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Soft to hard magnetic anisotropy in nanostructured magnets

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The effective anisotropy of hard-soft magnetic nanostructures is analyzed using the concept of the exchange correlation length of both phases. The dependence of coercivity on volume fraction, fluctuation length, temperature, and magnetic properties of the components is derived from the degree of magnetic coupling, defined through an effective interphase exchange constant. Coercivity and remanence measurements carried out on devitrified FeZrBCu amorphous alloys point out the transition from an uncoupled to a coupled regime by increasing the temperature in a very diluted system, according to the predictions of the analysis.
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A group of the more relevant magnetic materials is composed of two phases with different magnetic properties, which fluctuate spatially with the correlation length of nanometers.[1] Softer magnetic materials consist of Fe-rich nanocrystallites embedded in a soft amorphous matrix.[2] Harder magnets are formed by mixing at nanoscale highly anisotropic rare-earth-transition metal crystallites with a soft magnetic matrix, which enhances both magnetization and Curie temperature.[3] Complementary, pinning magnets, after a rather complicated annealing and quenching treatment, consist of a cellular structure with a softer Sm_2Co_{17} phase embedded in a hard $SmCo_5$ matrix.[4]

It is remarkable that nanocrystalline material obtained by devitrification of amorphous alloys $Fe_{79}Zr_7B_{14}$ and $Fe_{79}Nd_7B_{14}$ are examples of extremely soft and extremely hard magnetic materials, with coercivities of 10^{-3} and 10^4 Oe, respectively. This broad range—of seven orders of magnitude—is covered by substituting Nd by Zr only at 7 at. %, remaining free in the compound $Fe_{79}B_{14}$. Both materials are nanostructured, the former consists of Fe nanocrystals with anisotropy constant $k=10^4\ \mathrm{J\,m^{-3}}$, embedded in an amorphous matrix of FeZrB, with $k=10^2\ \mathrm{J\,m^{-3}}$; whereas the later is formed of $Fe_2Nd_{14}B_1$ nanocrystals with $k=5\ 10^6\ \mathrm{J\,m^{-3}}$, embedded in a matrix of Fe. In both cases the magnetic anisotropy constant of crystallites is two orders of magnitude larger than that of the matrix. One should also notice that the anisotropy constant of $Fe_2Nd_{14}B_1$ is only two and a half orders of magnitude larger than that of Fe. Therefore, the difference in coercivity is due to nanostructure effects rather than to single compositional reasons. Different types of approximations to the micromagnetic calculations have been attempted.[5] The aim of this paper is to summarize by means of a proposed approximation the parameters which determine the general trend of coercivity as well as its thermal dependence in nanostructured two-phase systems. Since in the problem addressed here exchange and anisotropy are the more relevant energy terms in order to find quite general predictions, magnetostatic interactions, even though they can be important,[6] have been disregarded. Finally some experimental results carried out on Fe nanocrystals which were very diluted in a FeZrBCu amorphous matrix summarize the most important conclusions of the theoretical description.

In a single-phase nanocrystalline ferromagnetic system the magnetic behavior is governed by the ratio of the crystal size d to the exchange correlation length or wall thickness $L=(A/k)^{1/2}$, A and k being the exchange and anisotropy constant of the single crystal. Let us analyze the two possible cases.

(A) *Coupled grains.* If $L>d$, and the orientational distribution of the crystallites is random, the effect of the exchange is a reduction of the effective anisotropy constant. This decrease leads to an increase of the exchange correlation length which becomes $L^*=(A/k^{\mathrm{eff}})^{1/2}$, where k^{eff} is given by[7]

$$k^{\mathrm{eff}}=k/(N^{1/2})=k^4d^6/A^3, \tag{1a}$$

where N is the number of crystallites in the volume L^{*3}, $N=(L^*/d)^3$.

