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Anomalous low temperature stair like coercivity decrease due to magnetostatic coupling between superconducting and ferromagnetic particles in mixed powders

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Magnetization curves of mixed Nb and FeSi based micrometric particles have been analyzed. The influence of the dispersion of Nb particles on the mixture remanence and coercivity has been studied above and below the Nb superconducting critical temperature. The hysteresis loop shows, at 5 K and low applied fields, a decrease of both remanence and coercivity with respect to the one of pure ferromagnetic powders as well as a stair like profile. These features are explained as a consequence of the diamagnetic hysteresis loop of Nb giving rise to local stray fields acting on the ferromagnetic particles at its nearest neighboring. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4733558]

I. INTRODUCTION

Ferromagnetic powders with adjustable shape and size can be utilized for different applications, e.g., flux enhancement at high frequencies. However, decreasing the sample dimensions leads to an intrinsic magnetic hardening[1] that can be ascribed to (i) a random anisotropy effect, (ii) the introduction of stresses and defects associated with the usual preparation procedure, and (iii) the unavoidable influence of the inter-particle magnetostatic interactions,[2] that play an important role in patterned structures for magnetic recording media influencing the switching field distribution and limiting the device density.[3]

With respect to soft ferromagnetic materials, it was observed that outstanding soft material[4–6] was obtained by Fe_3Si nanocrystals dispersed in an amorphous phase obtained by the partial devitrification of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy, which yielded coercivities as low as a few mOe. However, the same alloy when prepared as powders exhibits coercivities of 160 Oe after 60 h ball milling.[7]

A possible way of controlling the magnetization curve is by mixing powders with different properties such as ferromagnetic-antiferromagnetic[8] or soft-hard ferromagnetic particles.[2] The hysteresis behaviour of multiphase nano or micro-structured systems depends first on the morphology and intrinsic properties of each one of the phases, but, in addition, depends crucially on the magnitude and characteristics of the exchange[4,6] and magnetostatic interactions.[2]

Here we report the magnetic response of a mixture of a 75% mass (by weight) ferromagnetic $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, (FeSi) powder, obtained by atomization, with 25% mass Nb powder; the latter is a type II superconductor at temperatures below 9 K (T_c). Since the magnetic behaviour of the Nb particles drastically changes on increasing temperature above T_c, the magnetostatic interactions also must be modified and consequently their influence on magnetization curve can be probed through changes of the hysteresis loop below and above T_c. A noticeable reduction of the remanence and coercivity as well as a stair-like shape of the hysteresis loop is observed for temperatures below T_c, whereas the influence is almost negligible above this temperature. The results are discussed in terms of the magnetostatic interactions between both phases by using stray field fluctuations considerations.

II. EXPERIMENT

$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (atomic percent) starting material was atomized in a confined nozzle atomizer[9] where the liquid melt solidifies rapidly at high cooling rate (10^3–10^5 K s^{-1}). The resulting powder was allowed to cool in the inert gas of the atomizer. It was later sieved to achieve separation into different size ranges. In this work, the small, ~25 μm size, particles were been used after a 1 h 700 °C annealing. The annealing process leads to phase stabilization as published elsewhere.[9] Nb powders, 99.8% purity, from Sigma Aldrich and 300 μm average size, were mixed with the 25μm FeSi powders and dispersed by vibration forming a mixture 25% Nb and 75% FeSi expressed in mass percent.

Magnetization was measured using VSM-PPMS 6000 Quantum Design magnetometer. The sample studied was prepared by pressing the mixture to form a cylinder 0.75 mm height and 2.7 mm diameter. The field is applied along the cylinder axis or z-axis.

