

## Thermal dependence of coercivity in soft magnetic nanocrystals

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An important group of soft magnetic nanocrystals is that formed by  $\alpha$ -Fe(Si) nanocrystals (around 10-nm grain size) embedded in a residual amorphous matrix. A simple phenomenological theory that takes into account the two-phase character based on the random anisotropy approximation has been developed. The percentage of crystallized material  $x$  is taken into account and a quantitative expression for the thermal dependence of coercivity, considering the two-phase character of the samples, has been obtained. The good fit between the experimental curves and the theoretical ones of nanocrystalline  $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Ta}_3$  samples with different crystallized volume fraction is discussed.  
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The two-phase system consisting of nanocrystallites randomly distributed in a soft magnetic amorphous phase is an important group of soft magnetic materials. Two limit cases can be considered within the random anisotropy model, (i) high anisotropy and weak exchange interactions. This is the case of rare-earth-based amorphous samples or rare-earth disordered alloys, for which the exchange gives rise to magnetic phases characterized by frozen moments in scattered directions (spermagnet). A noticeable effort has been recently done, mainly computational and numerical, in order to understand the magnetic properties of these types of compounds.<sup>1</sup> (ii) Low anisotropy compared with the exchange interactions. This is typically the case of three-dimensional (3D)-based amorphous alloys for which the effect of the random distribution of the easy axis orientation is a remarkable decrease of the average structural anisotropy.<sup>2</sup> As Herzer<sup>3</sup> has shown, the coercivity dependence on grain size for Fe-based nanocrystals, obtained by partial devitrification of melt spun amorphous alloys, has been found to behave as predicted by the approximation developed by Alben and co-workers<sup>4</sup> for the case of weak anisotropy. According to this approximation, there exists long-range ferromagnetic order with very low anisotropy as concerns the micromagnetic scale and, therefore, the fluctuations of the spontaneous magnetization within each domain can be roughly disregarded.<sup>3</sup> As has been shown,<sup>1</sup> the condition for an equilibrium ferromagnetic state in a random anisotropy system is the existence of a coherent anisotropy. In our case, the coherent component of the anisotropy  $K_c$  appears from the magnetoelastic energy associated with the macroscopic stresses frozen in during the rapid quenching of the liquid alloy. This coherent anisotropy is assumed to be much smaller than the crystalline anisotropy of the nanocrystals. This assumption seems to be quite reasonable after considering the low value of the magnetostriction,  $10^{-7}$ , achieved in the softer nanocrystalline state.<sup>3</sup> A typical value of the

residual stresses in the as-quenched state is 100 MPa, which relaxes towards a few MPa after structural relaxation and leads to magnetoelastic anisotropies between 1 and  $10 \text{ J m}^{-3}$ , much smaller than the crystalline anisotropy constant close to  $10^5 \text{ J m}^{-3}$ . Under these conditions the domain width remains larger than the wall thickness, as has been experimentally shown by domain observations.<sup>3</sup>

Yoshizawa and co-workers<sup>5</sup> revealed that the presence of small additions of Cu and Nb to some FeSiB-based alloys can allow the creation of a two-phase material by the devitrification of the conventional amorphous alloy. After crystallization, the sample consists of small (around 10-nm grain size) nanocrystals embedded in the residual amorphous matrix. Its outstanding magnetic softness has been explained by Herzer<sup>3</sup> as related to the ratio of the exchange correlation length (or domain-wall thickness)  $L$  to the orientation fluctuation length of randomly distributed local easy axes, which in this case is roughly the average crystallite size  $D$ . For  $L \gg D$ , the macroscopic structural anisotropy averages out and the domain wall can move without becoming pinned. For some particular compositions and for a critical crystallized volume fraction  $x$ , when the average magnetostriction vanishes the magnetoelastic contributions to the macroscopic anisotropy also become negligible.

Although it was pointed out that the relevant exchange interaction between the grains is determined mainly by the intergranular amorphous matrix,<sup>3</sup> the original model does not explicitly describe this circumstance. The model was later extended in order to take into account more accurately the two-phase character of the microstructure in terms of the volume fraction of the crystallites<sup>6</sup> and an approach in order to describe the exchange interaction between the crystallites via the amorphous matrix.<sup>3</sup> The objective of the present work is to discuss these previous approaches in order to formulate a theoretical description of the temperature variation of coercivity that is most sensitive to the intergranular exchange

coupling. These results will be used to analyze the experimental behavior of nanocrystalline  $\text{Fe}_{73.5}\text{Cu}_1\text{Ta}_3\text{B}_9\text{Si}_{13.5}$  samples with different crystallized volume fractions.

