Relation between structure, charge ordering and magnetotransport properties in Nd$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Cr$_x$O$_3$ manganites

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Abstract

The relationships between incommensurability, charge ordering and magnetotransport properties in Nd$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Cr$_x$O$_3$ manganites have been studied by electron diffraction and lattice imaging versus temperature with 0.02 $\leq x \leq$ 0.07. All compositions show an incommensurate superstructure over the whole temperature domain, despite the fact that they are ferromagnetic and conductive below 140 K. The $q$-vector ($\frac{1}{2}$ - $\delta$) decreases with increasing temperature for all compositions $x$. For a given temperature $q$ also decreases with $x$. Lattice images obtained at low temperature give a clear view of the characteristics of the incommensurate structure. They also provide a better understanding of the charge ordering process. The low-temperature form of the Cr-doped manganites is not a perfectly doubled cell, but defects inducing a tripled cell occur pseudo-periodically. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: CMR; Charge ordering; Manganites

1. Introduction

During the last decade there has been an enormous interest in the properties of the lanthanide manganites Ln$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr, Ba, Pb) because of the discovery of ‘colossal’ magnetoresistance (CMR) in one of these compounds [1]. Especially, the charge ordering (CO) phenomena in the Ln$_{0.5}$Ca$_{0.5}$MnO$_3$ manganites have been of considerable interest [2–8]. It has been shown that this charge ordering has an influence on the magnetotransport properties of these materials [9–13]. Also, a detailed study of the structure of these manganites is absolutely necessary to understand their behaviour, since tiny structural distortions or modifications of their electronic charge distribution may influence their transport and magnetic properties dramatically. An earlier study of Chen and Cheong [3] has shown that the antiferro (AFM)-to ferromagnetic (FM) transition in La$_{0.5}$Ca$_{0.5}$MnO$_3$ is structurally associated with a commensurate to incommensurate charge ordering phase transition. Another study [14] however, reported that an
Incommensurate modulated structure is also observed for the \( \text{Sm}_{0.5} \text{Ca}_{0.5} \text{MnO}_3 \) manganite in spite of the fact that this oxide does not exhibit a FM-to-AFM transition. So at this point in time, the relationship between ferromagnetism, antiferromagnetism, and charge and orbital ordering in these manganites is not clearly understood.

The present article is devoted to an electron microscopy study of structures of the \( \text{Nd}_{0.5} \text{Ca}_{0.5} \text{Mn}_{1-x} \text{Cr}_x \text{O}_3 \) manganites versus temperature. The \( \text{Nd}_{0.5} \text{Ca}_{0.5} \text{MnO}_3 \) composition is very interesting because it has been shown that for this material a phase transition takes place below \( T_{\text{CO}} \) [15]. When this composition is doped with Cr, the physical properties are altered. The Cr-doped materials become conducting at low temperatures (\( T < 140 \) K). Conductivity means a mobility of the charges and this is not in agreement with a charge ordering process, which assumes a localisation of the charges. Secondly the Cr-doped materials with \( x > 0.02 \) show strong ferromagnetism at temperatures below 140 K and ferromagnetism suppresses charge ordering.

Because of all these properties the \( \text{Nd}_{0.5} \) \( \text{Ca}_{0.5} \) \( \text{Mn}_{1-x} \) \( \text{Cr}_x \) \( \text{O}_3 \) manganites are very suitable to study the relationships between ferromagnetism, conductivity, charge ordering and incommensurate structures.

## 2. Experimental procedure

The synthesis of polycrystalline \( \text{Nd}_{0.5} \text{Ca}_{0.5} \text{Mn}_{1-x} \text{Cr}_x \text{O}_3 \) samples (\( x = 0, 0.02, 0.05, 0.07 \) and 0.12) was carried out, starting from stoichiometric mixtures of \( \text{Nd}_2 \text{O}_3 \), \( \text{CaO} \), \( \text{Cr}_2 \text{O}_3 \) and \( \text{Mn}_2 \text{O}_3 \). The mixtures were heated at 1000 °C to achieve decarbonation. Then, the samples were pressed into pellets and sintered, in two steps, at 1200 and 1500 °C for 12 h. They were slowly cooled down to 800 °C and finally quenched to room temperature.

The electron diffraction (ED) versus temperature and the dark field lattice images at 150 K were carried out with a Philips CM20 electron microscope operating at 200 kV and equipped with a double tilt liquid \( \text{N}_2 \) sample holder (tilt \( \pm 30^\circ \), \( \pm 45^\circ \) and 90 K \( \leq T \leq 300 \) K). The FFT and inverse FFT were calculated using the Digital Micrograph 2.5 program of Gatan.

