Giant energy product in nanostructured two-phase magnets

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(Received 25 August 1993)

Exchange hardening of nanostructured two-phase systems composed of an aligned hard phase and a soft phase with high magnetization is investigated using an approach which yields analytic nucleation fields from the micromagnetic vector equation, and accounts for interactions between the soft regions. In suitable structures the nucleation field is proportional to the volume-averaged anisotropy constant. For example, a multilayer composed of alternating 2.4 nm hard-magnetic $Sm_2Fe_{17}N_3$ layers and 9 nm $Fe_{65}Co_{35}$ layers can have an energy product as high as 1 MJ/m^3 (120 MG Oe), with a rare-earth content of only 5 wt %. Giant energy products may also be achieved in suitable cellular and disordered structures.

A key characteristic of a permanent magnet of volume V is the energy product $(BH)_{max} = (1/V) \int_{magnet} |B \cdot H| d\mathbf{r}$ which is twice the maximum magnetostatic energy available from a magnet of optimal shape. Energy product increases with coercivity H_c and remanence M_r but it can never exceed the value $\mu_0 M_r^2/4$ corresponding to an ideal rectangular hysteresis loop. An upper limit for the remanence is the spontaneous magnetization M_0 but if magnetization were the only consideration then α-iron with $\mu_0 M_0 = 2.15$ T would be used for permanent magnets with energy products as high as 920 kJ/m^3. In fact, the coercivity of bcc iron is so low that energy products of iron magnets are only of order 1 kJ/m^3. In the past it was necessary to resort to cumbersome bar and horseshoe shapes to avoid spontaneous demagnetization into a multidomain state by the magnet's own magnetostatic field.

Modern high-performance magnets[1] such as $Nd_2Fe_{14}B$ or $Sm_2Fe_{17}N_3$ overcome this problem by exchange-coupling iron atoms to rare-earth atoms in sites with strong uniaxial anisotropy. The rare-earth sublattice yields anisotropy fields which exceed the magnetostatic fields by an order of magnitude. The penalty, however, is a reduced magnetization due to the rare-earth and nonmagnetic elements. The light rare-earths' atomic moments are, at best, slightly larger than that of iron, but they occupy more than three times the volume. Nevertheless, it has been possible to use $Nd_2Fe_{14}B$, which has $\mu_0 M_0 = 1.61$ T and $\mu_0 M_0^2/4 = 516$ kJ/m^3 to achieve energy products as high as 405 kJ/m^3 in laboratory-scale magnets.[2]

The outlook for discovering new ternary phases with magnetization significantly higher than that of those available at present is poor. Interstitial modification with small atoms such as nitrogen or carbon is effective for enhancing Curie temperature and anisotropy, but the magnetization remains practically unchanged.[3,4] A different approach is necessary if further progress is to be possible.

Recently, magnetic hardening has been achieved in the nanocrystalline composites $Nd_2Fe_{14}B/Fe_3B$ and $Sm_2Fe_{17}N_3/Fe$ produced by melt spinning[5] and mechani-

cal alloying,[6] respectively. The idea behind these systems is that the comparatively low remanence $M_r \approx M_0/2$ of the isotropic hard phase can be improved by exchange coupling with a soft phase.[5-10] But the energy product, though improved with respect to the isotropic single-phase rare-earth material, does not reach the level attained in oriented rare-earth magnets.

Here we show how it should be possible to substantially increase the energy product in oriented nanostructured two-phase magnets by exploiting exchange coupling between hard and soft regions. We derive analytic results for the nucleation field and energy product, and suggest how the composites might best be structured.

To describe the magnetic reversal, we consider the free energy[11,12]

$$F = \int \left[A(\mathbf{r}) \left| \frac{\nabla M}{M_0} \right|^2 - K_1(\mathbf{r}) \frac{(M \cdot \mathbf{n})^2}{M_0^2} - \mu_0 M \cdot H \right] d\mathbf{r} \,,$$

(1)

where H denotes the internal field, which is the sum of the externally applied field and the magnetostatic "demagnetizing" field. $A(\mathbf{r})$ is the exchange stiffness, $M(\mathbf{r})$ with $|M(\mathbf{r})| = M_0$ is the local magnetization, and $K_1(\mathbf{r})$ is the first anisotropy constant. The unit vector in the easy-axis direction $\mathbf{n}$ is assumed not to depend on $\mathbf{r}$ (common c axis).[13] The hard and soft phases can have different values of the parameters A, M_0, and K_1 denoted by the suffixes h and s. Note that the ferromagnetic exchange interaction $[A(\mathbf{r}) > 0]$ in iron-rich intermetallics is dominated by the iron sublattice (cf. Ref. 3); we do not consider nonmagnetic regions which are able to cause oscillating coupling effects such as those observed in multilayers with giant magnetoresistance.

