# Composition and Microstructure Dependent Spin Reorientation in Nanocrystalline (Nd–Pr)-(Fe–Co)-B Alloys

Zhongwu Liu, *Student Member, IEEE,* and Hywel A. Davies

***Abstract*—The effects of composition, grain size and exchange coupling on the spin-reorientation temperature ($\mathrm{T_{SR}}$) for nanocrystalline (Nd–Pr)-(Fe–Co)-B alloys have been systematically studied. Although $\mathrm{T_{SR}}$ is usually considered to be an intrinsic magnetic property, it is nevertheless influenced by the microstructure when the grain size decreases to the nanometer level. The $\mathrm{T_{SR}}$ for all single phase nanocrystalline $Nd_{12}Fe_{82}B_6$ alloys were lower than the published value for a single crystal or for an aligned sintered NdFeB magnet. The results consistently demonstrate that the increasing degree of exchange coupling between the $RE_2Fe_{14}B$ nano-grains with decreasing grain size leads to a progressive decrease in $\mathrm{T_{SR}}$. As is the case for conventional NdFeB alloys, Pr substitution for Nd decreases $\mathrm{T_{SR}}$ linearly and rapidly with increasing Pr concentration but a spin reorientation still occurs at 75% Pr substitution ($\mathrm{T_{SR}} \approx 25$ K). Co substitution for Fe also decreases $\mathrm{T_{SR}}$, but to a lower degree than Pr for Nd. Introduction of an increasing volume fraction of soft magnetic $\alpha$-(Fe–Co) phase into the nanocrystalline $Nd_2Fe_{14}B$ alloy has no significant influence on the value of $\mathrm{T_{SR}}$ in spite of the influence of $\alpha$-(Fe–Co) on the exchange coupling.**

***Index Terms*—Exchange coupling, nanocrystalline, Nd–Fe–B, spin reorientation.**

## I. INTRODUCTION

THE INTERPLAY between the magnetocrystalline anisotropies of the different magnetically ordered sublattices leads to spin reorientation phenomena in which the easy axis of the magnetization changes at the spin reorientation temperature ($\mathrm{T_{SR}}$). For $Nd_2Fe_{14}B$, at 4.2 K, the easy magnetization lies in the plane $\{110\}$ at an angle $\theta \approx 30^\circ$ with respect to the $c$ axis. The angle $\theta$ decreases continuously with increasing temperature and a transition occurs at $\mathrm{T_{SR}}$, reported to be in the vicinity of 135 K, to a collinear magnetic structure [1].

Apart from scientific interest, the spin reorientation is also important because it determines the lower temperature limit for uniaxial anisotropy which is critical for technical applications of $RE_2Fe_{14}B$ in permanent magnets. The effects of substitutions of rare-earth elements or three-dimensional (3-D) transition metals on the spin reorientation of $Nd_2Fe_{14}B$-type compounds in single crystal or sintered magnetic forms have been examined extensively [2]–[4]. The substitution of Pr for Nd suppresses the spin reorientation because $Pr_2Fe_{14}B$ shows only uniaxial magnetocrystalline anisotropy below the Curie temperature [3]. The substitution of Co for Fe is found to decrease $\mathrm{T_{SR}}$ for $Nd_2(Fe–Co)_{14}B$ alloys [2]. However, the nanocrystalline REFeB alloys have received relatively little attention, notably, the effect of mean crystallite size $d_g$ on the spin reorientation, possibly because, normally, a spin reorientation is considered to be an intrinsic property, independent of the microstructure. Actually, Dahlgren *et al.* [5] measured the temperature dependence of the ac susceptibility and obtained a $\mathrm{T_{SR}} = 118$ K for a single phase $Nd_{11.76}Fe_{82.36}B_{5.88}$ alloy with a $d_g$ of 19 nm, produced by melt spinning. Lewis *et al.* [6] also obtained a $\mathrm{T_{SR}} = 116.5$ K for nanocrystalline melt spun $Nd_2Fe_{14}B$ alloy of unspecific $d_g$. Their results suggest a different behavior of the spin reorientation in nanocrystalline alloys, though no further work has been reported until now. In the present work we performed a systematic study of the effect of nanocrystallite size on the spin reorientation of (Nd–Pr)-(Fe–Co)-B alloys. These alloys have previously been comprehensively studied at Sheffield, with Pr employed to successfully increase the coercivity and Co to enhance the Curie temperature [7].

