atoms called ‘dumbbells’ [55, 56]. Figure 7(a) illustrates the relation of crystallographic axis in CaCu$_5$, Th$_2$Ni$_{17}$, and ThMn$_{12}$-type structures (a) and the crystal structure of NdFe$_{12}$N (b). The ‘dumbbell’ T-atoms shown with dotted circles in (a) align perpendicular to the plane of this page.

The hypothetical RFe$_{12}$ compounds have negative values for $\Theta_l$ and therefore the rare earth element with positive Stevens factor $\Theta_l$ should show the magnetocrystalline anisotropy suitable for hard magnetic application, namely, the easy direction of magnetization being along the c-axis ([001]) [63]. First-principles study shows that modification of the structure with interstitial atoms improves the magnetic properties of the ThMn$_{12}$-type R(Fe, M)$_{12}$ compounds, accompanying substantial changes in the crystal field parameters and compounds with negative $\Theta_l$ show the easy c-axis anisotropy and that N gives the best results when application as permanent magnets is considered [64]. After introducing nitrogen, NdFe$_{11}$TiN has the easy direction of magnetization parallel to the [001] axis at and above room temperature but its saturation magnetization $J_S = \mu_0M_S$ is 1.45 T, being significantly smaller than that of Nd$_2$Fe$_{14}$B (1.60 T) at room temperature, see table 1 [18, 65–70].

Hirayama et al succeeded to fabricate the binary NdFe$_{12}$ compound by establishing lattice coherency with a W underlayer to allow epitaxial growth of thin films of NdFe$_{12}$ [68]. They discovered that preparation of relatively thick films of thickness up to 360 nm with the [001] axis perpendicular to the film plane was possible on a single crystalline W underlayer grown on the MgO (001) substrate. The NdFe$_{12}$ single-crystalline films was interstitially nitrogenated to form NdFe$_{12}$N which possesses the saturation magnetization of 1.67 T and the anisotropy field of 6.4 MA m$^{-1}$ at room temperature, both of which surpass corresponding values of Nd$_2$Fe$_{14}$B. NdFe$_{12}$N also decomposes above about 560 °C.

Search for stable ThMn$_{12}$-type compounds without the undesirable decrease in magnetization has been rekindled and several multi-component compounds have been found to possess a large magnetization and good hard magnetic properties. Rapidly solidified alloy with the composition of (Nd$_{0.5}$Zr$_{0.5}$)$_{11.5}$Ti$_{0.5}$N has $J_S = 1.68$ T and $H_A = 6$ MA m$^{-1}$ [70–72]. Without using the interstitial modification, a Sm–Fe-based alloy (Sm$_{0.5}$Zr$_{0.5}$)$_{11.5}$Ti$_{0.5}$N is also reported to have a large $J_S$ of 1.63 T and $H_A$ of 5.9 MA m$^{-1}$ at room temperature [69]. Comparison with other typical hard
magnetic Fe-rich rare earth compounds are shown in table 1. Included in this table are values of the magnetic hardness factor, $\kappa$, which is identical with $HM^2/2AS$, for each compound at room temperature. This parameter is defined to represent the ratio of the magnetocrystalline anisotropy energy to the magnetostatic energy and its value needs to be greater than one for a compound to be considered as a hard magnetic material. Suzuki et al and Sakuma et al argued that replacement of a part of Nd at the 2a site with Zr atoms should contribute to stabilize the ThMn12 structure through a slight shrinkage of Fe(8i, 8j) hexagons surrounding the Nd 2a site (shown in figure 7(b) with a dotted line) [71, 72]. Harashima et al pointed out that the partial Co substitution for Fe lowers the formation energy of the ThMn12-type Nd(Fe, M)12 compounds based on their first-principles calculations and that Co does not cause a significant decrease in magnetic moments of Fe atoms surrounding Co [73]. Unfortunately, the very abundant light rare earth elements, La and Ce, have no magnetic moments in the T-rich R-T compounds and no significant contributions to the magnetocrystalline anisotropy. Therefore, the multi-component alloys with the stabilized ThMn12-type compounds with relatively abundant magnetic light rare earth elements, namely Pr, Nd, and Sm, seem to be promising for development of new rare earth-lean, high magnetization permanent magnets.

