Viewpoint Paper

Permanent magnets: Plugging the gap

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Abstract—Bulk permanent magnets are indispensable components of numerous consumer and industrial products for energy conversion. The market splits roughly 2:1 between Nd–Fe–B and hard ferrite, whose costs are currently in a ratio of more than 25:1. The escalation of rare earth costs presents an opportunity for new magnets with an energy product of 100–200 kJ m^{-3}, intermediate between ferrite (<38 kJ m^{-3}) and Nd–Fe–B (>200 kJ m^{-3}), provided the costs of raw materials and manufacturing are kept low.
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1. Introduction

Permanent magnets have evolved in the last 60 years from classroom curiosities, with a handful of specialized applications in small motors, dynamos and microwave generators to indispensable components of many mass-market consumer goods, medical devices and industrial products. The majority of these are some sort of electro-magnetic energy converter—motors, actuators or generators. Magnet ownership by an average middle-class family has shot up a hundred-fold, from one or two magnets to one or two hundred, although most people would be hard pressed is asked to say where their magnets are to be found. If we count the individually addressable patches of magnetization on computer hard discs, which are becoming increasingly indistinguishable from permanent magnets, then magnet ownership rockets by a further nine orders of magnitude!

The magnet revolution has been brought about by the development of new hard magnetic materials. By a "hard magnet" we mean one with a broad hysteresis loop, which is a plot of the magnetization M of the material vs. the magnetic field H acting on it. The loop is nonlinear, and it depends on time, temperature and the prior history of the magnet [1]. The breakthrough that occurred in the early 1950s in the Netherlands [2] was the shattering of the "shape barrier". Before that, mass-market magnets had to be manufactured in awkward shapes in order to avoid self-demagnetization. The bars and horseshoes of yesteryear were needed to

reduce the negative contribution to H from the demagnetizing field H_d produced by the magnet itself. This field is approximately related to the magnetization by the simple expression:

$$H_d \approx -\mathcal{N}M, \tag{1}$$

where $\mathcal{N}$ is a number between 0 and 1 that depends only on the magnet shape. Hence the field acting is $H = H_0 + H_d$ where H_0 is the externally applied field. A magnetic material which exhibits an $M(H)$ hysteresis loop that has the form of a square or a squat rectangle can be made in any desired shape without demagnetizing itself. We can properly speak of the form of the loop when both M and H are measured in the same units of kA m^{-1}.

The ideal hysteresis loop for a permanent magnet is illustrated in Figure 1. A true permanent magnet can be fabricated in any desired shape, which means that coercivity must exceed the saturation magnetization:

$$H_c > M_s. \tag{2}$$

This does not imply that magnets should made in shapes which minimize H_d. On the contrary, such a magnet would be just as useless as one which maximizes it, because neither produces any stray field [3]. Stray field is the raison d'être of a permanent magnet. The job of the magnet is to produce a magnetic field outside its volume, which we denote by the same symbol H_d used for the field it produces within its volume. It is the stray field which is channeled in a magnetic circuit to provide the forces, torques, electromotive forces or voltages on which magnet applications depend [1,3].
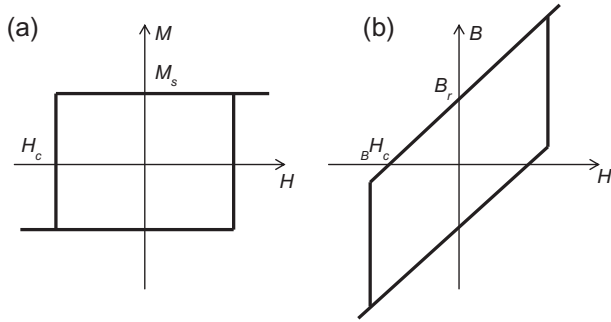
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Figure 1. Ideal hysteresis loops for a permanent magnet: (a) an $M(H)$ loop and (b) a $B(H)$ loop. The maximum possible energy product $|BH|_{MAX}$ is represented by the area of the largest square that can be drawn in the second quadrant.

