ILL RESEARCH PROPOSAL

Printed : 26/09/2012

Experiment Title : **Low temperature structure of charge ordered manganite**

Proposal Number

5-14-251

Proposer (to whom correspondence will be addressed)

Name and first name	Address	Phone / Fax / Email
DAOUD-ALADINE Aziz	**ISIS RAL, DIDCOT** STFC OX11 0QX DIDCOT ROYAUME-UNI	+44(0)1235445504 +44 (0)1235 44 5200 aziz.daoud-aladine@stfc.ac.uk New neutron user? **No** Phd student? **No** New ILL user? **No**

Co-proposers (mark the main proposer in each laboratory with an asterisk)

Name and first name	Laboratory	Country
PERRING Toby G	**ISIS RAL, DIDCOT**	**Royaume-Uni**
EWINGS Russell	**ISIS RAL, DIDCOT**	**Royaume-Uni**

Local contact(s) : **FERNANDEZ DIAZ Maria Theresa**

Suggested keyword number **5-14**

This proposal is :

[**X**] A new proposal.
[ ] A continuation proposal.
[ ] A resubmission.

The main research area of your proposal is: **Physics**

Do you need simulation support (C-lab)? **No** SAXS support through PSB : **No**

Need to use PSCM lab ? **No**

Industry : **NOT Related to industrial applications**

Instrument required	Days
D9	**8**

Requested starting time :

1. Jan/Feb **X** 2. Mar/Apr **X** 3. May/Jun **X**
4. Jul/Aug **X** 5. Sep/Oct **X** 6. Nov/Dec **X**

Unacceptable Dates :

Sample availability : **Available**

Sample description

Substance/Formula : **Pr1/2Ca1/2MnO3**

Mass (in mg) :

Size (in mm3) : **150**

State : **single crystal**

Surface area :

Space group : **Pbnm**

Unit cell dimension : a = **5.4** b = **5.4** c = **7.6**

T (k) = α = **90** β = **90** γ = **90**

Sample container : **stuck on a pin**

Safety aspects

No danger associated with sample.

Is there any danger associated with the proposed sample or its preparation at ILL ?

[ ] Yes [ ] Uncertain [**x**] No If Yes or Uncertain, please give details of the risks asociated :

Is the sample a transuranium sample [ ] Yes [**x**] No

Experimental details

Energy / wavelength range : **0.89 angstrom**

Resolution in energy or wavelength :

Range of momentum transfer :

Resolution in momentum transfer :

Sample environment equipement (supplied by ILL)

Environment equipment : **4-circle cryostat**

Temperature range (stability) : **10-300K** Pressure range :

Magnetic-field strength (stability)

Is there any danger associated with ancillary equipement ? [ ] Yes [ ] Uncertain [**x**] No

If Yes or Uncertain, please give details of the risks associated :

Submitted to other facilities :**No**

Societal Indicators :**Fundamental Science**

To be filled in by ILL

Sample environment code

C4

Comments by Health Physics Officer and Safety Engineer

Abstract

We have accumulated expertise in treating the diffraction data collected on twinned manganites as if it had collected on a single crystal. We obtained in the past good single crystal structural data at intermediate temperature (TN<T<TCO) on PrCaMnO3 charge ordered manganites, but we realize that we still miss one data collection at low temperature to get a complete view on the physics/ground state of these complex materials. The purpose of the experiment is to fill this gap.

Scientific Background: Perovskite manganese oxides formula $RE_{1-x}A_xMnO_3$ (RE=rare earth, A=Ca, Sr, Ba, Pb) continue to be widely studied not only for the colossal magnetoresistance (CMR) they can show (changes of resistivity of several orders of magnitude from insulating to metallic character in magnetic fields of a few Tesla) but also because of the rich physics arising from the ordering of spin, charge, orbital in the nominally Mn3+/Mn4+ mixed valent insulator materials [1]. Antiferromagnetic ordering, in the latter, has for a long time been intimately linked to *ionic* charge ordering and the orbital ordering on Mn3+ ions, the most ubiquitous example being found in manganites near half doping (i.e. $x = 0.5$) [2]. Yet, despite extensive studies, the electronic state and the mechanisms stabilizing this phase remain unclear. It has generally been indirectly studied looking at structural distortions taking place below the charge ordering transition at a temperature T_{CO}, or below the temperature where magnetic ordering sets in ($T_N < T_{CO}$).