(B) *Uncoupled grains.* If $L<d$, each crystallite magnetizes independently. However, there is a surface layer around the grain with depth L, in which as a consequence of the misalignment of the easy axis at both sides of the grain boundary the anisotropy decreases. The typical volume fraction of this surface layer at each crystallite is $x^*=6L/d$. As has been thoroughly analyzed this region provides lower nucleation fields for magnetization reversal.[8] The effective anisotropy constant can be in this case approximated by

TABLE I. Summary of the parameters for the different cases considered in the text.

Cases	Conditions fulfilled by the relevant length scales	Effective anisotropy constant K^{eff}	Physical systems
(A) Coupled grains	$L_2^* \gg D$ $L_1^* \gg d_1$	$\frac{k_1}{\sqrt{N}}$	Soft Fe-rich nanocrystalls in the optimum soft magnetic state
(B) Partially uncoupled grains	$L_2^* \gg D$ $L_1^* < d_1$	$k_1 x(1-x^*) + \frac{k_1 x x^*}{\sqrt{N}}$	Spring magnets AlNiCo magnets
(C) Uncoupled grains	$L_2^* < D$ or $L_2^* \approx D$	$k_1 x + k_2(1-x)$	Soft Fe-rich nanocrystals in the low dilution limit Hard nanocrystalline magnets

$$k^{\mathrm{eff}} = k(1-x^*) + kx^*/(N^{1/2}), \tag{1b}$$

where N is now the average number of crystallites in contact with each crystallite, which is always close to 6. Therefore, under this condition k^{eff} is of the order of k.

The coercivity of any ferromagnetic sample is related to k^{eff} and the spontaneous magnetization M_s through the relation

$$H_c = pk^{\mathrm{eff}}/\mu_0 M_s, \tag{2}$$

where p is a dimensionless factor which depends on the particular type of magnetization process.

Consider a two-phase system composed of an assembly of crystallites, with volume fraction x and average size d_1 (phase 1) embedded in a ferromagnetic phase with, at least, two orders of magnitude lower anisotropy (phase 2). The easy axis direction is assumed to fluctuate in orientation with length d_2 in phase 2, which is always smaller than L_2. The minimum L_2 considered here, which corresponds to the case of spring magnets with nanocrystalline Fe as phase 2, is of 30 nm. The different strength of the anisotropy allows us to disregard the contribution to the effective anisotropy of phase 2 for $x > 0.1$. Therefore, the effective exchange interactions between crystallites, belonging to phase 1, are only relevant with respect to a possible decrease of k^{eff}. The exchange constant A is assumed to be of the same order in both phases $A = 10^{-11}\ \mathrm{J\,m^{-1}}$. The distance between crystallites of phase 1 and D can be related to d_1 and x through the approximated expression

$$D = (d_1/x^{1/3}) - d_1. \tag{3}$$

The coupling between the hard crystallites is carried out through the softer matrix. The magnetic ordering effect coming from a certain crystallite which reaches the surface of another crystallite should be described as an effective exchange that we propose to write as

$$A^{\mathrm{eff}} = e^{-(D/L_2^*)} A = \gamma A, \tag{4}$$

where $A = (A_1 A_2)^{1/2}$ and $L_2^* = (A/k_2)^{1/2}$.

Such information should also decrease exponentially as it penetrates within the grain. The typical decreasing length is now $L_1^* = (A/k_1)^{1/2}$. It is worth noting that the decrease in A^{eff} can be due either to the decrease of A_2 because of the transition to the paramagnetic state of the matrix when the temperature is increased or to the high dilution of phase 1, which means $D \gg L_2^*$.

For the sake of simplicity, and following the standard procedure in the random anisotropy model for single-phase systems, the exponential functions are approximated by step functions, i.e., $\gamma = 1$ for $D < L_2^*$ and $\gamma = 0$ for $D > L_2^*$. Three relevant cases can be considered. These cases are summarized in Table I.