The fundamental magnetic field is really $\boldsymbol{B}$, not $\boldsymbol{H}$ (although it is the value of $\boldsymbol{H}$ and its history that determine the state of a piece of magnetic material). In free space the relation between the two is trivial:

$$\boldsymbol{B} = \mu_0 \boldsymbol{H}, \tag{3}$$

where μ_0 is the magnetic constant, also known as the permeability of free space, which is defined to be precisely $4\pi \times 10^{-7}$ T m A^{-1}. $\boldsymbol{B}$ is therefore measured in teslas. Bold type has just been introduced to indicate that $\boldsymbol{B}$ and $\boldsymbol{H}$ are vectors which only have to be parallel to each other free space. Within a magnetic material, the relation becomes:

$$\boldsymbol{B} = \mu_0 (\boldsymbol{H} + \boldsymbol{M}). \tag{4}$$

The B-field, also known as the magnetic flux density, obeys Maxwell's equation:

$$\nabla . \boldsymbol{B} = 0, \tag{5}$$

which states that the B-field is divergenceless. It has no sources or sinks, because free magnetic poles are never observed in nature. The "north" and "south" poles, or the equivalent positive and negative magnetic charge, are fictitious. Nevertheless, they are useful to envisage the H-field and magnetostatic calculations may be simplified by invoking them as a computational aide [3]. The $B(H)$ loop shown in Figure 1b corresponds to the $M(H)$ loop shown in Figure 1a.

It can be shown that the energy stored in the stray field created by a magnet is equal to $1/2 \int |BH| dV$, where the integral is over the magnet volume [3]. Assuming that H and M are uniform, Eqs. (1) and (4) give:

$$|BH| = \mu_0 M_s^2 (\mathcal{N} - \mathcal{N}^2). \tag{6}$$

Differentiating with respect to $\mathcal{N}$ to find the maximum, we obtain $\mathcal{N} = 1/2$, and $|BH|_{MAX} = 1/4 \mu_0 M_s^2$. A shape which corresponds to $\mathcal{N} = 1/2$ is a low cylinder of height roughly equal to its radius. Modern magnets are often this shape.

If the magnetization curve deviates from the ideal square loop of Figure 1a, the value of the maximum achievable energy product $|BH|_{max}$ is lower than this, so:

$$|BH|_{max} < 1/4 \mu_0 M_s^2. \tag{7}$$

For most applications, the figure of merit which we seek to maximize in a magnetic material is $|BH|_{max}$.

Nowadays, two families of magnets are produced on a large scale. One is the ferrite family [4], which was developed in the Netherlands 60 years ago [3]. The common phases are $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, which have the hexagonal magnetoplumbite structure. The energy product of these magnets does not exceed 38 kJ m^{-3}, but they are cheap and relatively easy to produce. Prices are less than \$5 kg^{-1}. Ferrites represent about one-third of the permanent magnet market, and the lion's share by mass of the million tonnes of magnets shipped each year.

Most of the remaining two-thirds are rare-earth permanent magnets, especially those based on $Nd_2Fe_{14}B$, an iron-rich tetragonal phase that was independently discovered in Japan [5] and in the USA [6] in 1982. The best laboratory Nd–Fe–B magnets have energy products as high as 470 kJ m^{-3}, close to the theoretical maximum of $|BH|_{MAX} = 512$ kJ m^{-3}. Commercial grades with values as high as 400 kJ m^{-3} are shipped. Production in 2010 amounted to 80,000 tonnes, but due to escalating rare-earth prices, Nd–Fe–B magnets now cost more than \$100 kg^{-1}. There is growing demand for superior grades with improved performance at elevated temperatures for energy-related applications such as electric vehicles and direct-drive wind turbines [7]. Adequate hysteresis is maintained at temperatures up to 200 °C by replacing some of the Nd by a heavy rare earth, Dy or Tb. Unfortunately, the supply situation for heavy rare earths is particularly precarious; the price of Dy or Tb is currently 10 times that of Nd, whose price is currently running at 10 times its historical level. The 3–10 wt.% of these elements in the formula is now the major component of the price of high-temperature grades of Nd–Fe–B.

