

NEW DIRECTIONS IN PERMANENT MAGNETISM

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Abstract-The prospects for further improvement in the energy product of permanent magnets are discussed. Some current research directions, including artificial nanostructures, nitride magnets and novel flux sources are briefly reviewed.

The story of the development of the energy product of permanent magnets [1] has been well-rehearsed at magnetism conferences. We see in Fig. 1 most of an S-shaped curve stepping from carbon steels, through cobalt steels, alnicos, ferrite and Sm-Co to Nd-Fe-B. The ferrites and rare-earth materials, after a period of assiduous development, reach the point where magnets can be produced with a nearly square hysteresis loop and an energy product which is not far below the theoretical limit; $\frac{1}{4} \mu_0 M_s^2$. This is the maximum value of the (BH) product for an ideal square loop when the coercivity exceeds half the remanence. In the case of $Nd_2Fe_{14}B$, for example, magnets with energy products of 400 kJ/m^3 are now available, compared to the limit of 516 kJ/m^3 for the pure phase. The progress depicted in Fig. 1 represents a doubling of energy product every twelve years. We can ask the questions 'How many more doublings of the energy product can be expected? Will we see 800 kJ/m^3 before 2000, and 1600 kJ/m^3 in the first decade of the next century?' Unfortunately, the answer to the second question is likely to be 'no'!

The alloy with the greatest magnetization at room temperature is bcc $Fe_{65}Co_{35}$, for which $M_s = 1.95 \text{ MA/m}$ ($\mu_0 M_s = 2.45 \text{ T}$). Iron itself has $\mu_0 M_s = 2.15 \text{ T}$, and if pure iron could be made with sufficient coercivity, its energy product could reach 920 kJ/m^3 . There are claims that a larger magnetization may exist in thin films of $\alpha''Fe_{16}N_2$ [2], but so far this material has not been prepared in the pure bulk as a pure phase so it has not been possible to study the bulk magnetization directly [3]. There are also considerable theoretical difficulties in accepting an average zero-temperature moment of $3.2 \mu_B/Fe$ as claimed in $\alpha''Fe_{16}N_2$, which is far beyond the $2.7 \mu_0$ which would be expected for strongly-ferromagnetic iron. In fact very large iron moments do exist on certain sites in iron nitrides and iron intermetallic compounds. A list of examples is given in table I.

Table I: Iron magnetic moments and hyperfine fields for high moment sites in iron compounds at $T \approx 0$.

Compound	Site	B_h (T)	μ_{Fe} (μ_B)	$\langle \mu \rangle$ (μ_B)
Fe_4N	1a	36.6	3.0	2.25
$Y_2Fe_{14}B$	8j ₂	36.0	2.8	2.20
Y_2Fe_{17}	4f	34.6	2.5	2.07
$Y_2Fe_{17}N_3$	4f	40.1	2.9 [†]	2.24

[†] calculated moment

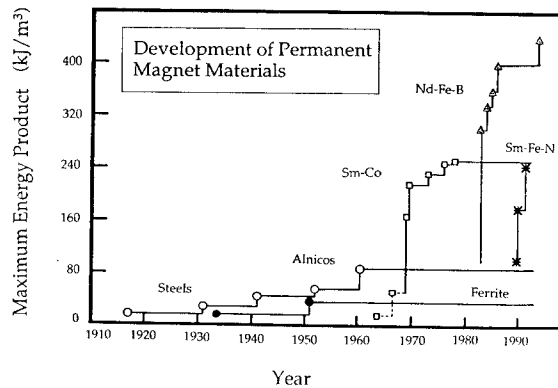


Figure 1: Progress in the energy product of permanent magnets during the 20th century.

But these large moments exist only on a small proportion of the iron sites in the compounds concerned. They reflect differences of electronegativity at different sites, and local charge transfers of 3d electron density. The charge deficit at the high moment sites is compensated elsewhere by a charge surplus at the low moment sites. An obvious chemical approach would be to substitute Mn for Fe, but the effect of doing this in intermetallics such as $Nd_2Fe_{14}B$ is to drastically reduce the Curie temperature because of the strong tendency of manganese to couple antiferromagnetically.