(A) *Coupled grains, verifying* $L_2^* \gg D$ *and* $L_1^* \gg d_1$. This is the typical case of soft Fe-rich nanocrystals at temperatures below the Curie temperature of the amorphous phase and at moderate or high x. The contribution to k^{eff} of the soft phase becomes negligible. According to the random anisotropy calculations of a single phase system and taking into account the modifications $N = x(L_1^{*3}/d_1^3)$ and $k = xk_1$, it is finally obtained that

$$k^{\mathrm{eff}} = x^2 k_1^4 d_1^6 / A^3. \tag{5}$$

(B) *Partially coupled grains, verifying* $L_2^* \gg D$ *and* $L_1^* < d_1$. These are typical conditions holding for nanocrystalline spring magnets as well as for AlNiCo type magnets. In this case the effect of the exchange between crystallites smoothing the anisotropy only affects a volume fraction x^* of them. Then, k^{eff} becomes

$$k^{\mathrm{eff}} = k_1 x(1-x^*) + k_1 x x^*/(N^{1/2}), \tag{6}$$

where N is the number of crystallites of phase 1 comprised in L_2^{*3}, $N = x(L_2^{*3}/d_1^3)$.

Notice that the remanent magnetization is proportional to $0.5M_1 x(1-x^*) + M_1 x x^* + M_2(1-x)$, where M_1 and M_2 are the spontaneous magnetizations of phases 1 and 2, respectively. The decrease of x, as well as the increase of x^*, decreases k^{eff} but increases the remanence as is normally observed in spring magnets where $M_2 > M_1$.

Expressions (5) and (6) account for the difference in coercivity, of seven orders of magnitude, between devitrified FeZrB and FeNdB. For $x=0.5$ and $d_1=7$ nm, k^{eff} takes, according to Eq. (6), a value of 0.5 J m^{-3} for $k_1=10^4$ J m^{-3} and $A=10^{-11}$; however, according to Eq. (7) for $k_1=10^7$, $L_1=1$ nm and k^{eff} becomes 4×10^6 J m^{-3}.

(C) *Uncoupled grains, verifying* $L_2^*<D$ *or* $L_2^*\approx D$. In this case the information coming from the grains either does not reach the surface of the other grains or does very weakly. This is the case of soft nanocrystals in the low dilution limit. In general, even at low values of x, L_2^* becomes greater than D. According to Eq. (3), for $x=0.1$, D is approximately equal to d_1 and therefore D is smaller than L_2^* if d_1 is smaller than 30 nm. Hence, when d_1 is of the order of 10 nm the condition $L_2^*<D$ only holds for very low values of x, i.e., $x<0.01$. In this limit the hard phase is expected to affect only the magnetization process of the sample (almost pure phase 2) through the pinning effect[9] exerted on the walls. Notice that under these conditions the contribution of the soft phase to the effective anisotropy may then be comparable to that of the hard phase.

$$k^{\mathrm{eff}}=k_1x+k_2(1-x). \qquad (7)$$

A different case is that of the so-called pinning magnets. In contrast to the previously considered cases, the microstructure of these magnets consists of a softer phase 1, basically composed of $\mathrm{Sm_2Co_{17}}$, surrounded by a hard phase 2 of $\mathrm{SmCo_5}$. In this case, $L_1^*>d_1$ and $L_2^*<D$, which means that the grain size of phase 1 is not large enough to keep a domain wall and magnetization reversal takes place in the hard phase. Therefore, the effective macroscopic anisotropy is that of the hard phase, the role of the softer phase being to increase the Curie temperature and saturation magnetization and hence the energy product.