About 5% of the rare-earth magnets produced belong to the Sm–Co family, which has been developed since the mid-1960s [8,9]. These magnets have a similar field of application to Dy-substituted Nd–Fe–B, offering improved temperature stability, but lower energy product.

There remains a small but steady demand for the old Alnico magnets [10]. An estimate of the breakdown of magnet production in terms of market value in 2010 is shown in Figure 2.

Processed magnets are frequently fully dense sintered, oriented blocks produced by power metallurgy or ceramic methods. An alignment step to orient the easy axes of all the crystallites is highly beneficial as without it the remanent magnetization is decreased by more than a factor of 2, and the energy product by a factor of 4 (Eq. (7)). However, there are benefits in loading the magnet powder in a polymer matrix, to make mouldable
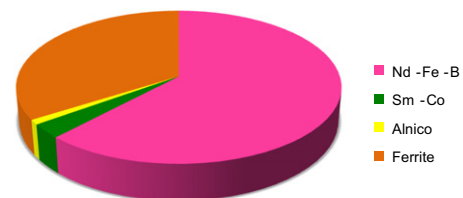

Figure 2. Estimated breakdown of the world market for permanent magnets in 2010. The total value is approximately \$9 bn (after Ref. [7]).
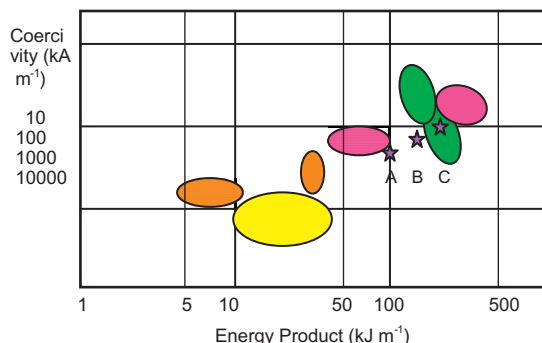
Figure 3. Ranges of energy product and coercivity for different types of permanent magnets. Colour code is the same as in Figure 2. Bonded magnets are shown stippled. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

or flexible magnets. The packing fraction of the magnetic material may reach 70%, so the magnetization is reduced in this proportion, and the energy product is reduced by a factor of 2. Figure 3 illustrates the range of energy products for the main classes of magnets produced today.

The escalating costs of rare earths is a manifestation of the "rare earth crisis" [11]. It is forcing attention to be paid to the possibilities of substitution, cost reduction and recycling. Broadly, three approaches are under investigation:

- Reduce the heavy rare-earth content of Nd–Fe–B-type magnets, while preserving their high-temperature performance. The heavy rare earths Dy or Tb are required if the coercivity is to remain stable with increasing temperature up to 200 °C.
- Seek a novel ultra-high-performance material to replace rare-earth magnets.
- Seek a new, low-cost material with a maximum energy product lying in the gap between ferrite and rare-earth magnets.

Considerable progress is being made with the first approach. By optimized processing and grain boundary engineering it should be reduce the heavy rare-earth content by about a factor of three from its present levels of upto 10 wt.% [12].

The second approach is problematic. $Nd_2Fe_{14}B$ is a close-to-ideal high-performance magnet [13]. It is largely made of iron, the cheap and abundant ferromagnetic element with the greatest magnetization. The anisotropy $K = 4.9$ MJ m^{-3} is mostly provided by the relatively inexpensive light rare earth Nd (which has an abundance similar to that of zinc), which couples with its moment parallel to that of iron, and only a small amount of a third element, boron, is required to stabilize a uniaxial structure, which has an easy axis of magnetization. All obvious candidates, including exchange spring nanocomposites, have been considered, and quite a lot of research has been done on them [14]. The difficulty is that an energy product in excess of 500 kJ m^{-3} requires $M_s > 1.3$ MA m^{-1}. The coercivity should be as large as this for a square loop, but an upper limit for the coercivity is set by the anisotropy field $H_a = 2K_1/\mu_0 M_s$, where K_1 is the uniaxial anisotropy constant. Past experience with new permanent magnet materials indicates that