III. RESULTS AND DISCUSSION

Figure 1 illustrates the hysteresis loop of the Nb powders, measured at 5 K, that is characteristic of type II superconductors. The Nb coercive field is close to 200 Oe. Both descendent branches of the hysteresis loop show a maximum of magnetization, $M = 5.8$ emu/g for applied fields of 400 Oe. The remanent magnetization is 1.2 emu/g. Figure 2 depicts the saturation hysteresis loops obtained for pure FeSi powders, for the 25%Nb-75%FeSi mixture and for pure Nb at 5 K (Fig. 2(a)) and 300 K (Fig. 2(b)). The low applied field region of both curves is shown in detail in Figures 3 and 4 where the Nb contribution has been omitted.

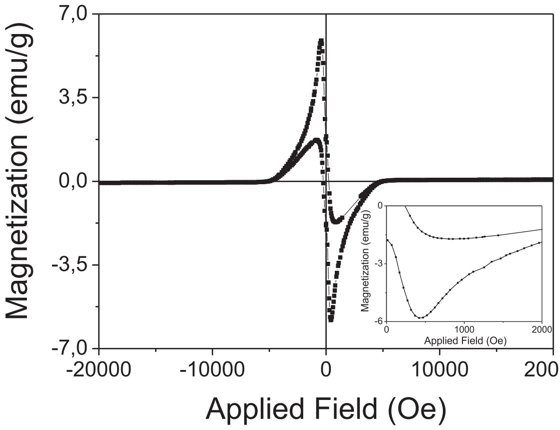

FIG. 1. Hysteresis loop for Nb powders, measured at 5 K. The inset shows a detail for the first branch.

Figures 2(a) and 2(b) indicate that at T = 5 K as well as at T = 300 K, the saturation magnetization of the mixture is approximately 0.75 times the saturation magnetization of the pure FeSi powders. Note that at T = 5 K and under the maximum applied field of 50 kOe, the Nb particles are paramagnetic. Therefore, the saturation magnetization relation experimentally observed between those of the mixture and the pure FeSi phases is in agreement with the mass percentage of the mixture, when the paramagnetic contribution of the Nb phase is neglected. It is important to note that from the shape of the curves shown in Figures 2(a) and 2(b) it turns out that long range magnetostatic interactions govern the magnetization curves through the macroscopic demagnetizing factor of the sample, *N*. The size of the FeSi particles is well above the single domain range and consequently magnetizes by nucleation and propagation of domains.

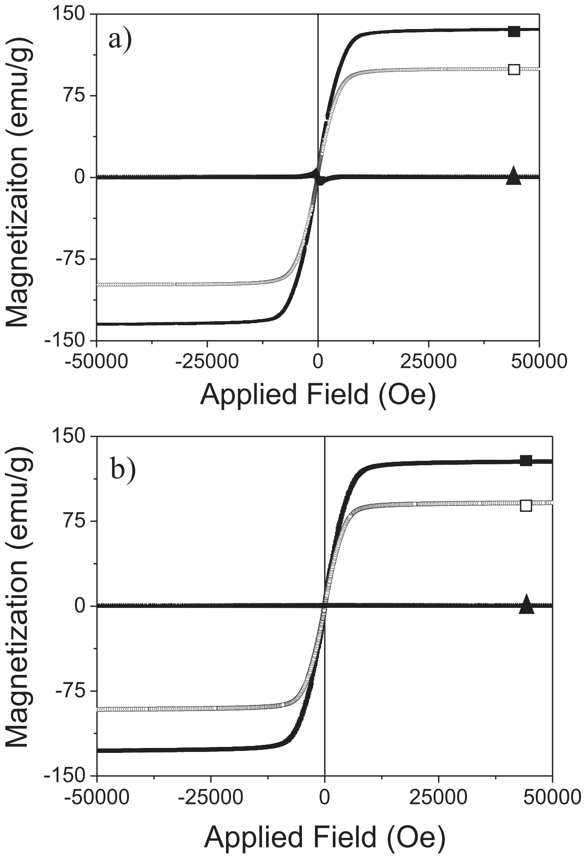

FIG. 2. Saturation magnetization hysteresis loops for pure FeSi (■), pure Nb (▲), and for the mixture 25%Nb-75%FeSi (○) measured at 5 K (a) and at 300 K (b).