An alternative approach is to raise the polarization of permanent magnets to above 2 T and to seek to exploit the large moments available on the heavy rare earths. Dysprosium and holmium each have an atomic moment of $10 \mu_B$. The atomic moment of terbium which is ferromagnetic below 220 K is $9 \mu_B$, and gadolinium with $T_C = 293 \text{ K}$ has a moment of $7 \mu_B$. The corresponding zero-temperature polarization of these ferromagnetic elements are not quite so attractive, because the 4f atoms occupy roughly three times the volume of the 3d atoms and magnetization, by definition, is magnetic moment per unit-volume; $Am^2/m^3 \equiv A/m$. The value of $\mu_0 M$ for Tb for example is 3.25 T. It is certainly worth exploring the rare-earth-rich corner of suitable phase diagrams for alloys which may have Curie points above room temperature and possess a large magnetization coupled with uniaxial anisotropy. A difficulty

is that the pure heavy rare-earth metals with hcp structures have a negative value of the electric field gradient A_2^0 , so that Tb, Dy and Ho all have easy-plane anisotropy. Only Er and Tm are easy axis, but the exchange coupling for these elements is quite weak on account of their small spin moment. The required ferromagnetic rare-earth rich intermetallic will have to have a local environment of the rare-earth which is quite different to that of the rare-earth metals themselves. The example of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ suggests that this might be achievable by interstitial modification.

Table II: Magnetic properties of permanent magnet materials

Compound	T_c (K)	$\mu_0 M_s$ (T)	$(1/4)\mu_0 M_s^2$ (kJ/m ³)	K_1 (kJ/m ³)	Ba (T)
$\text{SrFe}_{12}\text{O}_{19}$	745	0.48	45	350	1.8
NdFe_{14}B	585	1.61	516	4900	7.6
SmCo_5	993	1.05	219	17000	40
$\text{Sm}_2\text{Fe}_{17}\text{N}_3$	749	1.54	472	8600	14

The other approach to raising the energy product is more sophisticated. The rare-earth intermetallics used for permanent magnets have a polarization in the range 1.0-1.6 T, substantially less than αFe or Fe-Co alloys but they have a great surplus of anisotropy energy beyond that strictly necessary to produce coercivity. For a homogeneous ellipsoid, Brown's theorem states that

$$H_c \geq 2K_1/\mu_0 M_s - NM_s$$

The quantity $2K_1/\mu_0 M_s$ is the anisotropy field. In practice inhomogeneities greatly reduce the achievable coercivity, but the anisotropy field of the rare-earth intermetallics used for permanent magnets is typically an order of magnitude greater than the requisite coercivity (table II). In the case of compounds such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ where $A_2^0 > 0$ at the rare-earth site, the anisotropy can be further increased by appropriate substitution of heavy rare-earths with negative Stevens coefficient α_J (Tb, Dy). In these circumstances, the way to proceed is to make a two-phase nanostructure of the hard phase with a soft phase (Fig. 2) which possesses a greater magnetization. If the soft regions are sufficiently small and the grain boundaries between hard and soft regions are clean enough to allow exchange coupling of the 3d atoms in adjacent grains, then it is possible for the hard grains to stiffen the soft ones so that the whole nanostructured composite behaves as if it is magnetically hard [4]. The magnetization of the whole is $\langle M \rangle = f_h M_h + (1 - f_h) M_s$, where f_h is the volume fraction occupied by the hard phase, and M_h and M_s are the magnetization of the hard and soft phases respectively. A similar expression is found for the anisotropy in an ideal nanostructure $\langle K \rangle \approx f_h K_h$, since $K_s \approx 0$ [5].

Questions that arise are 'How small do the soft regions have to be so not as to act as nucleation centres for magnetization reversal, thereby destroying coercivity?' and 'Is it possible in practice to realize a nanostructure which would

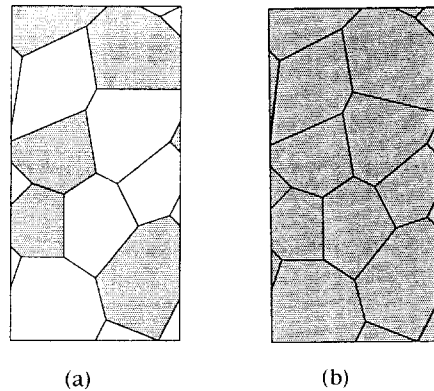


Figure 2: Ideal two-phase and single-plane nanostructures.

