

Coercivity, Time Dependence and Reversible Magnetization in Nd Rich Nd–Fe–B Alloys

Robert C. Woodward, Nicole T. Gorham, Robert Street, David C. Crew, Erol Girt, and Kannan M. Krishnan

Abstract—The coercivity, time dependent magnetic properties and reversible magnetization behavior for a series of neodymium enriched alloys based on $\text{Nd}_2\text{Fe}_{14}\text{B}$ has been investigated. These studies were carried out in an attempt to elucidate the dramatic increase in the coercivity in these materials with increasing dilution of the magnetic phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$). Good correlation between the coercivity and the relative average linear spacing between magnetic grains was found for all but the lowest Nd content. As the Nd content is increased the reversible magnetization associated with domain wall pinning decreases. At high dilutions the reversible magnetization behavior is consistent with the predictions of a Stoner-Wohlfarth model of an assembly of noninteracting single domain particles. The magnetic viscosity parameter, A , does not vary consistently with dilution or coercivity.

Index Terms—Coercivity, magnetic viscosity, magnetization processes, Nd–Fe–B.

I. INTRODUCTION

MAGNETIC materials based upon the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase dominate the permanent magnet industry with commercially available magnets having energy products of up to 50 MGOe. A large body of work has been performed in an effort to understand the origins of coercivity in $\text{Nd}_2\text{Fe}_{14}\text{B}$ materials, see review in [1]. Despite this work and the importance of this material the factors controlling the coercivity are not completely understood and the coercivity is limited to a fraction of the theoretical value [2].

The coercivities in the commercially available magnets are achieved by the combination of the high anisotropy of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and a suitable microstructure. In general this means the production of small grains of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, via for example powder metallurgy or melt spinning techniques, and the presence of a Nd rich grain boundary phase. Attempts to make magnets without this Nd rich phase generally result in materials with low coercivities.

In 1987 Sagawa and Hirosawa showed that it was possible to achieve dramatic increases in the coercivity by simply

increasing the volume of the intergranular phase. They developed boron rich sintered magnets that showed a remarkable increase in the coercivity as the boron content was increased from 8% to 37% [3]. The increase in coercivity was associated with the increase in the boron rich nonmagnetic intergranular phase which acted to isolate the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ grains.

A number of studies have been undertaken to investigate the effect of relatively small variations in the Nd or Pr content on the coercivity in melt-spun magnets [4]–[6]. However, even at the highest rare earth contents of 20% the coercivity for these materials was still well below the theoretical coercivity predicted for a Stoner–Wohlfarth assembly of isotropic noninteracting single domain particles [7].

In this paper the coercivity, time dependence and reversible magnetization behavior of materials with increasing volumes of Nd are described.

II. EXPERIMENTAL DETAILS

A series of alloys with a composition of $\text{Nd}_\delta\text{Fe}_{13.1}\text{B}$ ($\delta = 2.05, 3.8, 8.9, 38.1$ and 147.6) were prepared by melt-spinning and subsequent annealing of the amorphous or partially amorphous ribbons. The annealed ribbons consisted of α -Nd, $\text{Nd}_2\text{Fe}_{14}\text{B}$ with occasional traces of γ -Nd. The full details of the preparation and structure of the samples are given in [8], [9]. The ribbons were ground and the powder pressed into discs with a diameter of 4 mm and a height of 0.7 mm–2.4 mm. Magnetic measurements were made with the field applied parallel to the diameter of the discs using a demagnetization factor calculated from [10].

Hysteresis loops were measured in a VSM with a 12 T superconducting solenoid. Time dependence and reversible magnetization measurements were made in a VSM with a 5 T superconducting solenoid. Measurements along the demagnetization curve were made following saturation in 12 T. The procedure for the measurement and analysis of both the time dependence and the reversible magnetization are as described in [11] and [12] respectively.

III. RESULTS AND DISCUSSION

The hysteresis loops for the samples are shown in Fig. 1. Two of the samples, $\text{Nd}_{38.1}\text{Fe}_{13.1}\text{B}$ and $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$, show a two-phase behavior that is attributed to a slight degradation of the ribbons. This two-phase behavior was not present in earlier tests of the same materials [8], [9].

Assuming that the nonmagnetic Nd phase completely surrounds the hard magnetic phase it is possible to estimate the relative average linear separation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains from

Manuscript received February 7, 2001.

