Negative Magnetization in $\text{NdFe}_x\text{Ga}_{1-x}\text{O}_3$ Studied by XMCD

Fernando Bartolomé^{1,a*}, Laura Badía-Romano^{1,b}, María Parra-Borderías^{1,c},
Javier Rubín^{2,d}, Fabrice Wilhelm^{3,e}, Andrei Rogalev^{3,f} and Juan Bartolomé^{1,g}

¹ICMA-CSIC-Universidad de Zaragoza and Departamento de Física de la Materia Condensada,
Universidad de Zaragoza 50009, Zaragoza, Spain

² ICMA-CSIC-Universidad de Zaragoza and Departamento de Ciencia de Materiales e Ingeniería
Metalúrgica, Universidad de Zaragoza 50018, Zaragoza, Spain

³European Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France

^abartolome@unizar.es, ^blbadia@unizar.es, ^cmariapbor@gmail.com, ^djrubin@unizar.es,
^ewilhelm@esrf.fr, ^frogalev@esrf.fr, ^gbarto@unizar.es

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Abstract. Negative Magnetization (NM) in $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$ is reported using magnetization, ac-susceptibility and x-ray Magnetic Circular Dichroism measurements. The mechanism of NM in $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$ is the blocking of the weak-ferromagnetic domain walls and the polarization of the paramagnetic Nd sublattice by that of Fe at low temperatures.

Introduction

Magnetization reversal in magnetically ordered systems consists of a crossover from a positive value (parallel to the applied field) to a negative value (antiparallel to the applied field) as temperature is reduced below the magnetic ordering temperature. This phenomenon is also known as Negative Magnetization (NM). It was observed more than five decades ago in spinel ferrites [1] and more recently in other complex ferrimagnets or canted antiferromagnets (AF), including oxide perovskites such as manganites [2], chromites [3], or vanadates [4].

A recent review covers up-to-date experimental results [5], classifying the different mechanisms that give rise to NM. In particular, a special case corresponds to the existence of negative exchange between ferromagnetic/canted-antiferromagnetic and paramagnetic sublattices, namely, one of the sublattices remains paramagnetic below the magnetic ordering transition of the compound. The perovskite oxides RMO_3 where R = rare earth and M = magnetic transition metal, present interesting cases, since the exchange interactions follow the hierarchy of M-M, M-R, and R-R in descending strength [6]. In all cases the M-R coupling is capable of polarizing the paramagnetic R magnetic moment, while the R-R interaction gives rise to the R sublattice magnetic ordering at temperatures around 1 K. On the other hand, magnetic dilution of the M sublattice weakens the effective M-R interaction [7,8].

Element selective magnetometry is provided by the synchrotron based x-ray magnetic circular dichroism (XMCD). It is an ideal probe to study NM in this case, since one can directly observe the orientation of the R and M sublattices independently. This is of paramount relevance in understanding the contributions to the magnetization originated from different magnetic sublattices, R and M. In previous work we employed XMCD, measured at the Mn K-edge and Nd $L_{2,3}$ edges, to understand NM in the non-stoichiometric $\text{NdMnO}_{3.11}$ [8]. It was shown that the sublattice magnetization of Nd and Mn remain parallel at all temperatures, thus proving that competition is not the mechanism yielding NM in that case, but instead it is caused by compensation of two different magnetic phases.

In the present work we have studied one of the members of the diluted orthoferrite series $\text{NdFe}_x\text{Ga}_{1-x}\text{O}_3$, where the non-magnetic Ga randomly substitutes Fe [9]. It has been chosen since preliminary magnetization measurements showed that it undergoes a NM crossover. In contrast, the NdFeO_3 has a spin reorientation transition between 70 and 160 K, but it does not show NM as temperature is decreased. In both cases Nd remains paramagnetic, though polarized by the Fe

sublattice, down to the lowest temperature measured ($T = 2$ K) [9]. Thus, the substitution of Fe by Ga is causing the NM in the diluted systems. Magnetization measurements combined with XMCD allowed us to shed light on the NM mechanism in this paradigmatic case.

Experimental

Magnetization measurements were performed on the $x = 0.8$ compound in a SQUID magnetometer. The $M(T)$ data were obtained in the warming process, after cooling in zero magnetic field (ZFCW), and in a field (FCW). The ZFCW data measured with $H = 300$ Oe show magnetic positive magnetization, and the presence of the spin reorientation transition about 75 K, in agreement with previous measurements. Indeed, from a neutron diffraction study [9], it is known that the compound undergoes a para-antiferromagnetic transition at $T_N = 520$ K to the $G_x F_z$ spin configuration. This is a canted antiferromagnetic phase with a net magnetization of $1.3 \mu_B$ per Fe atom along the c axis. At zero applied field, a spontaneous spin reorientation transition sets in at $T_{SR1} = 88$ K down to $T_{SR2} = 53$ K. Below this temperature the spin configuration is $G_z F_x$, which is a canted antiferromagnet with net magnetization along the a axis.

In contrast, in the FCW measurement, performed at $H = 300$ Oe, NM clearly appears at low temperature, and crosses over to positive magnetization at $T_{cross} = 11$ K, recovering the $M(T)$ curve in the spin reorientation transition temperature region (Fig. 1a). In a second FCW measurement performed at $H = 3$ kOe the NM behavior is completely destroyed by the applied field, showing just positive magnetization (Fig. 1b).

