Effect of zirconium addition and microstructure refinement on the local magnetic properties of the $Nd_2Fe_{14}B$-based alloys

A P Menushenkov[1,4], V G Ivanov[1], I V Shchetinin[2], D G Zhukov[2], V P Menushenkov[2], I A Rudnev[1], F Wilhelm[3], A Rogalev[3] and A G Savchenko[2]

[1] National Research Nuclear University "MEPhI" (Moscow Engineering Physics Institute), Kashirskoe sh. 31, 115409 Moscow, Russia
[2] National University of Science and Technology "MISIS", Leninskiy pr. 4, 119049 Moscow, Russia
[3] European Synchrotron Radiation Facility (ESRF), CS40220, F-38043 GrenobleCedex 9, France

E-mail: APMenushenkov@mephi.ru

Abstract. The effect of Zr addition and microstructure refinement on the local magnetic properties of intermetallic compound $Nd_2Fe_{14}B$ in micro- and nano-crystalline alloys was studied by X-ray Magnetic Circular Dichroism. XMCD spectra were measured at the beamline ID-12 of ESRF (Grenoble, France) at the Fe-*K* and Nd-$L_{3,2}$ absorption edges in a magnetic field of 10 T at room temperature. The noticeable differences of XMCD amplitude signals, measured on the samples with different content of Zr and various parameters of the microstructure were found, which clearly indicates the influence of the both factors on the magnetic state of Nd and Fe ions in the $Nd_2Fe_{14}B$-based compounds.

1. Introduction

$Nd_2Fe_{14}B$-based alloys belong to the most popular and commercially used materials for highest performance permanent magnets [1]. Ability to change the properties of these alloys by the addition of different doping elements, as well as the use of various types of heat treatment for directed changes of their microstructure can significantly expand the scope of their practical use. For example, the Zr addition into $Nd_2Fe_{14}B$ increases the coercivity and remanence of the respective alloys [2]. Similar effect is also observed with grain size decreasing to the nano-scale range at melt spinning.

In the present work the comparative study of the effect of nano-structuring and Zr addition on local magnetic properties of $Nd_2Fe_{14}B$ alloys was performed by means of X-ray Magnetic Circular Dichroism (XMCD) at the *K*-edge of Fe and $L_{2,3}$-edges of Nd.

2. Experiment

Samples of hard magnetic alloys with a nominal compositions $Nd_2Fe_{14}B$ and $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ were prepared by copper mold casting and quenching from the liquid state on the rapidly rotating steel disc. X-ray diffraction (XRD) studies were carried out using the diffractometer Rigaku Ultima-IV focusing a Bragg-Brentano, with $Co_{K\alpha}$-radiation and a graphite monochromator in the diffracted beam.

[4] To whom any correspondence should be addressed.

The grain size in the micro- and nano-structure phases was detected by a JEM-1400 transmission electron microscope (TEM). Measurements of magnetic properties were performed using physical property measurement system PPMS (EverCoolII, Quantum Design) in fields up to 9 T.

To get a deeper insight into microscopic magnetic properties of these systems, we have used an element-selective technique, such as X-ray Magnetic Circular Dichrtoism (XMCD) [3-5]. XMCD spectra at the $L_{2,3}$ edges of Nd and at the *K*-edge of Fe have been measured at the ID-12 beamline of the European Synchrotron Radiation Facility, Grenoble, France [5]. The source was the helical undulator APPLE-II, which emits either right or left circularly polarized X-rays with a polarization rate in excess of 97%. The X-ray absorption spectra at the $L_{2,3}$-edges of Nd and at the *K*-edge of Fe were recorded using the total fluorescence yield detection mode in backscattering geometry. XMCD spectra were obtained as direct difference of absorption spectra recorded with right and left-circularly polarized photons and a magnetic field (10 Tesla) generated by a superconducting solenoid was applied along the X-ray beam direction. To make sure that the obtained XMCD spectra are free of any experimental artefact, the same measurements were repeated for opposite direction of applied magnetic field. The samples were kept at room temperature. Since the penetration depth of the X-rays is smaller than the sample thickness, the recorded XAS and XMCD spectra were corrected for so-called self-absorption effects. The correction took into account the chemical composition and thickness of the sample, incidence angle of the X-ray beam, and the solid angle of the detector [6].

3. Results and discussion

According to XRD studies the microcrystalline as-cast $Nd_2Fe_{14}B$ and $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ samples consist of single $Nd_2Fe_{14}B$ phase ($P4_2/mnm$, tP68). The measurement of magnetic properties of as-cast samples exhibited nearly zero coercivity and remanence. Quenching from the liquid state led to the formation of an amorphous phase in $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ sample together with small amount of soft magnetic phases, such as α-Fe and Nd_2Fe_{17}. Melt spinning resulted in an increase of the coercive force and residual magnetization, however, the magnetic hysteresis loop exhibits an inflection that could be due to the presence of soft magnetic amorphous phase (Fig. 1).