We start from the perfectly aligned state where $M(\mathbf{r}) = M_0 \mathbf{n}$. If a sufficiently high internal field is reached, the aligned state becomes unstable, and magnetic reversal begins (nucleation). Nucleation is a necessary but not sufficient condition for complete magnetic reversal. It sets a *lower* limit to the coercive field, $H_c \geq H_N$, since there is a possibility that the reversed nucleus will

not propagate.[14–16] The energy product can be estimated from the hysteresis loop by putting $H_c = H_N$.

In special cases, the nucleation problem [Eq. (1)] has been solved in one, two, or three dimensions by series expansion or an appropriate ansatz.[12,14,17–19] Here we take the vector identity,

$$M(\mathbf{r}) = M_0(\mathbf{r})(m_x(\mathbf{r})\mathbf{e}_x + m_y(\mathbf{r})\mathbf{e}_y + \sqrt{1 - m_x^2 - m_y^2}\,\mathbf{e}_z) ,$$

(2)

and expand the free-energy density with respect to the small transverse components $m_x, m_y \ll 1$,[20] and minimize the free energy to yield the micromagnetic equation,

$$\nabla\Psi(A(\mathbf{r})\nabla\mathbf{m}) - K_1(\mathbf{r})\mathbf{m} + \tfrac{1}{2}\mu_0 M_0(\mathbf{r})H_N\mathbf{m} = 0 ,$$

(3)

with $\mathbf{m} = m_x(\mathbf{r})\mathbf{e}_x + m_y(\mathbf{r})\mathbf{e}_y$. Note that $\mathbf{n} = \mathbf{e}_z$ does not enter the micromagnetic vector equation, so long as $\mathbf{H}$ is applied in the $-\mathbf{n}$ direction (cf. Ref. 11). This equation represents an eigenvalue problem, and to find H_N it is sufficient to solve the differential equation,

$$-\frac{2A(\mathbf{r})}{\mu_0 M_0(\mathbf{r})}\nabla^2\Psi + \frac{2K_1(\mathbf{r})}{\mu_0 M_0(\mathbf{r})}\Psi = H_N\Psi ,$$

(4)

with the interface boundary condition $A_s(\mathbf{e}\cdot\nabla)\Psi_s = A_h(\mathbf{e}\cdot\nabla)\Psi_h$. Here Ψ represents m_x or m_y or any linear combination of the two, and $\mathbf{e}$ is the unit vector normal to the interface. The boundary condition reflects the fact that phases with strong exchange stiffness tend to realize a more homogeneous magnetization state ($\nabla\Psi$ and $\nabla\mathbf{m}$ small). Apart from a minor generalization of the boundary condition, Eq. (4) corresponds to Schrödinger's equation for a particle moving in a three-dimensional potential $2K_1(\mathbf{r})/\mu_0 M_0(\mathbf{r})$, which allows us to apply ideas familiar from quantum mechanics to discuss micromagnetics. In particular, the nucleation field corresponds to the quantum-mechanical ground-state energy, and the small transverse magnetization or nucleation mode Ψ has its analog in the wave function.

