## VERWEY-LIKE TRANSITION IN A LITHIUM BATTERY MATERIAL: THE SPINEL LiMn<sub>2</sub>O<sub>4</sub>

J. Rodríguez-Carvajal<sup>1</sup>, G. Rousse<sup>2</sup>, C. Masquelier<sup>2</sup>, M. Hervieu<sup>3</sup>

## <sup>1</sup>Laboratoire Léon Brillouin (CEA-CNRS)

<sup>2</sup> Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay Cedex, France.
<sup>3</sup> CRISMAT, ISMRA, 6 Bld du Maréchal Juin, 14050 Caen Cedex, France.

An increasing interest has developed around Li-Mn-O spinels due to their potential use as positive electrode materials in lithium rechargeable batteries. A vast majority of the studies devoted to these compounds deals with their electrochemical characteristics in lithium cells<sup>[1]</sup>; only very recently, their structural and physical properties have also been studied<sup>[2-4]</sup>. The stoichiometric compound LiMn<sub>2</sub>O<sub>4</sub> presents a first order structural transition close to room temperature (RT) that was attributed to a Jahn-Teller distortion<sup>[4]</sup>. In the case of Mn-perovskites close to the composition  $(R_{1/2}D_{1/2})MnO_3$  (R: trivalent rare earth, D: divalent ion), structural phase transitions accompanied by sharp modifications of electronic and magnetic properties have been attributed to charge-ordering<sup>[5]</sup>. This phenomenon is supposed to be due to the Coulomb interaction that overcomes the kinetic energy of carriers below a certain temperature (Wigner crystallization) producing an alternating Mn<sup>3+</sup>-Mn<sup>4+</sup> NaCl-like lattice. This mechanism was first invoked by Verwey in 1941 to explain the low temperature transition in magnetite  $Fe_3O_4$  as a  $Fe^{2+}-Fe^{3+}$  ordering within the B-sites of the spinel structure<sup>[6]</sup>. In spite of a different lattice organization of Mn ions in the spinel as compared to Mn-perovkites, it is reasonable to expect some kind of similar electronic behaviors in both families.

To date, the structural details of charge-ordered Mnperovskites are quite limited, since the superstructure reflections in neutron powder diffraction patterns are barely visible and single crystals show complicated twinning effects. It is extremely important to know whether the ionic picture usually invoked to describe the charge ordering in these materials is supported by structural experimental evidence. For instance, the simple NaCl-like ordering picture of Mn<sup>3+</sup> and Mn<sup>4+</sup> ions in La<sub>1/2</sub>Ca<sub>1/2</sub>MnO<sub>3</sub> has not yet been confirmed definitively even if experimental data are not in contradiction with such a picture<sup>[7]</sup>. We have recently shown that the ionic picture is well supported in the case of LiMn<sub>2</sub>O<sub>4</sub> spinel and we have demonstrated that the charge-ordered state is not complete at  $230K^{[8]}$ 9]

DSC (Differential Scanning Calorimetry) experiments confirmed the presence of a first order transition

around RT. With a cooling rate of 5 K/mn, the cubic  $\rightarrow$  orthorhombic transformation starts at 290K with a hysteresis of 10K (fig.1). An increase of resistivity is observed upon cooling to the low temperature phase (fig.1). The activation energy of the low temperature form is slightly higher but similar to that of the high temperature. The charge carriers are very probably Jahn-Teller small polarons.



Figure 1: DSC and resistivity of LiMn<sub>2</sub>O<sub>4</sub>

Neutron diffraction experiments were performed using the high-resolution powder diffractometer 3T2. The high temperature form was carefully studied at 350K  $(a=8.2495(2)\text{\AA})$  to confirm the crystalline quality and the stoichiometry of the sample (fig.2). The refined value of the oxygen occupation was the nominal value within the experimental error. The unique Mn-O distance is 1.9609(3) Å, which is intermediate between what is expected for Mn<sup>3+</sup>-O and Mn<sup>4+</sup>-O bond lengths. Neutron powder diffraction at low temperature showed many small superstructure reflections (fig.2). The indexing of the pattern using solely the neutron data was ambiguous and gave several reasonable solutions due to the strong overlap between neighboring reflections. The information provided by electron diffraction at different temperatures was of capital importance for finding a " $3a \times 3a \times a$ " supercell and extinction conditions compatible with the space group *Fddd*.



