



	<b>Experiment title:</b> Charge ordered induced monoclinic distortion in the GMR compounds $\text{Nd}_x\text{Ca}_{1-x}\text{MnO}_3$ ( $x=0.66,0.7$ )	<b>Experiment number:</b> 01-01/210
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 7 Feb 2000 to: 10 Feb 2000	<b>Date of report:</b> 29.2.2000
<b>Shifts:</b> 9	<b>Local contact(s):</b> Hermann Emerich	<i>Received at ESRF:</i>
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## Report:

The aim of this experiment was to confirm the monoclinic charge ordered phase previously anticipated from high resolution neutron powder experiments performed on D2B and D1A at the Institut Laue Langevin [1,2]. In this monoclinic phase, the CO state consists of an alternating sequence of two types of  $\text{MnO}_6$  octahedra along the  $c$  axis where rows of  $\text{MnO}_6$  octahedra are uniquely occupied by  $\text{Mn}^{3+}$  ions and therefore strongly "Jahn-Teller distorted" (Fig.1). This original CO structure has been however recently subject to controversy as the doubling of one cell parameter would have been observed at low temperatures with electron diffraction technique [3]. In order to assess about the real crystallographic structure of  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  in the CO state, we performed high resolution measurement at low temperatures (down to 10K) on the powder diffraction station of SNBL. Moreover, we wanted to study the thermal dependence of the monoclinic distortion by measuring selected peaks (e.g. 202 and 20-2) at different temperatures between 10K and RT and eventually correlate the crystallographic transition with the onset of the magnetic ordering of Mn moments at  $\sim 130$  K (ferromagnetic in  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , antiferromagnetic followed by canting antiferromagnetic in  $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ).

From high resolution synchrotron powder diffraction experiments performed on BM01B, we were able to confirm the occurrence of the CO monoclinic state in  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (see Fig.1) and  $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ , below 160 K and 200K respectively. In the latter case, due to lack of time, we only performed rapid data collection of the (202)/(20-2) reflexions down to 150K.

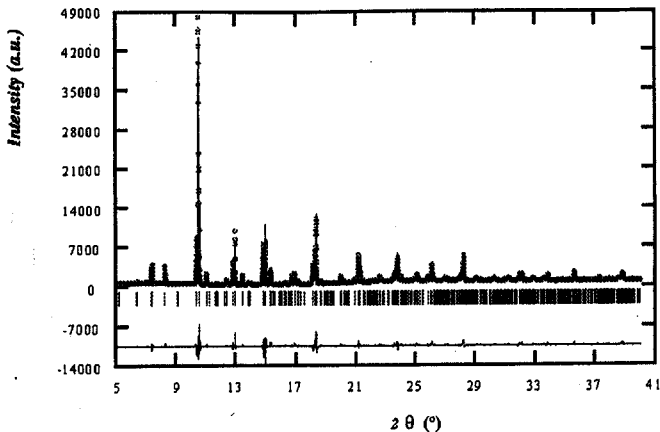


Fig. 1: Observed and calculated pattern of the CO monoclinic phase of  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  measured at 50 K and  $\lambda=0.49852 \text{ \AA}$ . The space group is  $P12_1/m1$  with cell parameters  $a=5.4924 \text{ \AA}$ ,  $b=7.6319 \text{ \AA}$ ,  $c=5.3978 \text{ \AA}$  and  $\beta=90.2097^\circ$ . In this calculation, we used the model obtained from neutron diffraction measurements (see ref 1) and just refined the instrumental parameters.

In  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , a far more spectacular effect was observed below 30 K. Indeed, just after cooling down the sample to 10K and switching the synchrotron beam on, we clearly observed the splitting of the (202)/(20-2) reflexion which unambiguously supports our CO monoclinic picture. However, after 2 hours under synchrotron radiation, the phase appeared to have been completely transformed to the same orthorhombic state as observed at room temperature (see Fig. 2). This photoinduced crystallographic transition has to be related to the melting of the charge ordering. Since  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  is a ferromagnetic insulator down to 2K, the same picture as reported for the parent compound  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  [4] does not seem to be valid any more. After this observation, most of experimental time was devoted to the confirmation of the photoinduced character of this transition (e.g. reproducibility of the effect, measurement with an attenuator, sequential switching on/off of the radiation beam, temperature dependence). In any case, this new observation deserves further studies, in particular an energy dependent study (down to the MnK edge). A similar study on the  $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  would be also desirable since this latter compound exhibits a completely different magnetic structure as  $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ . This would give us indication on the possible correlation between the magnetism and this photoinduced transition.

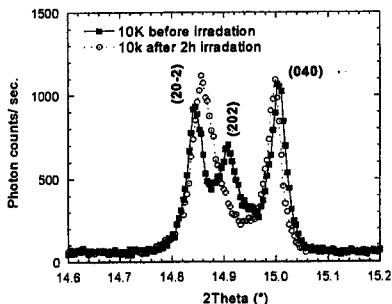


Fig. 2: Monoclinic-to-orthorhombic photoinduced transition

- [1] Millange et. al., J. Solid. State. Chem 127 (1996) 131
- [2] Suard et. al., In preparation
- [3] Hervieu, private communication
- [4] Cox et. al., Phys. Rev. B 57 (1998) 3305