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Tailoring the ground state of the ferrimagnet $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$

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ABSTRACT

We report on the magnetic and structural properties of $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$ in polycrystal, single crystal and thin film samples. We found that this material is a ferrimagnet ($T_c \approx 100$ K) which possesses a very distinctive and uncommon feature in its virgin curve of the hysteresis loops. We observe that bellow 20 K it lies outside the hysteresis cycle, and this feature was found to be an indication of a microscopically irreversible process possibly involving the interplay of competing antiferromagnetic interactions that hinder the initial movement of domain walls. This initial magnetic state is overcome by applying a temperature dependent characteristic field. Above this field, an isothermal magnetic demagnetization of the samples yield a ground state different from the initial thermally demagnetized one.

1. Introduction

The physics and chemistry of complex oxides have been largely studied due to the rich phenomena resulting from their combined magnetic, charge and orbital degrees of freedom. Among these complex oxides, those with perovskite structure ABO_3 have been extensively studied. They are the archetype of superconducting oxides, giant magnetoresistive oxides and the materials for the emergent field of novel device functions [1].

The size and oxidation state of A and B cations determine the symmetry of the perovskite structure, that departs from cubic when a tilting of the octahedral arrangement of oxygen around the B cation occurs [2]. Also, the partial replacement of A or B site cations by isovalent or aliovalent A′ and B′ atoms could result in a double perovskite structure with lower symmetry. In double perovskites with general formula $A_2(BB')O_6$, B and B′ atoms occupy two different crystallographic sites, and an ordered or disordered occupancy of them depends on the oxidation state and size difference between B and B′ ions [3,4].

Many of the magnetic interactions found in transition metal oxide perovskites are due to superexchange and/or super-superexchange interactions mediated through the oxygen orbitals. In some materials the relative strength and arrangement of these interactions determine the magnetic structure, range of the ordering temperatures and the possibility of frustration [5–9]. In particular, the effective spin lattice, ferro- or antiferromagnetic interactions among transition metal ions, depends on a delicate balance provided by the charge in the linking orbital, the bond angle, the degree of orbital overlap, the distance between interacting ions and their spin state [10,11]. In the specific case of the perovskite structure, the typical bond angles and distances usually favors antiferromagnetic superexchange interactions [11]. However, in some particular cases, when there is more than one electronic pathway in the linking orbitals, a destructive interference leads to the cancellation of the antiferromagnetic interaction. In these cases, a weak ferromagnetic coupling becomes relevant [12].

In transition metal oxides, the competing effects of a ferromagnetic interaction and local frustration leads to a spin glass like behavior [13]. The main signatures of this frustration are made evident in the time evolution from metastable magnetic states [14]. However, in bulk ferro/ferrimagnetic samples, a local frustration is normally hard to visualize due to the magnetic history dependence of the metastable states created by the pining of domain walls.

Also in some transition metal oxides the competition between a ferro- and antiferromagnetic ground states leads to a nonequilibrium glassy behavior that arises from a kinetic arrest of a ferromagnetic to antiferromagnetic phase transition [15]. These materials are identified as magnetic glasses [16] consisting of ferro- (or ferri-) magnetic and antiferromagnetic clusters frozen randomly with a dynamics similar to that of structural glasses.

This paper will present a detailed magnetic study of the ferrimagnetic double perovskite $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$ [17,18] showing evidence of a frustrated magnetic state at low temperatures. The properties of this compound were explored using

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polycrystalline, single crystalline and thin film samples. The main result is the observation that below 20 K there is evidence of a microscopically irreversible process involving the interplay of competing antiferromagnetic interactions that hinders the initial magnetic polarization or the movement of domain walls and determines the microscopic nature of the strong pinning centers found in this system [19]. This material results in a model system for studying the seldom found ferrimagnetic Ni^{2+} oxides and the low temperature glassy or magnetically disordered state present in many complex transition metal oxides.

2. Experimental details

We prepared polycrystalline samples of $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$ by conventional solid-state reaction. Stoichiometric amounts of La_2O_3, $Ni(NO_3)_2 \cdot 6H_2O$ and Sb_2O_3 were ground and fired at 1400 °C for 12 h in air. The single crystals were grown by the floating zone technique in a double ellipsoidal mirror furnace. The thin films were grown using RF magnetron sputtering in an Ar/O_2 atmosphere on (100) $SrTiO_3$ substrates at 700–800 °C. We checked the composition of all the investigated samples by EDS. Only the thin films showed a 10% Ni^{2+} deficiency not present in the stoichiometric target material. We carried out the structural analysis using powder X-ray diffraction (XRD) at room temperature. The magnetic measurements were performed in an QD-MPMS SQUID magnetometer in the range 2–300 K and -5 to 5 T.

