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Ferrimagnetism and spin excitation in a Ni–Mn partially inverted spinel prepared using a modified polymeric precursor method

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HIGHLIGHTS

- Ni–Mn oxide partially-inverted spinel made by modified polymeric precursor method.
- Magnetic measurements showed a ferrimagnetic and a parasitic magnetic transition.
- NPD revealed a magnetic structure consistent with a star-like moment arrangement.
- INS measurements indicated four distinct temperature-dependent magnetic regimes.

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ABSTRACT

We demonstrate that a Ni–Mn oxide partially inverted spinel $(Ni_{1-\nu}Mn_{\nu})[Ni_{\nu}Mn_{2-\nu}]O_4$ having inversion degree $\nu \approx 0.8$ and produced by a modified polymeric precursor method exhibits behaviour previously reported only in monophased samples. The structure of the specimen was determined using Rietveld analysis of X-ray and neutron powder diffraction data, showing that at room temperature the material crystallizes in the $Fd\bar{3}m$ space group with a lattice constant $a = 8.392$ Å. Combining magnetization measurements with neutron powder diffraction, we show that the magnetic structure of this spinel is associated with the interplay between the ferromagnetic and antiferromagnetic lattices which coexist due to the cations' presence on both tetrahedral and octahedral sites. Our analysis of the neutron diffraction data confirms the postulated magnetic structure involving a star-like moment arrangement, arising from competition for the *B* (octahedral) spinel sites by the Ni and Mn cations. Finally, we show that strong magnetic fluctuations are observed in the inelastic neutron scattering data.

1. Introduction

Oxide spinels can exhibit a variety of magnetic moment configurations in the ground state, including collinear, canted and spiral ferromagnetic (FM), and antiferromagnetic (AFM) structures [1]. They are also known to be very attractive candidates for applications in spintronics [2], due to a large tunnelling magnetoresistance (TMR) response and high Curie temperatures (T_c) combining to produce either conductive or insulating behaviour. Indeed, the renewed interest in spinels with non-collinear magnetic structures is related to the multiferroic properties produced by the modulation of spiral spin configurations.

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The relation between the crystallographic and magnetic properties in advanced oxide spinel materials such as manganites is still not fully understood. It is interesting, therefore, to study such compounds in order to establish any eventual correlation which may lead to potential applications, as was the case, for instance, with the giant-magnetoresistance ferromagnetic perovskites [3] and in the application of mesoporous $NiMn_2O_x$ to electrochemical energy storage and catalytic decomposition [4].

Spinel-type structures occur in three common forms. The first has formula $(A)[B_2]O_4$, where the notation (A) denotes a tetrahedral site occupied by cation *A* and having four oxygens as nearest neighbours, while $[B_2]$ denotes an octahedral site occupied by two *B* cations with six oxygen atoms as nearest neighbours [5–8]. Using the same notation, the second structure—known as a *perfectly inverted spinel*—has formula $(B)[AB]O_4$. There is also an intermediate structural possibility, represented by $(A_{1-\nu}B_\nu)[A_\nu B_{1-\nu}]O_4$; here ν is the inversion degree, which can be affected by the atmosphere and heat treatment used in its preparation [9,10]. Generally, spinel systems crystallize as face-centred cubic (FCC) or body-centred tetragonal (BCT) structures in which the oxide anions (O^{2-}) occupy preferential positions, while the metallic cations (A^{2+} and B^{3+}) are distributed in tetrahedral and octahedral sites, respectively.

$NiMn_2O_4$ possesses a spinel-type structure with a certain degree of inversion and showing a rich magnetic response, including AFM, FM or ferrimagnetism, depending on the cation occupancy and oxygen content [10,11]. The complexity of the magnetic behaviour is related to the fact that Ni^{2+} and Mn^{3+} ($3d^4$) occupy octahedral sites, while Mn^{2+} ($3d^5$) and Mn^{4+} ($3d^3$) have a preference for tetrahedral sites. However, the ferri-paramagnetic transition temperature in this material is extremely dependent on the synthesis process. For instance, ferrimagnetic behaviour has been observed, with strong antiferromagnetic interactions producing large negative Curie–Weiss temperatures [5,7,12] and Curie temperatures varying from 100 K to 145 K [7,12–14]. Therefore, a controlled synthesis process opens the possibility for materials to be developed with desirable structural and micro-structural properties, and therefore may generate a better understanding of the magnetic behaviour of these systems.

