ESRF	**Experiment title:** Pairing of charge- and orbital-ordered stripes in $La_{0.33}Ca_{0.66}MnO_3$	**Experiment number**: HE-829
Beamline: ID20	**Date of experiment**: from: 2/5/2000 to: 8/5/2000	**Date of report**: 4/9/2000
Shifts: 18	**Local contact(s)**: Emilio Lorenzo, Luigi Paolasini	*Received at ESRF:*

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Report:

During this experiment we studied strain relaxed thick films of $La_{1/3}Ca_{2/3}MnO_3$ which were grown on $SrTiO_3$ $(110)_c$ and $NdGaO_3$ $(100)_o$ substrates by pulsed laser ablation (subscript c stands for cubic, o for orthorhombic). A 5000 Å thick film on $SrTiO_3$ with a mosaic spread of ~ 0.7° has been used for the detailed experiments.
We observed superlattice reflections at reduced wave vectors of (0,1/3,0) in accordance with electron[1,3,4] – as well as neutron- and x-ray-powder diffraction[2], which reveal the existence of a displacement modulation and may be associated with charge ordering. There are two competing models which describe the ordering of the charge carriers in $La_{1-x}Ca_xMnO_3$ ($x \geq 0.5$). Mori *et al.*[1] suggested a bi-stripe model for which stable pairs of $Mn^{3+}O_6$ stripes are separated periodically by stripes of non-distorted $Mn^{4+}O_6$ octahedra. This model was contradicted by Radaelli *et al.*[2] and Wang *et al.*[3], which found support for a Wigner-crystal-like arrangement of the Mn^{3+} and Mn^{4+} cations with the Mn^{3+} stripes in the a-b plane arranged as far apart as possible.
In this experiment we observed resonant scattering at the Mn K-edge on the "forbidden" $(010)_o$ reflection. It is presumably related to orbital ordering , since it shows features characteristic of resonant scattering from orbital ordering. A rotation of the polarization of the scattered radiation by 90° with respect to the incident one is found and a two-fold symmetric azimuthal dependence of the resonant σ-π component, which is shown in Fig.1. This observation is in favor of the Wigner-crystal model since in the bi-stripe model (0k0) Bragg peaks, k odd, are allowed Bragg peaks (the n and b glide planes of the Pbnm space group vanish in the bi-stripe model).
The σ-σ component of (010) does not have a strong azimuthal dependence, and - as it is shown in Fig. 2 – there is an absorption dip on the Mn-K edge, characteristic for "normal" Bragg peaks. As $(010)_{\sigma\sigma}$ is non-resonant, it can be attributed to the longitudinal component of a lattice modulation induced by charge and orbital order. The second peak at higher energy in the σ-π scan is due to band structure effects.

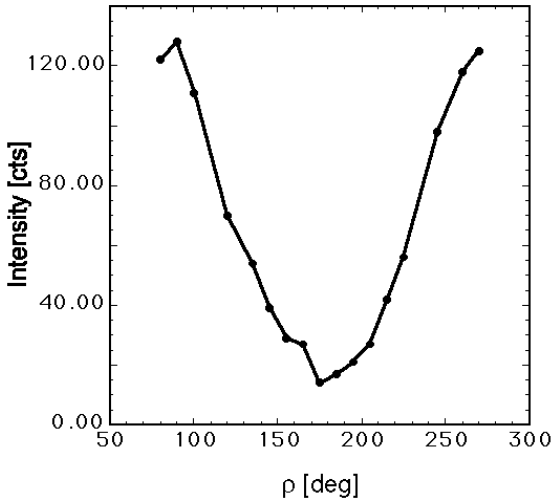

Fig.1: Azimuthal dependence of the (010) peak in σ-π position at T=100K.