allow for a further improvement in the energy product. There are three characteristic lengthscales in micromagnetism, the exchange length $l_{ex} = (A/\mu_0 M^2)^{1/2}$, the domain wall width $\delta_w = \pi(A/K_1)^{1/2}$ and the critical single-domain particle size $d_c = 72 (AK_1)^{1/2}/\mu_0 M^2$. The two latter quantities can be expressed in terms of the dimensionless hardness parameter $\kappa = (K_1/\mu_0 M^2)^{1/2}$, as $\pi l_{ex}/\kappa$ and $72 \kappa l_{ex}$ respectively. Initial estimates in a one-dimensional model [4], analytical calculations in the case where the hard phase is aligned with a common c-axis throughout the sample [5] and 3-dimensional numerical simulations [6] all indicate that the relevant length scale for exchange hardening is the domain wall width of the hard phase. This coincides roughly with the exchange length for the materials in question (table III). For most effective

Table III: Micromagnetic properties of permanent magnet materials

	κ	l_{ex} (nm)	δ_w (nm)	d_c (μm)
$\text{SrFe}_{12}\text{O}_{19}$	1.9	5.7	9.4	0.78
$\text{Nd}_2\text{Fe}_{14}\text{B}$	1.6	2.1	4.2	0.24
SmCo_5	4.4	5.3	3.7	1.68
$\text{Sm}_2\text{Fe}_{17}\text{N}_3$	2.2	2.6	3.6	0.41

exchange hardening, the soft regions should be no more than about twice the domain wall width δ_w , say about 10 nm. Furthermore, the hard regions should have a common easy axis for maximum effect. These are tough conditions to meet. The present situation is that exchange hardening has now been demonstrated in a number of systems prepared by melt spinning or mechanical alloying. In all of these, the orientations of the hard grains are essentially random. Oriented structures such as multilayers have been suggested [5], but not yet built.

Returning to Fig 1, it seems likely that the energy product will soon saturate in a classic S shape curve which will fit, more or less, into the 20th century.

Energy product is just one touchstone of progress in permanent magnetism. Even if there are no further advances in $(BH)_{\max}$, there remains considerable scope for finding new materials, process routes and applications. Materials with higher Curie temperatures, stronger anisotropy, better corrosion resistance and lower cost would be welcome. There is a gap in terms of performance/cost ratio between the best oriented ferrites and isotropic melt-spun Nd-Fe-B. Isotropic rare-earth magnets make inefficient use of expensive material [7] since their energy product seldom exceeds 20% of the theoretical maximum value, $\frac{1}{4} \mu_0 M_s^2$. Here the two-phase and single-phase nanostructures offer interesting prospects. In the two-phase systems, much of the rare-earth alloy is replaced by iron, or an iron-based alloy. The first such system was melt-spun $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ [8] but subsequent studies have covered melt-spun [9] or mechanically-alloyed [10] $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{Fe}$, melt-spun [11] or mechanically-alloyed [12] $\text{Sm}_2\text{Fe}_{17}\text{N}_3/\alpha\text{Fe}$ as well as several cobalt-based systems [13]. Some data on mechanically-alloyed material as a function of the proportion of αFe content are shown in Fig 3. The problem is to achieve an adequate coercivity with a suitably large remanence. Unfortunately M_r and H_c usually vary in opposite senses as a function of composition. Improved control of the nanostructure, especially nanoscale refinement of the grain size of the soft phase as discussed above is required to make the best of these isotropic magnets.

Another approach to improving the properties of isotropic rare-earth magnets is a single phase nanostructure (Fig 2b) where exchange coupling between the nanocrystallites leads to a magnetization which deviates somewhat from the local easy axes, leading to remanence enhancement. Again the relevant lengthscale is the domain wall width δ_w , and the coercivity diminishes as the remanence is enhanced. The first report of isotropic remanence enhancement was in Si-doped Nd-Fe-B [14], but the effect has subsequently been demonstrated in the pure phase and in Ga-doped material [9]. Improvements in properties can be expected as more homogeneous and uniform nanostructures are produced.

Since the performance of a magnet depends essentially on its remanence M_r and the squareness of its demagnetization curve, it is always worthwhile to improve the crystallite alignment and density of sintered or bonded magnets. Techniques such as transverse pressing and rubber isotropic pressing [15] lead to significant improvements in magnet properties. The process of making anisotropic Nd-Fe-B by the hydrogen disproportionation, desorption and recombination process (HDDR) is another significant advance [16], which lacks a clear theoretical explanation.