Chemical methods for metallic oxide preparation have been used for several years as an excellent alternative to traditional solid-state reaction routes, the latter invariably producing unreactive, inhomogeneous samples with undesirable secondary phases and large grains. On the other hand, the modified polymeric precursor (MPP) method has been used reliably to produce high quality samples without these shortcomings [15]. The MPP method involves the polyesterification of a metal chelate complex using a hydroxycarboxylic acid and a polyhydroxy alcohol in an aqueous solution of metal ions to produce a polymeric gel. Subsequent heat treatment produces an amorphous powder which is then calcined to achieve a product of the desired unsegregated phase. This material is an extremely homogeneous, very fine, agglomerate-free ceramic powder which is reactive at temperatures significantly lower than those required for powders obtained by traditional routes [15].

Another point of interest in the study of $NiMn_2O_4$ is that it can present different physical behaviours depending on the size and shape of the final material. Bulk systems usually exhibit a ferrimagnetic to paramagnetic transition at about 100 K followed by a parasitic ferrimagnetic transition at lower temperatures, around 70 K [7], while nanoscale materials exhibit only one ferrimagnetic to paramagnetic transition around 105 K [8]. Interestingly, thin films seem to exhibit both behaviours, depending on the heat treatment [16].

In this paper we present results obtained from X-ray (XPD) and neutron powder diffraction (NPD) measurements on a ceramic oxide of nominal composition $NiMn_2O_4$, prepared using the MPP method. We show that the use of this method can improve the purity of the resulting material. Its magnetic behaviour was determined from magnetization measurements as functions of temperature (M–T) and applied magnetic field (M–H). By correlating the nuclear and magnetic structures obtained using Rietveld analysis to the bulk magnetic data, we were able to confirm a star-like magnetic configuration formed by the Mn and Ni moments in this compound. Furthermore, inelastic neutron scattering showed the presence of collective magnetic excitations below 40 K.

2. Experimental

The synthesis procedure used to obtain nickel manganate was the modified polymeric precursor (MPP) method [15], wherein stoichiometric amounts of the reagents $MnCO_3$, $Co(NO_3)_3 \cdot H_2O$ and Ni_2O_3 (all $\geq$ 99.9% purity) were weighed and mixed with nitric acid while stirring at a temperature of 70 °C. After visually checking for the formation of a metallic cation solution, a citric acid solution was added to the reagents to enhance the metallic cation chelation, and ethylene glycol was used to enhance the polyesterification of metallic citrate. The pH of the resulting solution was adjusted to a value of 3 by adding ethylenediamine. Stirring was maintained at a temperature of 70 °C until the elimination of volatiles and water was complete. The homogeneous polymer gel produced was then air-dried in a furnace at 350 °C for 4 h. The resulting powder was macerated in an agate mortar, heated at 800 °C for 4 h and finally heated at 1000 °C for 16 h.

The homogeneity of the sample was confirmed with energy dispersive X-ray (EDX) mapping in a Leo Stereoscan 440 scanning electron microscope (SEM). X-ray diffraction (XRD) analysis was performed with a Rigaku DMAX-2100/PC diffractometer using CuK_α (K_β-filtered) radiation (λ = 1.5406 Å). Room temperature 2θ scans from 10° to 100° in steps of 0.02° and at fixed counting times of 1.6 s were recorded. More detailed crystallographic studies were later performed at the Brazilian Synchrotron Light Laboratory (LNLS) on the X-ray powder diffraction beamline [17], with energies in the Fe-absorption K-edge (λ = 1.6650 Å) and Mn K-edge (λ = 1.5406 Å), using a six-circle Huber diffractometer and a step size of 0.02°. A germanium (111) crystal analyzer was used to achieve high resolution, the X-ray scans being measured in the 2θ range 15°–120°. Structural refinements were carried out by the Rietveld method [18,19] using GSAS [20], based on JCPDS phase identification data (2003) and the ICSD (2003) structural database. The sample diffraction profiles were modelled using the pseudo-Voigt Thompson–Cox–Hastings (TCH) function [21].

The magnetic structure was inferred from data taken on the high resolution neutron powder diffractometer E9 at the Berlin Neutron Scattering Center (BENSC) at the Helmholtz-Zentrum Berlin (HZB). The data were measured in zero magnetic field as a function of temperature between 2 K and 280 K at a wavelength of 1.797 Å, giving a resolution (full width at half maximum, FWHM) of $\Delta d/d \sim 0.2\%$. Neutron data were analysed by the Rietveld method using the FULLPROF suite of programs [22].

Bulk magnetization measurements were performed using a Quantum Design 6000 magnetometer with both zero field cooling (ZFC) and field cooling (FC) between 10 K and 300 K using applied fields of 100 Oe, 500 Oe and 1 kOe. Magnetic hysteresis curves were measured between 10 K and 300 K in a field range of −9 kOe to +9 kOe. These measurements allowed the evolution of the magnetic properties of the material to be followed.

Finally, inelastic neutron scattering (INS) measurements were performed using the TOFTOF spectrometer [23] at the Garching research reactor (FRM-II), Munich. A wavelength of 5 Å and a chopper velocity of 16,000 rpm were selected as a compromise