

Element-specific magnetometry on negatively magnetized $\text{NdMnO}_{3+\delta}$

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Field-cooled x-ray magnetic circular dichroism experiments at several temperatures at the Mn K and Nd $L_{2,3}$ edges on nonstoichiometric $\text{NdMnO}_{3.11}$ have been performed. Our results show that Nd and Mn net magnetizations are parallel along the whole range of temperatures, ruling out the competition between the Nd and Mn sublattices as the origin of negative magnetization in $\text{NdMnO}_{3+\delta}$. © 2005 American Institute of Physics. [DOI: 10.1063/1.1850810]

The observation of a negative magnetization (opposed to the magnetic field) after a field-cooling (FC) process was described more than four decades ago in some spinel ferrites¹ and more recently in other complex ferrimagnetic systems as molecular magnets,² “fanned” amorphous alloys,³ or irradiated garnets.⁴ In the last years, negative magnetization has been found in non-stoichiometric $\text{NdMnO}_{3+\delta}$,⁵ and $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$,⁶ among other manganites.^{7–11}

All of these systems are complex ferri- or canted antiferromagnetic (AF) systems with at least two magnetic sublattices and some degree of disorder (structural or chemical). In most of the cases, the magnetization, $M(T)$, measured in a field-cooled process (FC) follows the general behavior shown for $\text{NdMnO}_{3.11}$ in Fig. 1. If the sample is cooled under a sufficiently high applied magnetic field, as $H_a=5$ T (upper panel), $M(T)$ continuously increases upon cooling below the Néel temperature $T_N=75$ K. The shape of the $M(T)$ curve reflects the complex nature of a canted antiferromagnet with two magnetic sublattices. However, if the magnetic field used in the FC process is below a certain maximum value H_{max} (7 kOe for $\text{NdMnO}_{3.11}$), the magnetization is parallel to H_a below T_N , but upon cooling, $M(T)$ increases, reaches a maximum and then diminishes to zero (bottom panel, $H=1$ kOe). Instead of the expected behavior of ferrimagnets presenting a compensation point, a negative net magnetization is developed below an “inversion” temperature in an obviously metastable situation. In contrast, the corresponding zero-field $M(T)$ (dotted line) is positive in the whole temperature range, though two maxima are observed (at $T \approx 42$ and 12 K), indicating a complicated temperature-dependent magnetism.

It is evident that at least two ingredients are needed for negative magnetization to appear. First, the competition between two antiferromagnetically coupled systems is needed. And second, an energy barrier must anchor the low-temperature magnetization in a direction opposed to that of the field, preventing the rotation of the moments and the appearance of a “normal” compensation point. In $\text{NdMnO}_{3.11}$ neither the nature of the two competing magnetic systems nor the origin of the energy barrier has been fully clarified.

In the pure compound, the Mn sublattice has been found to order at $T_N=77$ K in a canted AF structure C_xF_y .¹² Below T_N the Nd sublattice remains paramagnetic, as it is always the case in rare-earth orthoperovskites. The internal field created by the ordered Mn sublattice acts on the Nd one, but only below $T=13$ K the Nd sublattice is sufficiently polarized (with the F_y structure) to be detected by neutron diffraction.¹² The $H_a=1$ kOe magnetization curve shown in Fig. 1 has its positive maximum at $T \sim 40$ K, significantly higher than 13 K. A difficulty clearly arises from this result: the Nd net moment cannot be detected above 13 K and the magnetic competition leading to negative magnetization starts at three times that temperature. Thus, the natural identification of Nd and Mn sublattices as the two systems competing in $\text{NdMnO}_{3.11}$ may be wrong. It is worth to be noted that such a natural identification is usual in the literature reporting negative magnetization in manganites.^{7–11}

To solve this riddle, an element-specific magnetometry as x-ray circular magnetic dichroism (XMCD) is the technique of choice: the relative sign of the Nd and Mn net moments can be identified by inspection. In this article we

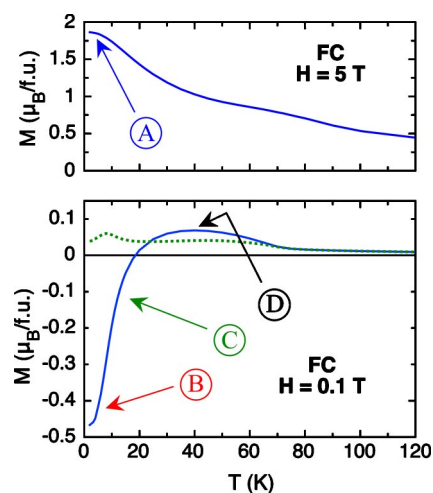


FIG. 1. Upper panel: FC magnetization of $\text{NdMnO}_{3.11}$ under $H_a=5$ T. Bottom panel: FC (full line) and zero-field-cooled (dotted line) magnetization of $\text{NdMnO}_{3+\delta}$ under $H_a=1$ kOe.

