Jahn-Teller Distortion, Charge Ordering, and Magnetic Transitions in Ca-Doped NdMnO$_3$

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Structural and magnetic properties of (Nd$_{1-x}$Ca$_x$)MnO$_3$, with $x = 0$, 0.38, and 0.55, have been investigated by means of neutron diffraction and ac magnetic susceptibility measurements. Ca doping induces a structural change to occur at around 250 K, that results in a much fatter unit cell and a significantly shorter axial Mn-O(1) bond length. Both antiferromagnetic and ferromagnetic behaviors were observed. Hole doping shifts the ordering temperature of the Mn spins to a much higher temperature and weakens the antiferromagnetic component as well. Reorientation of the Mn spins were also observed to occur at low temperatures for all three compounds studied.

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I. Introduction

Until recently, the interplay between magnetism and electric conductivity in the hole doped perovskite-type manganites that exhibit colossal magnetoresistance (CMR) is still under intensive investigations. Double exchange (DE) interactions [1-2] is now used to account for the simultaneous observation of itinerant electron behavior and ferromagnetism. Studies [3] have shown that magnetism in the CMR manganites is governed not only by ferromagnetic DE interaction, but also by superexchange (SE) interaction. A complicated magnetic behavior is then anticipated [4] for mixed valence systems, where competition between DE and SE interactions is significant. In this paper we present the results of studies made on Ca-doped NdMnO$_3$, using ac magnetic susceptibility and neutron diffraction measurements.

Polycrystalline samples of nominal composition Nd$_{1-x}$Ca$_x$MnO$_3$, with $x = 0$, 0.4, and 0.55, were prepared employing the standard solid-state reaction technique. The crystal structure of the compounds was determined using high-resolution neutron powder diffraction and Rietveld analysis [5]. The data were collected on BT-1, the 32-detector powder diffractometer at the NIST Center for Neutron Research, employing neutrons of wavelength 1.5401 Å and angular collimations of 15$^\circ$-20$^\circ$.7$^\circ$ acceptance. Neutron magnetic diffraction was performed as well. The data were collected on the BT-2 triple-axis spectrometer, using a conventional setup. AC susceptibility was measured on a conventional ac susceptometer, employing a weak driving field.

Structural analysis was performed using the General Structure Analysis System (GSAS) program. Each diffraction pattern was initially refined using several types of symmetry, each
belongs to a different space group. The refinements were finally carried out assuming the symmetry of space group \( \text{Pbnm} \). All three compounds crystallize into an orthorhombic phase. Careful analysis of the occupancy factors shows that both the Nd and O sites are almost fully occupied. The chemical compositions that we obtained for the three compounds are \( \text{NdMnO}_{2,997} \) \((x = 0)\), \( \text{Nd}_{0.62}\text{Ca}_{0.38}\text{MnO}_{2.995} \) \((x = 0.38)\), and \( \text{Nd}_{0.45}\text{Ca}_{0.55}\text{MnO}_{2.998} \) \((x = 0.55)\). We estimated that the impurity level to be less than 2% for all three samples. Shown in Fig. 1 are portions of the nuclear density map of the \( x = 0.55 \) compound at 170 K. These plots reveal the three characteristic Mn-O bonds of the \( \text{MnO}_6 \) octahedral. It shows that all three bond-lengths are unequal with the axial bond is about 1.8% shorter than the two slightly uneven equatorial bonds, indicating the existence of Jahn-Teller distortion in the system. The degree of distortion was found to be higher for the doped compounds than for the undoped one, as expected [6].

FIG. 1. Portions of the difference density map, where the three characteristic Mn-O bonds of the \( \text{MnO}_6 \) octahedral are seen.
FIG. 2. Temperature dependence of the ac susceptibility, measured using a weak driving field.

