Experimental Report

Proposal: **5-41-421** **Council:** 10/2006

Title: Re-investigation of the magnetic structure of prototype half-doped charge ordered Pr1/2Ca1/2MnO3 manganites

This proposal is a new proposal

Researh Area: Physics

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Samples: Pr1/2Ca1/2MnO3

Instrument	Req. Days	All. Days	From	To
D10	5	5	05/03/2007	10/03/2007

Abstract:

Half-doped R1/2Ca1/2MnO3 manganites (R:Y, Pr, Nd…) represent the prototype example of charge ordered materials. However, the concomitant charge and orbital ordering of the Mn 3d electrons at the Mn atomic level constitutes an old picture, which is nowadays admitted to be oversimplified. At present, several different alternatives are proposed, among which a novel picture, Zener Polaron ordering describing instead the localization of the charge inside ferromagnetic Mn dimmers. Zener Polaron ordering goes as far as calling back to question the unchallenged collinear CE-type magnetic structure: the model would rather support an alternative non-collinear spin arrangements of ferromagnetic Mn pairs instead of the collinear arrangement of high spin Mn ions. As the two competing magnetic structures are found undistinguishable from neutron powder diffraction, it appears highly desirable to perform the magnetic structure determination from single crystal neutron diffraction data.

Re-investigation of the magnetic structure of prototype half-doped charge ordered $Pr_{1/2}Ca_{1/2}MnO_3$ manganites.

The ground sate of prototype half-doped charge ordered $Pr_{1/2}Ca_{1/2}MnO_3$ manganites as described in the fifties [1] is re-investigated. The implication of this picture on the crystallographic structure has been the subject of many debates, implying an extremely difficult distinction between two models associated to ionic Mn^{3+}/Mn^{4+} charge ordering and corroborating the original views[2] and Zener polaron ordering[3], respectively. The D10 study intends to verify some consequences for the magnetism, as it is expected by changing the standard description of CO as ionic CO, by the ZP ordering picture. Powder experiments[4] and recent *ab initio* theories[5] pointed out that for ZP ordering, there are degenerate non-collinear magnetic structure solutions competing the collinear CE-type structure associated to the ionic picture (see fig.1).

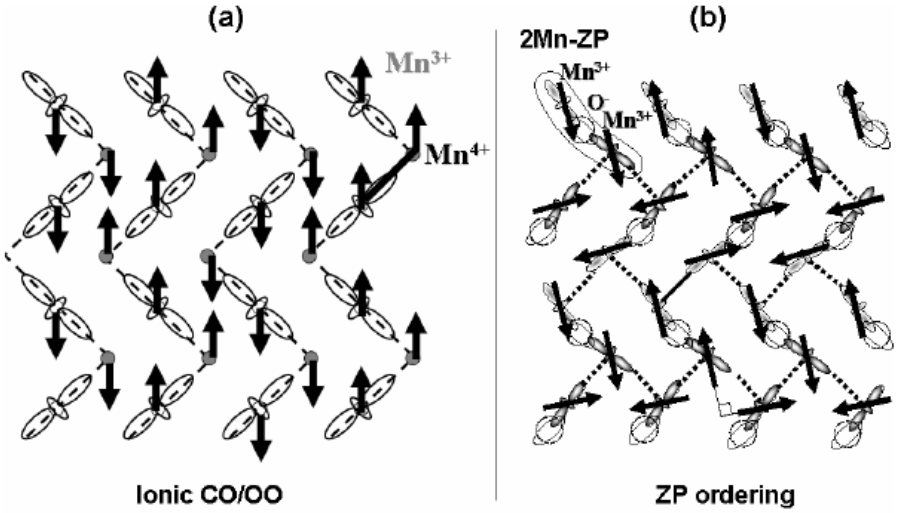
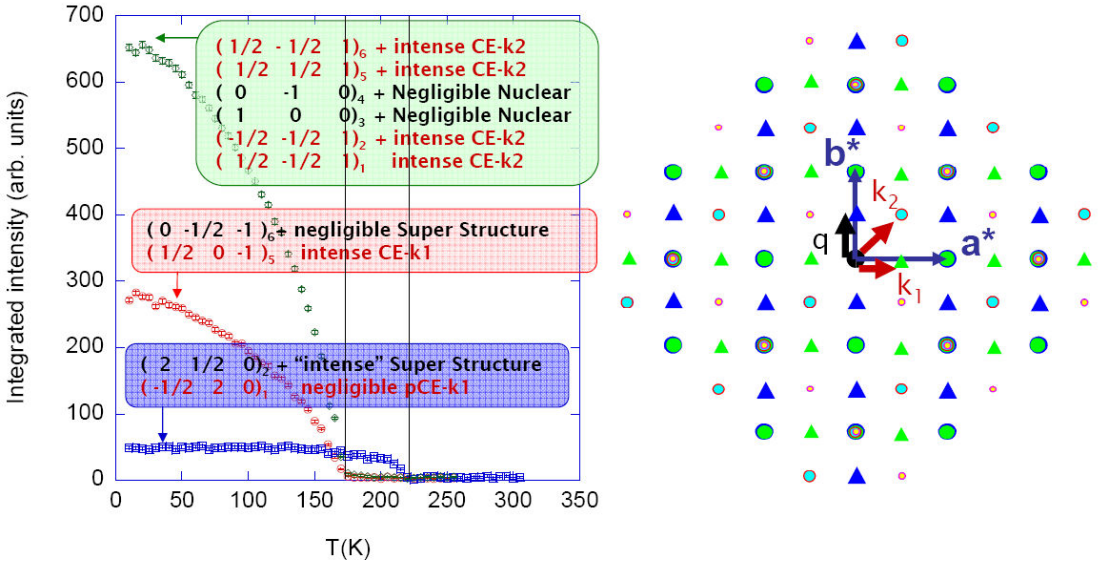


