Magnetization process in a two-phase exchange-coupled system: A microscopic study

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The magnetization process in an exchange-coupled α-Fe+$Nd_2Fe_{14}B$ nanocomposite has been studied by Mössbauer spectroscopy. Measurements in fields of up to 2 T confirm that the magnetization of the soft phase is strongly coupled to that of the hard phase. Analysis of magnetization curves and magic-angle spectra of saturated samples shows that the remanence is dominated by the hard phase. [S0021-8979(97)94208-0]

INTRODUCTION

Nanocomposite magnets containing fine grained hard and soft magnetic phases in intimate contact have been shown to exhibit some unusual properties. Their remanence ratio ($M_r/M_{\rm sat}$) can be as much as 0.7, well above the value of 0.5 expected for an isotropic uniaxial powder, and leading to the term ''HIREM'' being used to describe them.[1] They also show an unusual tendency to recover from the application of a reverse field, the magnetization ''springs'' back almost to its original value even after the application of a reverse field large enough to halve the magnetization.

Normally, the presence of a soft magnetic impurity in a hard magnet leads to a degradation of performance as the soft phase provides easy nucleation sites for magnetization reversal. However, if the hard and soft grains are small enough (typically less than the thickness of a domain wall) then it is no longer possible to start a reversal in the soft phase and the magnetizations of the two phases are locked together.[2] In an optimized sample, the soft phase (e.g., α-Fe) has a high magnetization and provides the saturation magnetization, while the hard phase (e.g., $Nd_2Fe_{14}B$) provides the resistance to reversal. This is the mesoscopic analogue of most hard magnet alloys, where the rare-earth provides anisotropy and iron provides magnetization.

Several numerical models have been developed to describe the magnetization process in an exchange-coupled magnet[3] and they lead to the following results: Although an isotropic powder of a hard phase can yield a remanence ratio of no more than 0.5 by having the magnetization of each grain oriented within the upper hemisphere (i.e., never worse that perpendicular to the bulk magnetization), the soft phase in which it is dispersed responds to the average of several neighboring hard grains and tends, on average, to have its local magnetization closer to the bulk direction and so contributes more than 0.5 of its $M_{\rm sat}$. When a reverse field is applied, the initial response is primarily in the soft phase with little effect on the hard grains, so that after the field is removed, the magnetization of the soft phase returns to its initial value as the hard grains, which define the zero-field magnetization of the soft phase, are still in their original orientations.

While the agreement between microscopic models and bulk behavior is quite good, we felt it would be appropriate to test the models at a microscopic level. To this end we set out to follow the rotation of the magnetization in an exchange-coupled system by Mössbauer spectroscopy. This technique allows us to see the magnetization direction through the intensities of lines 2 and 5 of the magnetically split 6-line spectrum. Furthermore, if the spectra of the two magnetic phases are sufficiently well separated, we can monitor the magnetization direction in each phase independently. We report here on an exchange coupled α-Fe+$Nd_2Fe_{14}B$ nanocomposite, chosen because of the complete separation of lines 5 and 6 in this combination and also because the Mössbauer spectra of both components have been extensively studied and excellent fits are available.

EXPERIMENTAL METHODS

An arc-melted ingot of $Nd_{10}Fe_{85}B_5$ was crushed and ball-milled under argon for 20 h in a SPEX 8000 mixer-mill, the resulting amorphous powder was then crystallized by annealing at 600 °C for 30 min. Mössbauer spectroscopy and thermogravimetric analysis (TGA) in a small field gradient confirmed that the only phases present were: α-Fe ($\sim$27% by weight) $Nd_2Fe_{14}B$ ($\sim$68%) with the balance being $Nd_{1.1}Fe_4B_4$. The sample for applied-field Mössbauer was prepared by mixing the annealed powder with epoxy to form a disc 16 mm in diameter and 2 mm thick. A piece of this was used for magnetization measurements. Despite the high concentration of a magnetically soft phase, the hysteresis loop showed conventional single magnetic phase behavior, and demagnetization curves measured following saturation (Fig. 1) show magnetization recovery typical of an exchange-spring system. A remanence of 103 J/T/kg was observed at zero internal field (a field of 0.4 T was used to cancel demagnetizing field of the sample, determined from fits to the Mössbauer spectra). This is 60% of the expected saturation value calculated from the phase composition, demonstrating that the sample exhibits significantly enhanced remanence.