years of optimization are usually needed to achieve a coercivity that is even a quarter of the anisotropy field, because permanent magnetism and hysteresis are metastable phenomena that depend on subtle details of the microstructure which can only be optimized by painstaking experimentation [15]. An empirical criterion for a permanent magnet is that the hardness parameter κ should be greater than unity [1,3]:

$$\kappa = (K/\mu_0 M_s^2)^{1/2} > 1. \tag{8}$$

This implies that $K > \mu_0 M_s^2 > 2$ MJ m^{-3}. Such large values of K demand magnetocrystalline anisotropy, which arises from spin–orbit coupling. The maximum anisotropy that can be achieved by controlling the shape of nanoscale magnetized regions, the approach adopted for Alnico [10], is only a quarter as large. Strong spin–orbit coupling requires the presence of a heavy element such as a member of the 4d, 4f or 5d series [3]. These are costly elements, as may be seen from the periodic table in Figure 4. Nd–Fe–B is really hard to beat.

Strictly speaking, the absolute minimum condition for a true permanent magnet is $H_a > H_c > M_s$, which reduces to $\kappa > 1/\sqrt{2}$. The maximum energy product could even be obtained for a magnet with $\mathcal{N} = 1/2$ provided $H_c > M_s/2$ ($\kappa > 1/2$). However, all existing materials have $\kappa > 1$ ($SrFe_{12}O_{19}$, 1.33; $SmCo_5$, 4.3; Sm_2Co_{17}, 1.89; $Nd_2Fe_{14}B$, 1.54). A breakthrough in magnet processing that would relax the condition (8) is conceivable, but on past experience it seems highly unlikely.

In this Viewpoint article we will therefore accept the condition (8) and explore the third approach. Can we hope to find a new, cheap material that is significantly better than ferrite?

2. New magnets with moderate performance

The prospect is to fill the gap between ferrite and rare-earth magnets with something cheap and effective. Such a material could enhance the performance and reduce the weight of devices that currently use ferrite, and greatly cut the cost of devices that currently use rare-earth magnets, at the expense of some increase in weight.

A point worth emphasizing is that our quest is to make M, the magnetic moment per unit volume, as large as possible, while satisfying the condition (8), $K > \mu_0 M_s^2$, without the use of expensive elements. Furthermore the material needs to be thermally stable and posses a Curie temperature in excess of 550 K if it is to have a realistic prospect of being adopted for practical purposes.

A modern approach to the problem of finding such a material would be to begin with combinatorial computational materials science to screen thousands of alloys, and identify perhaps a dozen candidate materials which satisfy the constraints of Curie temperature, magnetization, anisotropy and cost, and then proceed to try to make them in the laboratory. However, little use seems to have been made of this approach so far. It should be tried.

Instead we will discuss a few plausible candidate materials, analyse why they fall short, and see what might be done about it. In Table 1, we set out the basic
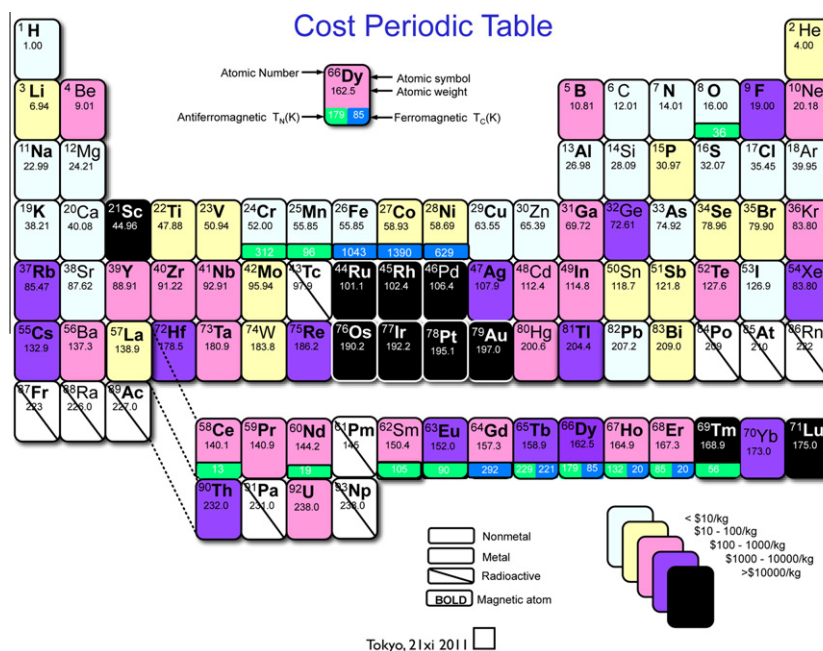
Figure 4. The cost periodic table (November 2011), including information on the magnetic properties of the elements.

requirements for new materials with three levels of energy product.