Figure 1

As for the crystal structure[3], and as indicated by recent powder studies[4], an unambiguous magnetic structure determination requires here single crystal diffraction, where great care must be taken to deal correctly with the generally unavoidable twinning of manganite crystals in the treatment of twinning in manganite samples and off-stoechiometry of $Pr_{1-x}Ca_xMnO_3$ samples, which are hard to obtain with x=0.5. Off-stoichiometric has a spectacular influence on the magnetic structure around half-doping [6], transforms to the CE arrangement into a related pseudo-CE arrangement in $Pr_{0.67}Ca_{0.33}MnO_3$. Hence, the distinction of the magnetic structures of Fig.1 needs to be studied exactly at half-doping.

The best way to check this composition with neutrons is the intensity ratio between l even (pseudo-CE) and l odd (CE) magnetic reflections, because Pr and Ca have almost the same neutron scattering length. Fig.2b explains the indexation of one twin contribution in the scheme of the reciprocal space of the twinned crystal, (blue twin). The charge ordered super structure gives extra superlattice reflexions (blue triangles) indexed with a propagation vector q=(0 ½ 0), while the magnetic structure diffracts at positions indexed by two propagation vectors k_1=(½ 0 0) k_2=(½ ½ 0). The reciprocal space contains reflections mixing either the nuclear contributions of the 6 twins (big circles), reflections containing 4-k_2 contributions overlapping 2 two

other nuclear contributions (small circles), and reflexions mixing the k_1 contribution of a twin with a sperlattice reflexion of another twin (green triangles). Fig.2a shows the measure of the total intensity of few of these overlapped reflections as function of temperature, which shows the two structural and magnetic transitions expected at T_{CO}=230K and T_N=170K. This measurement confirms the absence of pseudo-CE component and hence, the proximity to the exact x=0.5 composition from the following observations: firstly, the CE-type magnetic components (l even, labelled as CE-k_1 and CE-k_2) are appearing below T_N on the top of negligible nuclear contributions (red and green boxes), secondly, the k_1-pseudo-CE component of one twin (l even) does not disturb the evolution of the superlattice intensity of the other twin at T_N (blue box).