According to Herzer<sup>3</sup> and Alben and co-workers,<sup>4</sup> the average structural anisotropy  $\langle K \rangle$  relevant to the magnetization process is determined by the mean-square-root anisotropy fluctuation within the volume of the exchange length  $L_{\text{ex}}$ . For crystallites embedded with a volume fraction  $x$  into an amorphous matrix, the averaged anisotropy for grain sizes  $D$  smaller than  $L_{\text{ex}}$  finally reads

$$\langle K \rangle = \frac{xK_1}{N^{1/2}}, \quad (1)$$

where  $K_1$  is the local anisotropy constant of the crystallites and

$$N = x \left( \frac{L_{\text{ex}}}{D} \right)^3 \quad (2)$$

is the number of grains of size  $D$  within the volume of the exchange length that is self-consistently related to the averaged anisotropy by

$$L_{\text{ex}} = \left( \frac{\gamma A}{\langle K \rangle} \right)^{1/2}, \quad (3)$$

where  $A$  denotes the exchange stiffness constant of the crystallites. The parameter  $\gamma$  remains open within the scaling nature of the random anisotropy model. For a single phase system it depends on the crystal symmetry of the grains and is in the order of one (maximum  $\pi^{1/2}$ , if we consider  $L_{\text{ex}}$  to the Bloch wall thickness). It can be easily incorporated into an effective exchange stiffness constant

$$A_{\text{eff}} = \gamma A. \quad (4)$$

Accordingly, we have simply set  $\gamma=1$  as in previous works.<sup>3,7</sup> The combination of the above equations readily gives

$$\langle K \rangle = \frac{x^2 K_1^4 D^6}{A_{\text{eff}}^3}, \quad (5)$$

As already mentioned above, the model leaves open the precise numerical value to use for the effective exchange stiffness  $A_{\text{eff}}$  between the grains. For well coupled grains this deficiency is less significant when, e.g., describing the grain-size dependence. Yet for a two-phase system, in particular at elevated temperature, where  $A_{\text{eff}}$  is also determined by the magnetic nature of the intergranular phase, a more elaborate approach becomes inevitable, especially if we attack the temperature dependence of coercivity. Herzer already pointed out in his original approach<sup>3</sup> that at elevated temperatures,  $A_{\text{eff}}$  is rather determined by the exchange constant of the amorphous matrix (being the weakest link in the chain) than that of the bcc crystallites; i.e.,<sup>3</sup>

$$A_{\text{eff}} \propto M_{\text{am}}^2 \propto \left( 1 - \frac{T}{T_c^{\text{am}}} \right)^{2\beta}, \quad (6)$$

where  $\beta$  is the Heisenberg exponent and  $M_{\text{am}}$  and  $T_c^{\text{am}}$  denote the saturation magnetization and the Curie temperature of the

amorphous matrix. In this way he was able to explain the increase of coercivity when approaching the Curie temperature of the amorphous matrix. Yet this model equates the exchange constant of the residual matrix with that of an isolated system and is not able to describe the experimental data above the Curie temperature of the residual matrix.

In fact, the coupling between the grains depends on the magnetization and exchange correlation length of the intergranular region as recently analyzed by Hernando and co-workers.<sup>8</sup> For a system of coupled grains the thermal dependence of  $A_{\text{eff}}$  is governed by the thermal dependence of the square of the spontaneous magnetization of the intergranular region. When the sample is full crystallized,  $x=1$ ,  $A_{\text{eff}}$  coincides with  $A$ , however for  $x<1$ ,  $A_{\text{eff}}$  should range between  $A$  and  $A_{\text{am}}$ . Notice that if the system is coupled at low temperature it is because the exchange correlation length of the intergranular region  $L_{\text{am}}$  is larger than the intergranular distance. As  $L_{\text{am}}$  increases with temperature it remains larger than the intergranular distance for increasing temperatures. Therefore, the way in which the coupling can decrease with increasing temperature is restricted to the decrease of the saturation magnetization of the intergranular regions. The saturation magnetization of the intergranular region  $M_{\text{am}}$  and then the effective exchange constant  $A_{\text{eff}}(x)$  are assumed to decrease with temperature as indicated by Eq. (6), and depend on the crystallized fraction through both compositional dependence and influence of the grain's magnetization.  $T_c^{\text{am}}(x)$  ranges from  $T_c^{\text{am}}$  for  $x=0$  to  $T_c^{\text{cryst}}$  for  $x=1$ , where  $T_c^{\text{cryst}}$  holds for the Curie temperature of the crystallites.