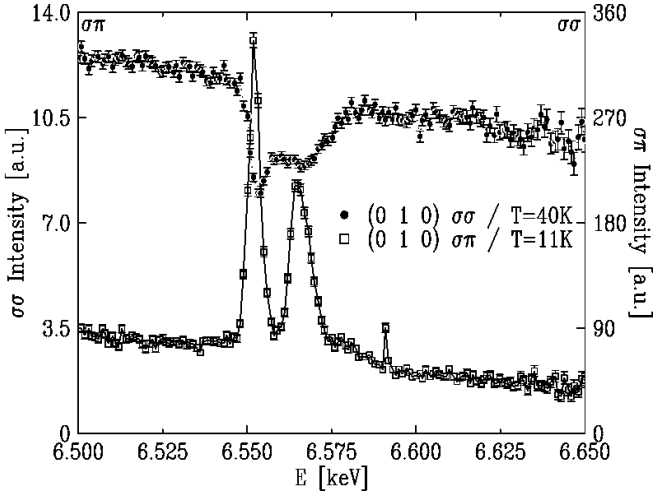

Fig.2: Energy scans on (010), once in σ→π position at 11K, and the other one in σ→σ at 40K.

The temperature dependence of the (2, 7/3, 0), $(010)_{\sigma\text{-}\sigma}$ and $(010)_{\sigma\text{-}\pi}$ reflections measured on heating is shown in Fig.3. From the figure we can observe that the charge order transition is clearly continuous in the thick film. It disappears almost completely at the charge ordering transition temperature T_{CO}~260K. But the temperature dependence of (010) is very surprising. The σ-σ component does not disappear at the charge order transition, instead, it slightly increases again at ~ 250K, whereas the σ-π component nearly does not vary at all up to 270K (Fig. 3).

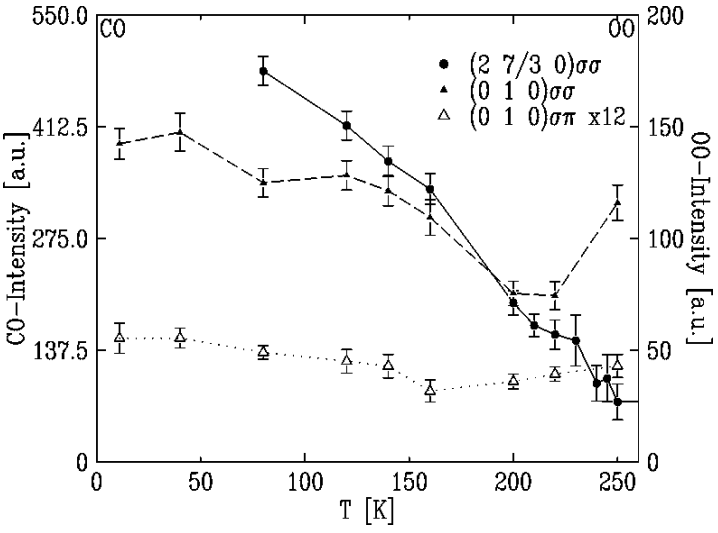

Fig.3: Temperature dependence of the charge and 'orbital' order peaks. The intensity of the (010)σπ peak has been multiplied by 12.

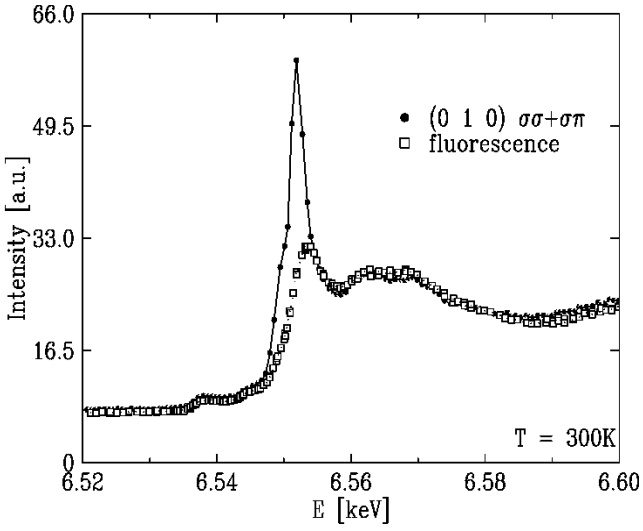

Fig.4: Energy dependence of the (010) peak without analyzer, and the fluorescence at backscattering position, respectively.

