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Nd^{3+} crystal-field study of weakly doped $Nd_{1-x}Ca_xMnO_3$

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ABSTRACT

Nd^{3+} crystal-field excitations in $Nd_{1-x}Ca_xMnO_3$ ($x=0.025$, 0.05 and 0.1) single crystals are studied via infrared transmission as a function of temperature and external magnetic field. We report excitations associated with Nd^{3+} sites as detected in $NdMnO_3$ and excitations due to Ca doping. The latter reveal phase separation between the usual A-type antiferromagnetic states and the insulating canted (ferromagnetic) spin states in the vicinity of doped Ca^{2+} ions. Both Nd^{3+} crystal-field levels could be described using calculated parameters for $NdMnO_3$. Also, while oxygen stoichiometry and coherent Jahn–Teller distortions seem not to be affected by Ca doping, increased absorption bandwidths characterize the doped crystals.

1. Introduction

Whenever $RMnO_3$ manganites are doped with divalent cations A^{2+} resulting in $R_{1-x}A_xMnO_3$ (R = lanthanides and A = Ba, Sr, or Ca), the obtained Mn^{4+} ions weaken the impact of Jahn–Teller-type distortions in favor of double exchange interactions. In particular, simultaneous ferromagnetic and metallic attributes develop for $x\sim0.3$ compounds [1–3] along with a colossal negative magnetoresistance observed near the concomitant paramagnetic insulator–ferromagnetic metallic phase transition [4]. In addition, Mn–O bond lengths are also affected, giving rise to temperature-dependent structural disorder in which the precise roles of the lattice, charge and orbital configurations are still debated [5]. The low-doping regime is of particular interest because it gives one a simple way to probe the physical mechanisms that are believed to play an important role in the large-doping regime. Recent theoretical and experimental studies have recourse to phase separation [6]. On the other hand, in the framework of the mean field theory, the low-doping regime is rather related to a canted antiferromagnetic homogeneous state [7]. It is worth noting that the low-doping regime of $LaMnO_3$ is also associated with ferromagnetic insulating states [8] not explained by the double exchange magnetic interaction. They rather reflect orbital ordering [9] and important electron–phonon coupling [10,11].

In contrast with $La_{1-x}Ca_xMnO_3$, $Nd_{1-x}Ca_xMnO_3$ and $Nd_{1-x}Sr_xMnO_3$ are likely to show a closer competition such as orbital, charge ordering and antiferromagnetic superexchange [12,13]. At $T<T_N$, the parent $NdMnO_3$ (D_{2h}^{16}-*Pbnm* space group) is an antiferromagnetic compound characterized by static Jahn–Teller distortions [14]. Its A-type structure is related to a layered structure with MnO_2 in-plane ferromagnetic interaction and MnO_2 inter-plane antiferromagnetic interaction [15,16]. Raman active phonons of $Nd_{1-x}Ca_xMnO_3$ [17,18] are sensitive to the magnetic evolution of the Mn^{3+} sublattice as a function of temperature. In particular, for $x=0$, 0.025 and 0.05, the most intense $\sim607\,cm^{-1}$ Raman active B_{2g} phonon softens below $T_N\sim80$ K, following the paramagnetic to canted antiferromagnetic phase transition. While magnetization measurements for the $x=0.1$ compound reveal an overall antiferromagnetic transition, its Raman B_{2g} mode does not soften below T_N. The latter fact suggests a disruption of long-range antiferromagnetism [18]. The lightly doped $Nd_{1-x}Ca_xMnO_3$ ($x=0.08$ and 0.12) have been investigated by several means including X-ray, neutron powder diffraction, magnetization and AC magnetic susceptibility measurements [19]. These compounds exhibit a complex magnetic behavior at low temperatures. This behavior is well described in the framework of the magnetic phase separation model which predicts the simultaneous presence of antiferromagnetic and ferromagnetic phases (with opposite f–d exchange interaction terms). In the ferromagnetic phase, the neodymium magnetic moments start to be ordered near T_N parallel to the moments of the manganese ions. On the other hand, the antiferromagnetic phase is related to magnetic moments aligned in the opposite direction.