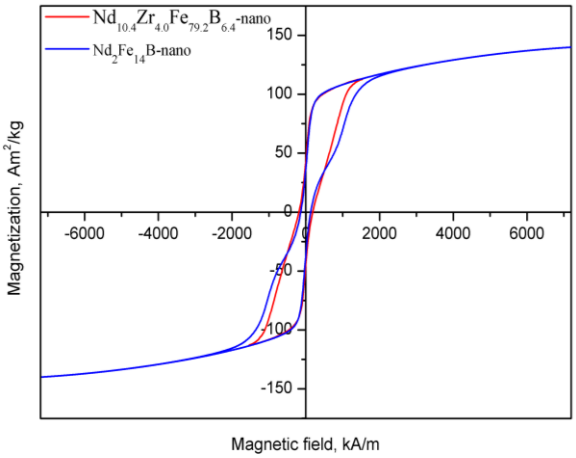

Figure 1. Magnetic hysteresis loops of melt spun $Nd_2Fe_{14}B$ and $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ samples

The results of a comparative analysis of XMCD spectra of Zr-doped and undoped $Nd_2Fe_{14}B$ samples are presented below. The effect of melt spinning of $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ alloy on element selective magnetic properties is also analyzed.

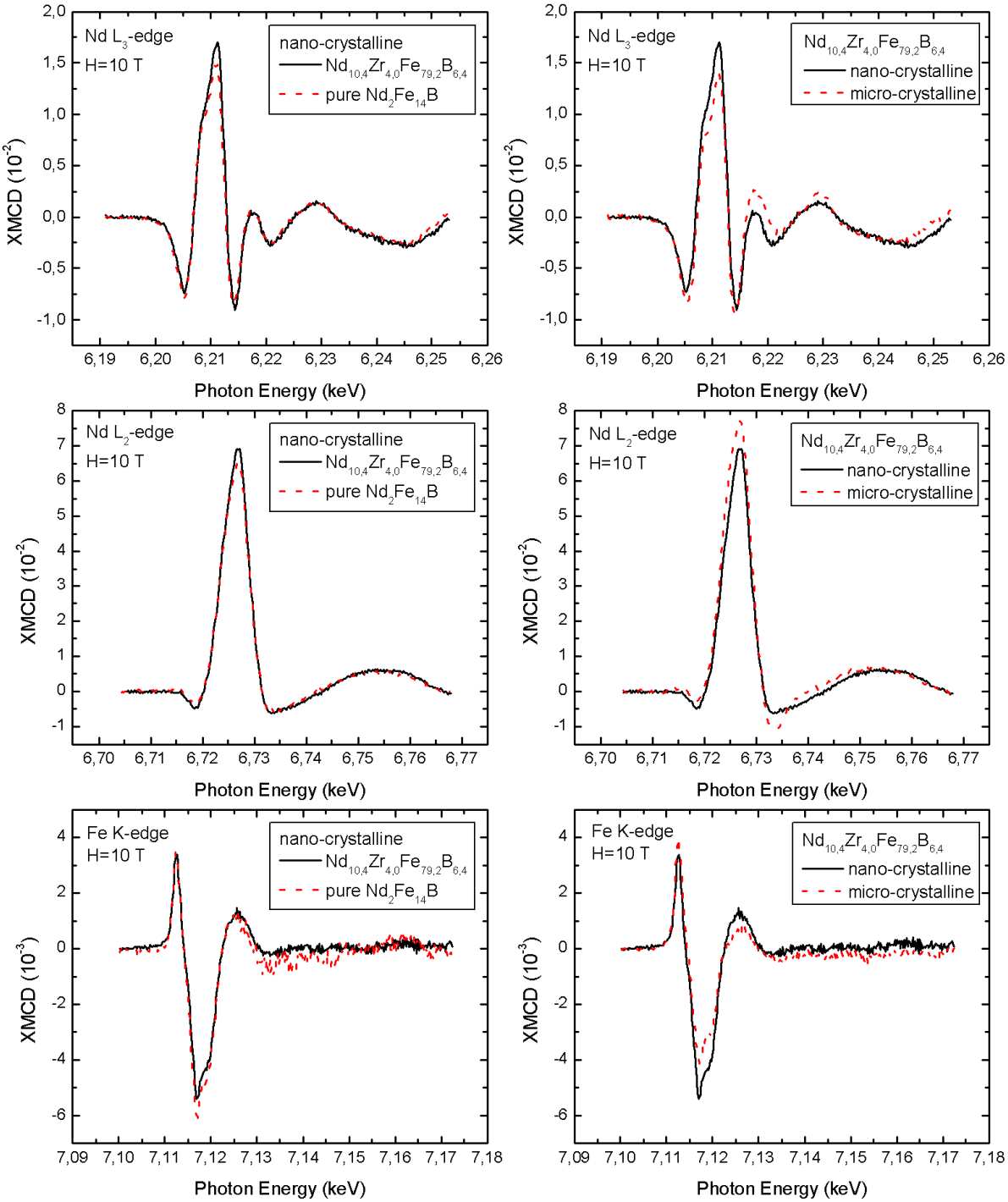

Figure 2. Comparative XMCD spectra measured at Nd-$L_{3,2}$ and *K*-Fe absorption edges in a magnetic field of 10 T for doped $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ and pure $Nd_2Fe_{14}B$ nano-crystalline samples (left panel), and for nano- and micro-crystalline samples of $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ (right panel).