The thermal dependence of coercivity in nanostructured two-phase systems presents some interesting anomalies due to the thermal dependence of the coupling as illustrated by expression (4). Notice that L_2^* and therefore γ increase with temperature, whereas A decreases with temperature. Consider first a totally coupled system at low temperature, $L_2^*>D$ and $L_1^*>d_1$. Since L_2^* increases with temperature,[10] the same relation $L_2^*>D$ holds, or according to the step function approximation $\gamma=1$, at any higher temperature. However, A decreases as M_1M_2 with increasing temperature, therefore, the system remains coupled up to T^* for which $k^{\mathrm{eff}}=k_1$. According to Eq. (5) this happens for $A=x^{2/3}k_1d_1^2$. In the case of soft nanocrystals the Curie temperature of the amorphous matrix T_{c_2} is 400 K lower than that of the Fe crystallites. Hence, A goes to zero very fast at the proximity of T_{c_2}, k^{eff} rises up to reach k_1 indicating the decoupling of the crystallites which become either single domains or superparamagnetic particles. This effect has been experimentally observed as a sharp maximum in the coercivity of the sample in the vicinity of T_{c_2}.[11]

The effect predicted by relation (4) is more interesting for systems uncoupled at low temperature, verifying $L_2^*<D$ and $L_1^*>d_1$. Initially $\gamma=0$, as L_2^* increases with T, at a certain temperature L_2^* overcomes D. From this temperature the system becomes coupled, i.e., $\gamma=1$. Thus, expression (4) predicts the possibility of inducing coupling by heating extremely diluted systems. In this paper we report an example of a system in which the exchange coupling increases with increasing temperature. This system is a highly diluted FeZrBCu nanocrystal.

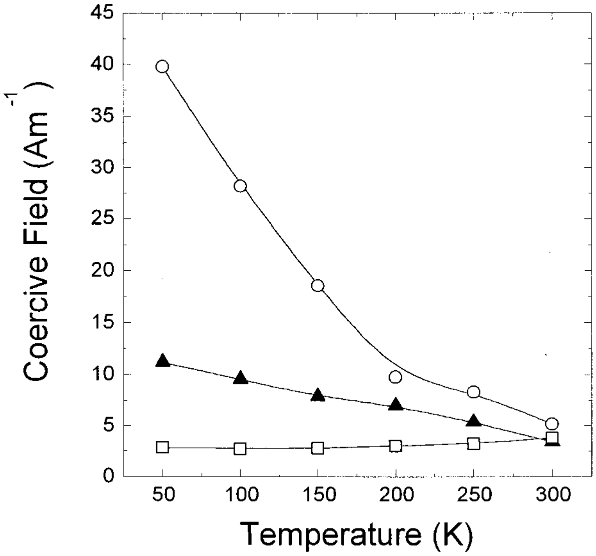

FIG. 1. Temperature dependence of the coercive field for the sample $\mathrm{Fe_{85}Zr_7B_6Cu_2}$ annealed at (○) 593 K, (▲) 633 K, and (□) 793 K.

Amorphous ribbons of composition $\mathrm{Fe_{85}Zr_7B_6Cu_2}$ were annealed under high vacuum. The thermal dependence of coercivity and remanence was measured in ribbon shaped samples at temperatures from 50 K up to room temperature by means of a Förster coercimeter and are shown, respectively, in Figs. 1 and 2. The crystalline fraction was estimated from magnetic measurements at 520 K in a vibrating sample magnetometer. This temperature was chosen because it is far above the Curie temperature of the amorphous matrix

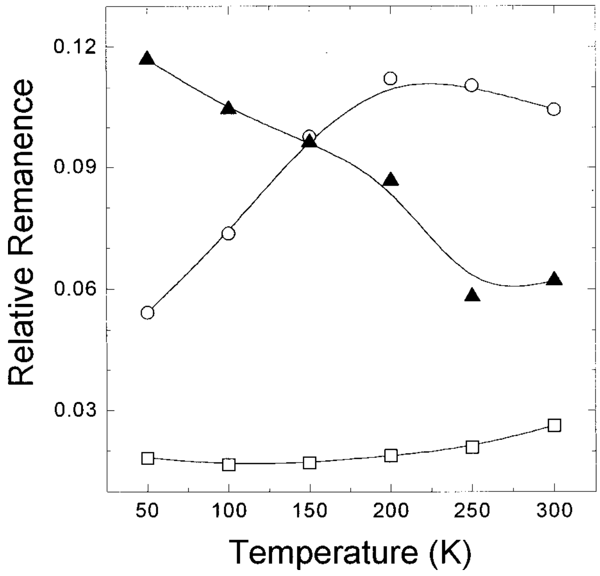

FIG. 2. Temperature dependence of the relative remanence for the sample $\mathrm{Fe_{85}Zr_7B_6Cu_2}$ annealed at (○) 593 K, (▲) 633 K, and (□) 793 K.