Many grades of Sm-Co and Nd-Fe-B are now in commercial production. Sm-Fe-N is not yet established commercially, although a number of preparation routes for magnets with useful properties have been established on a laboratory scale. These are summarized in Fig 4. They can

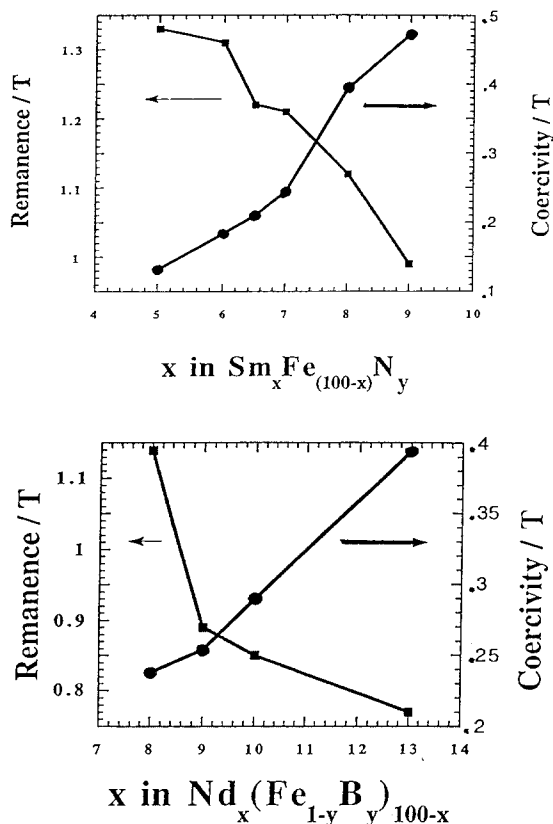
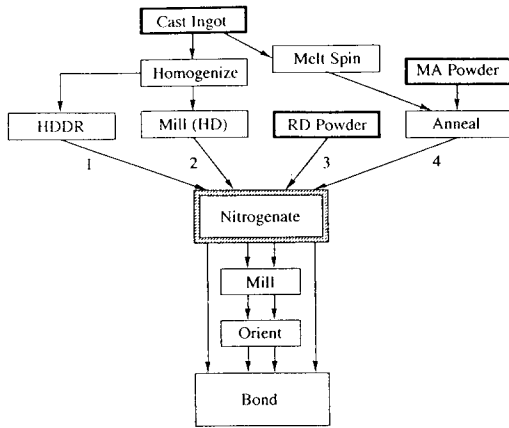


Figure 3: Remanence and coercivity of two-phase exchange-coupled magnets made by mechanical-alloying.

be divided into those (mechanical alloying, HDDR, melt spinning) which produce isotropic nanocrystalline coercive powder, and those which yield monocrystalline powder particles in the size range of a few microns which can be oriented. Data on such a powder is shown in Fig 5. In both cases, the potential is for bonded magnets. It appears likely that one further decisive advance in processing will be required to establish a market for Sm-Fe-N. This could be the development of precipitation hardening, as in $\text{Sm}_2\text{Fe}_{17}$ -based magnets which would eliminate the milling step after nitriding, or the production of anisotropic powder by HDDR, as in Nd-Fe-B.

It is interesting that certain nonmagnetic substitutions in $\text{Sm}_2\text{Fe}_{17}$ such as Al [17] and Ga [18] are able to increase the Curie temperature and change the sign of K_1 from negative (easy-plane) to positive (easy-axis), at the cost of a reduction in M_s . The anisotropy produced by the above substitutions is insufficient to yield useful permanent magnet properties, but this can be achieved in combination with interstitial nitrogen or carbon.



1, 4 = Isotropic magnets
2, 3 = Oriented magnets

Figure 4: Processing routes for Sm-Fe-N magnets.

A new family of rare-earth intermetallics are the monoclinic $R_3(Fe, Ti)_{29}$ compounds whose crystal structure is made up by stacking units with 2:17 and 1:12 composition [19]. Interstitial nitrogen or carbon can be introduced by gas-solid reaction, resulting in the increase of Curie temperature and change of anisotropy now familiar in the iron based 2:17 and 1:12 compounds [20]. The $Sm_3(Fe, Ti)N_x$ compounds exhibit significant coercivity [21], but they seem to offer no practical advantage compared to $Sm_2Fe_{17}N_x$. They are the first rare-earth intermetallic magnets with low crystal symmetry, and it is interesting to note that any ferromagnet with orthorhombic symmetry or lower will always have an easy anisotropy axis, never an easy phase, regardless of the sign of $\alpha_J A_2^0$.

