

**Experiment title:**SEARCHING FOR EVIDENCES OF ZENER PAIRS IN  $\text{Mn}_2\text{OBO}_3$ **Experiment****number:**

HE2339

<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 8 February to: 11 February	<b>Date of report:</b>
<b>Shifts:</b> 6	<b>Local contact(s):</b> Dr. Michela Brunelli	<i>Received at ESRF:</i>

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**Report:****Introduction:**

The  $\text{Mn}_2\text{OBO}_3$  is a mixed valent compound with warwickite structure, characterized by the presence of one-dimensional ribbons of edge sharing  $[\text{MnO}_6]$  octahedra. The ribbons are connected by corner sharing and the trigonal  $\text{BO}_3$  groups, defining two inequivalent sites for the Mn ions.

In this compound, a strong Jahn-Teller distortion with an axial elongation of the  $\text{Mn}(1)\text{O}_6$  octahedra [1] signals a charge ordering of the kind  $\text{Mn}^{3+}(1)\text{Mn}^{2+}(2)\text{OBO}_3$ . In addition, an inhomogeneous AF transition takes place at  $T_N=105$  K [2,3] that becomes long-ranged at 35 K [3].

[1] - R. Norrestam, M. Kritikos, A. Sjödin, J. Solid State Chem. **114**, 311, (1995).

[2] - J. P. Attfield, A. M. T. Bell, L. M. Rodríguez-Martínez, J. M. Greneche, R. J. Cernik, J. F. Clarke, D. A. Perkins, Nature **396**, 655, (1998).

[3] - B. Rivas-Murias, F. Rivadulla, M. Sánchez-Andújar, A. Castro-Couceiro, M. A. Señarís-Rodríguez, J. Rivas, Chem. Mat. **18**, 4547, (2006) and references therein.

Also, on the basis of ESR results, it has been proposed that for  $T > 105$  K Zener pairs (ZP) are present in this compound [3]:  $Mn^{3+}$ - $Mn^{2+}$  pairs sharing the extra electron of the divalent cation, similar to the  $Mn^{3+}$ - $Mn^{4+}$  ZP found in Mn perovskites [4]. In these ZP the extra electron of the  $Mn^{2+}$  cation would be localized between the empty  $d_{x^2-y^2}$  orbital of the  $Mn^{3+}$  cation of one ribbon and the half-filled  $e_g$  orbital of the  $Mn^{2+}$  cation of another ribbon [3]

In order to deepen in the structural details of this oxyborate and look for structural evidences of such ZP, we have carried out high resolution powder diffraction experiments using synchrotron radiation.

### Experimental details:

The compound was prepared as polycrystalline powder. The sample was introduced in a capillary of 0.3 mm of diameter to perform high resolution X-Ray powder diffraction studies in the ID31 beam line. The wavelength used was  $\lambda = 0.3994$  Å and the range of scan was  $1-40^\circ$  ( $2\theta$ ) with a step of  $0.003^\circ$ . The SHRPD patterns were recorded from room temperature to 5 K, paying specially attention to temperatures close to the Neel temperature, 105 K. The SHRPD patterns were refined by the Rietveld method using the Rietan software.

### Results:

The corresponding refinements indicate that this compound presents a monoclinic symmetry (space group:  $P2_1/n$ ) in the whole temperature range studied ( $5K \leq T \leq 300K$ ). In figure 1 we show the powder diffraction pattern of this compound at room temperature and the corresponding Rietveld refinement. We have to note that the (h k 0) and (0 k l) reflections show an asymmetric broadening towards the higher and smaller  $2\theta$  angles, respectively. Therefore, these reflections were refined independently and a split pseudo-Voigt function was used to describe the peak profile.

Figure 2 shows the thermal evolution of the cell parameters and the cell volume. There are several notable features in the temperature dependence of the lattice parameters ( $a = 9.2913(2)$  Å,  $b = 9.5270(2)$  Å,  $c = 3.2352(1)$  Å and  $\beta = 90.753(1)$ ) at 5 K): (i) contraction of  $a$  and expansion of  $c$  as temperature increases, (ii) a minimum in  $b$  around 60 K, (iii) expansion of the cell volume as temperature increases, (iv) strong temperature dependence for  $b$  and  $c$  parameters and (v) weak temperature dependence for  $a$  parameter. Although the cell parameters do not show clear

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[4] - A. Daoud-Aladine, J. Rodriguez-Carvajal, L. Pinsard-Gaudart, M. T. Fernandez-Diaz, A. Revcolevschi, Phys. Rev. Lett. **89**, 97205, (2002).

evidences of the presence of ZP, the anomalous anisotropic thermal expansion of the lattice parameters could be related to electronic changes in the manganese cations. In this context, the anomalous temperature dependence for the *a* and *b* parameters (while the *c* parameter follows the expected behaviour) can be due to formation of ZP located in a plane parallel to **ab**, as we have previously proposed [3].

On the other hand, we have studied the thermal evolution of the Mn-O bond lengths and Mn-O-Mn angles involved in the ZP (see figure 3), and we have observed discontinuous changes, specially in the Mn<sup>2+</sup>(2)-O(4) length and in the Mn(2)-O-Mn(1) angle: on heating from very low temperature, the former suddenly diminish, while the latter suddenly increases.

Taking into account that, according to the Virial theorem, a transition from *localized* to *itinerant* electronic behaviour would result in discontinuous changes in the equilibrium bond lengths and bond angles (with  $(\text{Mn-O})_{\text{localized}} > (\text{Mn-O})_{\text{itinerant}}$ , and  $(\text{Mn-O-Mn})_{\text{localized}} < (\text{Mn-O-Mn})_{\text{itinerant}}$  [5], our results would be in favour of the formation of ZP at around 105 K.