### Table 1. Magnetic properties of some newly reported Fe-rich light-rare earth compounds at room temperature compared with typical hard magnetic compounds.

| Material                             | $J_S$ (T) | $K_1$ (MJ m$^{-3}$) | $H_A$ (MA m$^{-1}$) | $\kappa$ | $(BH)^{\text{Theo.}}$ (kJ m$^{-3}$) |
|-------------------------------------|-----------|---------------------|---------------------|----------|----------------------------------|
| Nd$_2$Fe$_{14}$B [18]              | 1.60      | 4.3                 | 5.33                | 1.5      | 509                              |
| SmFe$_2$Ti [65]                    | 1.21      | 4.0                 | 6.6                 | 1.9      | 291                              |
| Sm$_2$Fe$_7$N$_3$ [66]             | 1.57      | 16.2                | 20.6                | 2.9      | 490                              |
| NdFe$_2$TiN [67]                   | 1.45      | 6.7                 | 9.2                 | 2.0      | 418                              |
| NdFe$_2$N [68]                     | 1.66      | 5.3                 | 6.4                 | 1.6      | 548                              |
| (SmZr)(FeCo)$_{10}$N$_x$ [69]      | 1.63      | 5.3                 | 5.9                 | 1.6      | 529                              |
| (NdZr)(FeCo)$_{11.5}$Ti$_{0.5}$N [70] | 1.68    | 4.0                 | 4.8                 | 1.3      | 562                              |

*a* $(\text{Sm–Zr})(\text{Fe–Co})_{10}N_x = (\text{Sm}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.7}\text{Co}_{0.3})_{10}N_x$.

*b* $(\text{Nd–Zr})(\text{Fe–Co})_{11.5}Ti_{0.5}N = (\text{Nd}_{0.7}\text{Zr}_{0.3})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}Ti_{0.5}N$.

$c\,\kappa = \sqrt{2H_{c}/M_S} = \sqrt{2H_{c}/M_S}$.

Figure 8. Illustration of conventional IPM rotor of magnetic flux weakening topology using high-coercivity permanent magnets (a) and non-conventional IPM rotor with flux-intensifying topology using variable-flux (low coercivity) permanent magnets (b) after Kato et al [78] (modified).

5. A brief view on applications of permanent magnets and niches for new materials

In order to have a newly developed material be utilized in real commercial applications, understandings of application technologies and foreseeable niches for the new material are crucially important. The application fields of PM materials extend to a very wide area. According to production volume, the top five areas are automobiles (other than electric vehicles), disc drives for information-storage devices, hybrid and electric vehicles (HEV and EV), electric bicycles, and transducers (including loudspeakers) [74]. Wind power generators and other energy-generation or energy-storage devices are expected to be near-future applications that use a large volume of high-energy materials. Among these, the markets for disc drives, electric vehicles, electric bicycles, and a large portion of energy generation/storage devices are growing and have been created by the development of high-coercivity sintered Nd–Fe–B-type PMs through the introduction of Dy [75] at a very early stage of material development.

PM synchronous machines have a greater efficiency than induction motors and less cogging torque and lower mechanical noise levels than variable reluctance motors [76]. Most drive motors for electric vehicles use interior PM (IPM)-type rotors (figure 8(a)) wherein magnets are inserted in thin slots with the
anisotropic axis perpendicular to the short axis of the slots [77]. IPM rotors have saliency that can yield additional reluctance torque, improving the efficiency of the motor, and in the low-revolution-speed regime. On the other hand, PMs are subject to strong armature fields that act in the demagnetizing direction [4]. The required coercivity of PMs should strongly depend on the rotor topology, but the typical values of intrinsic coercivity $H_{cJ}$ required at the operating temperature for HEV applications would be around 600 kA m$^{-1}$ if sintered Nd–Dy–Fe–B magnets with a room temperature coercivity of 2.4 MA m$^{-1}$ (3 T) are required for operations at 200 °C and if average temperature coefficient of $-0.5$ % K$^{-1}$ is assumed for the intrinsic coercivity. Servomotors with surface PM (SPM)-type rotors having a very small saliency are also commonly used in electric-power steering devices for all kinds of automobiles.