Finally, some remarks about permanent magnet applications are appropriate. The field of nanomagnetism is certainly an exciting frontier where new basic knowledge is likely to emerge. Some of this may prove to be of practical relevance in the rational design of processing routes leading to magnets with desired microstructures and improved properties. But the micromagnetic problem is difficult to solve analytically or computationally in a way that is relevant to the properties of real materials. In fact, much of the progress in permanent magnet processing has been made empirically, by systematic experimentation with the theoretical rationale emerging afterwards. A sound understanding of crystal field theory has not been indispensable for developing rare-earth magnets in the past, although it may prove to be useful in future. Theory has contributed more to the development of intrinsic magnetic properties than to coercive microstructures. However it is in the applications area that theory and simulation are again closely linked to practical results. Calculations of magnetic circuits are facilitated by the fact that rare-earth magnets are

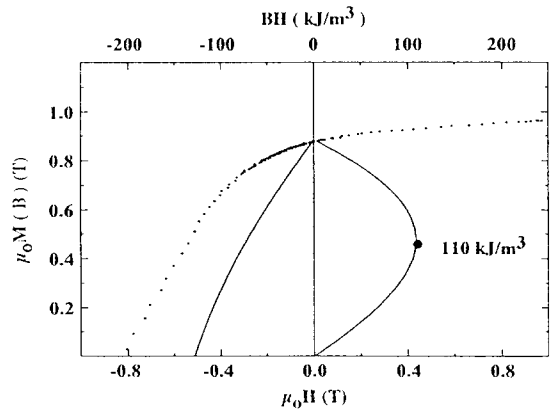
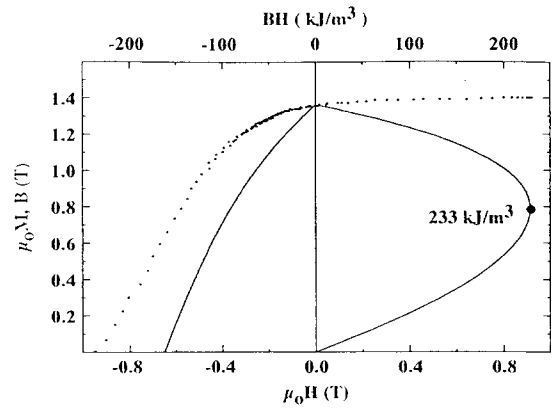


Figure 5: B:H curves and energy products for $Sm_2Fe_{17}N_3$ powder and a teflon-bonded magnet made from this powder.

magnetically transparent to a first approximation, and insensitive to the fields they themselves produce. Furthermore modern finite element and finite difference methods [22] and advanced numerical design techniques ensure that the performance of a magnetic circuit can be predicted in some detail before it is built.

Although a great many applications of Nd-Fe-B magnets exist, a large fraction of magnet production, perhaps as much as one-third, goes into just one area - voice coil actuators for hard disk drives. This illustrates how one new mass application can influence the whole magnet market. It might be in an automobile component, a high-speed elevator, a battery-powered bicycle or a magnetic toothbrush!

There is also scope to develop new static magnetic field devices based on permanent magnets [23]. An example is provided by the permanent magnet flux sources based on the 'magic mangle' [24]. This is a simple, but versatile device which uses four rotatable, transversely-magnetized rods to generate a uniform, variable magnetic field, field gradient or

'magic mangle' [24]. This is a simple, but versatile device which uses four rotatable, transversely-magnetized rods to generate a uniform, variable magnetic field, field gradient or quadrupole field in a readily accessible region of space. The principle is that for long dipole sources, the magnitude of the field produced at (\mathbf{r} , θ)

$$H_r = (\lambda/2\pi r^2) \cos \theta$$

$$H_\theta = (\lambda/2\pi r^2) \sin \theta$$

depends only on r , not on θ . λ is the dipole moment per unit length in Am. The directions of the components produced by the individual cylinders can be modified by rotating them, so a variable field can be produced in any direction in the plane perpendicular to their axes.

In summary, permanent magnetism is a field which still has a long life span and which will continue to flourish after the saturation of the energy product. Close links between materials development, magnet processing and applications are a recipe for stimulating progress.

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