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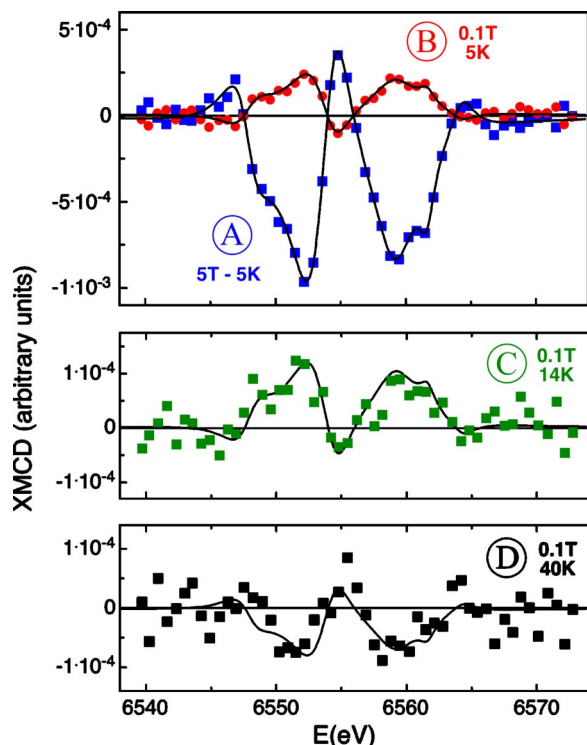


FIG. 2. Mn K -edge XMCD signals measured at different FC points, as labeled in Fig. 1. Upper panel: A: 5 K and 5 T (■) and B: 5 K and 0.1 T (•). Medium panel: point C: 14 K and 0.1 T (■). Lower panel: point D: 40 K and 0.1 T (■). The lines are guides to the eye.

present an XMCD study performed at the Nd L_2 and Mn K absorption edges on $\text{NdMnO}_{3.11}$ at relevant fields and temperatures.

XMCD on the hard x-ray range is sensitive to the bulk of the sample. $\text{NdMnO}_{3+\delta}$ was prepared by means of a ceramic procedure. A stoichiometric mixture of Nd_2O_3 and MnO_3 was calcined in air at 1000 °C for 2 days, pressed to 5 kbar into pellets and sintered in air at 1300 °C for 6 h. The oxygen content was determined by thermogravimetric analysis, yielding $\delta=0.11(1)$.¹³ XMCD was performed at the ID12 beamline of the ESRF in Grenoble, by recording the total fluorescence yield in backscattering geometry. The absorption of $\text{NdMnO}_{3.11}$ was measured at both Nd and Mn edges with circular positively (μ_+) and negatively (μ_-) polarized light. XMCD is then obtained as the difference $\mu_- - \mu_+$ at the four states labeled “A”–“D” in Fig. 1. “A” is a positively magnetized state, which will be used as reference. It corresponds to FC to $T=5$ K under $H=5$ T. Then the sample was heated up to 200 K to reset it magnetically, and a FC to $T=5$ K under $H_a=0.1$ T was performed. XMCD was measured at the Mn K and Nd L_2 , corresponding to point “B” (•). After that, the temperature was raised to 14 K, the XMCD measurements corresponding to point “C” were performed (■), and finally the temperature was raised to 40 K and point “D” was measured (■). In order to eliminate any possible experimental artifact, the whole cycle was repeated with applied fields in the opposite directions ($H_a=-5$ T and $H_a=-0.1$ T) after corresponding magnetic resets at 200 K. The data shown in Figs. 2 and 3 are the results of about 40 h of beamtime including thermal and magnetic cycles.

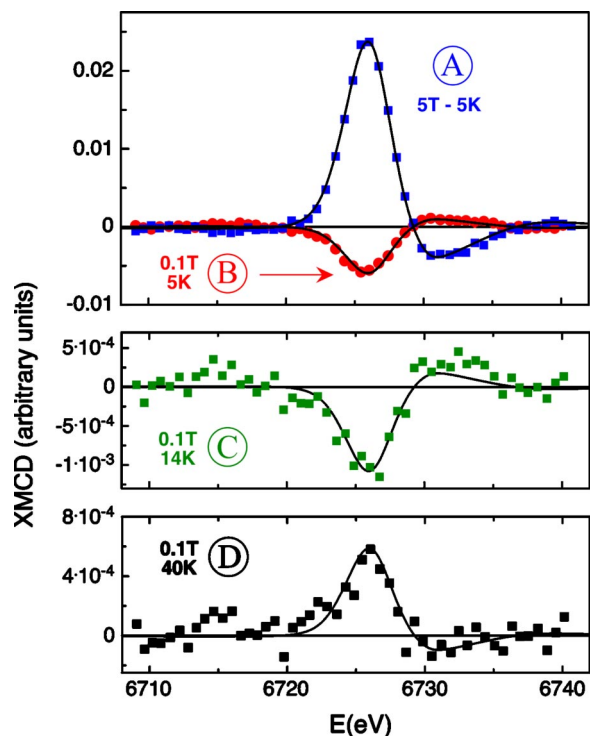


FIG. 3. Nd L_2 -edge XMCD signals measured at different FC points, as labeled in Fig. 1. Upper panel: A: 5 K and 5 T (■) and B: 5 K and 0.1 T (•). Medium panel: point C: 14 K and 0.1 T (■). Lower panel: point D: 40 K and 0.1 T (■). The lines are guides to the eye.

The XMCD signals measured at A at the Mn K and Nd L_2 edges are shown in the upper panel of Figs. 2 and 3, respectively (■). Both curves show the typical shapes of the XMCD at the Mn K and Nd L_2 edges, with positive sign (i.e., the one that is encountered when Mn and Nd net moments are parallel to the bulk magnetization, as it is the case in the ferromagnetic compounds $\text{Mn}_3\text{ZnC}^{14}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$).¹⁵ A fitted sum of several Lorentzian peaks (full line) is used as a guide to the eye in both cases. It is worth to note that this result already shows that after a FC process under $H_a=5$ T, Mn and Nd net moments are parallel in $\text{NdMnO}_{3.11}$.

The upper panel of Figs. 2 and 3 shows that XMCD signals recorded at B are changed in sign, both in Mn and Nd edges, indicating that the net magnetization of Nd and Mn at B are both antiparallel to the corresponding magnetizations at A, but one parallel to each other. This experimental result directly rules out the explanation of negative magnetization as a competition between Mn and Nd sublattices in $\text{NdMnO}_{3.11}$. The guide to the eye used for B XMCD signals is the same function as in A, scaled by a factor ~ -0.25 for Mn and Nd. Middle and bottom panels of Figs. 2 and 3 show the same result: the net magnetization of Nd and Mn are parallel to each other in the whole range of temperatures, following the sign of the magnetization. Again, the guide to the eye is the same function as in A, scaled by an adequate factor. Although absolute magnetic moments cannot be directly obtained from XMCD, the dichroic signal is proportional to the net moment of the corresponding sublattice, and one obtains the Mn and Nd net magnetic moments shown in

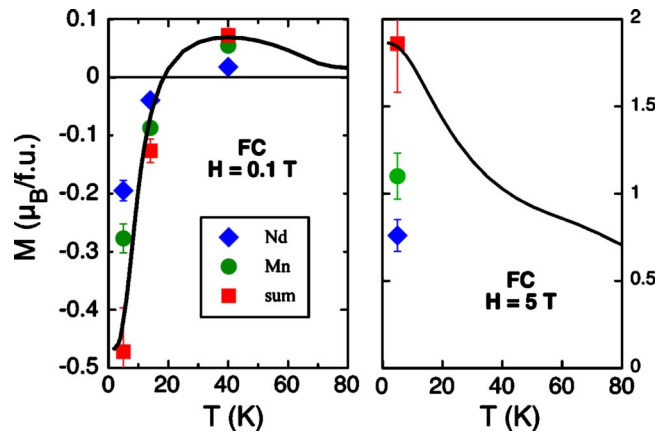


FIG. 4. Nd and Mn moments as obtained by comparison of the XMCD signals and the bulk magnetization at 0.1 (left) and 5 T (right).

Fig. 4 by imposing coherence between XMCD and the experimental bulk magnetization simultaneously at the four measured states.

Our XMCD results imply that negatively magnetized $\text{NdMnO}_{3.11}$ is not a metastable state in a typical compensated ferrimagnet. Indeed, the magnetic systems giving rise to negative magnetization have to be identified. In a previous study,⁵ we performed temperature dependent neutron diffraction on $\text{NdMnO}_{3+\delta}$ (including $\delta=0.11$) and the count rate on the small-angle region of the patterns clearly undergoes an enhancement at low temperature which we interpreted as the evidence of ferromagnetic clusters segregated within the antiferromagnetic matrix. Phase-separated $\text{NdMnO}_{3.11}$ would be a rather complex magnetic system: Nd and Mn sublattices have their own net moment, in both phases, ferro and canted antiferromagnetic, all with different temperature dependencies. However, phase separation gives a way to describe the negative magnetization in $\text{NdMnO}_{3.11}$. Indeed, in $\text{NdMnO}_{3+\delta}$ the physical origin of negative magnetization is linked to nonstoichiometry, as the effect is not found in stoichiometric NdMnO_3 , and phase separation in $\text{Mn}^{3+}-\text{Mn}^{4+}$ mixed valence manganites has been extensively reported.¹⁶ Moreover, the presence of ferromagnetic clusters within the antiferromagnetic matrix gives also a possible origin to freezing of magnetic moments and glassy phenomena, needed also as the second ingredient for negative magnetization. In this

model, it remains unexplained, however, why the interaction between the net moments of the ferromagnetic clusters and the canted AF matrix would be antiferromagnetic. A model based on phase separation and the occurrence of a spin-reorientation leading to negative magnetization in low-doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ has been recently proposed,⁶ which is in principle compatible with our results.

The XMCD experiments rules out the simple competition between the Nd and Mn sublattices as the origin of negative magnetization in $\text{NdMnO}_{3.11}$: the compensation takes place between two different phases instead of between two ferrimagnetically coupled sublattices. We conjecture that the numerous examples of negatively magnetized manganites recently found⁷⁻¹¹ belong to this kind described here.

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