This work was supported in part by the Australian Research Council and the U.S. Department of Energy, Division of Material Sciences, Office of Basic Energy Sciences under Contracts DE-AC02-98CH10886 and DE-AC03-76SF00098.

R. C. Woodward, N. T. Gorham, and R. Street are with the Department of Physics at the University of Western Australia, Nedlands 6907, Australia (e-mail: woodward@physics.uwa.edu).

D. C. Crew is with the Materials and Chemical Sciences Division, Energy Science and Technology Department, Brookhaven National Laboratory, Upton, NY 11973.

E. Girt and K. M. Krishnan are with the Materials Science Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720.

Publisher Item Identifier S 0018-9464(01)06834-0.

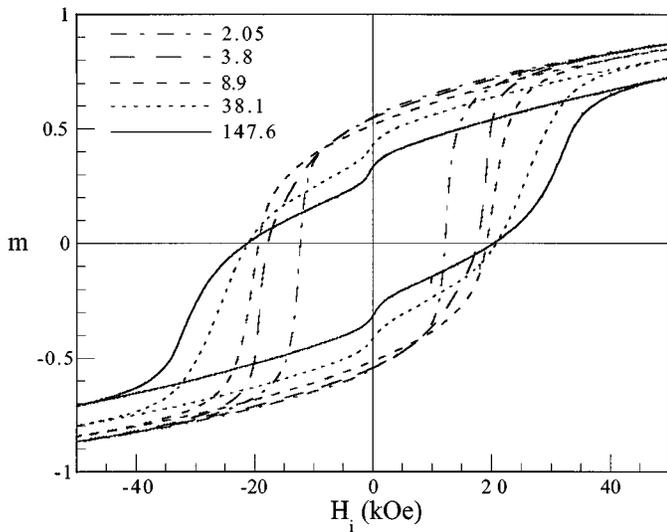


Fig. 1. Hysteresis loops for $\text{Nd}_\delta\text{Fe}_{13.1}\text{B}$ ($\delta = 2.05, 3.8, 8.9, 38.1$ and 147.6). m is in reduced units (M/M_s).

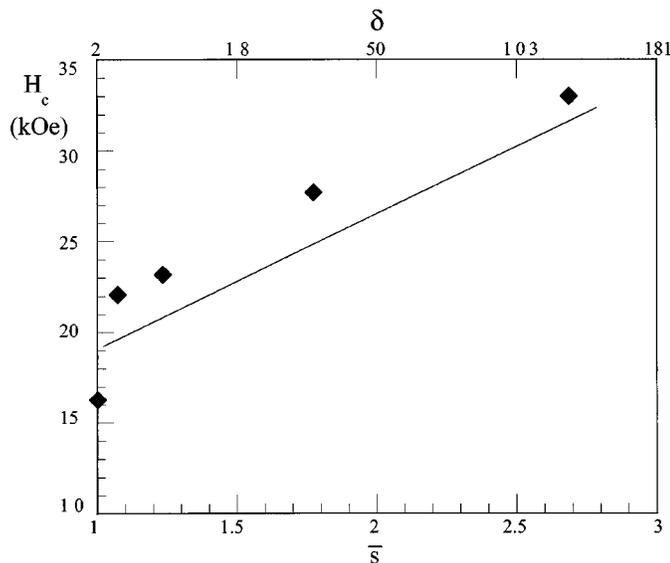


Fig. 2. Coercivity, H_c , as a function of relative average linear separation of the hard phase, \bar{s} , and neodymium composition, δ , for $\text{Nd}_\delta\text{Fe}_{13.1}\text{B}$.

the chemical composition. The average linear separation relative to the size of the hard magnetic grains (\bar{s}) is given by:

$$\bar{s} = \sqrt[3]{\frac{\text{volume of material}}{\text{volume of Nd}_2\text{Fe}_{14}\text{B}}} \quad (1)$$

The coercivity of the samples versus the relative average linear separation is shown in Fig. 2. The coercivity of the hard phase is determined as the high field peak in the susceptibility.

There is a rapid jump in the coercivity between $\text{Nd}_{2.05}\text{Fe}_{13.1}\text{B}$ and $\text{Nd}_{3.8}\text{Fe}_{13.1}\text{B}$. The detail of the change in coercivity between these two compositions can be found by plotting the data from previous work [4]–[6] in a similar manner to Fig. 2, this is shown in Fig. 3.

