

**MS38 O1**

**Magnetic ordering in charge-ordered manganites: ionic vs Zener polarons pictures** Juan Rodríguez-Carvajal, *Institut Laue-Langevin, BP156, 38042 Grenoble Cedex 9, France.* E-mail: [jrc@ill.fr](mailto:jrc@ill.fr)

**Keywords:** magnetic ordering, neutron diffraction, charge ordering

In the  $R_{1-x}D_xMnO_3$  ( $R^{3+}$ ,  $D^{2+}$ ,  $x \approx 1/2$ ) manganites, belonging to the  $ABO_3$  perovskite family, the structural phase transition at  $T_{CO}$  is commonly interpreted (ionic picture) as a concomitant charge and orbital ordering (CO/OO) process driven by a co-operative Jahn-Teller effect and Coulomb repulsion forces. The low temperature phase is supposed to contain well separated  $Mn^{3+}$  and  $Mn^{4+}$  ionic species ordered in a well defined pattern [1, 2]. It is expected, from that model, that  $Mn^{3+}O_6$  octahedra should be strongly distorted and with average Mn-O distance around 2.02 Å, whereas  $Mn^{4+}O_6$  octahedra, having an average Mn-O distance of 1.90 Å, should be nearly undistorted. The so called CO transition may also be interpreted in terms of the formation of Zener polarons (ZP) that order spatially at  $T_{CO}$  [3]. This last picture combines the spatial ordering of the charge density with a partial delocalisation of electrons between few Mn-ions coupling them ferromagnetically. This last interpretation comes from the combination of a structural model obtained from single crystal neutron diffraction demonstrating that the expected distortions from the ionic picture do not occur [3] and the magnetic susceptibility of manganites in which  $T_{CO}$  is higher than the magnetic ordering temperature. In such compounds there are two paramagnetic regions separated by  $T_{CO}$ . The consequences of the ZP picture concerning magnetic ordering will be discussed. The talk will review what is known about the magnetic ordering in manganites, mostly around compositions close to half-doped; the problems related to the degeneracy of solutions in neutron powder diffraction giving rise to nearly the same diffraction pattern for physically different magnetic structures, and new results concerning the magnetic ordering in manganites without chemical disorder in the A-site.

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**MS38 O2**

**Probing Novel Order Parameters in Multiferroics with X-ray Resonant Scattering** D.F. McMorrow<sup>a</sup>, T. Beale<sup>d</sup>, S. Bland<sup>d</sup>, A.T. Boothroyd<sup>e</sup>, R. Ewings<sup>e</sup>, T.Forrest<sup>a</sup>, P.D. Hatton<sup>d</sup>, Y. Joly<sup>f</sup>, D. Mannix<sup>b</sup>, R., D. Prabhakaran<sup>e</sup>, H. Walker<sup>a</sup>, S.B. Wilkins<sup>c</sup>, <sup>a</sup>*Department of Physics, University College London, UK*, <sup>b</sup>*XMaS CRG Beam line, ESRF, France*, <sup>c</sup>*Brookhaven National Laboratory, USA*, <sup>d</sup>*Department of Physics, University of Durham, UK*, <sup>e</sup>*Clarendon Laboratory, University of Oxford, UK*, <sup>f</sup>*CNRS-Grenoble, Grenoble, France.*  
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**Keywords:** Multiferroic, Resonant Scattering

X-ray scattering techniques have been used to study the multiferroic compound  $TbMnO_3$ . A comprehensive set of experimental data will be presented, including non-resonant x-ray magnetic scattering and resonant scattering at the Mn (K and L) and Tb (L and M) absorption edges. From these measurements a complete description is obtained of the relevant order parameters in the different ordered phases of  $TbMnO_3$ . A critical discussion will be given of how these data relate to the known magnetic and structural properties of  $TbMnO_3$ , and to theories of the origin of multiferroicity in this compound.

**MS38 O3**

**Charge Ordering and Isosymmetrical Phase Transitions in Mixed Valence Vanadates  $MV_4O_8$  ( $M=Y, Yb$ )** Karen Friese<sup>a</sup>, Yasushi Kanke<sup>b</sup>, Andy N. Fitch<sup>c</sup>, Andrzej Grzechnik<sup>a</sup>, <sup>a</sup>*Department of Condensed Matter Physics, University of the Basque Country, Bilbao, Spain;* <sup>b</sup>*Advanced Materials Laboratory, National Institute of Material Science, Tsukuba, Japan;* <sup>c</sup>*European Synchrotron Radiation Facility, Grenoble, France.* E-mail: [karen.friese@ehu.es](mailto:karen.friese@ehu.es)

**Keywords:** charge ordering, phase transitions and structure, magnetic materials

The  $\alpha$ - and  $\beta$ -phases of  $YV_4O_8$  and  $YbV_4O_8$  (space group  $P12_1/n1$  for the  $\alpha$ - and  $A2_1/d11$  for the  $\beta$ -phases) are composed of essentially identical  $V_4O_8$  octahedral frameworks and differ only in the arrangement of the trivalent cations [1,2]. As a consequence, one-dimensional disorder and a co-existence of the two polytypic modifications is frequently observed [3,4]. Magnetic susceptibility measurements show anomalies at approximately 190 K for  $\beta$ - $YV_4O_8$  and 183 K for  $\beta$ - $YbV_4O_8$ , which can be attributed to a paramagnetic-paramagnetic transition. At about 80 K, a further magnetic anomaly is observed for both compounds. For  $\alpha$ - $YV_4O_8$ , on the other hand, magnetic anomalies are observed at approximately 78 and 50 K (measurements for  $\alpha$ - $YbV_4O_8$  have not been performed yet).

