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Coercivity extrema in melt-spun CuCo ribbons: Effects of the magnetic moment distribution

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Measurements of magnetization loops on melt-spun CuCo ribbons revealed a minimum in the temperature dependence of the coercivity. A coherent interpretation was given through Monte Carlo simulations of a dispersed system of noninteracting, uniaxial magnetic granules embedded in a nonmagnetic matrix. The coercivity is implicitly defined by the balance between the negative magnetization of superparamagnetic granules and the remaining magnetization of blocked granules after saturation in the positive field direction. When the temperature rises in a system made of a large amount of small granules and a small amount of big granules, unblocking predominates over thermal fluctuations and the coercivity decreases until a certain temperature at which most of the small granules are superparamagnetic; above this temperature, thermal fluctuations predominate, and the coercivity increases almost linearly with the temperature until the final unblocking of the big granules. © *1999 American Institute of Physics.* [S0021-8979(99)04618-6]

I. INTRODUCTION

Magnetic granular alloys consist of an assembly of ferromagnetic granules dispersed in a nonmagnetic matrix. At high temperatures, the granules are superparamagnetic and the magnetization loop displays no hysteresis. On lowering the temperature, the granules become blocked at certain temperatures which depend on their moment and anisotropy field and on the time scale of the experiment. As a consequence, the superparamagnetism disappears and the magnetization loop displays a remanence and a coercivity which are very sensitive to the actual distribution of magnetic moments.[1] Since the blocking temperatures are higher for bigger granules, the distribution of magnetic moments greatly affect the magnetic and transport properties of granular alloys.[2–4]

This study focuses on the hysteretic behavior of tiny precipitates of Co embedded in a matrix of Cu. The magnetization loop of a melt-spun CuCo ribbon was measured at various temperatures after a heat treatment. As usually observed, the remanence decreases when the temperature rises. Surprisingly, however, the coercivity drops to a minimum and then increases almost linearly with the temperature, approaching a presumed maximum.

The maximum in the thermal dependence of the coercivity has previously been observed on crystalline samples obtained by annealing Fe–Si–B–Cu–Ta[5] and Fe–Zr[6] amorphous alloys. However, a different mechanism drives the behavior of these ferromagnetic materials. According to Hernando *et al.*,[7] the coercivity increases with the temperature due to the ferromagnetic–paramagnetic transition of the remaining amorphous matrix and the consequent enhancement of the effective anisotropy field. Once the nanocrystallites become exchange isolated, they behave as single-domain granules and the coercivity decreases.

Although it is tempting to interpret the coercivity behavior of CuCo as a consequence of correlations among the magnetic moments, the matrix of Cu is not ferromagnetic. Accordingly, a simpler interpretation is proposed by taking into account a so-called bimodal distribution of independent magnetic moments. Transmission electron microscopy images of melt-spun CuCo ribbons have often revealed a polycrystalline microstructure with a Cu grain size of the order of 1 μm possessing such a bimodal distribution of sizes of Co precipitates,[8–10] i.e., a large amount of small Co precipitates of an average size of about 2 nm that are dispersed within the Cu grains and a small amount of big Co precipitates of an average size of 30 nm that have grown at the Cu grain boundaries. The balance between the negative magnetization of the small and superparamagnetic Co precipitates and the remaining magnetization of the big and blocked Co precipitates is suggested as the cause of the observed temperature dependence of the coercivity and of its connection with the remanence.