With little excess Nd the coercivity is fairly small. As the amount of Nd is increased the coercivity rises rapidly until

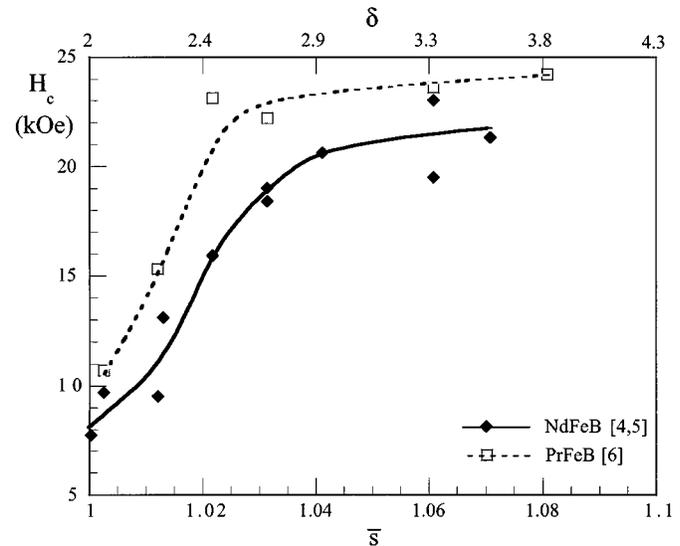


Fig. 3. Coercivity, H_c , as a function of relative average linear separation of the hard phase, \bar{s} , and rare earth composition, δ , for $\text{Nd}_\delta\text{Fe}_{13.1}\text{B}$ [4], [5] and $\text{Pr}_\delta\text{Fe}_{13.1}\text{B}$ [6].

$\delta \sim 2.9$. As more Nd is added the coercivity continues to rise but at a significantly reduced rate. These two regimes correspond to differences in the terms which dominate the intergranular interactions. For $\delta < 2.9$ the intergranular exchange interactions dominate. As more Nd is added the grains become exchange decoupled by the paramagnetic Nd phase and so with $\delta > 2.9$ the dipolar coupling between grains dominates and determines the coercivity.

The examination of the interdependence of the reversible and irreversible magnetization has been used to determine magnetization processes in magnetic materials [12]. The shape of the reversible magnetization curves (M_{rev} vs. M_{irr} at constant H) and the behavior of the parameter η defined as

$$\eta = \left. \frac{\partial M_{rev}}{\partial M_{irr}} \right|_H \quad (2)$$

can be compared to the behavior expected for coherent rotation and reversible domain wall movement.

The reversible magnetization curves obtained during demagnetization are shown in Fig. 4. $\text{Nd}_{2.05}\text{Fe}_{13.1}\text{B}$ and $\text{Nd}_{3.8}\text{Fe}_{13.1}\text{B}$ show a small minimum that is indicative of reversible domain wall processes occurring during the demagnetization [12]. The effect of these reversible domain wall processes also result in the positive values of η at low field as shown in Fig. 5. In general the peak in η reduces as the dilution is increased. The lower peak in η for $\text{Nd}_{2.05}\text{Fe}_{13.1}\text{B}$ is associated with its smaller grain size compared to the other samples [9].

The reversible magnetization behavior in $\text{Nd}_{38.1}\text{Fe}_{13.1}\text{B}$ and $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$ shows no evidence of stable domain walls during demagnetization and M_{rev} is due only to coherent rotation. The behavior of η for $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$ is very similar to that predicted for a Stoner–Wohlfarth assembly of NdFeB particles.

In sintered NdFeB magnets reversible magnetization behavior that is qualitatively similar to the Stoner–Wohlfarth behavior can be achieved if the nucleation field exceeds the

