Road to Phase-specific Magnetism in Nanocomposite Magnetic Materials

D. Haskel,[1] Y. Choi,[1] Z. Islam,[1] D.R. Lee,[1] J.C. Lang,[1] D. Keavney,[1] G. Srajer,[1] B.M. Ma[2]

[1]Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL, U.S.A.

[2]Magnequench, Inc., Research Triangle Park, NC, U.S.A.

Introduction

Permanent magnetic materials have evolved dramatically during the past few decades. From Ba-Sr ferrites to SmCo and $Nd_2Fe_{14}B$ rare-earth-based magnets, the magnetic flux density per unit volume has systematically increased as higher remanent magnetizations and coercive fields have been attained in artificially engineered materials. A good permanent magnet is one that has high remanent magnetization and is difficult to demagnetize. In the case of $Nd_2Fe_{14}B$, for example, the Fe atoms (which are the majority in the compound) dominate the remanent magnetization, while the large orbital moment at the Nd sites introduces magneto-crystalline anisotropy through spin-orbit coupling, yielding high coercivity [1].

New conceptual designs for permanent magnets, in which separate phases of soft and hard magnetic materials are brought into contact, are being investigated. The soft magnetic material provides high magnetization, while the hard magnetic material provides coercivity. If the two phases are sufficiently coupled to one another (by exchange), the composite system behaves like a unit with both desired qualities. This concept was successfully tested in the artificial, layered structures of so-called "exchange spring magnets," in which thin films of, for example, soft Fe and hard Sm_2Co_7 are epitaxially grown, resulting in strong ferromagnetic coupling at their interface [2]. Such thin film magnets will likely prove useful in a variety of applications. Other applications, however, require large magnet sizes that can be achieved only through the synthesis of large-scale bulk materials. A large effort in the area of nanocomposite magnets is underway, where the material microstructure is controlled to yield nanoscale segregation of soft and hard magnetic phases. The quality of the interfacial exchange coupling between these grains is the key to achieving the desired improved magnetic properties.

The $Nd_2Fe_{14}B/\alpha$-Fe compound is a prototype nanocomposite material for new-generation permanent magnets. Theoretically, the (2-14-1) phase provides hardness, while the soft α-Fe phase enhances the magnetization. Understanding the properties of the nanocomposite requires the ability to determine synthesis-induced changes in the magnetic properties of each phase and in their coupled behavior. While changes in the Nd-containing (2-14-1) phase can be addressed through element-specific x-ray magnetic circular dichroism (XMCD) measurements at Nd absorption edges, information on the α-Fe phase is masked by the appearance of Fe in both phases. The concept proposed here is to separate the magnetic signals of each phase by measuring helicity-dependent resonant Bragg scattering at selected Q (scattering) vectors that isolate one phase from the other in reciprocal space.

We demonstrate that despite the abundance of Bragg reflections associated with the large unit cell of the (2-14-1) phase, the separation of the phases in reciprocal space is achievable. The challenges involved in retrieving magnetic information in the diffraction channel from these polycrystalline samples are outlined here.

Methods and Materials

The two alloys used in these measurements are $Nd_{11.8}Fe_{82.3}B_{5.9}$ and $Nd_9Fe_{86.5}B_{4.5}$. The former corresponds to the stoichiometric (2-14-1) phase, while the latter includes about 25% of an α-Fe secondary phase. Magnetization measurements show that the nanocomposite with the 25% α-Fe phase has about 10% increased remanent magnetization. The coercivity, however, is decreased relative to that of the stoichiometric sample by about 15%, which is probably indicative of weak interphase coupling. The polycrystalline powders were embedded in a thermoplastic resin and cast into discs for stability during saturation in a 4-T magnetic field, applied in the plane of the discs. Measurements were done in remanence at room temperature at beamline station 4-ID-D at the APS. Higher energy harmonics were rejected with double Pd mirrors at 6.5 mrad. Powder diffraction was collected by using the powder mode of SPEC. Fluorescence background, which was the dominant source of background for the Fe K-edge resonant diffraction measurements, was rejected first with a Ge(111) analyzer crystal and later with an energy-dispersive Ge solid-state detector. The latter allowed us to simultaneously measure diffraction and absorption in fluorescence geometry. Helicity-dependent resonant Bragg scattering was attempted by reversing the x-ray helicity at each energy point through Fe K-edge and Nd $L_{2,3}$-edge resonances while maintaining a Bragg diffraction condition of either one of the phases. XMCD measurements were done simultaneously by measuring the asymmetry in the fluorescence for opposite helicities of circularly polarized CP x-rays.