In the electron diffraction study versus temperature all the patterns were recorded under the same experimental conditions, i.e. increasing the temperature from 90 to 300 K, in steps of 4°C (\( x = 0.02 \)) or 10°C, waiting for temperature stabilisation during minimum 3 min before each ED recording, made with a constant electron beam adjustment.

Resistance measurements were performed from room temperature down to 30 K by the four-probe method on sintered bars in the earth magnetic field. All bars have the same \( 2 \times 2 \times 10 \) mm\(^3\) dimensions. The magnetisation versus temperature was registered during heating with a vibrating sample magnetometer after a magnetic field of 1.4 or 0.01 T was applied at 4.2 K (Fig. 1).

## 3. Results and discussion

### 3.1. Charge ordering in \( \text{Nd}_{0.5} \text{Ca}_{0.5} \text{Mn}_{0.98} \text{Cr}_{0.02} \text{O}_3 \)

When \( \text{Nd}_{0.5} \) \( \text{Ca}_{0.5} \) \( \text{MnO}_3 \) is doped with small amounts of Cr, satellite reflections appear in the vicinity of the \( \frac{1}{2} 0 0 \) superstructure reflections, i.e. the structure becomes incommensurate. The modulation vector can be written as \( q = (\frac{1}{2} - \delta) a^* \). The intensity of the incommensurate satellites scales with the intensity of the basic \( \text{Pnma} \) reflections as can be clearly seen from the enlarged Fig. 2. This shows that the satellites are not to be considered as a splitting of the \( \frac{1}{2} 0 0 \) reflection, but as satellites of the basic \( \text{Pnma} \) spots. The \( \frac{1}{2} 0 0 \) superstructure reflections present in the undoped material [15] then have to be considered as the end members of the series with \( q = 0.5a^* \). Such a modulation is best described using a notation based on four indices \( h \ k \ l \ m \); in Fig. 2 the \( 2 0 2 \bar{1} \) satellite belongs to the \( 2 0 2 \) reflection, whereas the \( 1 0 1 1 \) satellite belongs to reflection \( 1 0 1 \). In some patterns also the second-order satellites are visible, indicating that the modulation is not purely sinusoidal. Sometimes the satellites are not exactly along \( a^* \), but slightly inclined, i.e. \( q \) has a component along \( c^* \) (indicated by the 3.6° tilt between two satellites in Fig. 2). The origin of this orientation anomaly will be discussed when considering the HREM at low temperature.

The position of the satellites changes continuously with temperature. This evolution is visible in the
ED patterns of Fig. 3. The shift of the 0 0 2 $\bar{1}$ spot (upper arrow) is visualised with respect to the unsplit position (lower arrow). The evolution of the $q$-value for $x = 0.02$ as a function of temperature is summarised in Fig. 1c. This curve presents the ‘naked’ measurements on a single sample during a heating run from 97 K till room temperature. The curve starts at $q = 0.472$ for $T = 97$ K and is then continuously descending till $q = 0.369$ is reached at $T = 244$ K.

This continuous descent of the $q$-value can be correlated with the charge ordering process, similarly it was also done for related compounds [2,3,13,14]. The fact that the intensity of the reflections drastically drops and becomes streaked at
3.2. Evolution of the charge ordering process with increased Cr-doping

To verify whether charge ordering disappears when the Cr-doping is increased — as expected from the \( M(T) \) and \( R(T) \) measurements (Figs. 1a and b) — a systematic exploration of the modulated structure of the doped manganites \( \text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3 \), following the same process as described above, has been carried out for four different \( x \)-values varying from \( x = 0.02 \) to 0.12. The results for \( x = 0.02, 0.05 \) and 0.07 are summarised in Fig. 1c, where the \( q \)-values are drawn versus temperature (97 K \( \leq T \leq 270 \) K). Based on these results, the following remarks can be made:

1. The structure is incommensurate for all \( x \)-values in spite of the fact that for \( T < 140 \) K the compounds become strongly ferromagnetic, which is a disadvantage for charge ordering. One would expect that when ferromagnetism becomes stronger charge ordering would be suppressed and the incommensurate reflections would become weaker; however, such a phenomenon is not observed in any of the crystals studied.

2. In the \( x = 0.05 \) compound ferromagnetism and CO go together, but apparently this has no influence on the behaviour of the \( q \)-value, because a similar descent is observed as that with other \( x \)-values.