It should be emphasized that these are minimum requirements. In particular, we should not forget that the $|BH|_{max}$ achieved with real hysteresis loops always falls short of the ideal $|BH|_{MAX}$ for a square loop.

Table 2 summarizes the properties of a few interesting uniaxial ferromagnetic compounds. It is possible to achieve any individual target value, but no material quite manages to combine the required T_C, M_s, K and energy product.

The magnetization of all the materials in Table 2 meets the minimum target value of M_s, except for Mn_2Ga, which has a ferrimagnetic structure [17]. Manganese is an abundant element which forms alloys which may exhibit high Curie temperatures. Atomic moments can be higher than those of either iron or cobalt. The difficulty is that the Mn atoms on high-moment sites tend to couple antiferromagnetically. Ferromagnetic coupling occurs for long bond lengths, as in tetragonal MnAl, but there half the volume is occupied by nonmagnetic Al; the magnetization in this and other equiatomic compounds is necessarily small [3], although it may suffice for target A in Table 1. A nonmagnetic constituent will normally reduce the magnetization of an alloy since it occupies volume without contributing to the magnetic moment. Interstitial elements (B, C, N) may be exceptions. Hexagonal MnBi is another interesting material, but although the materials cost per kg looks affordable, bismuth is a scarce element obtained as a

byproduct of lead, with an annual production of only 8000 tonnes. It makes little sense to try to develop MnBi as a mass-market permanent magnet, because the bismuth cost would then rise to prohibitive levels. The same argument can be made for gallium in Mn_2Ga, or any related composition with Ga or Ge.

One lesson to be taken from Table 2 is that the rare earths are not indispensable for strong uniaxial anisotropy. Provided the axial distortion of the structure is sufficient, useful uniaxial anisotropy may be found for Mn, Fe or Co. Mn_2Ga, which has the tetragonal $D0_{22}$ structure, which may be regarded as a severely distorted $C1_b$ half-Heusler structure, and YCo_5, which has the hexagonal $D2_d$ stucture, are cases in point. Both have $K > 2$ MJ m^{-3}. The contribution of the $3d$ sublattice in magnets such as $SmCo_5$ and $Nd_2Fe_{14}B$ to the overall uniaxial anistropy can be seen from the data on the yttrium analogues in Table 2. The presence of a heavy nonmagnetic atom may help to enhance the spin–orbit coupling at the $3d$ site by hybridization, but examples in the Table 2 show that it is by no means essential.

However, the anisotropy needed to make a magnet permanent rises quadratically with the magnetization (Eq. (8)). For $\alpha''Fe_{16}N_2$, an interstitial compound that is only stable at low temperature and is very difficult to prepare in bulk in single-phase form [18], but which has a magnetization approaching 2 MA m^{-1}, Eq. (8) requires $K > 5$ MJ m^{-3}. Unfortunately this is 5 times the measured value. Interstitial $D0_{11}$ Fe_3C also has κ much too small to make a true permanent magnet. Co_3C may be a bit better [19].

The tetragonal $L1_0$ structure is potentially interesting, but if only half the atoms in the alternating c-plane layers are magnetic, as in τMnAl, the magnetization is inevitably limited. Tetragonal MnAl is a permanent magnet material but $|BH|_{MAX}$ is only 112 kJ m^{-3}. Developments that have taken place stabilizing the τ phase with carbon have produced material with $|BH|_{max}$ of up to 50 kJ m^{-3}

Table 1. Some target specifications for new magnet materials.