First we consider an ideally soft inclusion (diameter D, $K_s = 0$) in a hard matrix (Fig. 1). The initial state is one where the magnetization of the matrix and inclusion are perfectly aligned. Introducing spherical coordinates and taking the limit $\Psi \to 0$ as $r \to \infty$ we obtain the eigenvalue
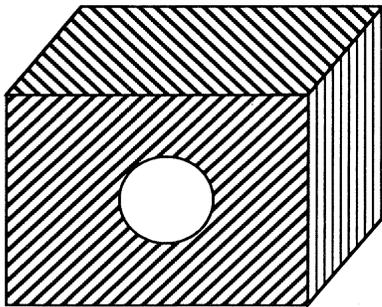
equation,

$$\frac{A_s}{A_h}\left[\frac{D}{2}\sqrt{\mu_0 M_s H_N/2A_s}\cot\left[\frac{D}{2}\sqrt{\mu_0 M_s H_N/2A_s}\right] - 1\right]$$
$$+1 + \frac{D}{2}\sqrt{(2K_h - \mu_0 M_h H_N)/2A_h} = 0 ,$$

(5)

which can be solved numerically (Fig. 2). The nucleation field reaches a plateau below $D \approx \delta_h$, where δ_h is the Bloch wall width of the hard phase.

Taking values appropriate to $Sm_2Fe_{17}N_3$, the intermetallic with the most favorable combination of magnetization and anisotropy,[3,21] inclusions smaller than 3 nm in diameter will have coercivity equal to the anisotropy field of the matrix (≈ 20 T). Even at a diameter $D = 7$ nm, the soft inclusion retains a coercivity $\mu_0 H_N = 7$ T. For larger inclusions the coercivity falls off as $1/D^2$; inhomogeneous magnetostatic fields can initiate nucleation at diameters greater than 20 nm.

For sufficiently small reverse fields $|H| < H_N(D)$, the single soft inclusion is ideally aligned along e_z and slightly enhances the remanence, provided $M_s > M_h$. To obtain a significant remanence enhancement it is necessary to generalize to large numbers of spherical inclusions per unit volume (Fig. 3). The remanence is

$$M_r = f_h M_h + f_s M_s ,$$

(6)

where f_s and $f_h = (1 - f_s)$ are the volume fractions of the soft and hard phases, respectively, but when the distance between neighboring inclusions becomes too small, the soft regions interact and coercivity is destroyed. This behavior is illustrated schematically in Fig. 4. In the case of well-separated inclusions, the lowest-lying magnetization mode which is responsible for nucleation decreases exponentially in the hard region. But when the distance between the soft inclusions is small, the magnetization modes can tunnel through the hard region, which no longer acts as an effective potential barrier. In fact, this micromagnetic exchange interaction can reduce the nu-
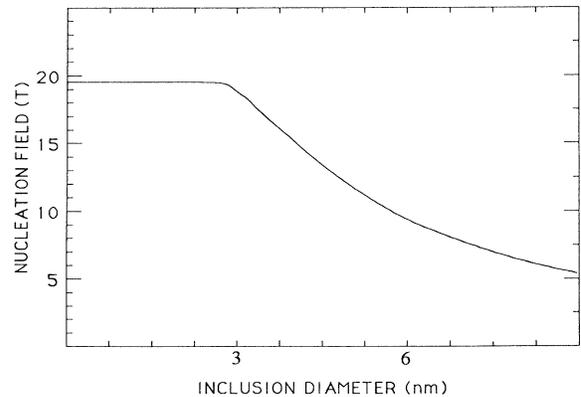

FIG. 1. Spherical soft inclusion with diameter D in a hard-magnetic matrix (dashed region).

FIG. 2. Nucleation field H_N as a function of D, the diameter of the inclusion in Fig. 1. The values assumed are for the $Sm_2Fe_{17}N_3/Fe$ system: $\mu_0 M_s = 2.15$ T, $\mu_0 M_h = 1.55$ T, $A_s/A_h = 1.5$, $K_s = 0$, and $K_h = 12$ kJ/m^3.
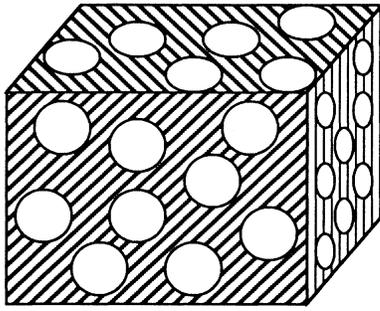
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FIG. 3. A possible structure of remanence enhancement, with many inclusions per unit volume.

cleation field considerably when the thickness of the hard region is less than δ_h.

