ILL RESEARCH PROPOSAL

Printed : 29/09/2006

Experiment Title : **Do Zener polarons exist in half-dop ed CMR manganites?**

Proposal Number

4-01-640

Proposer (to whom correspondence will be addressed)

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New neutron user? **No**

New ILL user? **No**

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

Name and first name	Laboratory	Country
BULL Martyn J.	**RAL, CCLRC , DIDCOT**	**Royaume-Uni**
DAOUD-ALADINE Aziz	**ISIS RAL, DIDCOT**	**Royaume-Uni**
HILL John	**DEPT PHYS, BROOKHAVEN NAT LAB, UPTON**	**États-Unis**

Local contact(s) : **FREEMAN Paul**

Suggested keyword number **4-01**

This proposal is :

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

The main research area of your proposal is

[ ] Biology [ ] Chemistry [**x**] Physics [ ] Materials [ ] Methods and instrumentation
[ ] Engineering [ ] Soft condensed matter [ ] Other :

Industry : **NOT Related to industrial applications**

Instrument required	Days
IN8	**10**

Requested starting time :

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

Unacceptable Dates : **Second half of May onwards**

Sample availability **Now**

Sample description

Substance/Formula : **Pr0.5 Ca0.5 Mn O3**

Mass (in mg) : **1500**

Size (in mm3) : **250**

State : **single crystal**

Surface area :

Space group : **pseudo-cubic**

Unit cell dimension : a = **3.84** b = **3.84** c = **3.84**

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

Sample container :

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 - 40 meV**

Resolution in energy or wavelength : **1-3 meV**

Range of momentum transfer : **1 - 4 Ang^-1**

Resolution in momentum transfer : **0.05 - 0.2 Ang^-1**

Sample environment equipement (supplied by ILL)

Environment equipment : **standard orange cryostat 1.5 - 300 K**

Temperature range (stability) : **4K**

Pressure range : **ambient**

Magnetic-field strength (stability) **0 T**

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

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

To be filled in by ILL

Sample environment code	Comments by Health Physics Officer and Safety Engineer
CO	

Abstract

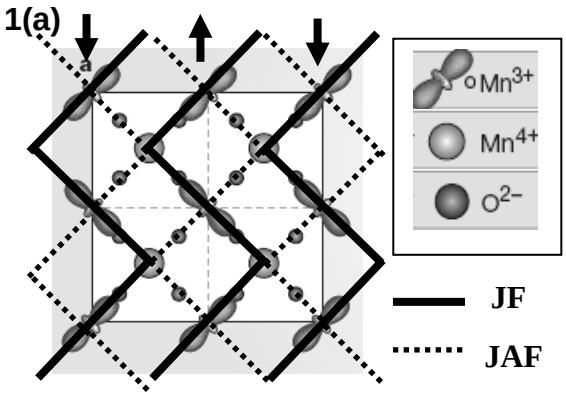
We propose to test for the existence of Zener polarons in Pr0.5Ca0.5MnO3, a manganite that is conventionally expected to show long-range charge ordering. The Zener polaron model, which has recently come to prominence, provides an alternative picture in which pairs of Mn moments are strongly bound to form a single entity with spin 7/2, and which interact magnetically. Distinguishing between the conventional picture of an ordered lattice of Mn3+ and Mn4+ moments with CE-type orbital and charge ordering, and that of an ordered lattice of Zener polarons, is a subtle problem for diffraction, but is in principle straightforward using inelastic magnetic neutron scattering. Zener polarons provide a different approach to understanding ordering in manganites, and this proposal addresses the controversy that surrounds their existence.

Perovskite manganites formula $RE_{1-x}A_xMnO_3$ (RE=rare earth, A=Ca, Sr, Ba, Pb) remain a topic of great interest not just because of the colossal magnetoresistance (CMR) that they can show – up to several orders of magnitude change in resistivity in a few Tesla – but because of the fundamental physics of the metal-insulator transition [1]. These can include photon, electric field, magnetic field and strain-field induced insulator-metal transitions. Each Mn ion has 3 electrons in the t_{2g} *d*-orbitals, and a fraction (1-*x*) have one in the higher energy e_g orbitals, whose spins are aligned parallel to the local t_{2g} moment by strong intrasite exchange. The essential physics is a competition between delocalisation of the e_g electrons, favouring a homogeneous, fully spin polarized, ferromagnetic metal, and localisation due to lattice distortions trapping the e_g electrons to form polarons [2]. For $x \sim 0.3$ the materials are typically ferromagnetic metals, with a sea of polarons in the insulating paramagnetic phase. In the half doped state, $x \sim 0.5$, the polarons typically order to give a charge and orbitally ordered insulating state for $T < T_{CO}$, the charge-ordering temperature.