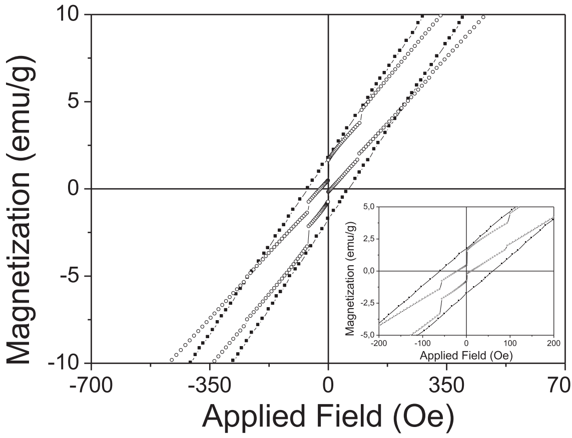

FIG. 3. Detail of the hysteresis loops obtained at 5 K for pure FeSi (■) powders and for the mixture 25%Nb-75%FeSi (○).

As shown in Figure 3, the coercivity of the mixture at 5 K is 15 Oe, lower than that of pure FeSi powders that reaches 60 Oe. The remanence of the mixture, 0.60 emu/g is less than one half that the measured for the pure FeSi phase, 1.80 emu/g. Hence, the hysteresis loop of the mixture undergoes a noticeable narrowing at low fields (between 150 and −150 Oe) respect to that of the pure FeSi phase. The effect of Nb powders, for temperatures above its critical temperature, seems to be opposite and exhibits a trend to increase both remanence and coercivity (Figure 4). This last observation coincides with the expected effect produced by the introduction of non magnetic inclusion in a ferromagnetic system that necessarily leads to a shortening of the exchange correlation length and subsequent hardening.[6]

A second and intriguing characteristic of the hysteresis loop of the mixture, measured at 5 K, is the stair-like profile of both hysteresis branches that can be seen in Figure 3. This type of magnetization curves is also characteristic of other

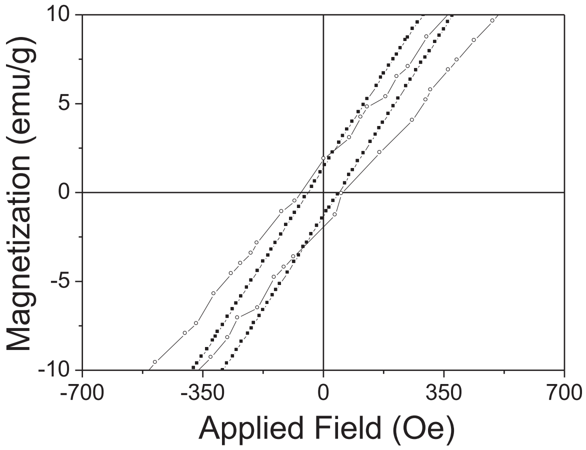

FIG. 4. Detail of the hysteresis loops obtained at 300 K for pure FeSi (■) powders and for the mixture 25%Nb-75%FeSi (○).

very different magnetic systems as for example antiferromagnetic structures with a dispersion of metamagnetic field transitions and systems exhibiting magnetic avalanches.[10–14] However, stair-like hysteresis profiles have been found and reported to be originated generally by magnetostatic interactions.[15]

Since the narrowing in the hysteresis loop as well as the stair-like behaviour disappears at 300 K, it turns out that both effects must likely be associated with the presence of the superconducting Nb particles. Therefore, they must be explained in terms of the diamagnetism of the superconducting particles that modify the macroscopic magnetization and gives rise to peculiar discrete magnetostatic interactions between first neighbours of the two different phases.[2,15]