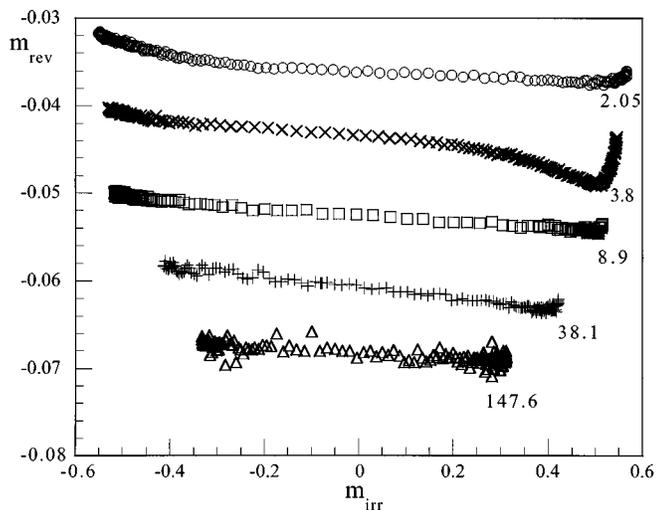


Fig. 4. Reversible magnetization (m_{rev}) curves for $\text{Nd}_\delta\text{Fe}_{13.1}\text{B}$ ($\delta = 2.05, 3.8, 8.9, 38.1$ and 147.6) at -3 kOe. m_{rev} and m_{irr} are in reduced units (M/M_s). Note curves shifted in m_{rev} for clarity.

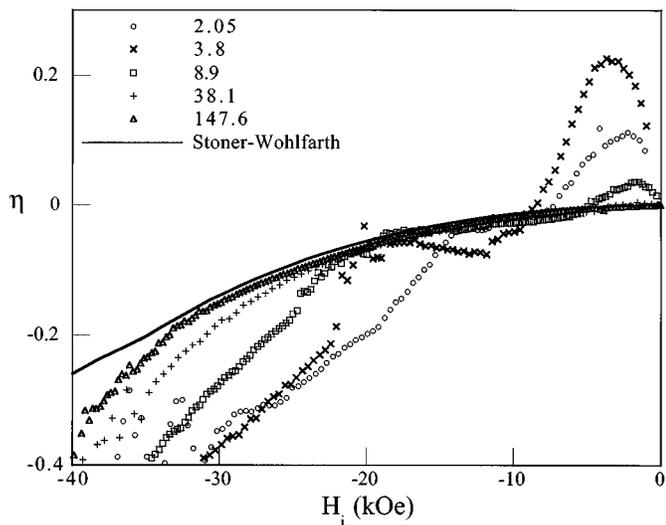


Fig. 5. η versus field for $\text{Nd}_\delta\text{Fe}_{13.1}\text{B}$ ($\delta = 2.05, 3.8, 8.9, 38.1, 147.6$) on demagnetization with the prediction from a Stoner–Wohlfarth model [12].

pinning field, and hence domain walls are no longer stable during demagnetization. This can be accomplished in materials showing domain wall pinning at room temperature by measuring the sample at low temperatures so that the anisotropy constant, and therefore nucleation field, is increased [13].

Investigations were carried out to see if the Stoner–Wohlfarth like behavior of $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$ was due to its increased coercivity or due to the dilution of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase so that the reduced dipolar fields were no longer sufficient to pin the domain walls. The reversible magnetization behavior was measured at high temperatures (373 and 484 K). At these temperatures the coercivity of the $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$ sample dropped to 23 kOe and 16 kOe respectively. If scaled to M_s and H_c the reversible magnetization curves and η curves are all similar to the room temperature measurements for $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$ and all exhibit Stoner–Wohlfarth like behavior. This suggests that the reversible magnetization behavior in $\text{Nd}_{147.6}\text{Fe}_{13.1}\text{B}$ is due to

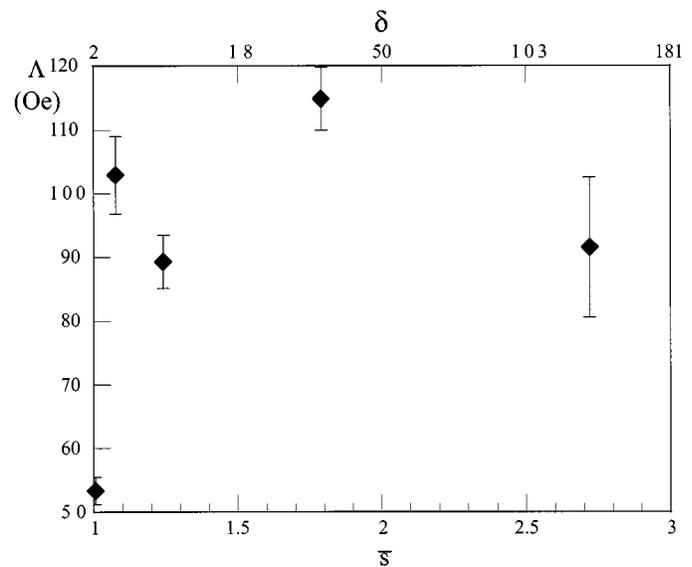


Fig. 6. Magnetic viscosity parameter (Λ) as a function of relative average linear separation of the hard phase, $\bar{\delta}$, and neodymium composition, δ .

the reduction in the dipolar interactions between grains caused by the dilution.