The importance of this case is related to the fact that a nanocrystalline single phase system ( $x=1$ ) that is coupled at low temperature,  $L_{\text{ex}}>D$ , is also coupled at any higher temperature. This behavior is a consequence of the thermal dependence of  $L_{\text{ex}}$  which, as indicated by Eq. (3), always increases as  $T$  increases. Notice that  $\gamma A$  varies as  $A$  and therefore as  $(M_s^{\text{cryst}})^2$ . In this case,  $L$  increases with temperature as  $M_s^{(1-0.5n)}$ , where  $K_1$  is assumed to change as  $M_s^n$  with  $n=4$ , which is an exponent intermediate between those corresponding to uniaxial,  $n=3$ , and cubic,  $n=10$ , anisotropies. Notice that the differences between the thermal dependencies associated with these exponents is not remarkable and the value  $n=4$  can be considered as a good one to describe the general behavior.

In the general case the coercivity can be given for either magnetization rotation or wall motion by

$$H_c = p_c \left( \frac{\langle K \rangle + K_c}{\mu_0 M_s} \right) \left( 1 - \sqrt{\frac{25k_B T}{\langle K \rangle V}} \right), \quad (7)$$

where  $p_c$  is a dimensionless factor close to unity and  $V$  is the volume of the crystallites supposed to be single domain particles. The second factor takes into account the absence of coercivity in the superparamagnetic regime, and is only important in the case of fully uncoupled grains.

Considering the particular average value given by Eq. (5) corresponding to the case where the nanocrystallite size  $D$  is smaller than the structural correlation length and the nanocrystals are fully coupled between them, the coercivity becomes

$$H_c = p_c \frac{x^2 K_1^4 D^6}{\mu_0 M_s A_{\text{eff}}^3} + p_c \frac{K_c}{\mu_0 M_s}. \quad (8)$$

No superparamagnetic term should be taken into account because the effective ‘‘grain’’ volume is now all the sample volume. The thermal dependence of the second term in Eq. (8), associated with the coherent anisotropy, corresponds to the normal decrease of coercivity observed in soft amorphous materials, which is roughly determined through the thermal dependence of the magnetostriction constant divided by the magnetization. The interesting and anomalous thermal dependencies of coercivity are due to the modifications of the degree of exchange coupling between the grains, related to the first term in Eq. (8) for which the following discussion should be restricted.

Accordingly, and taking only into consideration the term in Eq. (8) associated with the average structural anisotropy, the coercive field should depend on temperature as

$$H_c(T) \propto M_s(T)^{4n-7} D^6. \quad (9a)$$

Then, in a coupled single phase system with random anisotropy, a decrease of coercivity with increasing temperature should be expected.

On the other hand, if the grain size is larger than the exchange correlation length ( $D > L_{\text{ex}}$ ), the effective anisotropy  $\langle K \rangle$  is given by the magnetocrystalline anisotropy of the grains  $K_1$ , which changes with temperature as  $M_s^n$ . Now through Eq. (7), the coercivity is expected to decrease with temperature as  $M_s(T)^{n-1}$ , if the superparamagnetic term is not important. In the general case we have

$$H_c(T) \propto M_s(T)^{n-1} \left( 1 - \sqrt{\frac{25k_B T}{K_1(0) M_s^n D^3}} \right) \quad (9b)$$

or

$$H_c(T) \propto M_s(T)^{n-1} \left( 1 - \sqrt{\frac{C(T/T_c)}{M_s^n}} \right), \quad (9c)$$

with  $C = 25k_B T_c / \langle K_1(0) \rangle D^3$  and where the volume of the crystallites has been taken as  $D^3$  and  $K_1(0)$  is the magnetocrystalline anisotropy constant at 0 K. Figure 1 shows the expected behavior, displaying the effect of superparamagnetism on the coercivity. The curves correspond to the values 0, 0.1, and 0.2 for  $C$ .

Since a coupled system remains coupled at any higher temperature, it is not possible to transit from the low to the high coercivity branches shown in Fig. 1. Herzl,<sup>6</sup> Shafer and co-workers,<sup>9</sup> Hernando and Kulik,<sup>10</sup> Slawska-Wanieska *et al.*,<sup>11</sup> Grossinger *et al.*,<sup>12</sup> González *et al.*,<sup>13</sup> and Suzuki *et al.*,<sup>14</sup> have reported the coercivity and its thermal dependence for nanocrystalline samples obtained by annealing Fe-Si-B-Cu-Ta, Fe-Zr, and Finement<sup>2</sup> amorphous alloys and they found an anomalous thermal dependence characterized by a rapid increase of coercivity with temperature in a certain temperature range. In particular, Hernando and Kulik<sup>10</sup> and Slawska-Wanieska *et al.*<sup>11</sup> have observed that for any particular  $x$  and  $D$  values, which depend on the annealing conditions, the coercive field shows an abrupt maximum. The maximum occurs at a temperature  $T_p$ , which is close to the Curie temperature of the amorphous matrix  $T_{\text{am}}$  for those