Let us start by estimating the remanence and coercivity decrease when magnetostatic interactions between both phases are neglected. From the measured remanence of the phases determined separately, one might conclude that the magnetization of FeSi and Nb particles are oriented along opposite directions in the remanent state; after considering the respective mass percentage, the expected mixture remanence is found to be 1 emu/g. However, the measured remanence of the experimental mixture is 0.6 emu/g. When the applied field is reversed to negative values, the slope of the descendent branch of the hysteresis of the pure FeSi powders in the vicinity of the coercive field is 3×10^{-2} emu/g Oe (Figure 3). The magnetization of the Nb phase is, according to Figure 1, smaller than the remanence, 1.1 emu/g. Considering 0.25% mass percentage of Nb in the mixture, this 1.1 emu/g leads to a value of 0.27 emu/g. Consequently, the expected decrease of the coercivity due to the Nb negative remanent contribution becomes 10 Oe, which would decrease the coercivity of pure FeSi down to 50 Oe, whereas the value experimentally determined is 15 Oe. It can be concluded that even though the diamagnetic contribution of the Nb superconducting particles accounts for the qualitative changes observed in the hysteresis loop the quantitative experimental observations require further insight to be satisfactorily explained.

Let us estimate the discrete, short range magnetostatic interactions induced by oppositely aligned Nb particles and surrounding FeSi particles. By considering the densities of FeSi, ρ_{FeSi}, to be approximately 7 g/cm^3 and of Nb, $\rho_{\mathrm{Nb}} = 8.14$ g/cm^3, it can be found that the number of 25 μm FeSi particles in the mixture per cubic centimetre is approximately 10^6, whereas the number of 300 μm Nb particles should be close to 10^3. Thus, the percentage of the total number of FeSi particles located at the first neighbourhood of all the Nb particles per unit volume becomes 10% for maximum packing factor. A more realistic estimation of the average yields 5% of FeSi particles that are actually located within the nearest neighbours shell.

All FeSi particles located outside the nearest neighbour locations of Nb particles, that are more than 90% of the total number of FeSi particles per unit volume, form the matrix. According to the curves shown in Figures 2 and 4, the magnetization process of the matrix is not noticeably modified, at least in a first order, by the presence of the Nb particles. For the sake of simplicity, it will be assumed that, according to Figures 2 and 3, the matrix magnetization, M_m, can be roughly expressed in emu/g as $M_m = (H_{ap}/4\pi N\rho_{FeSi}) = 3 \times 10^{-2} H_{ap}$. As concerns the short range magnetostatic interactions, three different phases can be distinguished: the FeSi matrix, the FeSi interface formed by those particles located at the shell of nearest neighbouring of Nb particles, and the Nb phase. The magnetic field acting on the FeSi particles forming the interface is the sum of the fields produced by the spherical matrix-interface plus the Nb particle, sum that can be approximated as

$$\begin{aligned} H_{shell} &= \frac{4\pi\rho_{FeSi}M_m}{3} + \frac{4\pi\rho_{Nb}M_{Nb}R^3}{3(R+r)^3}(3\cos^2\theta - 1) \\ &= 27.7M_m + 25.4M_{Nb}(3\cos^2\theta - 1), \end{aligned} \quad (1)$$

where R and r hold for the Nb and FeSi particle radii, respectively, and θ is the angle formed by the position vector of the FeSi particle with origin at the centre of the Nb particle and the z axis.

Figure 5(a) indicates the magnetization of Nb and FeSi particles in the descendent branch of the hysteresis loop. As illustrated by Figure 5(a), the interface FeSi particles can be classified in three groups according to its angular position respect to the Nb central particle: (a) polar particles over which the field produced by the Nb magnetization is opposite to its magnetization, (b) equatorial particles over which the field is parallel to its magnetization, and (c) neutral particles located at angles θ for which $3\cos^2\theta$ is close to 1. Figure 5(b) shows the component z, parallel to the applied field, of the stray fields produced by the Nb particle at the first shell.