3. Results

3.1. Structural characterization

In spite of an earlier report of this structure as being orthorhombic [17], with a fully disordered arrangement of Ni^{2+} and Sb^{5+} ions, we found the crystalline symmetry to be monoclinic (space group $P2_1/n$) with a rock salt arrangement of BO_6 and $B'O_6$ octahedra described by the $a^-b^-c^+$ system of three octahedral tilts in the Glazer's notation. The $(Ni^{2+}/Sb^{5+})_{2d}O_6$ and $(Ni^{2+}/Sb^{5+})_{2c}O_6$ octahedra are rotated in phase along the primitive *c* axis and out-of phase along the primitive *a* and *b* axes. We performed a Rietveld refinement of the structure using the FULLPROF program [20], obtaining the lattice parameters $a = 5.6051(3)$ Å, $b = 5.6362(3)$ Å, $c = 7.9350(5)$ Å and $\beta = 89.986(4)°$. The occupancy of the two crystallographic sites 2*d* and 2*c* were refined allowing the Ni^{2+}/Sb^{5+} distribution to vary, in order to model the octahedral site disorder. We found that the 2*d* cation site is almost fully occupied by Ni^{2+} while the 2*c* site has an occupancy close to 1/3 of Ni^{2+} ions and 2/3 of Sb^{5+}. The resulting crystallographic formula can be written as $La_2(Ni_{0.976}Sb_{0.024})_{2d}$ $(Ni_{0.357}Sb_{0.643})_{2c}O_6$. It should be noted here that this space group does not allow a further ordering of the Ni^{2+} and Sb^{5+} ions at 2*c* site. Fig. 1 shows the structure of $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$ and also a schematic two dimensional square view of Ni^{2+}/Sb^{5+} distribution among 2*d* and 2*c* sites. From this picture it can be seen that Ni^{2+} ions have three types of Ni^{2+} neighbors: first next nearest neighbors (mediated by –O–, that is, superexchange), second next nearest neighbors (through a –O–O– bridge) and third next nearest neighbors (–O–Sb^{5+}–O–, super-superexchange).

Small crystals with a face parallel to the (103) planes could be extracted from the rod grown in the mirror furnace. The rocking curve on the (103) peak had a FWHM = 0.25° and the interplanar spacing showed a 0.05% reduction with respect to the bulk.

The thin films (100–130 nm thick) were grown epitaxially in the *c*-axis direction. From XRD we measured a 1.4% *c*-axis expansion as compared with bulk samples, considering a constant cell volume. This corresponds to a 1.5% $(Ni^{2+}/Sb^{5+})_{2d}$-$(Ni^{2+}/Sb^{5+})_{2c}$ distance reduction in the *ab*-plane, to match the Ti–Ti distance of the substrate. Rocking curves showed typically a FWHM = 0.4° indicating a good crystallographic quality of the $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$ films.

3.2. Magnetic characterization

We measured the magnetization as a function of temperature (*M* vs *T*) using a ZFC-FC procedure (i.e. cooling with zero applied field or with a finite applied field) for several powder samples, thin films and single crystals. The lower curve in Fig. 2(a) (open diamonds) shows a typical result for polycrystalline samples with a Curie–Weiss behavior at high temperature, $M/H = C/(T - T_{CW})$, with *C* the Curie constant and T_{CW} the Curie–Weiss temperature. The lower inset in Fig. 2(a) shows the magnetization derivative dM/dT used to determine the transition temperature to the ordered state, the Curie temperature, T_C. A Curie–Weiss fit of several polycrystalline samples gives $T_{CW} = 155(6)$ K and $T_C = 98(2)$ K. The effective magnetic moment, calculated from the Curie

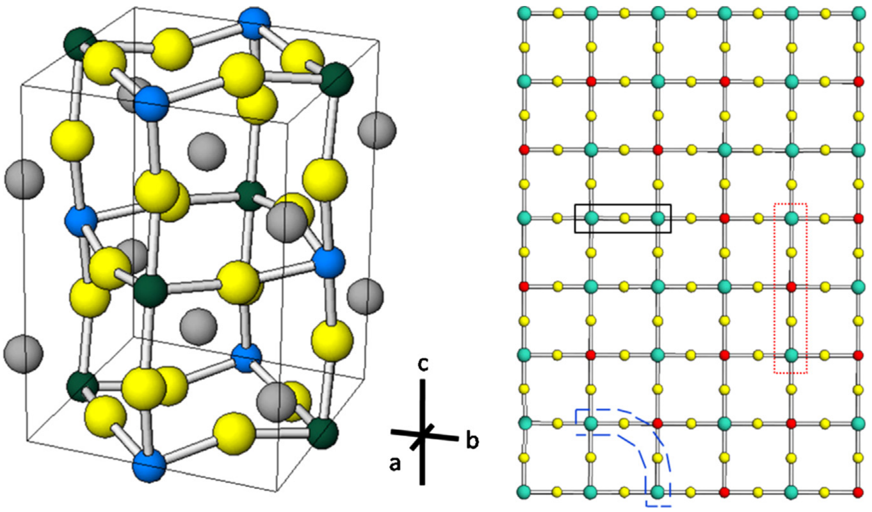

Fig. 1. Left: monoclinic structure of $La_2Ni(Ni_{1/3}Sb_{2/3})O_6$ double perovskite. Grey spheres: La^{3+}, yellow spheres: O^{2-}, light blue spheres: B_{2d} ions and green spheres: B_{2c} ions. Right: two dimensional scheme of the distribution of B ions over the 2d and 2c sites for $La_2(Ni)_{2d}(Ni_{1/3}Sb_{2/3})_{2c}O_6$ showing the different neighbors of the magnetic Ni^{2+} ions (turquoise spheres): first next nearest neighbors (1 nnn, black), second next nearest neighbors (2 nnn, dash blue line) and third next nearest neighbors (3 nnn, red dot line). Red spheres are Sb^{5+} ions and yellow spheres O^{2-} ions. For simplicity a square structure was supposed and lanthanum ions were omitted. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)