Surprisingly, despite its relevance to the defining properties of the CMR manganties, the nature of the charge-ordered state is far from well-understood. The picture widely used is of CE type charge and magnetic ordering (Fig. 1a). In a 2D plane of the pseudocubic lattice, half the Mn ions are Mn^{3+} (hence spin 3/2) and half are Mn^{4+} (spin 2); the ions have ferromagnetic (FM) coupling along zigzags, with antiferromagnetic (AFM) coupling between zigzags. Planes are then stacked antiferromagnetically. However, there are some puzzling experimental problems with this simple picture in various half-doped manganites. Bond valence sums applied to the Mn ions typically reveal Mn valences of approximately 3.4+ & 3.6+ rather than the expected 3+ & 4+ at the two sites [3]. X-ray resonant scattering at the Mn *K*-edge also conclude that the valences differ by the same amount [4]. An alternative model that has recently come to great prominence is one in which adjacent Mn^{3+} and Mn^{4+} ions pair up via delocalisation of the lone e_g electron to produce a single unit with spin 7/2 known as a Zener polaron. They form a herringbone pattern (Fig. 1b) with AFM coupling between parallel units, and FM coupling between perpendicular units. This idea emerged from a key single crystal neutron diffraction experiment on $Pr_{0.6}Ca_{0.4}MnO_3$ [5] which implied that the two Mn sites were identical. The concept of Zener polarons has received theoretical support from various *ab initio* calculations [6]. However the idea still remains very controversial [7].

We propose to use inelastic magnetic neutron scattering to distinguish between the two models. Trying to distinguish between a charge ordered (CO) and the Zener polaron (ZP) model by diffraction is extremely subtle, which in part accounts for the controversy. However, inelastic neutron scattering should be able to make the distinction. Fig 2a shows the spin wave dispersion relations for the charge ordered model (solid line); Fig. 2b shows the dispersion for the true Zener polaron model (i.e. arbitrarily strong interaction in the dimer unit) for two scenarios of the FM exchange constants between polarons [8]. The two cases – charge order and Zener polarons – are clearly distinguishable; in particular the ΓX and ΓY directions (parallel and perpendicular to the zigzags respectively) are nearly identical for the charge ordering (Fig. 2a), but are distinctly different for the Zener polaron model (Fig. 2b). Different scenarios for the ratios of the exchange constants for both cases are also distinguishable. An intermediate picture, with the ferromagnetic zigzags in Fig. 1a made from dimers with finite internal FM coupling *JF*, and weaker FM coupling between the dimers, *JF´*(but still AFM coupling between the Mn ions in adjacent zigzags), is shown as dotted lines in Fig. 2a. The signature distinguishing this dispersion from that for the charge ordered model is that relative to the gradient of the low energy dispersion near Γ points, the gap between the 'optic' branches along ΓY is sensitive to the ratio *JF´*/*JF*.

We propose to measure the spin waves at 4K in a 1.5g single crystal (22mm long, 4mm dia) of $Pr_{0.5}Ca_{0.5}MnO_3$, the fully stoichiometric doping of the material used in the paper that initiated the Zener polaron debate [5]. The spin wave bandwidth on the basis of exchange constants in other



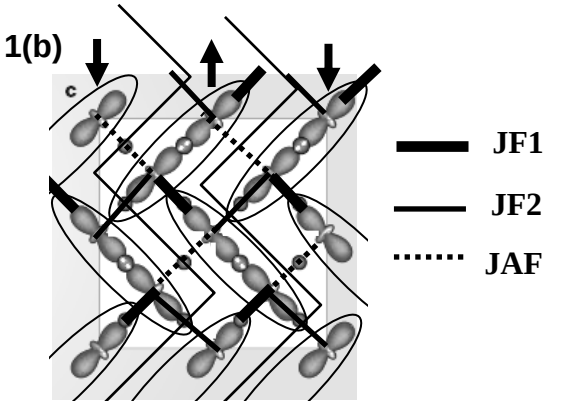
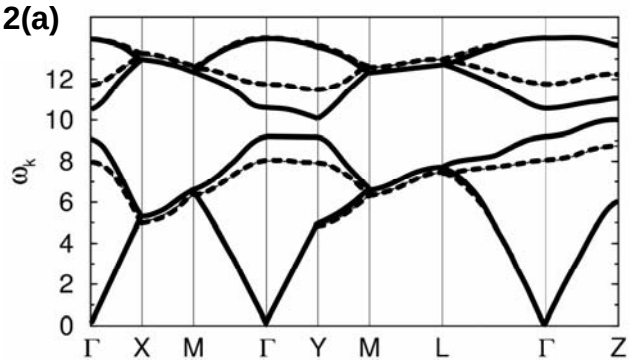