The celebrated Goodenough model for the half-doped manganites is shown in Fig. 1(a). It considers the electronic structure as a checkerboard of Mn3+/Mn4+ ions with an associated herring-bone pattern of occupied *eg* orbitals on Mn3+ sites controlling the sign of the superexchange interactions stabilizing the characteristic CE-type spin order: an antiferromagnetic arrangement of ferromagnetic (FM) zig-zag chains. Most *structural* studies have supported the same symmetry ($P2_1/m$), which is expected from Fig.1 (a) (though, bond-valence sums and resonant x-ray scattering invariably show markedly reduced (<25%) between the Mn sites nominally ascribed to the Mn^{3+} and Mn^{4+} sites [2]), until a distinctly different symmetry ($P2_1nm$) and MnO_6 distortions suggested an alternative scenario, the Zener polaron (ZP) picture [3]: it postulates instead, that pairs of nearest-neighbor Mn ions effectively share an electron through the Zener double exchange mechanism, creating strongly bound dimmers the Zener Polarons (ZP), which interact much more weakly (Fig. 1(b)). The idea emerged from a key **structural determination** from single crystal neutron diffraction on $Pr_{0.6}Ca_{0.4}MnO_3$ at T=180K **in the paramagnetic charge ordered (PM-CO)** state [4].

From a *structural* perspective, the Zener polaron ordering picture received theoretical support from *ab initio* calculations[5] but most modern diffraction techniques still dispute it. The discrepancy can be ascribed to the fact experiments have not all been applied in the same PM-CO phase in which the ZP order was deduced in Ref[4], or they are not employing the same methodology: an electron diffraction study in the PM-CO phase [6] confirms the model, but most resonant X-ray scattering experiments (where CO was mostly addressed in the magnetically ordered state), have discarded it. e.g. [7].

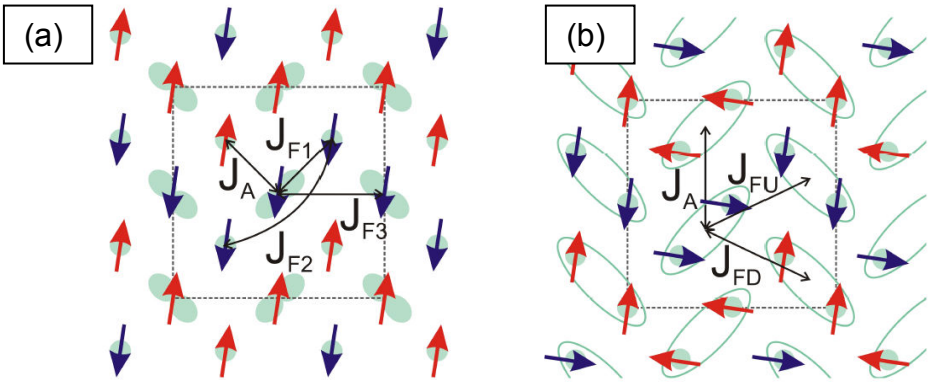

Figure 1: ionic CO model (a) and ZP ordering model(b)

Previous Work: In the past years, we attempted to distinguish the models differently, by investigating the different **ground state magnetism** that they sustain using *elastic and inelastic neutron scattering* data collected on high quality single crystals of the ideal half-doped composition $Pr_{0.5}Ca_{0.5}MnO_3$. The D10 data collected at $T = 10\ K < T_N$ in a smaller |Q| range than in Ref[4] (Exp. Rep. 5-41-421, 2008) do not permit a precise structural study, but enabled the first time refinement of the magnetic structure from single crystal data. It finally concludes that the CE-type magnetic order associated with ionic order fits better alternative non-collinear arrangements which could have been theoretically expected from the ZP model [3], illustrated in Fig. 1(b)). Our complete spin wave spectra in $Pr_{0.5}Ca_{0.5}MnO_3$ and its bilayer analogue $Pr(Ca_{0.9}Sr_{0.1})_2Mn_2O_7$ collected using time-of-flight on the chopper spectrometer ARCS at the SNS also unambiguously exclude any *magnetic* dimerisation [8]. Because the ground state magnetism discards ZP ordering, we came back to **structural investigations on D9 in the PM-CO phase [Exp. Rep. 5-41-569, 2012] (see Fig. 2)**, which verified that the superlattice intensities, like in Ref[4], supports the structural symmetry of the ZP order.