3. For each nominal composition, a variation of the modulation vector is observed in different crystals, but within a single crystal the modulation vector is constant.

4. The \( q \)-value is always incommensurate and decreases as the chromium doping \( (x) \) is increased. This strongly suggests that the undoped phase has also to be considered as a modulated structure, but with a commensurate \( q \)-vector \( (q = 0.5) \), as mentioned in Ref. [14].

5. The temperature where the reflections broaden and become streaked along \( a^* \) is in good agreement with the \( T_{\text{CO}} \) obtained by the physical properties for all \( x \)-values.

6. For \( x = 0.12 \) no clear modulation reflections were observed, even at \( T = 97 \) K; only a weak streaking along \( a^* \) with a maximum around \( q \approx 0.35 \) was present.

3.3. Lattice images at 150 K for \( \text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.98}\text{Cr}_{0.02}\text{O}_3 \)

Low-temperature \( (T \approx 150 \) K) HREM was performed for the compound with \( x = 0.02 \) in order to understand better the character of the charge ordering process and the structure of the incommensurate phase. The \([0 1 0]\) image shown in Fig. 4a shows a fringe system of \((0 0 l) \) planes, similar to that obtained for an over-oxidised \( \text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) [14]. To enhance the contrast of this fringe system some processing has been done. A FFT (Fig. 4d) has been obtained from the HREM image of Fig. 4a. Then a mask which only selected a few reflections (including the satellite reflections) was applied and an inverse FFT (Fig. 4d) has been calculated using the ‘masked’ FFT. This inverse FFT very clearly shows two characteristic phenomena:

- The sequence of bright and dark fringes is not regular. No well-ordered domains, where one bright fringe alternates with one grey fringe along \( a \) over a certain period, are visible. The distance between two bright fringes separated by one grey fringe is approximately 10.8 \( \AA \) \( (= 2 \times a_p \sqrt{2}) \), in agreement with a doubling of the \( a \) parameter. But in some regions two adjacent dark or bright fringes appear with an inter-distance of 5.4 \( \AA \) \( (= a_p \sqrt{2}) \), as indicated in the figure by the white arrows. We therefore have a mixing of fringes separated by 2 \( \times a_p \sqrt{2} \) and
fringes separated by $3 \times a_p \sqrt{2}$. Since this mixing tends to be uniform a $q$-vector slightly smaller than 0.5 results.

- Occasionally, a shift of the fringes along $a$ occurs. This is illustrated by the black arrow in Figs. 4a and c, where a dark fringe is connected to a bright fringe. The amplitude of the translation is $a_p \sqrt{2}$. As mentioned in Ref. [2] this shift implies that the modulation vector is no longer parallel to $a$, but has a small component along $c$.

This explains the inclination of the satellites with respect to $a^*$ observed in de ED patterns (see e.g. Fig. 2).

The clear presence of these two phenomena strongly support the structural model for the charge ordering process proposed by Barnabé et al. [2], where such images are interpreted by the presence of an excess Mn$^{4+}$ ($\text{Mn}^{4+}/\text{Mn}^{3+} > 1$). The additional Mn$^{4+}$ species are ordered in the form
of long-range ordered adjacent $[\text{Mn}^{4+}\text{O}]_\infty$ layers and submitted to a shearing mechanism along $\mathbf{a}$. 

4. Conclusion

This study of the oxides Nd$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Cr$_x$O$_3$ shows that the charge ordering process is progressive and corresponds to a broad temperature range where the structure is incommensurate. The incommensurability $q$-vector descends continuously as temperature is increased. With increasing temperature also the intensity of the incommensurate satellites reduces and at $T_{\text{CO}}$ the satellite reflections become streaked along $\mathbf{a}^\ast$. This temperature is in good agreement with the $T_{\text{CO}}$ obtained by physical properties measurements. With increased Cr-doping the $q$-vector decreases, but the fact that these Cr-doped compounds are ferromagnetic and conductive at low temperature seems to have no influence on the behaviour of the modulation vector $q$. It should be noted, however, that the resistivity is measured on a large amount of material compared to the amount studied by electron microscopy and that only a slight fraction has to be conductive to give the measured result. Lattice images obtained at low temperature allow a better understanding of the characteristics and features of the charge ordering process. However, further investigations with a better direct spatial resolution at lower temperatures and diffraction measurements below 100 K are necessary to obtain a complete image of this complex mechanism and its relationship with phenomena like conductivity and ferromagnetism.

Acknowledgements

W. Schuddinck is grateful to the FWO for financial support. This research has been performed within the framework of IUAP 4/10.

References