Following a ZFCW process, ac susceptibility as a function of temperature, at varying frequency ($9 < f < 900$ Hz) was measured to explore the spin dynamics in the neighborhood of T_{SR} and T_{cross} (Fig. 2). While at T_{cross} no feature is observed, in the SRT region a low temperature anomaly with two peaks at T_{SR1} and T_{SR2} , associated with the onset and completion of the SRT appears. A frequency dependent anomaly in the 100-150 K range is related to domain wall motion. Indeed, magnetic domains appear as soon as there is a non-zero net magnetic moment caused by the canting of the spins (F_z component at 150 K) [10]. The motion of the walls separating the different magnetic domains is driven by the ac exciting field giving rise to a non-zero out-of-phase component in the ac susceptibility at temperatures much higher than the SRT. The thermal dependence of the magnetic domain wall relaxation time constant follows an Arrhenius law with activation energy $U/k_B = 1629$ K, and $\tau_0 = 5 \times 10^{-9}$ s. Then, at temperatures of the order of 10 K, or below, the relaxation time becomes $\tau \approx 10^{60}$ s, i.e., the domain walls are strongly anchored to the lattice defects.

The XMCD measurements were performed at the ESRF ID12 beamline by recording the total fluorescence yield in backscattering geometry. The Fe K-edge and the Nd L_2 -edge XMCD spectra were measured after a FCW process at $H = 300$ Oe, at $T = 2$ K, well within the NM region (point A in Fig. 1(a)). XMCD was also measured in the Fe K-edge at $T = 60$ K, between the crossing temperature T_{cross} and T_{SR2} . (point B in Fig. 1(a)). The Fe K-edge XMCD probes the empty 4p states, and it is only due to the spin-orbit coupling. It is non-zero and reflects the uncompensated Fe sublattice magnetization caused by canting. The XMCD spectrum resembles that of $ZnFe_2O_4$ nanoferrite for the Fe(III) oxidation state at $T = 10$ K [12]: i.e., a minimum at $E_{photon} \approx 7126$ eV and a maximum at ≈ 7129 eV (see arrows in Fig. 3, points A and B), which implies that the non-zero Fe sublattice magnetization is aligned parallel to the applied field. It is noteworthy that it remains oriented parallel to the applied field above and below T_{cross} (at both points A and B).

In contrast, the Nd- L_2 edge XMCD signal in point A shows a minimum at $E_{photon} \approx 6725$ eV, that is indicative of antiparallel orientation of the Nd moment with respect to the applied field. Moreover, when the sample is warmed to state B, the Nd XMCD signal falls below the error bar. This proves that at $T = 60$ K the thermally induced fluctuations on the Nd moment dominates the polarizing effect of the Fe sublattice interaction.

When a field of $H = 3$ kOe is applied at $T = 2.2$ K (point C in Fig. 1b) NM is destroyed, while the XMCD for Nd reverses sign and yields a strong signal (Fig. 3. point C, right), thus it has a component parallel to the applied field. Curiously, the Fe K-edge XMCD still shows a large positive peak at $E_{\text{photon}} \approx 7129$ eV and the peaks at and after the white line energy maximum (not shown) maintain their sign (Fig. 3, point C). Thus the Fe moment has a parallel component to the applied field, but different to the one at $H = 300$ Oe. Thus the 3kOe field essentially reorients the Fe and Nd moments to yield parallel components to the field. It is interesting to note that this result nicely supports the field induced reorientation in a NdFeO_3 single crystal measured with THz time-domain spectroscopy, where it is shown that a field of the order of 2 kOe is sufficient to provoke the field induced spin reorientation [11].

Discussion and conclusions

From the previous works [12], [13] and present experimental results on $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$ one may conclude that during the FCW process: a) weak-ferromagnetic magnetic domains are formed below T_N that anchor at the defects in the sample, b) the domain walls become blocked at about 100 K ($\tau \approx 6 \times 10^{-2}$ s). Within the domains the magnetic moment of the Nd ion is polarized by uncompensated antiferromagnetic coupling to the Fe sublattice, and it grows in magnitude but remains oriented opposite to the Fe net moment. At the crossover temperature the polarized Nd sublattice magnetization compensates that of the Fe sublattice. Decreasing the temperature to $T < T_{\text{cross}}$, the Nd magnetization becomes larger than that of Fe, while it remains antiparallel, thus giving rise to the NM. In the undiluted NdFeO_3 , in the absence of the defects as introduced by the Ga substitution in the present work, no blocking takes place and no NM appears.

Therefore, we conclude that the mechanism for NM differs from that found by XMCD on $\text{NdMnO}_{3.1}$, which was based on the appearance of ferromagnetic clusters within the sample [2]. We cannot exclude that there is some clustering in the stoichiometric $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$, where Ga atoms were introduced to weaken interactions, similar to those found in the non stoichiometric $\text{NdMnO}_{3.1}$, but they seem not to play a role in the NM of $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$. Thus, the present XMCD study unambiguously demonstrates that the mechanism of NM in $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$ is the appearance of a metastable weak-ferromagnetic phase and the polarization of the paramagnetic Nd by AF exchange interaction with the Fe sublattice.

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Fig. 1. Magnetization of $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$. a) FCW measurement under $H = 300$ Oe (blue squares). ZFCW measurement under $H = 300$ Oe (green circles). b) FCW measurement under $H = 3$ kOe (red circles).

Fig. 2. Out-of-phase component of the ac-susceptibility of $\text{NdFe}_{0.8}\text{Ga}_{0.2}\text{O}_3$ as a function of temperature for three different excitation frequencies.

Fig. 3. XMCD measurements at the Fe K-edge (left) and at the Nd L₂ edge in NdFe_{0.8}Ga_{0.2}O₃ (right). A, B and C states refer to the points in Fig. 1.