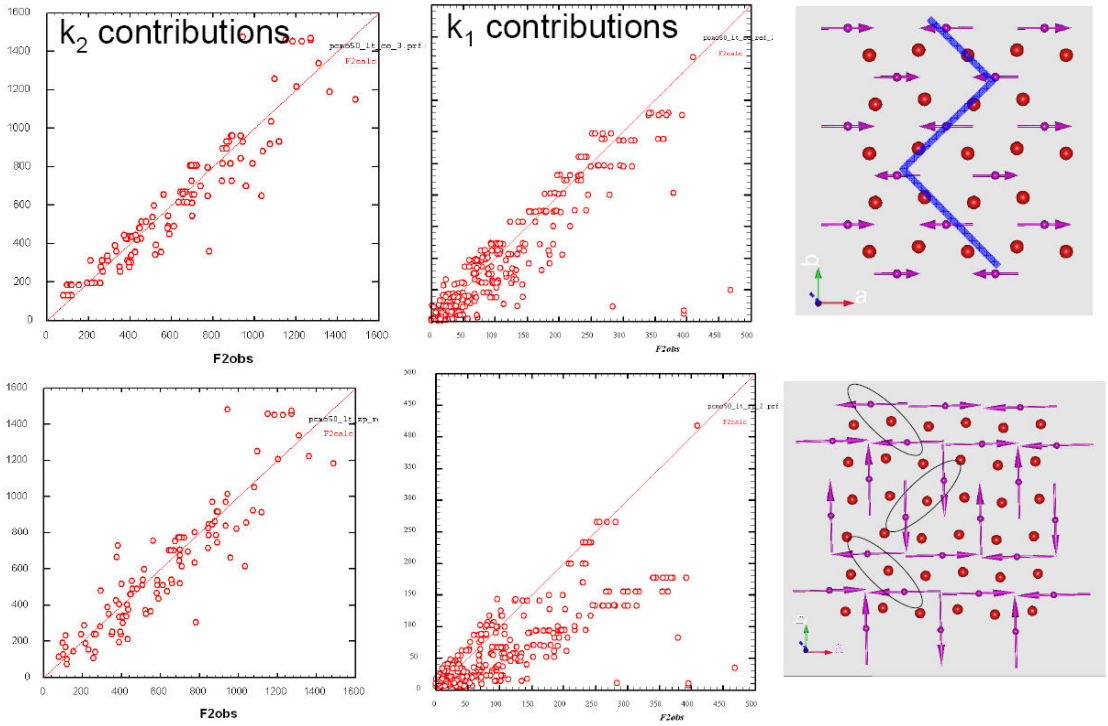


Sure that we dispose here of the desired pure half-doped $Pr_{0.5}Ca_{0.5}MnO_3$ material, we took complete data collections at T=RT (paramagnetic), 5K and T=190K (charge ordered paramagnetic) phases. Structural refinements at RT are good, providing accurate twin fractions. For the analysis of the magnetic structure, we focused on the analysis of the 5K phase ignoring the structural modulation at the first approximation. The data integration is complicated by the metric distortion, which splits the contributions of different twins that were overlapping at RT into non overlapped reflectons, preventing a standard/optimized integration using ellipsoids libraries, as constructed by the D10 integration program racer. Integration of split contributions is less precise, since we use the wider integration region corresponding to the full frame for each scan step, a procedure which picks more background, or which accounts aluminium powder lines as Bragg scattering, leading to more systematic errors in the data.

With these data, we've only compared the refinements of totally constrained magnetic models (2/3 parameters), constrained to fit the physics of each of the competing models model shown fig.1: collinear spins on AF-coupled zigzags (fig.1a, refined in Fig3, top) and 90º arrangements of pairs (fig.1b, refined in Fig3, bottom), which can be entirely described by few parameters corresponding to the moment values, and one parameter for the in-plane spin direction on a particular atom. The models are hardly discriminated on the k_2 reflections, but the collinear arrangement definitively fits better the set of k_1 reflections.

The preliminary conclusion gives a preference to the collinear order, which could be unfortunately compatible with both the ionic CO and the ZP ordering

pictures. So the experiment alone does not discriminate in between the two *magnetic* models straightforwardly. We hope we can ultimately discard them anyway, but for that, there are still several things to do: 1) iterate the integration/refinement procedure to remove any suspicious reflection (typically, powder rings) and attempt unconstrained refinements, or a structure solution, 2) analyse the superlattice peaks information, which is rather intense in the reflections set corresponding to negligible k1-pseudo CE contributions with l even (see Fig.2), in order to confirm/infirm the competing *structural* models. Both analyses are under way.



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