Figure 2: Details of the observed and calculated neutron diffraction patterns (l=1.2253 Å) of the high temperature charge-disordered phase (350K), and of the low temperature partially charge-ordered phase (230K) of LiMn<sub>2</sub>O<sub>4</sub>. Additional tick marks in the low temperature pattern correspond to the superstructure reflections.

The final atom positions can be found in reference [8]. The analysis of the structure obtained from the Rietveld refinement of our neutron data clearly shows the electron ordering nature of the phase transition and allows us to interpret the resistivity measurements. Two Mn-sites correspond to well-defined Mn<sup>4+</sup> ions (the average Mn-O distance is 1.91Å). The other three sites are not pure Mn<sup>3+</sup> ions. This is revealed by the average Mn-O distance for the three Mn-sites (2.00 Å) which is slightly smaller than what is expected for pure  $Mn^{3+}$  (2.02 Å). To simplify the visualization of the crystal structure we have represented in Fig. 3 an idealized projection along [001] of the Mn and Li sites within a unit cell. Neglecting the z-position of the atoms, it is apparent that octagonal cylinders surfaces (hole-rich regions), containing all the Mn<sup>4+</sup>, wrap two types of Mn<sup>3+</sup> columns (electron-rich regions) which are distinguished by the presence, or lack therein, of Li ions. The space between the octagonal cylinders is occupied by columns containing the Mn(1) site in the special position (16d).



Figure 3. Simplified projection of the charge-partiallyordered structure. Oxygen atoms have been removed from the drawing. Static holes  $(Mn^{4+}, blue \ circles)$  wrap columns of nearly pure  $Mn^{3+}$  ions along the *c*-axis. 8/72=1/9 of the total number of holes are mobile within the  $Mn^{3+}$  sublattices.

The average valence of Mn ions, obtained from chemical analysis and structure refinement at high temperature, indicates that the number of holes  $(Mn^{4+})$ in the eg-band is equal to the number of electrons  $(Mn^{3+})$  available for hopping. The crystal structure indicates that there are 64 localized holes per unit cell, so there are eight remaining holes per cell distributed within the remaining 80 Mn positions. Thus, a certain electron hopping should persist at low temperature as revealed by the previous analysis. This is consistent with the semiconducting characteristics of the compound below the transition temperature. The static distortion of the three  $Mn^{3+}O_6$  octahedra is consistent with a slightly attenuated Jahn-Teller effect<sup>[9]</sup> due to the remaining electron hopping towards the 8 holes per cell. The charge ordering process is, consequently, accompanied by the presence of an orbital ordering which is the manifestation of the Jahn-Teller polaronic nature of the mobile charges above and below the transition temperature.

To our knowledge this is the first time that a partial charge ordering transition is clearly observed in a Mn oxide. The electronic crystallization observed in this compound must be due to a combination of Coulomb interaction and another mechanism implying electron-lattice coupling as is the Jahn-Teller effect. The analysis of the crystal structure shows that the ionic model seems to be adequate and the usual  $Mn^{3+}$ -  $Mn^{4+}$  picture is well justified in LiMn<sub>2</sub>O<sub>4</sub>.

## References

- [1] M.M. Thackeray, *Prog. Solid St. Chem.* 25, 1 (1997), and references therein.
- [2] C. Masquelier et al., J. Solid State Chem. **123**, 255 (1996).
- [3] V. Massarotti et al., J. Solid State Chem. 131, 94 (1997).
- [4] H. Yamaguchi, A. Yamada, and H. Uwe, *Phys. Rev.* B58, 8 (1998).
- [5] Y. Tomioka et al., Phys Rev Lett 74, 5108 (1995)
- [6] E.J.W. Verwey, and P.W. Haaymann, *Physica* **8**, 979 (1941).
- [7] P. Radaelli, D.E. Cox, M. Marezio, and S.-W Cheong, *Phys Rev B* 55, 3015 (1997)
- [8] J. Rodriguez-Carvajal et al., Phys Rev Lett 81, 4660-4663 (1998)
- [9] J. Rodriguez-Carvajal et al., Phys. Rev. **B57**, R3189 (1998)