## II. EXPERIMENTAL PROCEDURES

$(Nd_{1-y}Pr_y)_z(Fe_{1-x}Co_x)_{94-z}B_6$ alloy ingots were produced from the constituent elements (purity $\geq$99.9%) by argon arc melting. Each ingot was remelted at least six times to ensure homogeneity. Nanocrystalline ribbons with single phase, nanocomposite and RE-rich compositions and various grain sizes, were produced by melt spinning, using roll speeds ($V_r$) within the range 16–25 m/s. The mean grain sizes $d_g$ for the $RE_2(Fe–Co)_{14}B$ (2/14/1) phase were determined by X-ray line broadening analysis [8] and transmission electron microscopy.

The $\mathrm{T_{SR}}$ for all alloys were determined as the inflection point in the magnetization $M$ versus temperature $T$ curves, evaluated from the derivative $\partial M/\partial T$ [6], as shown in Fig. 1 for curve a). The $M \sim T$ curves were measured in each case for selected single ribbon samples by VSM under a small constant field H of 0.1 T with a temperature ramp rate of 3 K/min. The $M - H$ curves for single ribbons were measured in the temperature range 4.2–250 K with a high field VSM, coupled to a magnet having a maximum applied field of 9 T.

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Z. Liu is with the Department of Engineering Materials, University of Sheffield, Sheffield S1 3JD, U.K. (e-mail: mtp00zl@Sheffield.ac.uk).

H. A. Davies is with the Department of Engineering Materials and Centre for Advanced Magnetic Materials and Device, University of Sheffield, Sheffield S1 3JD, U.K. (e-mail: h.a.davies@Sheffield.ac.uk, http://www.shef.ac.uk).

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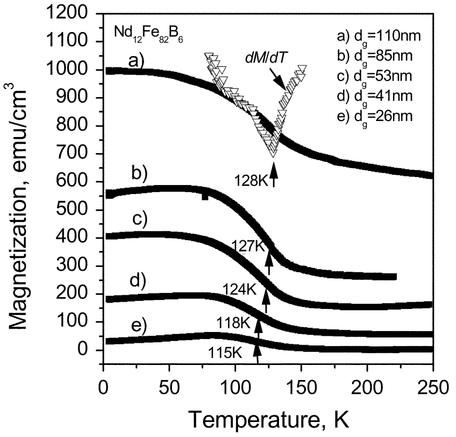

Fig. 1. $M \sim T$ curves measured at 0.1 T for $Nd_{12}Fe_{82}B_6$ alloys with various $d_g$. The $dM/dT$ plot is the derivation of curve (a). $T_{SR}$ is determined as the inflection point from $M$ versus $T$ curve.

TABLE I
SPIN-REORIENTATION TEMPERATURE FOR Pr AND Co SUBSTITUTED ALLOYS WITH COARSE AND FINE CRYSTALLITES

| Alloy | Coarse grains | | Fine grains | |
|---|---|---|---|---|
| | $d_g$, nm | $T_{SR}$, K | $d_g$, nm | $T_{SR}$, K |
| $Nd_{12}Fe_{82}B_6$ | 110 | 128 | 26 | 115 |
| $Nd_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ | >80 | 122 | 27 | 115 |
| $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ | >100 | 97 | 28 | 93 |
| $(Nd_{0.50}Pr_{0.50})_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ | >80 | 63 | 27 | 58 |
| $(Nd_{0.25}Pr_{0.75})_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ | >100 | 26 | 33 | 25 |