$|BH|_{MAX}$ kJ m^{-3}	T_C K	M_s MA m^{-1}	K kJ m^{-3}	Raw materials cost \$ kg^{-1}
A 100	>550	570	500	10
B 150	>550	690	750	20
C 200	>550	800	1000	30

Table 2. Properties of some uniaxial ferromagnets [3,16,17].

	MnAl	MnBi	Mn_2Ga	$Y_2Fe_{14}B$	$\alpha''Fe_{16}N_2$	Fe_3C	YCo_5
M_s (MA m^{-1})	0.60	0.58	0.47	1.10	1.92	1.09	0.85
K_1 (MJ m^{-3})	1.7	0.90	2.35	1.1	1.0	0.45	6.5
T_C (K)	650	628	>770	590	810	56	987
κ	1.95	1.46	2.35	0.85	0.43	0.55	2.7
Raw materials cost ($ kg^{-1})	<10	<20	>100	<30	<10	<10	<50

[20]. MnAl magnets are machinable and light. The $L1_0$ alloys CoPt and FePt are suitable for permanent magnets. In fact PtCo was discovered in 1936 (by Jellinghaus), and it was probably the first true permanent magnet. The values of M_s and κ are 0.80 MA m^{-1} and 2.47 for CoPt and 1.14 MA m^{-1} and 2.02 for FePt, respectively. Energy products of up to 100 kJ m^{-3} are reported for these materials [16], but the materials cost is prohibitive for any mass-market application.

A feature of $L1_0$ materials is that they undergo a tetragonal to face-centred cubic (fcc) phase transition at an elevated temperature T_t. The permanent magnetism obviously disappears in the cubic phase, and the maximum operating temperature has to be one where there is no tendency for atomic disordering in the sites of the tetragonal structure. A particularly interesting example of an $L1_0$ compound is τFeNi. It is found in iron meteorites which have had billions of years to reach thermal equilibrium. The value of T_t is only 320 °C [21]. The phase been prepared by neutron irradiation of fcc FeNi [22]. The value of K is 0.32 MJ m^{-3}, and $\kappa \approx 0.4$.

Included in Table 2 are compounds with the $Nd_2Fe_{14}B$- or $SmCo_5$-type structures having the nonmagnetic Y atom in place of the rare earth. Replacement of the magnetic rare earth by some mixture of the cheaper nonmagnetic elements Y, La or Ce could offer significant cost savings. Cobalt, which costs approximately $30 kg^{-1}, is a constraint on the application of $D2_d$ structure MCo_5 materials.

It is worth emphasizing that the relative amounts of the different rare earths obtained from a mine depends on the relative proportion of the metals in the ore, which in turn reflects the *local* crystal abundances. The Sm:Nd ratio is typically about 1:5, so Sm may be now regarded as a byproduct of Nd production, and in the absence of balanced demand it may fetch a lower price than Nd. This is the case at present (late 2011). Since the production of Sm–Co magnets is currently about 5% of that of Nd–Fe–B (Fig. 2), it may be economically viable to use Sm–Co instead of Nd–Fe–B, despite the relatively costly Co. Sm–Co magnets are traditionally more expensive than Nd–Fe–B, because of higher raw materials and manufacturing costs. However, the price of Sm is currently lower than that of Nd, and 17 times less than that of Dy, an element with similar crustal abundance. At the moment, the raw materials costs for Nd–Fe–B with 9% Dy are $340 kg^{-1}, compared with $75 kg^{-1} for a 2:17 Sm–Co magnet. This illustrates the importance of matching demand to the relative distribution of the rare-earth elements in the ores that are being mined, in order to make the best use of nature's gifts.

Another example where the price is unrelated to the abundance is the Dy/Tb pair. Although the abundance of Tb is five times less than that of Dy it sells for almost the same price because it serves a similar purpose—to increase the anisotropy constant of Nd–Fe–B magnets and thereby improve their high-temperature performance. It has no other significant use, except for small amounts required for phosphors. The current rare-earth crisis is largely a problem of heavy rare earth supply. There are abundant ores containing the light rare earths Pr, Nd and Sm in various parts of the world, but known reserves of the heavy rare earths Dy and Tb outside China are very limited in relation to possible demand over the next ten years.