The energy scan taken at T=300K without analyzer (Fig.4) doesn't show the characteristic absorption dip of the dominant σ-σ component as at T=40K (Fig.2). Therefore, there must be a phase transition above 270K where the σ-σ component disappears. After subtracting the fluorescence, the disappearance of the second peak (as in the energy scan on (010)σπ at 11K) in the resulting curve (Fig.5) reveals also a change in the spectral distribution of the σ-π component.

As is shown in Fig. 6, the melting of the charge order goes hand-in-hand with a commensurate-incommensurate-like phase transition, where the modulation ξ of the wave vector q=(2π/a)(2, 2+ξ, 0) is shifted to longer wavelengths while the peak width is rapidly broadening near T_{CO}=260K, indicating that the correlation length of the charge order drops. The position of the peaks is not corrected yet for the temperature dependence of the lattice parameters. Below 100 K its position is constant and presumably close to K=2.33 r.l.u. after correction. This type of transition has been reported previously by Chen *et al.* also in other compounds of manganites with a charge-ordered phase [4]. This behavior together with the temperature dependence of the integrated intensity of the CO peak proves that our 5300 Å thick film behaves like the previously studied powder samples.

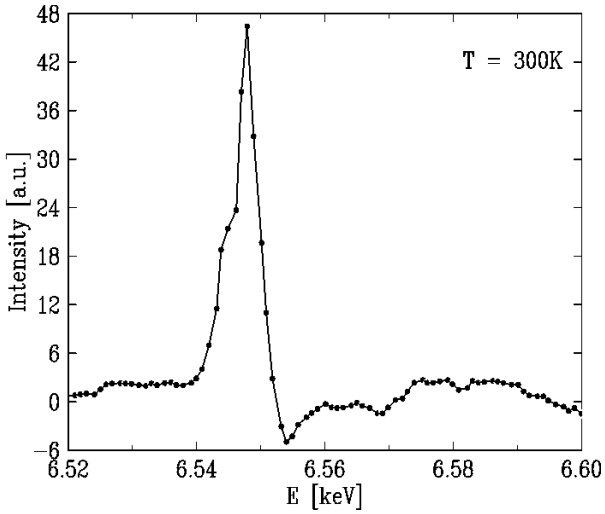

Fig. 5: Energy dependence of the (010) peak at 300K with the fluorescence subtracted

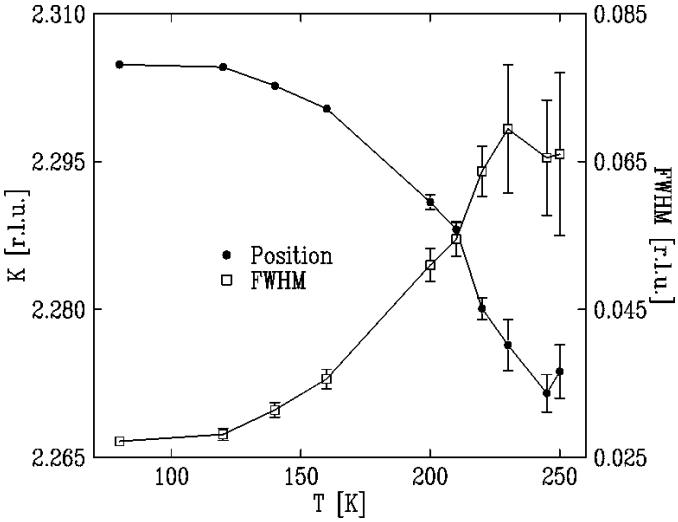

Fig. 6: Temperature dependence of position and peak width in [010] direction of the CO reflection (2, 7/3, 0)

References:

1. S. Mori *et al.*, Nature **392**, 473 (1998)
2. P.G. Radaelli *et al.*, Phys. Rev. B **59**, 14440 (1999).
3. R. Wang *et al.*, Phys. Rev. B **61**, 11946 (2000).
4 C.H. Chen et al., Phys. Rev. Letters, **81**, 4792 (2000)