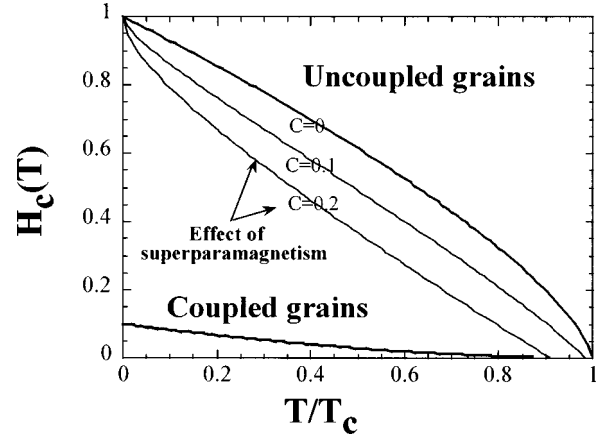


FIG. 1. Simulation of the thermal dependence of the coercivity, reduced to the value of the uncoupled grains at 0 K as described by the first term of Eq. (7), in a nanocrystalline system with uniaxial anisotropy ( $n=3$ ). The superparamagnetic behavior reduces the coercivity at all temperatures and causes it to vanish above the blocking temperature. The value of  $C$  is explained in the text. Coupling between the grains drastically reduces the coercivity that displays a different thermal behavior.

values of  $x$  that correspond to an intercrystallite spacing  $d > 5$  nm, according to Eq. (6). Nevertheless, when  $x$  increases the corresponding distance between the surfaces of neighboring crystallites verifies  $d < 5$  nm and the maximum of coercivity is observed at temperatures well above  $T_{\text{am}}$ , i.e.,  $T_p = T_{\text{am}} + 100$  °C. This behavior points out the role played by the amorphous matrix as exchange transmitter and should be understood in the framework of the two-phase theory.

In this case the initially coupled system at low temperature ( $L_{\text{ex}} < D$ ) crosses over to an uncoupled regime at the temperature for which  $L_{\text{ex}} = D$ . The decrease of  $L_{\text{ex}}$  with increasing temperature, assuming that the Curie temperature of the amorphous is below the Curie temperature of the crystallites is, through Eq. (3), given by

$$L_{\text{ex}}(T) \propto \frac{M_s^{\text{am}}}{M_s^{0.5n}} \quad (10)$$

The temperature of decoupling,  $T_t$  [obtained considering  $L_{\text{ex}}(T) = D$ ], is closely related to the Curie temperature of the intergranular region and verifies from Eqs. (3) and (6):

$$\left( 1 - \frac{T_t}{T_c^{\text{am}}} \right) = D \left( 1 - \frac{T_t}{T_c^{\text{cryst}}} \right)^{0.5n}. \quad (11)$$

It is true that the evolution of the magnetization of the amorphous phase, under the influence of the crystalline grains, is very different than that of the ideal Heisenberg ferromagnet given by Eq. (6), but we can leave this point aside for the moment.

The coupling through the amorphous matrix lowers the coercive field well below the independent particle’s approximation at low temperatures

$$H_{c1} = p_c \frac{x^2 K_1^4 D^6}{\mu_0 M_s A(x)_{\text{eff}}^3}, \quad (12)$$

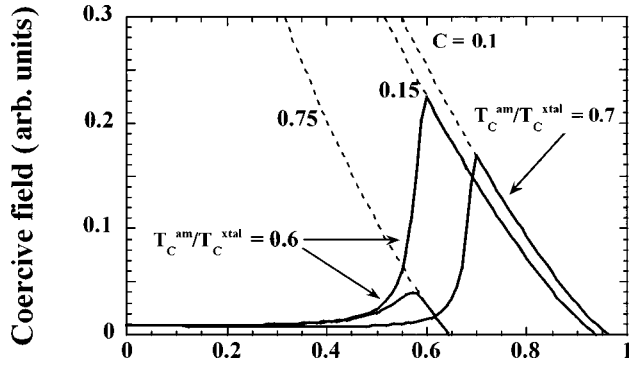


FIG. 2. Simulation of the coercivity of nanocrystalline materials with different amounts of nanocrystals and hence different Curie temperatures of the amorphous matrix. The magnetization of the grains has been assumed to vary as  $(M_s^{\text{cryst}})^4$ . The dashed curves represent the uncoupled values of  $H_c$  for different blocking temperatures.

but can grow larger than the latter near the Curie temperature of the amorphous phase.