and well below the crystallization temperature and the Curie temperature of the crystalline phase. The average grain diameter was calculated from the x-ray diffraction patterns by means of the Schërrer formula.

In the samples annealed at 593 and 633 K the crystalline fraction is measured to be 4×10^{-4} and 5×10^{-3}, respectively. Therefore, considering that the average grain diameter is of the order of 20 nm, the distance between crystallites is calculated to be about 260 and 100 nm, respectively. These distances are of the same order as the typical domain wall thickness in amorphous materials. Therefore, these samples fulfill the conditions listed in (C) and the effect of crystallites is a pinning effect on the domain walls. The pinning increases as the domain wall thickness L_2^*, approaches D, then takes a maximum for $L_2^*=D$ and decreases due to the averaging effect of the exchange for further increases of L_2^*.[9] Therefore, the coercivity consists of two contributions. (i) The intrinsic contribution or that from the amorphous phase free of crystallites. This contribution is expected to decrease with temperature as a power of M_2 as indicated by Eq. (1a). (ii) A pinning contribution which is expected to either decrease with temperature for $L_2^*>D$ or increase for $L_2^*<D$. The experimental results shown in Fig. 1 indicate that the pinning effect is maximum for the sample annealed at 593 K ($L_2^*\approx D$ at 0 K). The fast decrease of coercivity with temperature corresponds to the decrease of pinning effect with the increase of L_2^*. In the sample annealed at 633 K, L_2^* is slightly larger than D,[12] the pinning effect is smaller, and the thermal dependence of coercivity is governed through the thermal dependence of the intrinsic coercivity. In the sample annealed at 793 K the crystalline fraction is 0.54, whereas, the average grain diameter is 21 nm. Thus, the average distance between grains is $D=5$ nm. Therefore, in this sample $L_2^*\gg D$, at 0 K, the coupling between grains is strong and the pinning effect is negligible. The thermal dependence of coercivity is due to a decrease of the coupling associated with the decrease of A_2, as is reinforced by the behavior of the reduced remanence shown in Fig. 2. The increase of L_2^* increases the remanence in the sample annealed at 593 K due to the enlargement of the coupling, just as it decreases the coercivity, whereas in the sample annealed at 633 K the thermal decrease of the remanence reflects the decrease of the spontaneous magnetization of the amorphous matrix M_2. The sample annealed at 793 K is in the structural optimum state from the soft magnetic point of view. As the sample is finite it is easily splitted in domains which reduces the remanence. The coupling between crystallites decreases with increasing temperature due to the descent of A_2 and, therefore, the remanence approaches the uncoupled value of $0.83M_1$ (as 0.83 is the theoretical reduced remanence of an assembly of randomly oriented cubic particles).

In summary, the parameters governing the effective anisotropy and coercivity of nanostructured soft-hard two phases systems have been indicated. The experimental thermal dependence of the coercivity can be explained through expression (4) proposed for the coupling. Moreover, the capability of expression (4) to account for the induction of coupling by increasing temperature has been experimentally tested.

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[10] Since A_2 decreases with temperature much slower than k_2 and providing that A_1 remains approximately constant in this temperature range, L_2^* will increase with temperature.

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[12] Notice that according to Eqs. (5) and (7) when $k_2(1-x)>k_1x$ as is the case for $x=10^{-3}$, the decrease of the anisotropy induced by the coupling between crystallites at $L_2^*>D$ is macroscopically negligible when compared to the pinning effects.