The field acting on the Nb particles that is given by the sum of the field produced by the matrix-shell spherical interface plus the field produced by the *n* FeSi particles contained at the first shell is

$$H_{Nb} = 4\pi\rho_{FeSi}\left[\frac{M_m}{3} + \sum_i \frac{M_{shell}r^3}{3(R+r)^3}(3\cos^2\theta_i - 1)\right], \quad (2)$$

M_{shell} is the magnetization of the FeSi particles of the first shell that is determined by H_{shell} therefore through relation (1), by M_m and M_{Nb}. But M_{Nb} depends on H_{Nb} and therefore, according to relation (2), on M_m and M_{shell}. Whereas M_m can be approximated by the expression $M_m = 3 \times 10^{-2}\, H_{ap}$, the values of M_{Nb} and M_{shell} cannot be generally expressed as a function of H_{ap}.

According to relation (1), H_{shell} will be influenced by M_{Nb} only for values of the magnetization matrix close to the magnetization of the Nb particles. Since the maximum magnetization of Nb is 5.8 emu/g, the interaction effects are only relevant in the range for which M_m varies between 6 and -6 emu/g, that corresponds to applied fields in the interval between 250 and -250 Oe.[16] Within this range of applied fields, H_{shell} can be oriented either along the plus or the minus directions depending on the angular position of the FeSi particles in the shell.

Along the descendent branch of the hysteresis loop and in the range for which M_m and M_{Nb} are oriented along

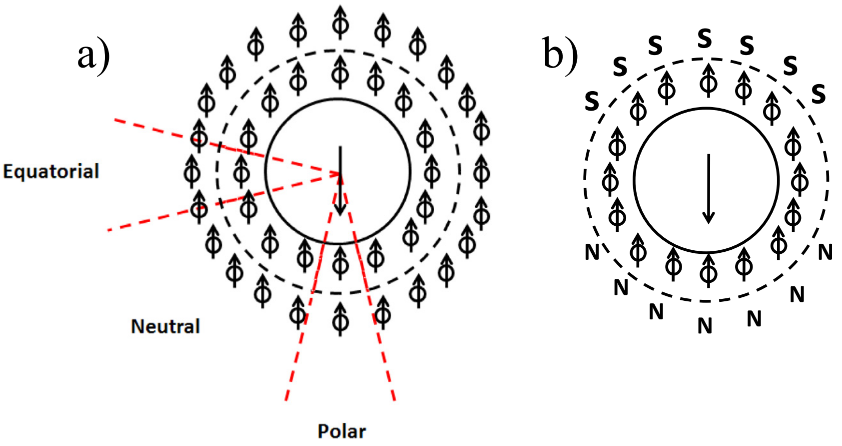

FIG. 5. Magnetization of one Nb particle and FeSi particles around in the descendent branch of the hysteresis loop when the effective field acting on Nb particles is below 700 Oe. The nearest neighbour shell and the boundary between this shell and matrix are pointed out (a). Parallel component to the applied field of the stray fields produced by the Nb particle at the first shell (b).

opposite directions, relation (1), shows that at the polar positions H_{shell} vanishes for $M_m = 1.8 M_{Nb}$. The coercive field of the shell particles, achieved for $H_{shell} = -60$ Oe, can correspond to positive applied fields, since according to Eq. (1) this condition becomes

$$-60 = 27.7M_m - 50.8M_{Nb}(3\cos^2\theta - 1) = (27.7 - 50.8\alpha)M_m, \quad (3)$$

where $\alpha = M_{Nb}/M_m$.