Mössbauer measurements were carried out at room temperature on a conventional constant acceleration spectrometer. A field of up to 2.2 T was applied perpendicular to the γ beam using a Harvey-Wells electromagnet. The 1 GBq ^{57}CoRh source was located well out of the pole gap so that stray fields at the source never exceeded 100 mT. The

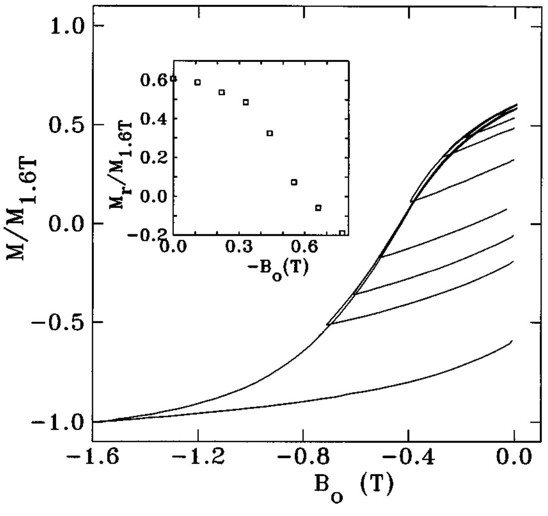

FIG. 1. Demagnetization curves normalized to the magnetization in 1.6 T, for the exchange-coupled sample studied here, showing single magnetic phase response despite the 27 wt. % of α-Fe present. The inset shows the loss of remanence in zero field after exposure to increasing reverse fields. Note that little irreversible loss occurs for reverse fields of less than 0.4 T.

sample was initially magnetized perpendicular to the disc surface in 2.2 T and then spectra were recorded with the field applied parallel to the disc surface to observe the rotation of the magnetization. Spectra were fitted using a conventional nonlinear least-squares minimization routine with the hyperfine parameters of all three phases fixed to values determined from standards.[4] The adjustable parameters were: baseline, linewidth, relative proportions of each phase, intensity of lines 2 and 5 (R) for each of the two magnetic phases and a field shift to include the effect of the externally applied field. Typical spectra are shown in Fig. 2.

RESULTS AND DISCUSSION

The demagnetization curves in Fig. 1 show that the remanent magnetization largely recovers for reverse external fields of up to 0.4 T but is rapidly destroyed in larger fields, with 0.55 T being sufficient to reduce the remanence to zero. A field of 1.6 T is sufficient to close the hysteresis loop. These curves set the scale for the expected changes in the Mössbauer spectra.

Inspection of the spectra in Fig. 2 shows that the combination of α-Fe and $Nd_2Fe_{14}B$ is ideally suited to the study of magnetization rotation in an exchange-spring system as lines 5 and 6 for each phase are clearly separated. In each case, the right-hand component of the doublets centered at 3 mm/s and 5 mm/s belongs to α-Fe while the left-hand component is due to $Nd_2Fe_{14}B$. Fig. 3 shows the fitted intensities of lines 2 and 5 (R) for the two magnetic components in the sample for various fields with data from a pure iron foil for comparison. The behavior of the pure foil is as expected, with the remanent field of 0.6 mT in the electromagnet being nearly enough to saturate the magnetization. The maximum value of 3.6 (less than the theoretical value of 4.0) was limited by absorption saturation effects in the rather thick foil used.

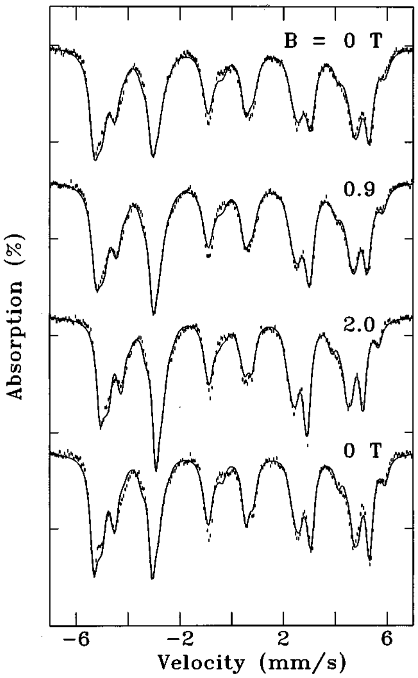

FIG. 2. Mössbauer spectra for a sample initially magnetized parallel to the γ beam, exposed to increasing fields perpendicular to the beam. The bottom spectrum was taken in zero field after measuring in 2.0 T. Note the clear separation of α-Fe from $Nd_2Fe_{14}B$ in lines 5 and 6 of the spectra, in each case, the high velocity component of the doublet is due to α-Fe.