II. EXPERIMENT

A melt-spun $Cu_{90}Co_{10}$ ribbon, obtained by planar flow casting in He atmosphere on a CuZr wheel, was annealed at 500 °C for 60 min in order to produce big Co rich precipitates. The magnetization loop measurements were carried out on a SQUID with a field range of ± 50 kOe at various temperatures between 4.6 and 244 K. The temperature dependencies of the coercivity H_c and the remanence M_r are

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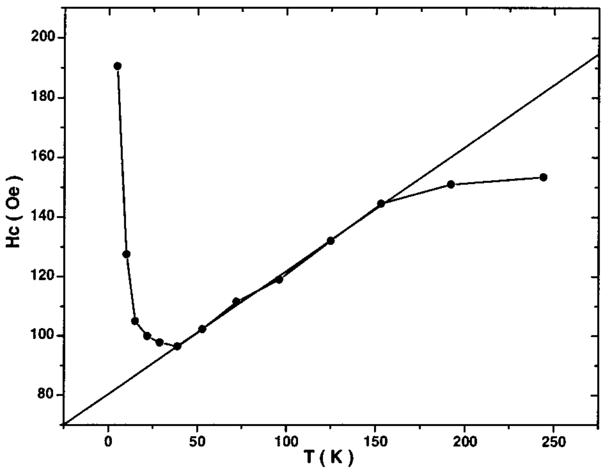

FIG. 1. Temperature dependence of the coercivity for $Cu_{90}Co_{10}$ annealed at 500 °C for 60 min. Note the linear behavior after the minimum.

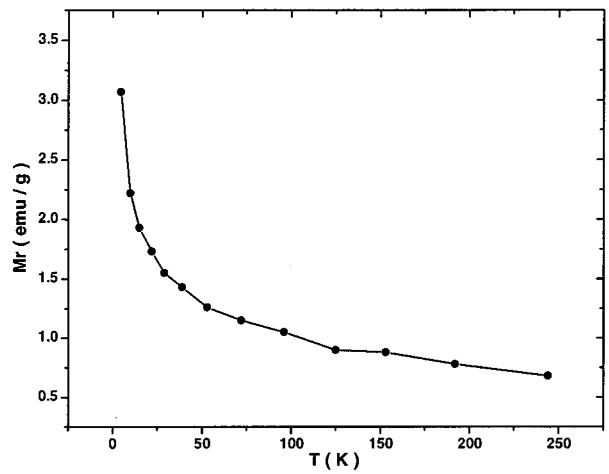

FIG. 2. Temperature dependence of the remanence for $Cu_{90}Co_{10}$ annealed at 500 °C for 60 min. The low temperature saturation magnetization is $M_s = 14.2$ emu/g.

shown in Figs. 1 and 2, respectively. Both the coercivity and the remanence steeply decrease when the temperature rises until 40 K. Above this temperature, the remanence still decreases but at a much slower rate, whereas the coercivity increases almost linearly with the temperature, approaching a presumed maximum beyond 244 K. Their thermal behavior will be explained in terms of a bimodal distribution of magnetic moments through Monte Carlo simulations and a balance model of the coercivity.

III. MONTE CARLO SIMULATIONS

Monte Carlo algorithms are commonly used for simulating the dynamics of magnetic granular alloys.[11–14] The simplest model describes a system of noninteracting, uniaxial magnetic granules of volume V embedded in a nonmagnetic matrix, assuming that the magnetization I_s within the granules is homogeneous, stable, and rotates coherently. The free energy of a granule with magnetic moment μ $(=I_s \times V)$ is

$$E = \frac{1}{2} H_a \mu \sin^2(\psi) - H\mu \cos(\theta), \tag{1}$$

in which H_a is the uniaxial anisotropy field, ψ is the angle between the magnetic moment and the easy axis, H is the applied field, and θ is the angle between the magnetic moment and the applied field. It can be shown that the minimum energy is attained when the magnetic moment lies in the plane determined by the easy axis and the applied field. The absolute minimum E_a, the relative minimum E_r, and the saddle-point E_s are calculated using the Newton–Raphson technique. The transition probabilities for rotating from one minimum to the other are[15]

$$p_{a\rightarrow r} = \exp[-(E_s - E_a)/kT], \tag{2}$$

$$p_{r\rightarrow a} = \exp[-(E_s - E_r)/kT]. \tag{3}$$

According to the usual criterion,[1] the change from the superparamagnetic to the stable behavior of the magnetic granule occurs when the energy barrier $E_s - E_r$ becomes equal to $25kT$, in which case T is called the blocking temperature of the moment μ. The probabilities of localizing the magnetic moment around the energy minima are obtained from the principle of detailed balance