To characterize the structural response to these magnetic transitions, powder diffraction diagrams of the four phases have been measured in the temperature range from 290 K to 10 K at the European Synchrotron Radiation Facility, Grenoble, France (the beamline ID31). Our studies show no indication of a change in symmetry for all four phases (space group  $P12_1/n1$  for the  $\alpha$ - and  $A2_1/d11$  for the  $\beta$ -phases) in the whole temperature range, yet significant discontinuities in the lattice parameters indicate that some of the magnetic anomalies are accompanied by isosymmetrical phase transitions.

In addition, single crystal diffraction experiments have been carried out on  $\beta$ - $YbV_4O_8$  at the Institute for Synchrotron Radiation (Karlsruhe, Germany). The results confirm the existence of an isosymmetrical phase transition at approximately 180 K, which can be attributed to charge ordering. In the high temperature phase, the four symmetrically independent V-sites are partially occupied by tri- and tetravalent vanadium ions. At the phase transition, the tetravalent vanadium concentrates on one octahedron (V21) while the three trivalent vanadium ions fully occupy the remaining octahedra. This charge ordering is accompanied by discontinuous changes in the V-V, Yb-Yb and Yb-V interatomic distances.

Currently, we are investigating whether comparable phase transitions with a similar underlying mechanism are also present in the other three compounds.

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#### MS38 O4

##### **R<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> pyrochlores under high pressure.**

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**Keywords:** magnetic frustration, high-pressure structure, neutron diffraction

R<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> (R=rare earth) pyrochlores show geometric magnetic frustration and a threshold transition from a ferromagnetic metal to an insulating spin glass state tuned by the rare earth ionic radius  $r_c$ . We studied their crystal structure under pressure by powder X ray diffraction using the synchrotron radiation, showing that they remain cubic with Fd-3m symmetry up to 36 GPa. The pressure induced changes in their microscopic magnetic state were studied throughout the threshold by powder neutron diffraction combined with  $\mu$ SR. In Gd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, ferromagnet at the verge of the threshold ( $r \sim r_c$ ), ferromagnetic long range order coexists with strong fluctuations and is strongly unstable under pressure [1]. In Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> insulating spin glass ( $r < r_c$ ), diluting Tb<sup>3+</sup> ion by La<sup>3+</sup> allows us to cross the threshold, inducing a canted ferromagnetic state akin to an ordered spin ice, where the Tb moments lie close to the local (111) anisotropy axes [2]. The spin glass state is recovered under pressure. In Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> ferromagnet with ( $r > r_c$ ), a reentrant magnetic state is stabilized well below the Curie temperature, associated with a giant anomalous Hall effect [3]. We present new results in Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> by neutron diffraction (at ambient and under pressure), small angle neutron scattering and  $\mu$ SR. Combining these three probes on the same sample allows us to precise the microscopic nature of the reentrant state and its evolution with temperature and pressure.

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#### MS38 O5

**Simultaneous antiferromagnetic Fe<sup>3+</sup> and Nd<sup>3+</sup> ordering in NdFe<sub>3</sub>(<sup>11</sup>BO<sub>3</sub>)<sub>4</sub> investigated by single crystal neutron diffraction,** J. Schefer<sup>a</sup>, M Janoschek<sup>a</sup>, V Pomjakushin<sup>a</sup>, P Fischer<sup>a\*</sup>, D Sheptyakov<sup>a</sup>, L Keller<sup>a</sup>, B

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**Keywords:** Magnetic Structure Determination, Neutron Diffraction, Antiferromagnetism

As promising materials for optoelectronics and with respect to interesting magnetic properties due to competing magnetic sublattices and magnetoelectric interactions, the family of borates RM<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> with R = rare earths or Y, La-Lu and M = Al, Ga, Cr, Fe, Sc is of current interest. GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> has been found [1,2] to exhibit a structural phase transition at 156 K, antiferromagnetic order of the magnetic Fe<sup>3+</sup> moments at 36 K, followed by a spin reorientation phase transition at 9 K. Moreover there is evidence for an induced ferroelectric phase in this material in external magnetic fields which demonstrates a strong correlation between the magnetic order and the dielectric properties of GdM<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>. Concerning technical applications such compounds, e.g. YAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, may be important materials for laser techniques and optical second harmonic generation [3].

By means of magnetic susceptibility and specific heat measurements, x-ray and unpolarized neutron diffraction investigations on powder and single-crystal samples, simultaneous long-range antiferromagnetic Fe and Nd ordering in NdFe<sub>3</sub>(<sup>11</sup>BO<sub>3</sub>)<sub>4</sub> with R 3 2 chemical structure has been found at temperatures below T<sub>N</sub> = 30.5(5) K down to 1.6 K. At temperatures down to 20 K to the propagation vector is  $\mathbf{k}_{\text{hex}} = [0,0,3/2]$  and becomes slightly incommensurate at lower temperatures. Symmetry analysis yields magnetic spiral configurations with the magnetic moments oriented parallel to hexagonal basal plane according to the irreducible representations  $\tau_3$  in the commensurate case. This is in agreement with the easy directions of magnetization perpendicular to the c-axis as determined by magnetic susceptibility measurements. At 1.6 K the magnetic Fe moment amounts to 4.9  $\mu_B$  close to the free ion moment of Fe<sup>3+</sup>. The magnetic Nd<sup>3+</sup> moment saturates presumably due to crystal-field effects at 2.7  $\mu_B$  [4]. There remains some doubt that the chemical structure is R 3 instead of R 3 2, a problem most likely to be solved by neutron single crystal diffraction at TriCS/SINQ and HEIDI/FRM-2.

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