The examples considered in Table 2 are all intermetallic or interstitial metallic compounds. One might ask whether there is any prospect of finding an oxide permanent magnet with better properties than hexagonal ferrite. Part of the reason for the low magnetization of $SrFe_{12}O_{19}$ ($M_s = 0.38$ MA m^{-1}) is the fact that much of the volume is occupied by large O^{2-} anions, which carry no magnetic moment. Another problem, however, is that the oxide is ferrimagnetic rather than ferromagnetic. If the moments of the Fe^{3+} sublattices were all aligned, the magnetization would be 3 times as great and energy products of 300 kJ m^{-3} could be envisioned. How could we ensure that the 3d moments in an oxide couple parallel, with a high Curie temperature? Ferromagnetic oxides are not unknown; CrO_2 is the textbook example, with a 2/3 full t_{2g} band for Cr^{4+} [3]. Most other oxide ferromagnets, such as the perovskite manganites, rely on mixed valence to provide ferromagnetic double-exchange coupling. Further efforts might throw up a uniaxial, ferromagnetic mixed-valence oxide with a high T_C, but it seems unlikely as oxides have already been intensively investigated [23].

Finally, it is worth remarking that the specifications of materials used for perpendicular magnetic recording with bit-patterned media and perpendicular magnetic random-access memory are increasingly coming to resemble those for permanent magnets. The stability condition for 10-year data retention:

$$\Delta = KV/kT > 60 \qquad (9)$$

demands $K > 0.5$ MJ m^{-3} in media where the free layer volume or bit volume is <500 nm^3 (10 nm × 10 nm × 5 nm). Thin-film materials CoPt, FePt have been considered for this purpose, but thin films of Pt-free materials with less expensive elements such as $MnGa_2$ can be envisaged [24]. For perpendicular media, the anisotropy field $2K/\mu_0 M_s$ must overcome the demagnetizing field $H_d \approx -M_s$, so that $K > 1/2\mu_0 M_s^2$. In the case of Mn_2Ga, this condition reads $K > 0.14$ MJ m^{-3}, which is comfortably satisfied. The bits could even be a factor of 2 smaller. Unlike bulk applications, one can consider using a much wider range of materials in Table 2 for thin films because cost is no longer such a severe constraint. The quantities of materials used in a thin-film memory are

tiny, perhaps of the order of 1 μg, 7 orders of magnitude less than in a bulk energy conversion device. Nevertheless, if either Pt- or Pd-based alloys were to be widely adopted for magnetic media or memory, there would be a strain on the global market for scarce platinum group metals. A cubic meter would provide 5 billion people with a 20 cm^2 of a film 10 nm thick, but this would represent half the world's annual production of Pt.

3. Conclusions

Despite everything that has already been done on the topic, it is possible to be optimistic about the prospects of developing a relatively cheap magnet that could hit targets A–C in Table 1 and Figure 3. In τMnAl we already have a material which, given an effort comparable to that which has been devoted to optimizing Nd$_2$Fe$_{14}$B where $|BH|_{max}/|BH|_{MAX}$ is now 0.93, should be able to meet target A. Whether or not the process will be cost effective remains to be seen.

The pressure to come up with some new magnets that has been generated by the rare-earth crisis looks set to continue in the medium term. Ultimately the supply situation for the light rare earths is expected to ease as new mines are opened [25], and new reserves such as those on the sea-bed are exploited [26]. The heavy rare earths Dy and Tb are more problematic, so long as demand relative to Nd outweighs their relative abundance in available ores [25]. The current elevated and unstable prices of these elements is likely to act as a disincentive to developing new, high-volume applications of Nd–Fe–B magnets such as direct-drive wind turbines and electric vehicles.

Computation methods of combinational materials science may be the key to further progress. We need to see if some cheap new ternary or quaternary phases can be found. Binaries have been exhaustively explored, and the possibilities there are well known.

As scientists looking for new perpendicular media and those seeking new low-cost permanent magnets are converging onto some sort of common ground, it can be expected that in the future one community will increasingly learn from the other.

Acknowledgements

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