In the plateau region (Fig. 2), where the soft regions are very small, the problem can be treated in perturbation theory.[22] As in quantum mechanics, the lowest-order eigenvalue correction is obtained by using the normalized unperturbed function Ψ_0, so an effective anisotropy constant K_{eff},

$$K_{eff} = \int \Psi^*(\mathbf{r})K_1(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r} , \tag{7a}$$

$$= \langle K_1(\mathbf{r}) \rangle = f_s K_s + f_h K_h , \tag{7b}$$

is introduced. The nucleation field is given by

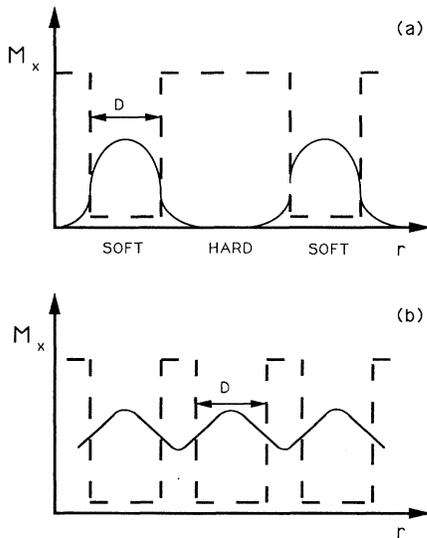$$H_N = 2\langle K_1(\mathbf{r}) \rangle / \mu_c \langle M_0(\mathbf{r}) \rangle$$

or

FIG. 4. Schematic diagram showing the effect of interaction between different soft regions. (a) The distance between the inclusions is large, and the magnetization node decreases exponentially in the hard region. (b) The distance between the inclusions is small, and micromagnetic exchange reduces the coercivity.
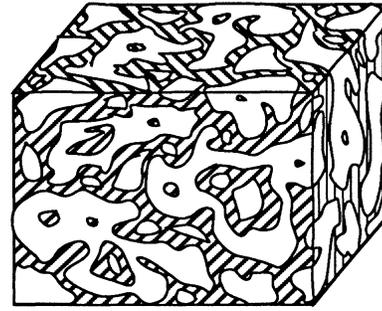

FIG. 5. An oriented, disordered two-phase magnet with common c axis. The size of the soft and hard regions is smaller than the Bloch wall thickness δ_h of the hard phase.

$$\mu_0 H_N = 2\frac{f_s K_s + f_h K_h}{f_s M_s + f_h M_h} . \tag{8}$$

If we neglect further pinning of the nucleus, we obtain a rectangular hysteresis loop with $H_c = H_N$ and $M_r = \langle M_0(\mathbf{r}) \rangle$. The energy product depends on the shape of the magnet, but the optimal value is given by $\mu_0 M_r^2/4$ for $H_N > M_r/2$ and $\mu_0 H_N M_r/2$ for $H_N < M_r/2$. Using Eqs. (6) and (8) we find the highest-energy product obtained for $H_N = M_r/2$. Putting $K_s = 0$ yields

$$(BH)_{max} = \frac{1}{4}\mu_0 M_s^2 \left[1 - \frac{\mu_0(M_s - M_h)M_s}{2K_h} \right] . \tag{9}$$

Due to the large K_h, the second term in the parentheses is small so the energy product approaches the ultimate value of $\mu_0 M_s^2$. The corresponding volume fraction of the hard phase is

$$f_h = \frac{\mu_0 M_s^2}{4K_h} . \tag{10}$$

If we consider the $Sm_2Fe_{17}N_3/Fe$ system and take values $\mu_0 M_s = 2.15$ T, $\mu_0 M_h = 1.55$ T, and $K_h = 12$ MJ/m³, we obtain a theoretical energy product of 880 kJ/m³ (110 MG Oe) for a volume fraction of only 7% of
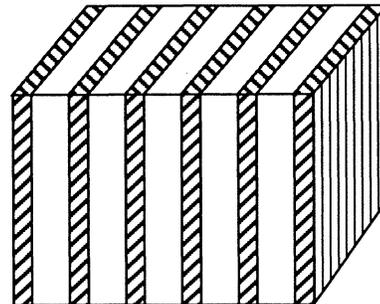

FIG. 6. A multilayer structure composed of alternating hard- and soft- magnetic regions. The multilayer periodicity should not exceed ~ 10 nm.

the hard phase. A further increase of the energy product is possible if iron is replaced by $Fe_{65}Co_{35}$ with $\mu_0 M_0 = 2.43$ T; the theoretical energy product of the $Sm_2Fe_{17}N_3/Fe_{65}Co_{35}$ system might be as high as 1090 kJ/m^3 (137 MG Oe), with $f_h = 9\%$. It is remarkable that these optimum magnets are composed nearly entirely of $3d$ metals, with only about 2 wt % samarium.