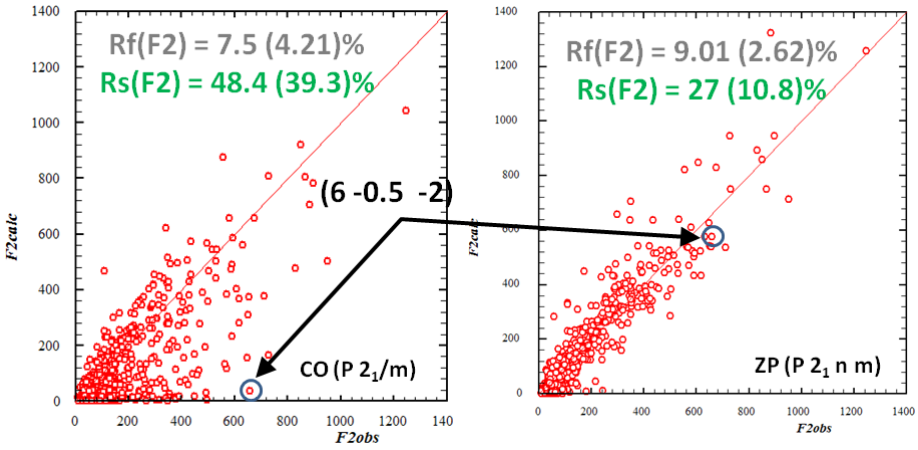

Figure 2: F_{obs} vs F_{cal} plot of the superstructure peaks intensities and their Bragg factors (Rs), in $Pr_{1/2}Ca_{1/2}MnO_3$, Bragg factors for main peaks (Rf) and values for $Pr_{0.6}Ca_{0.4}MnO_3$ Ref[4] in parenthesi. A reflection very sensitive to the symmetry is highlighted.

We conclude, combining all our unpublished result on the x=0.5 crystal, for a unique consistent explanation, which needs a last corroboration[9]: **the ZP picture would be valid above $T_N \sim 170K$ (structurally), but it is modified below,** or said differently, there could be a subtle (note, symmetry allowed) hidden structural transition at T_N restoring/admixing some characteristics of the Goodenough model, at low temperatures.

Proposed experiments: Two experiments on D9 could unravel such a transition. The first is to seek qualitatively for accidents in the temperature dependence of a set of suitable supperlatice reflections (typically, those highlighted Fig. 2, well accounted for by the ZP symmetry but not by the $P2_1/m$ symmetry). For doing this, **we ask for 2 days of beam time on D9**. More quantitatively, we aim at a combined magnetic structure/superstructure refinement of high-Q D9 data at T=10K, using our D10 analysis to constrain the magnetic model. For this part, **we ask for 6 additional days of beam time,** (like what was allocated for the previous experiment at T=190K [Exp. Rep. 5-41-569, 2012]) **so a total of 8 days.**

[1] For a review, see e.g. Y. Tokura (Rep. Prog. Phys. **69** 797 (2006). **[2]** R.J.Goff et al, PRB **70** 140404 (2004); J.Herrero-Martin et al, PRB **70** 024408 (2004); P.G.Radaelli et al, PRB **55** 3015 (1997) **[3]** D.V.Efremov et al, Nature Materials 3 853 (2004). **[4]** A.Daoud-Aladine et al, PRL **89** 097205 (2002). **[5]** G.Zheng & C.H.Patterson, PRB **67** 220404 (2003); V.Ferrari et al, PRL **91** 227202 (2003). **[6]** L.Wu et al, PRB **76**, 174210 (2007); **[7]** M. García-Fernández et al, PRL **103** 097205 (2009). **[8]** T.G.Perring and R.A.Ewings et al, in preparation; G.E.Johnstone, T.G.Perring et al, submitted to PRL. **[9]** A. Daoud-Aladine and T.G. Perring et al. in preparation

Publication

26/09/2012

Proposal: **5-14-251** **Council:** 10/2012

Title: Low temperature structure of charge ordered manganite

This proposal is a new proposal

Researh Area: Physics

Industry: **Not related to industrial application**

Main proposer: **DAOUD-ALADINE Aziz**

ISIS RAL, DIDCOT
CHILTON

OX11 0QX
DIDCOT

Phone: +44(0)1235445504
Fax: +44 (0)1235 44 5200
E-mail: aziz.daoud-aladine@stfc.ac.uk

New neutron user? No
New ILL user? No

Local Contact: FERNANDEZ DIAZ Maria Theresa

Instrument	Req. Days
D9	8

Publication:

Incommensurate magnetism in the coupled spin tetrahedra system Cu2Te2O5Cl2,Zaharko O. Rønnow H.M. Daoud-Aladine A. Streule S. Jurányi F. Mesot J. Berger H. Brown P.J.,Fizika Nizkikh Temperatur,(2005),31,1068-1072

Zener polaron ordering in half-doped manganites,Daoud-Aladine A. Rodríguez-Carvajal J. Pinsard-Gaudart L. Fernández-Díaz M.T. Revcolevschi A.,Physical Review Letters,(2002),89,097205-1-097205-4

Ordering of ferromagnetic Mn-Mn dimers vs. Mn3+/Mn4+ charge ordering in the Pr1-xCaxMnO3 (x,0.5) perovskites,Daoud-Aladine A. Rodríguez-Carvajal J. Pinsard-Gaudart L. Fernández-Díaz M.T. Revcolevschi A.,Applied Physics A,(2002),74,S1758-S1760