Discussion

Figure 1 shows powder diffraction data from the two samples collected at E = 7.112 keV by using an energy-dispersive solid-state detector (single-element Ge) that isolates the elastic scattered x-rays from the fluorescence background. Total counts in the detector were less than 25 kilocounts per second. The vertical lines indicate simulated Bragg reflections of the (2-14-1) phase. The high-symmetry α-Fe phase has only one Bragg peak in this angular range. Peak broadening is intrinsic, determined by the nanocrystalline nature of the sample (particle size). Only slightly sharper peaks were measured with a Ge(111) analyzer crystal. To prove that the two phases can be practically separated in reciprocal space despite the abundance of (2-14-1) peaks and their large intrinsic broadening, we performed resonant scattering measurements through the Nd L_3 and Fe K edges at fixed Q values corresponding to (2-14-1) and α-Fe phases. Figure 2 shows the results of these measurements. While all three Bragg peaks resonate through the Fe K-edge resonance (both phases contain Fe), the α-Fe (110) Bragg peak does not significantly resonate through the Nd L_3 resonance. This is expected, since this phase does not contain Nd atoms, but it proves the case that the (2-14-1) phase contributions at this Q vector are indeed very small (the resonance response is about 5% of that measured at the 214 and 410 Bragg peaks of the 2-14-1 phase). The separation of the Fe magnetic signals in each phase was attempted by helicity-dependent Bragg scattering measurements, whereby the x-ray helicity is switched between left and right at each energy point while the energy is scanned through the Fe K-edge resonance,
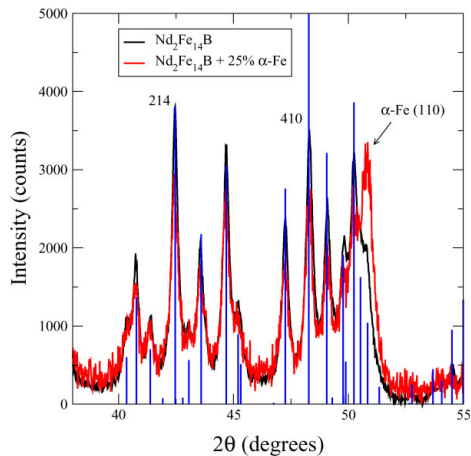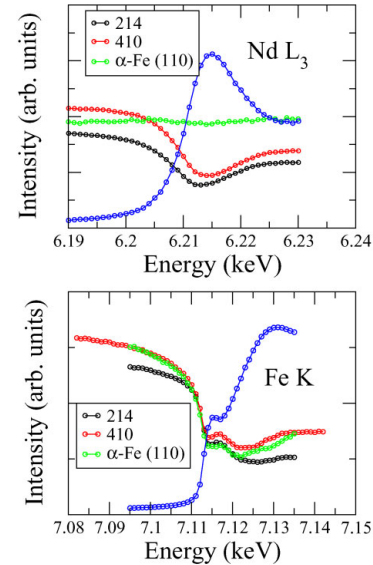

FIG. 2. *Resonance diffraction scans through Nd L_3 edge (top) and Fe K edge (bottom) at selected Bragg peaks of the (2-14-1) and α-Fe phases. The absence of resonant behavior in the α-Fe (110) Bragg peak through the Nd L_3 edge indicates that the two phases can be separated in reciprocal space. Phase-specific Fe magnetism can, in principle, be obtained by helicity-dependent resonance Bragg scattering for selected reflections that isolate one or the other phase.*

maintaining a given Bragg condition. Despite the clear remanent magnetization of the samples (Fig. 3), we were unable to reliably measure a dichroic effect in the elastic scattering channel for these powder samples. The dichroic effect at the Fe K edge is about 0.3% and hence requires significant counting statistics (10^6 counts). The weak intensity of the powder peaks, at approximately 1000 counts per second with the polarizing diamond phase retarder in the beam, requires long counting times and stability.

The difference in the scattering intensity for the left and right helicities theoretically removes the pure (and much stronger) charge scattering signal, which, in ferromagnets, occurs at the same scattering vector as the charge-magnetic interference signal nominally measured in the difference signal [3]. However, a light asymmetry in the linear polarization content of the beam for nominally left and right helicities can result in pure charge-scattering contamination of the charge-magnetic interference signal. Since charge scattering is independent of the applied field direction and since charge-magnetic scattering reverses sign upon field reversal, this contamination can be removed by reversing the applied magnetic field. Applying this method for the hard nanocomposites requires a 4-T magnet/diffractometer setup with large angular acceptance, which was not available. Instead, we

FIG. 1. *X-ray powder diffraction of nanocomposite samples (E = 7.112 keV). Data were collected with an energy-dispersive Ge detector to isolate elastic scattered x-rays from fluorescence x-rays. Vertical lines are simulated Bragg peak positions for the (2-14-1) phase. Broadening is intrinsic, due to the nanocrystalline nature of the samples.*
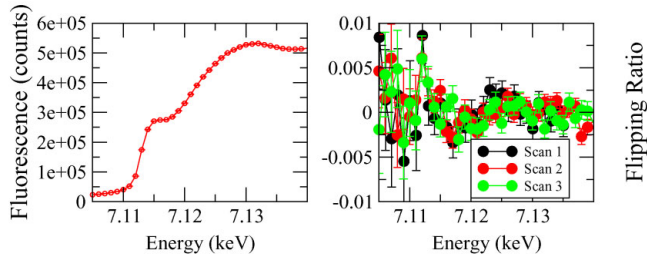
FIG. 3. Absorption (left) and remanent XMCD (right) signals at the Fe K edge of the $Nd_9Fe_{86.5}B_{4.5}$ (25% α-Fe) nanocomposite sample. Data were measured in fluorescence geometry with an energy-dispersive Ge detector. The remanent magnetic signal is comparable to that of a pure Fe sample.

reversed the direction of remanent magnetization relative to the incidence photon wave vector by rotating the sample 180°. Since the resonant diffraction through the Fe K edge is strongly damped by absorption (Fig. 2), slight changes in the scattering geometry/irradiated area that are introduced with such rotations invalidate the subtraction procedure. The ability to reverse the applied field direction without changing the sample position is essential to measure this signal reliably. Recently, we used this method to measure Fe K-edge helicity-dependent Bragg scattering in soft magnetic single crystals of Fe_3O_4 (magnetite). Additional gains can be achieved by using area detectors and integrating over the powder rings to improve counting statistics and decrease the measurement time. Further improvements should also be attained by means of digital lock-in methods to detect the energy-dependent amplitude variations in the helicity-modulated scattered intensity.

Acknowledgments

References

[1] J.F. Herbst, Rev. Mod. Phys. **63**, 819 (1991).
[2] J.S. Jiang et al., IEEE Trans. Magn. **35**, 3229 (1999).
[3] D. Haskel et al., Phys. Rev. Lett. **87**, 207201 (2001).