A weak point of traditional IPM motors used in HEVs and EVs is that, although they generate a large torque in the low-revolution-speed region, the torque decreases sharply when the revolution speed increases above a constant torque region. At high rotation speeds, the large magnetic flux of the PMs generates a large voltage in the drive coils in the stator, counteracting the input voltage from the drive power unit. The flux-weakening operation is the conventional way to reduce magnetic flux crossing the stator coils to suppress the induced voltage due to the permanent magnets, but it causes large losses in the motor torque and efficiency. To eliminate this dilemma, various motor designs have been proposed, including variable-characteristic machines wherein PMs are used for flux strengthening along the salient axis in which the magnetic flux of the PMs are intentionally demagnetized in the high-rotation-speed region and remagnetized in the low-revolution-speed region. An illustration of such a variable-characteristic machine is shown in figure 8(b) after an example proposed by Kato et al [78]. For such a variable-characteristic operation, completely different properties are required for PMs compared with conventional IPM motors. Motors with new designs and concepts, including PM-assisted reluctance motors that allow the use of weaker PMs such as ferrites [76], remain in the development stage, and IPM-type motors are projected to be the mainstream choice in coming years. The high-coercivity Nd–Fe–B-type anisotropic magnets with the largest possible remanence are required for large-scale applications that have been developed using these very materials, and this situation is expected to continue in the coming years.

The question is whether new permanent magnets with significantly different characteristics from Nd–Fe–B can find any niche market in the newly developed machines. The Ce- or La-based Fe-rich compounds with relatively large magnetization and magnetocrystalline anisotropy generated by the Fe-sublattice may be interesting if they provide coercivity greater that those achievable in the alnico or Fe–Cr–Co-type permanent magnets (see figure 6). Regarding the rare-earth free magnets, the Mn-based compounds MnBi [79] and MnAl(C) [80] have only a small $J_S$ of $-0.7$ T and are eliminated from consideration to be developed as PMs for HEV and EV applications. A combination of the shape anisotropy with the intrinsic magnetocrystalline anisotropy of 3d-metals was investigated in Co nanorods [81], where the requirement to maintain magnetic space among particles to yield the shape anisotropy yielded a reduced remanence of 0.8–0.9 T compared with the saturation magnetization of Co metals (1.8 T). High-magnetization Fe-rich hard magnetic materials such as Fe$_{16}$N$_2$ particles [82], tetragonal-FeCo thin films epitaxially grown on substrates [83, 84], and Li$_{10}$FeNi thin films [85] have the technical difficulties to be considered as the base materials on which industrially useful bulk permanent magnet materials can be developed. To make PMs for HEV/EV applications truly free from ‘environmentally critical’ elements with some of these hard magnetic materials, the identification of such new niche applications that may potentially creep into the mainstream is necessary. The potential for the utilization of novel PM materials may then be discovered.

6. Conclusions and outlook

Since the critical rare earth elements such as Dy in Nd–Fe–B permanent magnets are used to modify the intrinsic magnetic properties of the matrix hard magnetic phase to provide enough coercivity at elevated temperatures which the magnets encounter in their operating environments, to develop permanent magnets free from the critical elements is to develop large enough coercivity at the elevated temperatures by means of controlling nanostructures of the materials. Recent developments in understandings of atomistic description of local magnetic properties in inhomogeneity such as interfaces and surfaces in the permanent magnet materials and magnetization reversal behaviors at elevated temperatures have clearly suggested that suppression of thermal fluctuations of atomic magnetic moments at the surface or interface through enhancement of surface magnetocrystalline anisotropy of molecular-field (exchange) interactions by controlling the atomic environments can result in further enhancement of coercivity. Brief overview of current applications, particularly the high efficiency drive motors for HEVs or EVs, suggests that development of new permanent magnet other than the Dy-free Nd–Fe–B, namely the rare-earth-free permanent magnets, need to rely on emergence of new topologies of the motors. The new class of rare-earth-lean hard magnetic compounds, namely the 1–12 systems, attracts attention because of their excellent magnetic properties comparable or even exceeding those of Nd$_3$Fe$_{14}$B.

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