$$p_a \times p_{a\rightarrow r} = p_r \times p_{r\rightarrow a}. \tag{4}$$

Since $p_a + p_r = 1$, they are given by

$$p_a = \frac{1}{1 + \exp[(E_a - E_r)/kT]}, \tag{5}$$

$$p_r = \frac{1}{1 + \exp[(E_r - E_a)/kT]}. \tag{6}$$

Thermal averages are calculated using the Metropolis *et al.* algorithm.[16,17] In the superparamagnetic regime, the moment orientation is changed at random and the energy difference ΔE is calculated. If $\Delta E \leqslant 0$, the transition to the new orientation is accepted. If $\Delta E > 0$, a random number W is generated and the transition is accepted if $W < \exp(-\Delta E/kT)$. Otherwise, the old orientation is accepted. After a number of relaxation steps, thermal averages are calculated as arithmetic averages over the accepted configurations. In the blocked regime, transitions cannot occur over the energy barrier and the moment moves are solely allowed around the two minima. Hence, thermal averages are calculated as arithmetic averages weighted by the probabilities p_a and p_r.

The magnetization of a dispersed system with f_i granules of moment μ_i per unit volume is the average

$$M(H,T) = \sum_i f_i \mu_i m_i(H,T), \tag{7}$$

in which $m_i(H,T)$ is the thermal average of $\cos(\theta)$ calculated for a system of granules with moment μ_i.

Figure 3 shows the reduced magnetization loops calculated at different temperatures for an assembly of 1000 granules with moment $\mu = 25\,000\ \mu_B$ and anisotropy field $H_a = 3000$ Oe. The loop at $T = 0.01$ K practically coincides with

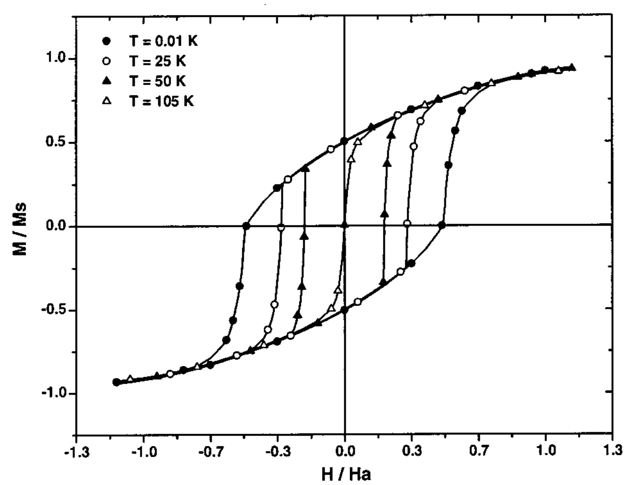

FIG. 3. Calculated magnetization loops at various temperatures for a system of granules with $\mu = 25\,000\ \mu_B$ and $H_a = 3000$ Oe.

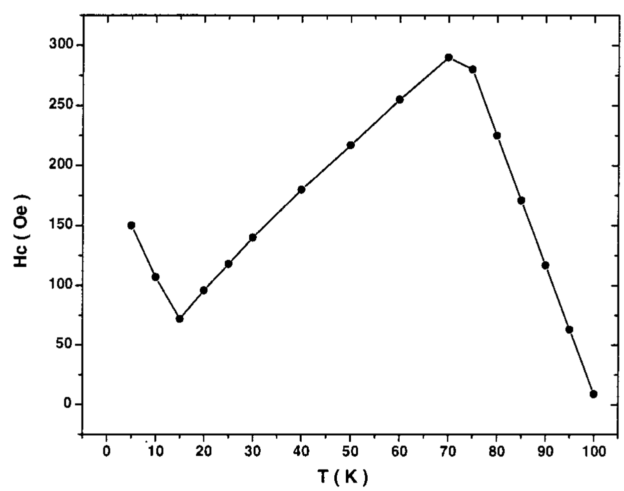

FIG. 5. Calculated coercivity as a function of the temperature for a dispersed system.