Fig. 1: (a) CE-type charge and magnetic order. Arrows show relative orientations of moments in the FM zigzags. (b) Zener polaron model; one FM zigzag indicated for clarity.



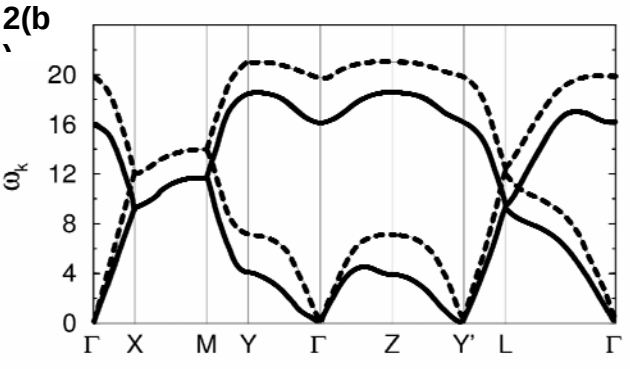


Fig. 2: (a) solid: dispersion for charge order ($JF = JAF = 1$; $JA_Z = 1$); dashed: dimer model described in text (JF=3/2, $JF' = 1/2$, $JA = 1$; $JA_Z = 1$) (b) Zener polaron model; solid: $JF1 = 1$, $JF2 = 0.33$, $JA = JA_Z = 1/2$; dashed: $JF1 = 1$, $JF2 = 0$, $JA = JA_Z = 1/2$. (Note that the Zener polarons form a frustrated lattice). See [8] for details.

insulating manganites is likely to be 15-40 meV, hence IN8 is needed. An unavoidable complication is twinning of the crystal; however the different dispersion and structure factors along different directions, and 'sweet spots' in Q and energy where only one or two domain contribute, mean that with sufficient data the different branches can be isolated. We are asking for 10 days to map the dispersion relations. The theorists who calculated Fig. 2 (ref. 8) are working with us to give the theoretical support needed for planning and analysis in this project. The results will have a direct bearing on the controversy surrounding the Zener polaron, in a manganite in which and localization/delocalization are finely balanced. (We note that recent spin wave data from $(La_{0.25}Sr_{0.75})_2MnO_4$ [9] is in the single layer manganites $La_{1-x}Sr_{1+x}MnO_4$ that do not show metallic behaviour for any x, and charge ordering is suppressed only at fields of ~30T.)

[1] "Colossal magnetoresistive oxides" ed. Y. Tokura (Gordon & breach, 2001) for a review.
[2] A.Millis, Nature **392** 147 (1998) and references therein.
[3] R.J.Goff et al, PRB **70** 140404 (2004); P.G.Radaelli et al, PRB **55** 3015 (1997).
[4] J.Herrero-Martin et al, PRB **70** 024408 (2004); J.Garcia et al, J.Phys.Cond.Mat **13** 3243 (2001)
[5] A.Daoud-Aladine et al, PRL **89** 097205 (2003).
[6] G. Zheng & C.H.Patterson, PRB **67** 220404 (2003); V. Ferrari et al., PRL **91** 227202 (2003).
[7] S.Grenier et al, PRB **69** 134419 (2004)
[8] O.Sikora & A.M.Oleś, Acta Physica Polonica A **106** 659 (2004), Physica B **359** 1300 (2005).
[9] D.Senff et al, PRL **96** 257201 (2006).

Publication

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This proposal is a new proposal

Researh Area: Physics

Industry: **Not related to industrial application**

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New neutron user? No
New ILL user? No

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Instrument	Req. Days
IN8	10

Publication: