



Negative magnetization and phase segregation in $\text{NdMnO}_{3+\delta}$

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Abstract

Magnetization and neutron diffraction as a function of temperature have been measured on $\text{NdMnO}_{3+\delta}$. The net magnetization below 25 K is antiparallel to the applied magnetic field when cooling under fields up to 7 kOe. A mechanism based on the presence of ferromagnetic clusters is proposed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Manganites; Negative magnetization; Phase segregation

Phase segregation of ferromagnetic clusters within the antiferromagnetic matrix on the low-doping regime of the RMnO_3 manganites has been recently inferred from a body of experimental evidence of transport, structural, and magnetic measurements (for a review see Ref. [1]). We report in this paper how the competition between different magnetic components taking place in this region of the phase diagram may induce unexpected magnetic phenomena, such as the exotic negative magnetization (opposite to the applied magnetic field) we have observed in $\text{NdMnO}_{3+\delta}$.

The $\text{NdMnO}_{3+\delta}$ sample 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, the resulting powder was pressed to 5 kbar into pellets and sintered in air at 1300°C for 6 h. The oxygen content was determined by TGA, yielding a value of $\delta = 0.11(1)$.

Negative magnetization was observed more than four decades ago in spinel ferrites [2], and more recently in other oxides [3] and molecular magnets [4]. Usually,

negative magnetization appears in complex ferri- or canted antiferromagnetic (AF) systems. Structurally, NdMnO_3 falls into this category [5,6]: the Mn sublattice has been found to order in a canted AF structure below $T_N = 77$ K. In most of these systems, the magnetization measured in a field-cooled process (FC) follows the same general behavior as we show for $\text{NdMnO}_{3.11}$ in Fig. 1. When cooling under a magnetic applied field (in Fig. 1, $H_a = 1$ kOe), which is smaller than a maximum value ($H_{\max} = 7$ kOe for $\text{NdMnO}_{3.11}$), the magnetization is parallel to H_a just below T_N . Upon cooling, the net magnetization increases, reaches a maximum and then diminishes to zero. Instead of the normal behavior of ferrimagnets presenting a compensation point, a negative net magnetization is developed below the so-called ‘inversion’ temperature, $T_i \approx 20$ K. The zero-field magnetization curve (ZFC) 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.

In non-doped stoichiometric lanthanide manganites, RMnO_3 , the strongest magnetic interaction is the AF Mn^{3+} - Mn^{3+} superexchange, which induces the AF order of Mn, the R system remaining paramagnetic. The R ions become polarized typically below ~ 30 K, due to the R–Mn interaction. Below T_N , as usual, the Mn net magnetization points parallel to the applied field. At the $T = 40$ K maximum of the FC curve, the net moment is $0.07\mu_B$ per formula unit. This value,

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¹This work was supported by Spanish CICYT under contracts no. MAT99-1142 and MAT99-0667-04-C04 and by means of the support to the Spanish CRG-D1B at ILL.

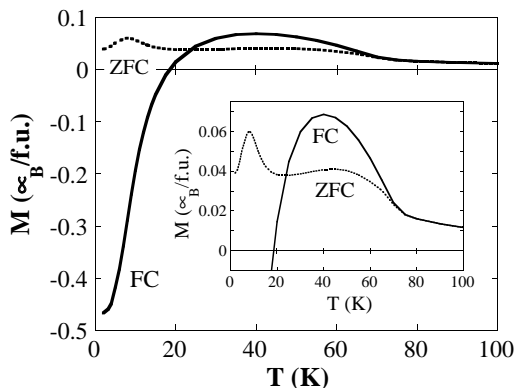


Fig. 1. FC (full line) and ZFC (dotted line) $\text{NdMnO}_{3.11}$ magnetization under $H_a = 1$ kOe.

indicating a very small canting, would be overcome at sufficiently low temperature by the Nd system if all the Nd moments were polarized by Nd–Mn interaction in a parallel fashion, antiparallel to the Mn net moment. However, the neutron diffraction experiments in Ref. [5] shows that Nd and Mn net moments are parallel, and a new mechanism, different to simple ferrimagnetism is necessary to explain our results.

The strong differences evidenced in the magnetic properties of samples of NdMnO_3 in recent studies [5,6] suggests a strong dependence of the magnetic properties on the stoichiometry. Ref. [6] indicates $\text{NdMnO}_{2.997}$, while Ref. [5] gives no data on δ determination. At first approximation, $\text{RMnO}_{3+\delta}$ systems have a 2δ Mn^{4+} concentration, giving rise to the ferromagnetic Mn^{3+} –O– Mn^{4+} interaction. At low Mn^{4+} concentration, manganites are unstable under phase segregation of ferromagnetic (FM) clusters within the AF phase of the parent compound. Moreover, the $\delta = 0.11$ value in our sample implies a Mn^{4+} concentration well above the critical value leading to ferromagnetism in doped manganites. This suggests that non-stoichiometric manganites are not only electronic but also chemically inhomogeneous systems, leading to the formation of an oxygen-poor AF matrix and FM oxygen-rich clusters. If the interaction between those two components is antiferromagnetic, a different temperature dependence of the magnetization would generate a phase-ferrimagnet. Moreover, it is plausible that the exchange anisotropy [7] originated by the interaction between FM clusters and the AF matrix generates an energy barrier between parallel and antiparallel orientations of M and H_a . If the thermal energy available at the compensation temperature is low compared to the exchange energy barrier, moment rotation is prevented at T_i , giving rise to net negative magnetization.

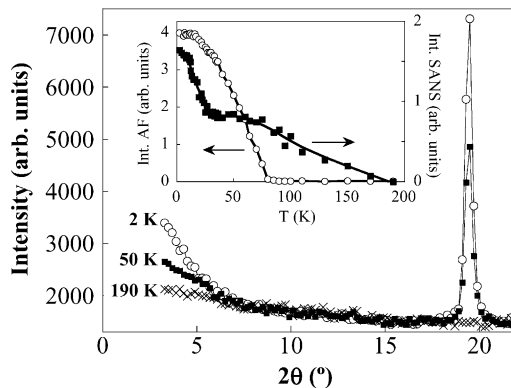


Fig. 2. Diffraction patterns obtained at $T = 2$ K (\circ), 50 K (\blacksquare), and 190 K (\times). Inset: integrated intensities of the (101) reflection (\circ) and the low-angle feature (\blacksquare). Both y-axes are in the same arbitrary units.

In order to provide evidence of the presence of such clusters in our sample, we have performed a temperature-dependent neutron diffraction study using the D1B diffractometer at the ILL. In Fig. 2, we show the low-angle part of the neutron diffraction patterns ($\lambda_n = 2.52$ Å) obtained at $T = 2$ K (\circ), 50 K (\blacksquare), and 190 K (\times). Below T_N , the (010) AF peak is visible. A low-angle magnetic contribution which significantly increases upon cooling is also present. This component is usually related to the presence of magnetic clusters [8]. The inset of Fig. 2 shows the integrated intensities of the (010) (\circ) and the low-angle scattering (\blacksquare) after subtraction of the nuclear scattering and background from the $T = 190$ K pattern. The (010) intensity shows the typical shape of an order parameter. This strongly contrasts with the shape of the low-angle component. It is non-zero well above T_N , showing no critical behavior, but indicating the presence of FM clusters in the sample. The low-temperature enhancement of the low-angle signal evidences the polarization of the Nd moments within the FM clusters below 30 K.

We interpret the phenomenon of negative magnetization upon FC as due to the extremely slow dynamics of FM clusters, which are antiferromagnetically coupled with the canted-AF matrix at low temperatures.

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