## III. RESULTS AND DISCUSSION

### A. *The Effect of Crystallite Size on* $T_{SR}$

Our data show clearly that the $T_{SR}$ is influenced by the scale of the microstructure when the grain size decreases to the nanometer level. Fig. 1 shows the $M \sim T$ curves for the $Nd_{12}Fe_{82}B_6$ alloy, which can be assumed to have a single phase (2/14/1) structure, produced at various $V_r$, and it is evident that decreasing $d_g$ leads to a lower $T_{SR}$. The $T_{SR}$ for all single phase nanocrystalline $Nd_{12}Fe_{82}B_6$ alloys were lower than 135 K. The $T_{SR}$ for various Pr- and Co-substituted single phase alloys with coarse and fine crystallites are listed in Table I. The results consistently demonstrate that decreasing $d_g$ diminishes $T_{SR}$, e.g., for $Nd_{12}Fe_{82}B_6$, $T_{SR}$ is 115 K for a $d_g$ of 26 nm, compared with 128 K for a $d_g$ of 110 nm. As is well established, decreasing $d_g$ enhances the exchange interaction between the hard phase grains [9], and thus we conclude that the increasing degree of exchange coupling between the 2/14/1 nanograins with decreasing $d_g$ leads to a progressive decrease in $T_{SR}$.

### B. *The Effect of Pr Substitution for Nd on* $T_{SR}$

Fig. 2 shows the $M \sim T$ curves for single phase $(Nd_{1-y}Pr_y)_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ alloys with $d_g < 35$ nm. Pr substitution for Nd decreases $T_{SR}$ linearly with increasing Pr concentration (Fig. 3); clearly a spin reorientation still occurs up to at least 75% Pr substitution. This result agrees with that obtained by Kim *et al.* [10] for sintered alloys but is significantly different from that reported by Yang *et al.* [3] for arc melted and annealed samples of RE-rich $(Nd_{1-y}Pr_y)_2Fe_{14}B$. The latter data indicated that $T_{SR}$ decreases to 0 K at $y = 0.57$. The hysteresis loops measured in the temperature range 10 K–200 K for the alloy $(Nd_{0.25}Pr_{0.75})_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ indicate a kink in the 2nd quadrant of demagnetization curve at 10 K (Fig. 4), which further demonstrates that a spin reorientation still occurs for the 75% Pr substituted alloy [11]. Fig. 3 indicates that $T_{SR}$ decreases approximately linearly with increasing Pr substitution for the 5% and 30% Co series alloys also.

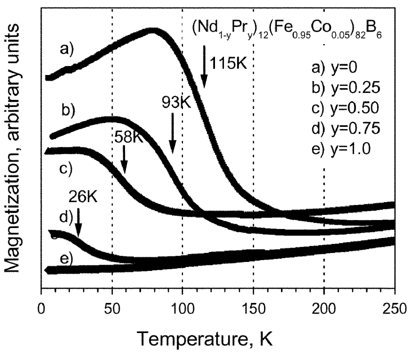

Fig. 2. $M \sim T$ curves for $(Nd_{1-y}P_y)_{12}(Fe_{0.95}Co_{0.05})_{82}B_6$ alloys with various Pr substitutions.

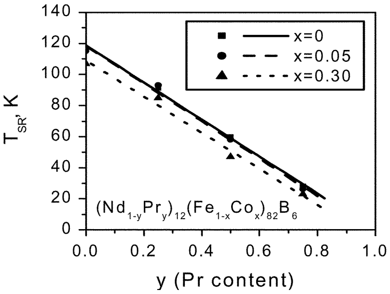

Fig. 3. Dependence of $T_{SR}$ on Pr (y) and Co (x) contents for $d_g < 35$ nm.

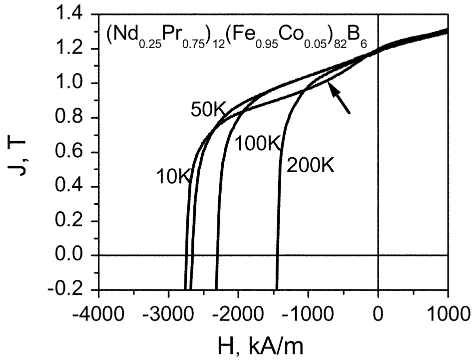

Fig. 4. Hysteresis loops at 10 K–200 K for 75% Pr and 5% Co substituted alloy with $d_g = 33$ nm.

### C. *The Effect of Co Substitution for Fe on* $T_{SR}$

Fig. 5 shows the $M \sim T$ curves for fi$(Nd_{0.25}Pr_{0.75})_{12}(Fe_{1-x}Co_x)_{82}B_6$ alloys with $d_g < 35$ nm. Increasing the Co content decreases $T_{SR}$ slightly. The same trends were observed for various Pr substituted alloys also (Fig. 4). The result is consistent with the published magnetic phase diagram for $(Nd–Pr)_2(Fe–Co)_{14}B$ alloys, in which increasing Co content is shown to result in a slow and monotonic decrease of $T_{SR}$ [12].