The nucleation field [Eq. (8)] is independent of the shape of the soft regions, so long as their size lies in the plateau region (Fig. 2). The hard regions act as a skeleton to stiffen the magnetization direction of the soft regions. The practical problem, however, is to realize a

structure where the soft regions are sufficiently small to avoid nucleation at small fields while having the hard regions crystallographically oriented. One conceivable solution is a disordered two-phase magnet (Fig. 5) with a common c axis throughout the hard regions, but it is difficult to see how this might be achieved in practice. A more realistic possibility may be a multilayered structure of alternating soft and hard-magnetic layers (Fig. 6). The micromagnetic multilayer problem is analogous to the periodic multiple quantum-well problem; assuming a uniform demagnetizing field the solution for the lowest eigenvalue H_N is given by the implicit equation,

$$\sqrt{(2K_h - \mu_0 M_h H_N)/2A_h}\,\tanh\left[\frac{\lambda_h}{2}\sqrt{(2K_h - \mu_0 M_h H_N)/2A_h}\,\right] = \frac{A_s}{A_h}\sqrt{\mu_0 M_s H_N/2A_s}\,\tan\left[\frac{\lambda_s}{2}\sqrt{\mu_0 M_s H_N/2A_s}\,\right],$$

$$(11)$$

where λ_h and λ_s denote the thickness of the hard and soft layers, respectively. Equation (11) permits direct numerical calculation of the critical thickness λ_c of the soft layer above which nucleation occurs, as a function of λ_h and the required coercivity H_N. For example, to obtain a megajoule magnet using $Sm_2Fe_{17}N_3$, we need a coercivity of 1.12 T with a remanence of 2.24 T which corresponds to 79 vol % $Fe_{65}Co_{35}$, thus fixing the ratio λ_s/λ_h. Taking $A_s = 1.67 \times 10^{-11}$ J/m and $A_h = 1.07 \times 10^{-11}$ J/m, we obtain the values $\lambda_h = 2.4$ nm and $\lambda_c = \lambda_s = 9.0$ nm. To achieve the same coercivity when $\lambda_h \to \infty$ we find $\lambda_c = 9.5$ nm, the difference being due to the micromagnetic coupling between the soft layers. The form of the megajoule magnet must, of course, correspond to the optimum operating point on the BH curve; it should approximate an ellipsoid with $c/a = 0.55$.

Equation (1) is based on classical micromagnetic considerations; the sizes of the hard and soft regions must be large compared to atomic dimensions so that a continuum model can be applied. The model must break down when λ_s or λ_h is smaller than about 1 nm. Furthermore,

the micromagnetic approach takes no account of thermal fluctuations of the free energy, which might be an important source of nucleation in rare-earth magnets at ambient temperature. Fortunately, the nanostructures we have been discussing are very likely to impede domain-wall propagation should a reverse nucleus form by thermal nucleation.[23] Besides, due to the small prefactor $(M_s - M_h)/M_s$, 0.28, for the $Sm_2Fe_{17}N_3/Fe$ system, the energy product is not much affected if the fraction of the hard phase is increased. We have still an energy product of almost 800 kJ/m^3 (100 MG Oe) in this system when $f_h = 30\%$, and we can use the extra hard material to improve the thermal stability and to create pinning centers.

In conclusion, it is likely that substantial improvements in the energy product of permanent magnets can be achieved by exchange hardening in nanoscale combinations of a soft phase and an oriented hard phase, structured according to the principles we have outlined.

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[23]A reversed nucleus will grow spontaneously if its radius exceeds $c\gamma/\mu_0 M_0^2$ where c is a constant of order unity and γ is the domain-wall energy. If $c = 1$ and $\gamma = 30$ mJ/m^2, the critical radius is 10 nm. However, the thermal energy needed to produce such a nucleus must be at least $4\pi r^2 \gamma$, or 4×10^5 K.