In this case, the independent model value  $H_{c2}$  [Eq. 9(b)]

$$H_{c2} = p_c \left( \frac{K_1}{\mu_0 M_s} \right) \left( 1 - \sqrt{\frac{CT}{T_c M_s}} \right) \quad (13)$$

is an upper limit that will never be surpassed. In this case, Eq. (13) contains, instead of  $K_1$ , the stray field energy  $M_s^2/\mu_0$ , giving  $C = K_B \mu_0 T_c / M_s^2 D^3$ , which couples the grains above  $T_c^{\text{am}}$  and which is much larger than  $K_1$ .<sup>4</sup> This expression was calculated by Herzer<sup>3</sup> assuming the system behaves superferro-paramagnetic above  $T_c^{\text{am}}$  and the interactions are of dipolar type. Moreover, when both mechanisms of magnetization reversal are of similar magnitude, we can consider that they can take place independently, so that the actual coercive field  $H_c$  is given by

$$H_c = \frac{1}{(H_{c1}^{-1} + H_{c2}^{-1})} = \frac{H_{c1} H_{c2}}{H_{c1} + H_{c2}}. \quad (14)$$

In this way we have calculated the behavior of the coercivity of a nanocrystalline material with different blocking temperatures and different ratios between the Curie temperatures of the amorphous to crystalline phases, namely, 0.5 and 0.6, which are typical values of the nanocrystalline compositions reported in the literature.<sup>9-13</sup> This change in  $T_c^{\text{am}}$  is assumed to be due to the influence of the increasing number of crystallites on the amorphous matrix, i.e., increase of  $x$ . The

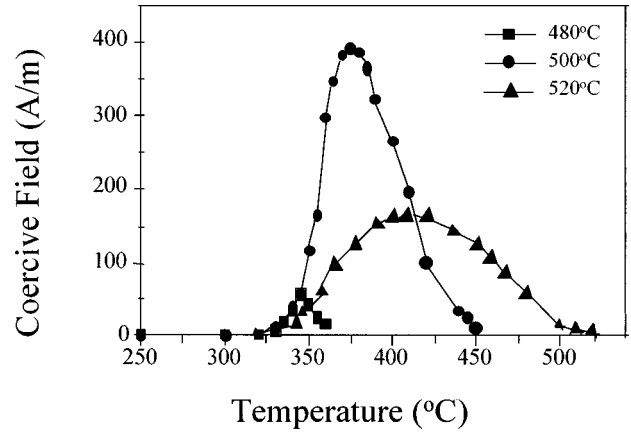


FIG. 3. Temperature dependence of the coercive field  $H_c$  for the  $\text{Fe}_{73.5}\text{Cu}_1\text{Ta}_3\text{Si}_{13.5}\text{B}_9$  1 h annealed samples at different temperatures.

anisotropy constant  $K_1$  in the coupled state (Eq. 12) is assumed to be of the uniaxial type, and to vary as  $(M_s^{\text{cryst}})^3$ , whereas in the uncoupled state (Eq. 13) the isolated grains are assumed to vary as  $(M_s^{\text{cryst}})^4$ . The magnetization dependence on temperature was assumed to be of the form  $(1 - T/T_c)^\beta$  with  $\beta = 0.36$  for both the amorphous and crystalline phases.

The results are displayed in Fig. 2 and the overall agreement with the experimental data of Fig. 3 is evident. However some comments are still needed. The broad maximum of  $H_c$  appearing in the sample treated at 520 °C is due to a broad distribution of Curie temperatures in the amorphous phase and cannot be taken into account properly by the oversimplified model we are using. The shift to high temperatures of the fall of  $H_c$  is mainly due to a change in the blocking temperature for superparamagnetic behavior.

This change can arise not only because of some grain growth in samples treated at higher temperature, but also as a consequence of the intergranular interaction, dipolar or other, which also increases as the nanocrystallization proceeds. That makes fully single domain particles. The simulation points out that the curves that differ only in the decay of  $H_{c1}$ , but follow the same trend in the increase (as those corresponding to the annealing at 480 and 500 °C), differ in the blocking temperature for superparamagnetic behavior. On the other hand, the curves that separate from the beginning of the increase of  $H_c$  (as those corresponding to the annealing at 500 and 520 °C) reveal a change in the Curie temperature of the amorphous matrix, as a consequence of the polarization produced by the crystallites.

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