For the $NdMnO_3$ and $Nd_{1-x}Sr_xMnO_3$ ($x=0.05$ and 0.1) compounds we have previously reported the lifting of the Nd^{3+}

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ground-state Kramers doublet degeneracy ($\sim$14 cm^{-1}) as a consequence of Mn^{3+}–Nd^{3+} interactions below T_N ($\sim$75 K) [20,21]. The Nd^{3+} crystal-field (CF) Hamiltonian parameters have been calculated using the measured CF levels, the Kramers doublet exchange splittings, the g-tensor components and ab-initio methods. The study of $Nd_{1-x}Sr_xMnO_3$ CF excitations revealed that new ferromagnetic domains and phase separation are generated as a result of Sr doping [21]. Compared to $Nd_{1-x}Sr_xMnO_3$, the radius of the A-site cation in $Nd_{1-x}Ca_xMnO_3$ is reduced (1.17 Å for Ca^{2+} vs. 1.236 Å for Sr^{2+}). This implies a decrease of the Mn–O–Mn angle (from 165° to 157°) and an increase of the Mn–O distance (from 1.936 Å to 1.945 Å). The latter consequences have several impacts including, for instance, the $x = 0.5$ compounds charge ordering transition effective temperatures [22].

In this paper, we present a study of Ca lightly doped $NdMnO_3$ CF excitations as a function of doping, temperature and external magnetic field. We aim to determine whether magnetic phase separation is present in $Nd_{1-x}Ca_xMnO_3$ and if there are similarities between the ferromagnetic domain CF excitations in both $Nd_{1-x}Ca_xMnO_3$ and $Nd_{1-x}Sr_xMnO_3$ compounds.

2. Experiments

The $Nd_{1-x}Ca_xMnO_3$ ($x = 0$, 0.025, 0.05 and 0.1) single crystals ($\sim$1mm, 2mm, and 200 μm) were grown using the floating zone method described in Ref. [23]. The infrared transmission measurements as a function of temperature were obtained in the 1800–5000 cm^{-1} range with a Fourier transform interferometer BOMEM DA3.002 equipped with an InSb detector, quartz-halogen and globar sources and a CaF_2 beamsplitter. For measurements under external magnetic field, with 1 cm^{-1} resolution, a Bruker Instruments model 113 Fourier transform spectrometer, equipped with tungsten and globar light sources, was used to collect and analyze the spectra. The samples were placed in the bore of a superconducting magnet and in a helium bath cryostat at 1.8 K, with the magnetic field parallel to the incident radiation. A composite Si bolometer mounted directly beneath the sample was used to measure the intensity of the transmitted light.

3. Results and discussion

Prior to the CF absorption measurements, we used micro-Raman spectroscopy in order to check the samples stoichiometries by monitoring the $Nd_{1-x}Ca_xMnO_3$ phonon frequencies as a function of temperature [18]. Both A_g and B_{2g} phonons, of stretching and bending types, related to octahedral distortions were detected. On the other hand, broad bands due to large non-coherent Jahn–Teller distortions resulting in disordered-induced phonon density of states were absent. This indicates the overall persistence of coherent Jahn–Teller distortions at low Ca doping. Softening of the 607 cm^{-1} phonon below $T_N$$\sim$80 K, as observed in $NdMnO_3$, $Nd_{0.975}Ca_{0.025}MnO_3$ and $Nd_{0.95}Ca_{0.05}MnO_3$, disappears in $Nd_{0.9}Ca_{0.1}MnO_3$ (Fig. 1(a) and (b)). Granado et al. [24] and Laverdière et al. [25] have studied, respectively, $La_{1-x}Mn_{1-x}O_3$ and $RMnO_3$ single crystals and have also reported the softening of the $\sim$607 cm^{-1} Raman active phonon. By scaling the frequency shift to the normalized square of the sublattice magnetization, they have associated this softening with spin–phonon coupling caused by phonon modulation of the nearest neighbors exchange integral. Absence of phonon softening in $Nd_{0.9}Ca_{0.1}MnO_3$ is a clear indication of long-range antiferromagnetism disruption at this doping concentration.