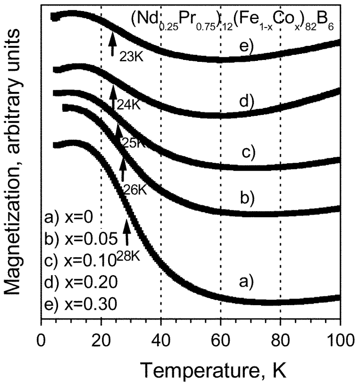

Fig. 5. $M \sim T$ curves for single phase alloys with various Co substitutions for Fe and $d_g < 35$ nm.

TABLE II

$T_{SR}$ FOR NANOCRYSTALLINE $(Nd_{0.75}Pr_{0.25})_x(Fe_{0.95}Co_{0.05})_{94-x}B_6$ ALLOYS HAVING $d_g < 35$ nm AND WITH VARIOUS PHASE CONSTITUENTS

| Alloy | x, RE content | Phase constituent | $T_{SR}$, K |
|---|---|---|---|
| RE-rich | 14 | 2/14/1+RE-rich phases | 92 |
| Single phase | 12 | 2/14/1 | 93 |
| Nanocomposite | 10 | 2/14/1+~13 vol.% α-(Fe,Co) | 93 |
| | 8 | 2/14/1+~22 vol.% α-(Fe,Co) | 92 |

The gradual drop in $T_{SR}$ with Co can be explained by the fact that the exchange field, $H_{exch}$, experienced by the $Nd^{3+}$ ion becomes smaller when the 3-D sublattices become "diluted" by cobalt, which has a lower magnetic moment than iron. It is known that $H_{exch}$ is directly proportional to the magnitude of the 3-D magnetization. Changes in $T_{SR}$ can be related to the changes in $H_{exch}$: the lower the $H_{exch}$, the lower the $T_{SR}$ [2].

### D. The Effect of Introducing α-(Fe–Co) or RE-Rich Phase on $T_{SR}$

Since enhanced exchange coupling between the $RE_2Fe_{14}B$ hard phases decreases the $T_{SR}$ for single phase alloys for $d_g$ below ~ 100 nm, it is of interest to investigate the exchange coupled nanocomposite (Fe–Co)-rich alloys and a partly decoupled RE-rich alloy.

Thus, we examined the $(Nd_{0.75}Pr_{0.25})_z(Fe_{0.95}Co_{0.05})_{94-z}B_6$ alloys with various rare earth contents, including a RE-rich alloy with $z = 14$ and nanocomposite alloys with $z = 8$ and 10, in order to compare with the $z = 12$ alloy. All of these alloys had similar $d_g$ (< 35 nm). The phase constituents and the $T_{SR}$ are shown in Table II. The results indicate that, introduction of an increasing volume fraction of soft magnetic α-(Fe–Co) phase into the nanocrystalline $RE_2Fe_{14}B$ alloy, which gives additional enhancement of remanence, has no significant influence on the value of $T_{SR}$ for the 2/14/1 phase which suggests that the soft phase grains are completely coupled to the hard grain neighbors. However, more surprisingly, introducing a small fraction of RE-rich phase, which partly decouples the hard phase grains, also apparently has no significant effect on $T_{SR}$; the reason for this is currently being investigated.

## IV. CONCLUSION

For nanocrystalline NdFeB-based alloys, the spin reorientation is influenced by the crystallite size of the 2/14/1 phase $d_g$. The $T_{SR}$ for all nanocrystalline alloys are lower than that for a single crystal or for an aligned sintered NdFeB magnet. The increasing degree of exchange coupling between the $RE_2Fe_{14}B$ nano-grains with decreasing $d_g$ leads to a progressive decrease in $T_{SR}$. Co substitution for Fe slightly decreases $T_{SR}$. Pr substitution for Nd decreases $T_{SR}$ linearly with increasing Pr but a spin reorientation still occurred up to at least 75% Pr substitution. The additional exchange coupling between hard and soft phases in a nanocomposite structure has no significant effect on the value of $T_{SR}$ for a given value of $d_g$.

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