Note that if $\alpha > 0.54$ the coefficient of M_m in relation (3) is negative and then is possible with positive H_{ap} to obtain negative H_{shell}. According to the curve shown in Figures 3, the remanence of M_m is 1.8 emu/g and gives rise, according to relation (2) and neglecting its second term, to H_{Nb} close to 60 Oe, that corresponds to a negative $M_{Nb} = 2$ emu/g (Fig. 1). Therefore, close to the region of zero applied field, α takes values above 1, thereby higher than 0.6. Hence, FeSi particles located at the polar regions of the first shell can switch the magnetization even under positive applied fields due to the magnetic field produced by the Nb particles. When the magnetization of a polar particle reverses the magnetostatic coupling between the FeSi particles forming the first shell it can give rise to the stair-like jumps between metastable states as experimentally observed and theoretically analysed in Ref. 15. For those applied field for which some particles of neutral (H_{ap} close to zero) and equatorial particles (H_{ap} negative) reverse the same type of jumps are expected to be induced.

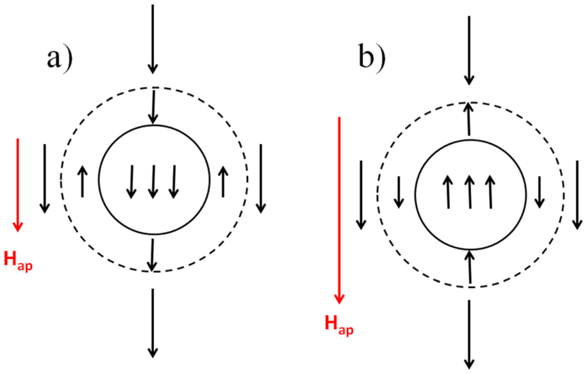

FIG. 6. The reversal of the Nb magnetization from negative to positive inducing the immediate reversal of the equatorial particles from positive to negative.

Note that, as shown in Figure 3, the strength of the magnetization jump steps (2.75 and 2.25 emu/g at the descendent and ascendant branches, respectively) roughly represents 2% of the total magnetization switch which is the order of either the total switch of the Nb phase magnetization or the switch of a fraction of the FeSi particles located at the first neighbouring positions of the Nb particles.

Following the descendent branch of the hysteresis loop is interesting to remark the effect produced on H_{Nb} by the reversal of the applied field to negative values. In this situation M_m is negative and the second term in Eq. (2) is also negative as the polar particles had eventually reversed the magnetization at positive applied fields (Figure 6). When the sum of both terms in relation (2) reaches the coercivity shown in Figure 1, that is 200 Oe, the magnetization of Nb vanishes. If the second term in Eq. (2) is neglected[17] the reversal of Nb magnetization would take place for $M_m = 6$ emu/g. However, when the second term is taken into account the reversal could take place at negative applied fields for which M_m could be as low as 2.5 emu/g. The reversal of the Nb magnetization from negative to positive would immediately induce the reversal of the equatorial particles from positive to negative, as illustrated in Figure 6.

IV. CONCLUSIONS

In conclusion, the dispersion of superconducting particles in a ferromagnetic powder gives rise to a narrowing of the hysteresis loop through the decrease of both remanence and coercivity. This perturbation of the magnetization process is only observed under applied fields for which the magnetization of both phases is similar. The diamagnetic hysteresis loop of the superconducting phase accounts for the qualitative behaviour. However, the explanation of the stair like profile of the magnetization curve as well as the quantitative changes measured in remanence and coercivity require magnetostatic coupling considerations. The analysis carried out in this report shows that the coupling only affects to a small fraction, 2%, of FeSi particles forming the interface between the FeSi matrix and the Nb inclusions. By increasing the temperature of the sample above the critical superconducting temperature, the effect of the Nb becomes opposite and a weak increase of both coercivity and remanence with respect to those of pure FeSi phase is appreciated. This hardening is expected when non magnetic inclusions are introduced in a ferromagnetic system. It has been shown that typical characteristics of the ferromagnetic powders hysteresis loop, as are coercivity and remanence, can be controlled at low temperature by mixing with adequate superconducting particles.

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[16] It is precisely for this range of applied fields and magnetization when the modification of the hysteresis curve due to the Nb inclusions is experimentally observed as depicted by Figure 3.
[17] This condition holds for a spherical symmetry distribution of the FeSi particles of the interface around the Nb particle.