the nonthermal loop of the Stoner–Wohlfarth model for which the remanence is $m_r = 0.5$ and the coercivity is $H_c = 0.479 H_a = 1437$ Oe.[18] The temperature dependence of the coercivity is represented in Fig. 4. The equation

$$H_c(T) = 0.479 H_a \left[1 - \left(\frac{50kT}{H_a \mu} \right)^{0.76} \right] \quad (8)$$

fits very well the coercivities in the simulated curves for the whole range of temperatures. The same equation is valid for all the tested values of the magnetic moment between 5000 and 65 000 μ_B. The exponent of 0.76 for the decrease in the coercivity with the temperature is between the values of 3/4 and 0.77 calculated, respectively, by Garcia-Otero *et al.*[19] and Pfeiffer.[20] Starting from the result by Pfeiffer, Chen *et al.*[21] obtained a much larger exponent of 1.155 when the anisotropy field is due to the uniaxial *surface* anisotropy.

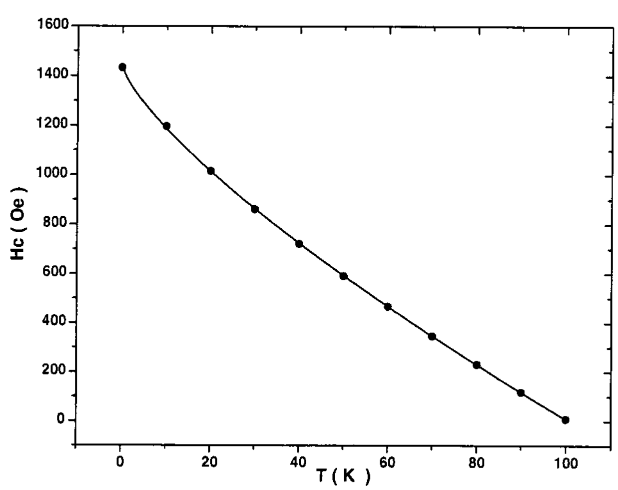

FIG. 4. Calculated coercivity as a function of the temperature for a system of granules with $\mu = 25\,000\ \mu_B$ and $H_a = 3000$ Oe.

The distribution of magnetic moments can very noticeably change the temperature dependence of the coercivity. For example, Fig. 5 shows the $H_c(T)$ curve for a dispersed system of granules with moments of 750, 1500, 3000, and 25 000 μ_B corresponding, respectively, to 55%, 15%, 10%, and 20% of the saturation magnetization. Initially, the coercivity decreases when the temperature rises, because a large amount of small granules are gradually unblocked; then, the coercivity increases almost linearly with the temperature due to the larger thermal fluctuations of the superparamagnetic moments; finally, the coercivity vanishes, because the big granules are also unblocked. When the remanence due to the blocked granules is a small fraction of the saturation magnetization as in this example, the coercive field is much smaller than the coercivity of blocked granules alone (compare Figs. 4 and 5).

IV. BALANCE MODEL OF COERCIVITY

The Monte Carlo simulations accurately reproduce the dependence of the coercivity on the temperature as predicted in the Néel relaxation model for a system of granules with the same magnetic moment.[19,20] For a dispersed system, however, the thermal behavior of the coercivity is very sensitive to the actual distribution of magnetic moments. In general, $H_c(T)$ is implicitly defined by the balance between the negative magnetization of superparamagnetic granules and the remaining magnetization of blocked granules after saturation in the positive field direction as

$$M(-H_c, T) = M_{spm}(-H_c, T) + M_b(-H_c, T) = 0. \quad (9)$$

When the temperature rises, two factors change this balance in opposite ways: (1) the additional unblocking increases M_{spm} and reduces M_b, whereas (2) the enlarged thermal fluctuations reduce M_{spm} much more than M_b. The first effect is compensated for by reducing the magnetic field and the second, by increasing it.