The behavior of the exchange-spring system is less easily accounted for. R_{Fe} responds much more slowly than in the pure foil, strong evidence that it is indeed exchange coupled to the hard phase. It also saturates in about 1.5 T, consistent with the magnetization curve in Fig. 1. The rather low saturation value of ~3.2 is due in part to absorption saturation effects, but exchange coupling to the hard phase

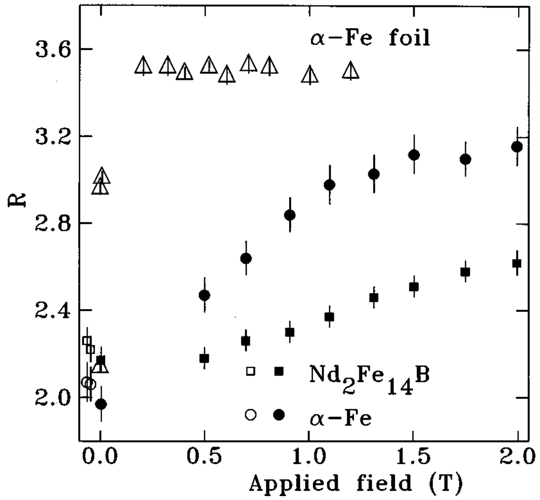

FIG. 3. Fitted intensities of lines 2 and 5 relative to 3 and 4 for the two phases in the sample. The response of a pure iron foil is shown as open triangles for comparison. The two pairs of open symbols plotted to the left of zero field show results obtained in zero field after the sample had been measured in 1.5 T and 2.0 T.

also restricts the degree to which the iron moments can orient parallel to the external field. By contrast, R_{2-14-1} increases quite slowly with the field, rising linearly with no sign of saturation, even in fields where the magnetization curve (Fig. 1) has clearly flattened. If the trend continues, then a field of $\sim$3.5 T would be needed before R_{2-14-1} would meet R_{Fe}. The recoil response is perhaps more surprising. The open points to the left of zero in Fig. 3 show results obtained in zero field after the sample had been exposed to external fields of 1.5 T and 2.0 T and in both cases the sample appears to return to its initial state, even though the magnetization curve shows a substantial remanence. The small change apparent in Fig. 3 is close to the fitting uncertainty.

The apparent contradiction between the Mössbauer and magnetization data is easily resolved when the structure of the sample is taken into account. Dispersing a ball-milled powder of an easy-axis magnet, such as $Nd_2Fe_{14}B$, in epoxy should yield a crystallographically isotropic sample, i.e., one with no preferred axis or direction and an as-cast, unmagnetized, sample will contain a uniform distribution of magnetization directions. Since the intensities of lines 2 and 5 are given by: $R=(4\sin^2\theta)/(1+\cos^2\theta)$, we obtain $R=2.0$. In the fully magnetized remanent state, the moments are distributed uniformly over a hemisphere giving a remanence ratio of 0.5 and R is still 2. If we now apply a reverse field to the sample, the magnetization within each grain will tend to tip, however, in an easy axis system, the only way a significant change in magnetization can occur is through a 180° flip which takes the magnetization from largely anti-parallel to largely parallel to the applied field. This type of flip has no effect on the Mössbauer spectrum. R is a function of $\sin^2\theta$ and $\cos^2\theta$ only and so a flip from θ to $\theta+180°$ leaves R unchanged. As the magnetization of an isotropic powder is reversed through a series of 180° flips, R remains equal to 2. Thus, in zero field, R is always independent of the state of magnetization of any isotropic powder of an easy axis material. The slow, linear increase in R apparent in Fig. 3 is due to the magnetization within grains canting away from the easy axis against the anisotropy field, in response to the applied field.

In order to check our interpretation, we made a series of 'magic angle'[5] measurements on the sample magnetized both parallel and perpendicular to the disc surface. We found R_{2-14-1} to be independent of both orientation and magnetization state, as expected for an isotropic powder of an easy-axis system. Furthermore, the constant value of 2.26 ± 0.01 obtained suggests that the offset from 2.0 apparent in Fig. 3 is due to saturation effects, probably due to the presence of large agglomerates. An anisotropic magnetization distribution would show up as an orientation dependence in R, while saturation due to a uniform thick sample would lead to an increase in R when the sample was tilted through 54.7°. Large spherical agglomerates appear the same thickness in all orientations, and no change in saturation occurs in any orientation. The soft phase showed a systematic anisotropic response consistent with some polarization of the moments, however the effect was small, and close to the statistical uncertainty of the fits.

In conclusion, we have shown that the magnetization of the soft α-Fe phase is locked to that of the hard $Nd_2Fe_{14}B$ phase and a substantial field is needed to change its orientation. The angular dependence of R coupled with the magnetization process in an isotropic powder of a uni-axial magnet precludes observation of the orientation of the magnetization in the hard phase. While it is likely that the majority of the remanence enhancement in a spring magnet is due to polarization of the soft phase, it is not possible to rule out some polarization of the hard phase from Mössbauer data as previously claimed.[6]

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