1.1. Effect of Zr *addition to the* $Nd_2Fe_{14}B$ *on XMCD spectra of nano-crystalline samples.*
XMCD spectra obtained for nano-crystalline samples at Nd-$L_{3,2}$ absorption edges have a greater amplitude for Zr-doped $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ than for undoped $Nd_2Fe_{14}B$ whereas the opposite effect is observed at the *K*-edge of Fe (Fig. 2, left panel). The highly structured XMCD spectra at the L_3 absorption edge of Nd are due to a variety of electronic transitions involved. The first minimum

(prepeak) corresponds to the quadrupolar transition $2p_{3/2} \rightarrow 4f_{5/2}$, and the main maximum – to dipolar transition $2p_{3/2} \rightarrow 5d_{5/2}$ [7]. The oscillating structure afterwards, apparently, corresponds to the transitions to hybridized Nd-Fe *p-d* band and/or manifests multiple scattering of a photoelectron wave from the nearest neighbors, so-called magnetic EXAFS. XMCD signal at the L_2 absorption edge of Nd is characterized by the pronounced main maximum, corresponding to dipolar transition $2p_{1/2} \rightarrow 5d_{3/2}$, and much weaker quadrupolar contributions [7]. The shape of the Fe *K*-edge XMCD signal could also be disentangled into quadrupolar and dipolar transitions, but this assignment is usually quite ambiguous.

Thus, the XMCD results indicate that doping of $Nd_2Fe_{14}B$ phase by Zr affects the magnetic state of both Nd and Fe sublattices via changes the overall electronic subsystem, in particular, the 5*d* states of Nd and the 4*p* states of Fe.

1.2. Effect of crystal grain's size of $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ *alloys on XMCD spectra.*

According to the TEM data an average grain size was estimated as 5-10 micron and 10-20 nm in micro- and nano- crystalline samples. Comparing XMCD spectra for micro- and nano- crystalline $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$ (Fig. 2, right panel), one can see that for nano-crystalline sample the signals are greater at Nd-L_3 and *K*-Fe edges and smaller at Nd-L_2 edge. This is apparently due to the different magnetic state of Nd and Fe ions in the bulk and at grain boundaries, since the transition to nanostructured state leads to growing contribution of ions at the grain boundaries.

It should be noted that XMCD spectra change differently under influence of nano-structuring and Zr doping.

4. Conclusion

Experimental *K*-Fe and Nd-$L_{3,2}$ XMCD spectra were measured in magnetic field of 10 T for nano- and micro-crystalline magnetic intermetallides $Nd_2Fe_{14}B$ and $Nd_{10,4}Zr_{4,0}Fe_{79,2}B_{6,4}$.

Noticeable differences in the amplitudes of XMCD signals were found for the samples with addition of zirconium and for nano-crystalline samples. This indicates the important role of the both factors in forming of the magnetic state of Nd and Fe ions in $Nd_2Fe_{14}B$-based compounds.

The results are helpful for understanding the magnetic moment formation and nature of the high coercivity state in $Nd_2Fe_{14}B$-based hard magnetic alloys and may be used to improve their functional magnetic properties.

Acknowledgements

The European Synchrotron Radiation Facility is acknowledged for providing beamtime in the framework of the project HC-2600. This work was partly supported by the Ministry of Education and Science of the Russian Federation within the framework of the state assignment 3.1540.2014/K and project 14.579.21.0043 (unique number of agreement RFMEFI57514X0043).

References

[1] Matsuura Y 2006 *JMMM* **303** 344
[2] Bao XQ, Zhu J, Li W, *et al.* 2009*Journal Rare Earths* **27** 843
[3] Sarafidis C, Wilhelm F, Rogalev A, *et al.* 2009 *J. Phys.: Condens. Matt.* **21** 236001
[4] Van der Laan G, Figueroa A I 2014 *Coordin. Chem. Rev.* **277-278** 95
[5] Rogalev A, Wilhelm F 2015 *The Physics of Metals and Metallography***116** 1285
[6] Wilhelm F, Jaouen N, Rogalev A, *et al.* 2007 *Phys. Rev.* B**76** 024425
[7] Bartolomé F, Tonnerre J M, Sève L, *et al.* 1998 *J. Appl. Phys.* **83** 7091