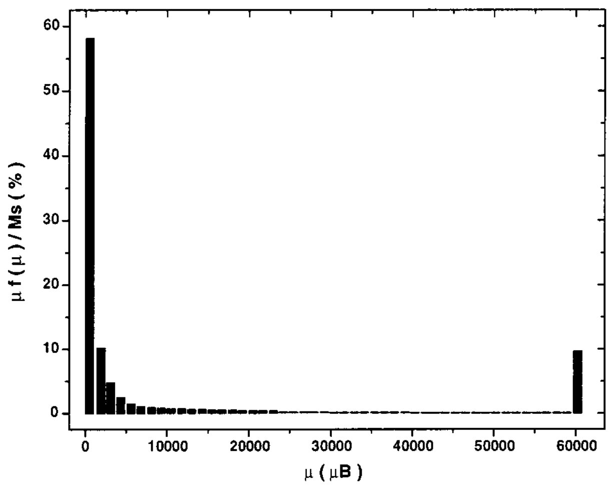

FIG. 6. Distribution function of magnetic moments as a fraction of the saturation magnetization for $Cu_{90}Co_{10}$ annealed at 500 °C for 60 min. Percentages are accumulated below 1000 μ_B and above 60 000 μ_B.

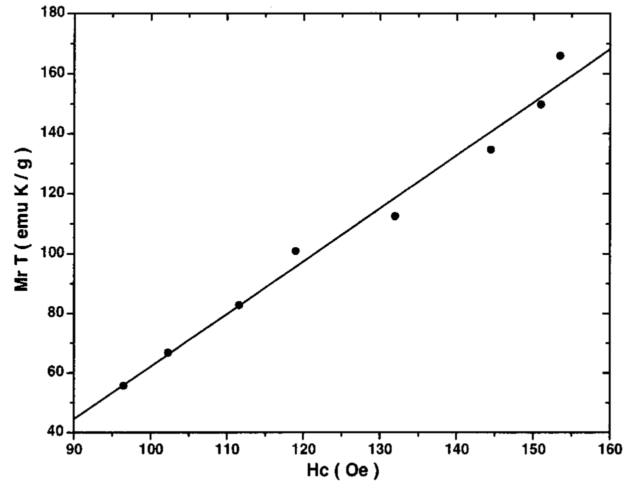

FIG. 7. Linear relationship between H_c and M_rT in the temperature range above the H_c minimum for $Cu_{90}Co_{10}$ annealed at 500 °C for 60 min.

So a coherent interpretation of the experimental results can be obtained in terms of the distribution of magnetic moments. Using a well known method recently renewed by Peleg *et al.*,[22] the remanence $M_r(T)$ is expressed as an integral of the distribution function of blocked moments at the temperature T approximately in the form[23]

$$M_r(T)=\frac{1}{2}\int_{50kT/H_a}^{\infty}\mu f(\mu)d\mu. \tag{10}$$

Consequently, the distribution function $f(\mu)$ is given by the temperature derivative of the remanence as

$$f(\mu)=-\frac{H_a}{25k\mu}\frac{dM_r}{dT}\quad\left(\mu=\frac{50kT}{H_a}\right). \tag{11}$$

Figure 6 shows the distribution function obtained from the experimental remanence curve (Fig. 2) as a fraction of the saturation magnetization $M_s=14.2$ emu/g. The granular structure consists of a large amount of small granules and a small amount of big granules, as often observed by transmission electron microscopy on melt-spun CuCo alloys.[8–10] In fact, expressing the accumulated magnetic moment distribution function $\int_0^{\mu}\mu f(\mu)d\mu$ as a percentage of M_s, it follows that 80% of the saturation magnetization is due to granules with a moment smaller than 10 000 μ_B, 10% is due to granules with a moment between 10 000 and 60 000 μ_B, and another 10% is due to granules with a moment larger than 60 000 μ_B. Evidently, this is the granular structure that could be expected from the behavior of the experimental coercivity curve (Fig. 1). Unblocking predominates over thermal fluctuations until a temperature of 40 K—exactly the blocking temperature of a moment of 10 000 μ_B—and the coercivity decreases; above this temperature, thermal fluctuations predominate and the coercivity increases. The final decrease of the coercivity is not observed, because the big granules remain stable even above 240 K—the blocking temperature of a moment of 60 000 μ_B.