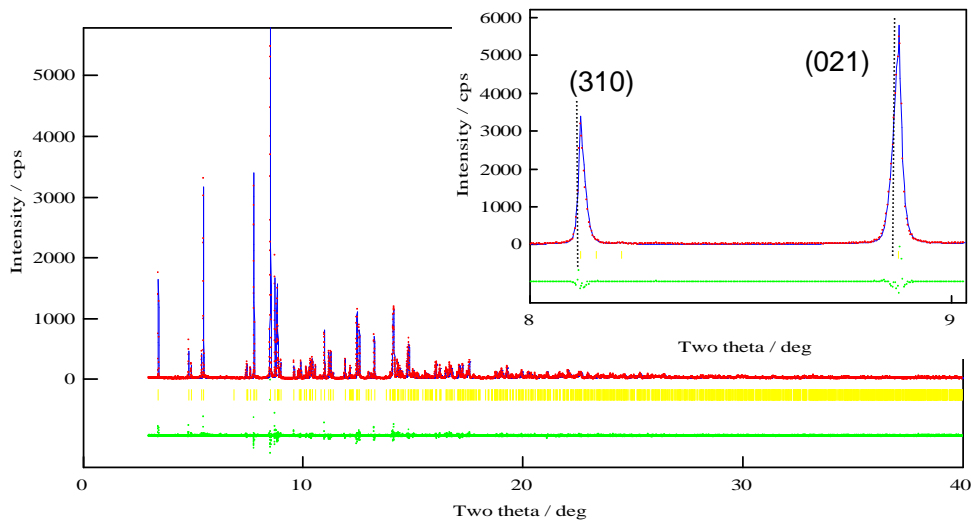
On the other hand, the effect of the ZP formation is very weak for the Mn<sup>3+</sup>(1)-O(4) bond, probably because it is a short bond length, that is under compression.

In conclusion, we have observed for the Mn<sub>2</sub>OBO<sub>3</sub> compound discontinuous changes in the Mn-O bond lengths and Mn-O-Mn bond angles, which are compatible with a transition from localized to itinerant electronic behaviour. These results confirm the formation of Zener pairs in this compound at around 105 K, as previously detected by ESR.

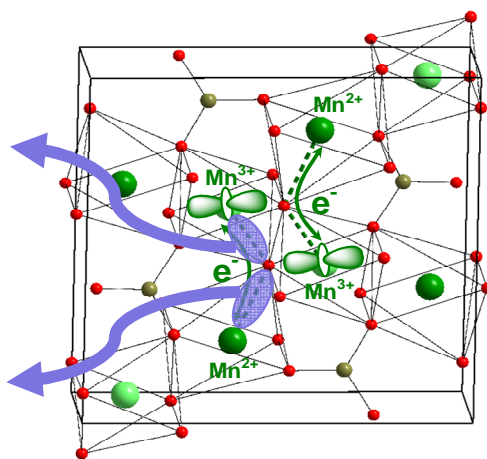
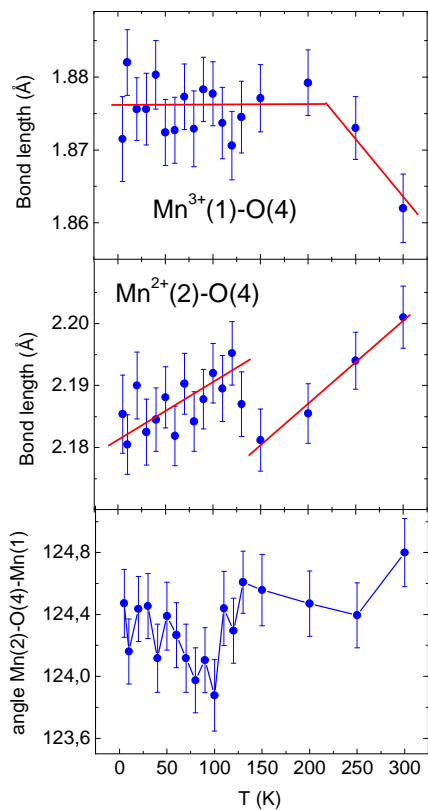
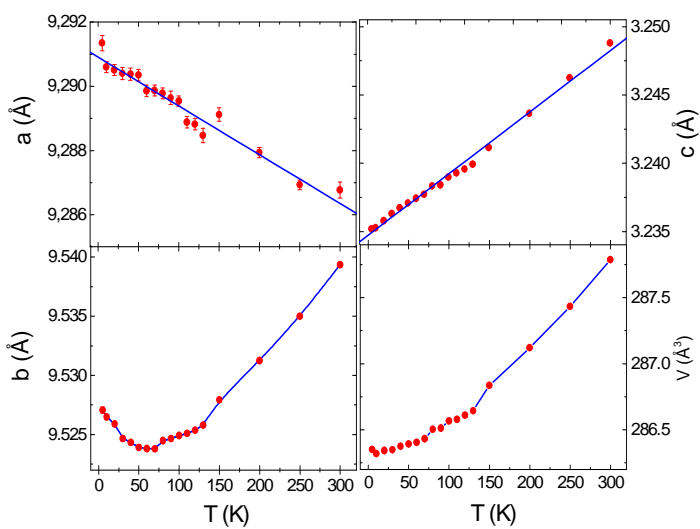
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[5] J. B. Goodenough in "Localized to Itinerant Electronic Transition in Perovskite Oxides", Structure and Bonding 98, Springer Verlag, Berlin (2001).

**Figure 1**



**Figure 2**



**Figure 3**