Figure 2 shows the temperature dependence of the in-phase component $\chi^0$ of the ac susceptibility. A number of peaks, which depend strongly on $x$, are clearly evident. For the undoped compound, the main feature seen is the sharp peak at 75 K, marked as $T_m$. This peak is associated with the ordering of the Mn spins (see below), and it has an antiferromagnetic (AFM) character, as a cusp is present. The values of $\chi^0$ increase significantly as the Mn spins order. Although downturn is seen at lower temperatures, $\chi^0$ remains finite to the lowest temperature studied. Suggesting that both ferromagnetic (FM) and AFM components are present. At lower temperatures, two small but definite peaks with maxima at 44 and 13 K are also clearly seen. The latter is associated with the reorientation of the Mn spin (see below), and the origin of the
former is not clear to us at this time. Hole doping significantly affects the peaks in $\chi^0(T)$. For the peak that characterizing the ordering of the Mn spins, the primary change is the reduction of the rate of decrease in $\chi^0$ below $T_m$. Much broader peaks were observed for the doped compounds, showing that the AFM component is weakened. An upturn in $\chi^0$ is seen at 75 K for the $x = 0.55$ compound, further indicating that the FM component becomes dominating.

Another major change seen in $\chi^0(T)$ by Ca-doping is the appearance of the peak at $\sim 250$ K, marked as $T_{CO}$. This peak is not seen in the undoped compound. It becomes more pronounced and occurs at a higher temperature as $x$ is increased. They are associated with the structural change, as shown in Fig. 3 where variations of the lattice parameters with temperature are shown. Distinct changes on the thermal dependence of the lattice parameters are seen at $\sim 230$ K and

![Lattice Parameters](image)

**FIG. 3.** Variation of the lattice constants with temperature, obtained from detailed structural analysis.
\( \sim 260 \) K for the \( x = 0.38 \) and 0.55 compounds, respectively. Below which \( a \) and \( b \) show negative thermal expansions, while \( c \) displays a sudden drop. Showing the occurrence of a structural change, which results in a fatter unit cell and significantly shorter Mn-O(1) bonds. These behaviors have been attributed [7] to direct results of the spatial ordering of the Mn\(^{3+}\) and Mn\(^{4+}\) ions, known as charge ordering. The effect is stronger in the \( x = 0.55 \) compound than it is in the \( x = 0.38 \) compound, as over the transition \( \Delta a/a \) and \( \Delta c/c \) changed by 0.21% and -0.43%, respectively, for the \( x = 0.55 \) compound compared to 0.03% and -0.11% for the \( x = 0.38 \) compound. No similar structural change, but monotonic decreases of the lattice parameters with reducing temperature due to thermal contraction, was found for the undoped compound. Ca doping resulting in a mixed valence state for the Mn ions, at \( x = 0.5 \) the system has an equal number of Mn\(^{3+}\) and Mn\(^{4+}\) ions, a strong charge-ordering effect may then be anticipated.

![Temperature dependence of the intensity of the representative magnetic peaks for the three compounds studied.](image-url)
A series of new peaks develop in the neutron-diffraction patterns as the temperature is reduced to below $T_m$ for all three compounds. The patterns observed for the undoped and Ca-doped compounds are quite different, indicating that Ca-doping significantly affects the magnetic structure of the Mn spins. Shown in Fig. 4 are the temperature dependence of the magnetic intensities $I_m$ of the representative peaks. The ordering temperatures of the Mn spins, as determined by the inflection points of the $I_m(T)$ curves, are $T_m \approx 75$, 130, and 120 K for the $x = 0$, 0.38, and 0.55 compounds, respectively. Correspondingly, there is a pronounced peak in $\chi^\theta(T)$ for each compound at the temperature specified. Clearly, Ca doping shifts the $T_m$ to a considerably higher temperature, presumably due to triggering of the DE interaction by doping. Compared to the La-based systems, these $T_m$ observed for Nd-based systems are lower. At even lower temperatures, the intensities for the $x = 0$ and 0.55 compounds show downturns to decrease with decreasing temperature. For each compound, the downturn is accompanied by further increases of the intensities of other magnetic peaks, as shown in the inset of each plot. These changes mark the onset of the reorientation of the Mn spins, which is completed at $\sim 4$ K.

To summarize, Jahn-Teller distortion was observed in the Ca-doped NdMnO$_3$ systems. Ca doping induces a structural change to occur around 250 K, believed to be due to the spatial ordering of the Mn$^{3+}$ and Mn$^{4+}$ ions, and shifts the ordering temperature of the Mn spins to a much higher temperature as well. Both ferromagnetic and antiferromagnetic components are present in the systems, indicating that the DE interaction may not be the only magnetic interaction operating in the system.

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References