A simple relationship between the remanence and coercivity can be obtained under very restrictive assumptions. When the anisotropy energy of the superparamagnetic granules is negligible compared with their thermal energy and, on the contrary, the thermal energy of the blocked granules is negligible compared with their anisotropy energy, the magnetization of superparamagnetic granules is given by

$$M_{spm}(H,T)=\int_0^{50kT/H_a}\mu\mathcal{L}\left(\frac{\mu H}{kT}\right)f(\mu)d\mu, \tag{12}$$

in which $\mathcal{L}(\mu H/kT)$ is the Langevin function, and the magnetization of blocked granules is approximately equal to the remanence:

$$M_b(H,T)\approx M_r(T)\quad(|H|\ll 0.479H_a). \tag{13}$$

Substituting Eqs. (12) and (13) in the balance Eq. (9), it takes the form

$$\int_0^{50kT/H_a}\mu\mathcal{L}\left(-\frac{\mu H_c}{kT}\right)f(\mu)d\mu+M_r(T)=0. \tag{14}$$

When the temperature is between the blocking temperatures of the small and big granules, the remanence $M_r(T)$ is almost constant and the temperature dependence of the upper limit of integration has little importance. Therefore, there is an approximate linear relationship between H_c and T, because the Langevin function depends only on the ratio H_c/T.

For small moments, $\mu H_c\ll kT$ and, therefore, $\mathcal{L}(-\mu H_c/kT)\approx-\mu H_c/3kT$. After simple algebraic manipulations, Eq. (14) can be written as

$$m_r\equiv\frac{M_r}{M_s}=\frac{H_c\overline{\mu}}{3kT}, \tag{15}$$

in which $\overline{\mu}$ is an average moment given by the ratio between the superparamagnetic averages of μ^2 and μ, $\overline{\mu}=\langle\mu^2\rangle_{spm}/\langle\mu\rangle_{spm}$.

Figure 7 shows a linear relationship between the experimental data of H_c and M_rT after the H_c minimum. The average moment takes a value of $\bar{\mu}=5550\ \mu_B$ which corresponds to a blocking temperature of 22 K and, therefore, is superparamagnetic in the range of temperatures above the H_c minimum. Allia *et al.*[24] derived a similar relationship from a mean-field model relating the hysteresis to the effect of long-range interactions among the magnetic granules. As shown in their Figs. 1 and 3, the linear Eq. (15) fits very well the experimental results on melt-spun CuCo ribbons. It is clear, however, that the existence of a distribution of independent magnetic moments like that shown in Fig. 6 is sufficient for the validity of the assumptions under which Eq. (15) was obtained.

V. CONCLUSIONS

The thermal behavior of the coercivity and remanence of melt-spun CuCo ribbons was explained through Monte Carlo simulations and a model of balance between the magnetizations of superparamagnetic and blocked granules of Co. When the temperature rises, the remanence initially decreases steeply due to the unblocking of a large fraction of small granules; then above a certain temperature T_m at which most of the small granules are superparamagnetic, the remanence gradually decreases as the unblocking of a much smaller fraction of larger and larger granules proceeds. This behavior characterizes a bimodal distribution of sizes. The coercivity also steeply decreases when the temperature rises until T_m, because initially the unblocking predominates over the thermal fluctuations of superparamagnetic moments; above T_m, the coercivity increases almost linearly with the temperature, because now the thermal fluctuations predominate over the unblocking. The expected maximum was not observed in the temperature range of the measurements, which indicates the presence of very large granules and brings additional support to the proposed interpretation in terms of a bimodal distribution of sizes. These results establish that the moment distribution must be taken into account in any in-depth analysis of magnetic granular alloys.

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