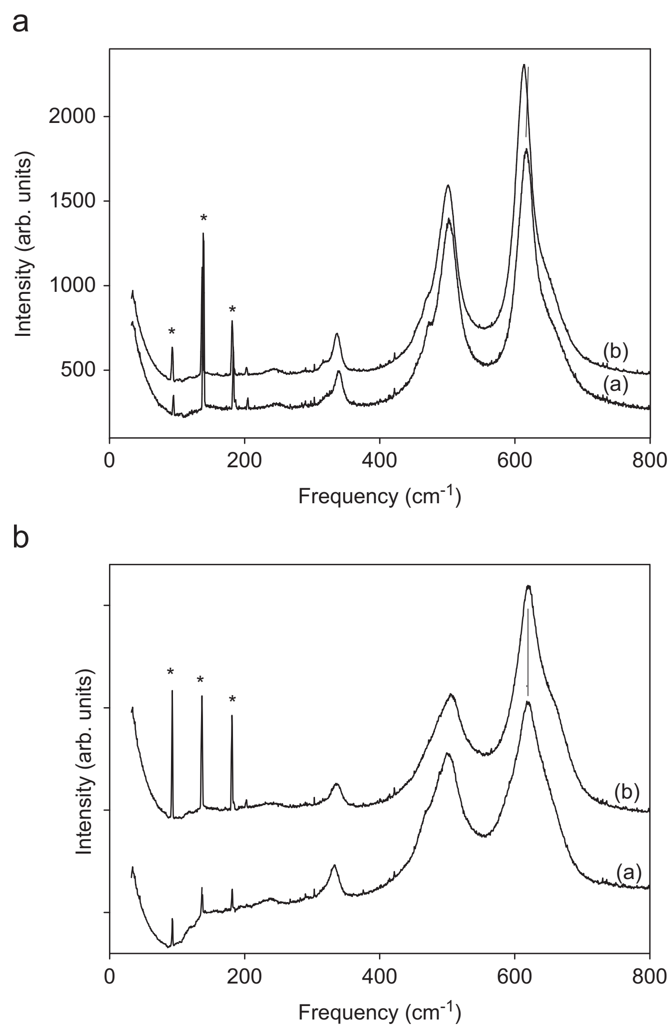

Fig. 1. (a) $Nd_{0.95}Ca_{0.05}MnO_3$ Raman active phonons at $T = 80$ K (a) and $T = 4.2$ K (b). Phonon softening is indicated by a vertical line. * indicates laser plasma lines. (b) $Nd_{0.9}Ca_{0.1}MnO_3$ Raman active phonons at $T = 80$ K (a) and $T = 4.2$ K (b). Absence of phonon softening is indicated by a vertical line. * indicates laser plasma lines.

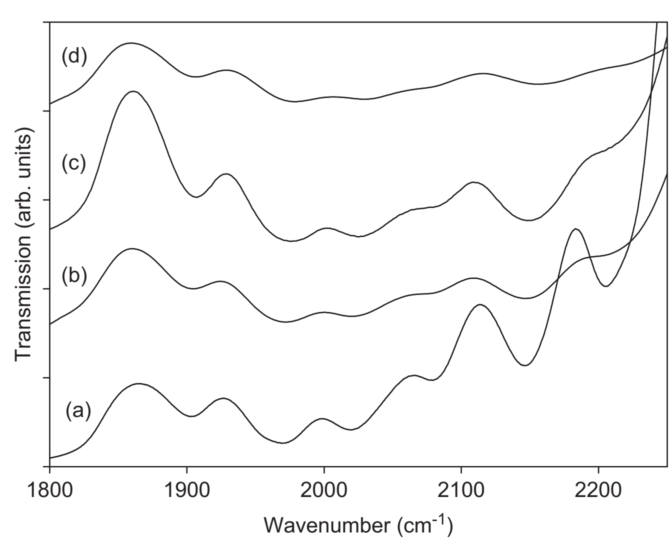

Fig. 2. $^4I_{9/2} \rightarrow {}^4I_{11/2}$ Nd^{3+} CF transitions in $Nd_{1-x}Ca_xMnO_3$ at $T = 300$ K: $x = 0$ (a), $x = 0.025$ (b), $x = 0.05$ (c) and $x = 0.1$ (d).