The magnetic viscosity parameter Λ :

$$\Lambda = \left. \frac{\partial H_i}{\partial M_{irr}} \right|_{M_{irr}} \quad (3)$$

was determined for each of the samples. For each of the samples the value of Λ was averaged over a range $-0.3 \leq m \leq 0.3$ and the results are plotted in Fig. 6. There is no consistently increasing variation of Λ with the average linear separation and hence with coercivity.

IV. CONCLUSIONS

The effective coercivity of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains increases as the dilution of the hard phase by Nd is increased. At high dilutions $\delta \geq 3.8$ the coercivity shows a linear relation to the relative average linear separation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. The reversible magnetization behavior approaches that predicted for a Stoner–Wohlfarth assembly of NdFeB particles as the dilution is increased.

REFERENCES

- [1] D. Givord and M. F. Rossignol, "Coercivity," in *Rare-Earth Iron Permanent Magnets*, J. M. D. Coey, Ed. Melbourne: Oxford Science Publications, 1996, ch. 5.
- [2] J. F. Herbst, " $\text{R}_2\text{Fe}_{14}\text{B}$ materials: Intrinsic properties and technological aspects," *Rev. Mod. Phys.*, vol. 63, pp. 819–898, 1991.
- [3] M. Sagawa and S. Hirosawa, "Magnetic hardening in sintered R–Fe–B permanent magnets," in *High Performance Permanent Magnet Materials Symp.* Pittsburgh, PA, USA: Mater. Res. Soc., 1987, pp. 161–179.
- [4] W. B. Muir, Z. Altounian, T. Gou-hua, and C. Wan-rong, "Magnetic properties of rapidly crystallized Nd–Fe–B glassy alloys," *J. Magn. Magn. Mater.*, vol. 81, pp. 168–172, 1989.
- [5] I. Ahmad, H. A. Davies, and R. A. Buckley, "The effect of Nd constant on the structure and properties of melt spun Nd rich NdFeB alloys," *J. Magn. Magn. Mater.*, vol. 157/158, pp. 31–32, 1996.
- [6] G. Mendoza-Suárez, H. A. Davies, and J. I. Escalante-García, " jH_c , J_r and $(\text{BH})_{\text{max}}$ relationship in PrFeB melt spun alloys," *J. Magn. Magn. Mater.*, vol. 218, pp. 97–102, 2000.

- [7] E. C. Stoner and E. P. Wohlfarth, "A mechanism of magnetic hysteresis in heterogeneous alloys," *Philos. Trans. R. Soc. London Ser. A*, vol. A240, pp. 599–642, 1948.
- [8] E. Girt, K. M. Krishnan, G. Thomas, and Z. Altounian, "Nanocomposite Nd-rich Nd–Fe–B alloys: Approaching ideal Stoner–Wohlfarth type behavior," *Appl. Phys. Lett.*, vol. 76, pp. 1746–1748, 2000.
- [9] E. Girt, K. M. Krishnan, G. Thomas, E. Girt, and Z. Altounian, "Coercivity limits and mechanism in nanocomposite Nd–Fe–B alloys," *J. Magn. Mater.*, to be published.
- [10] D. X. Chen, J. A. Brug, and R. F. Goldfarb, "Demagnetization factors for cylinders," *IEEE Trans. Magn.*, vol. 27, pp. 3601–3619, 1991.
- [11] L. Folks and R. Street, "Analysis and interpretation of time dependent magnetic phenomena," *J. Appl. Phys.*, vol. 76, pp. 6391–6395, 1994.
- [12] D. C. Crew, R. Street, and P. G. McCormick, "An investigation of reversible magnetization in NdFeB," *J. Appl. Phys.*, vol. 86, pp. 3278–3284, 1999.
- [13] D. C. Crew, R. Lewis, and D. O. Welch, "The effect of temperature on the magnetization reversal mechanism in PrFeB," *J. Appl. Phys.*, vol. 87, pp. 4783–4785, 2000.