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High Resolution Electron Microscopy evidence of stacking faults in O-$LiMnO_2$

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HREM study of stacking faults in O-$LiMnO_2$ is presented as a confirmation of the previous model obtained from XRD measurements.

Keywords: lithium battery; stacking faults; manganese oxide

INTRODUCTION

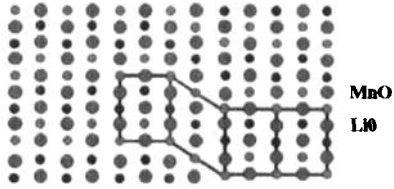
The synthesis of orthorhombic $LiMnO_2$ (O-$LiMnO_2$) very small crystals ($\Phi \approx 0.3$ μm) leads to peculiar X-ray diffraction patterns[1]. Cell parameter refinements made on thin unaltered reflections (with even k) showed that, compared to phases with bigger crystals, b and c cell parameters remain unchanged, whereas an important increase of the a parameter is observed. Other reflections (with $k = 2n+1$ and $h \neq 0$) are substantially widened, while the remaining peaks ($k = 2n+1$ and $h = 0$) present a strong asymmetry. These features could successfully be related to stacking faults corresponding to a $\vec{b}/2$ translation of O-$LiMnO_2$.

EXPERIMENTAL

The Electron Diffraction (ED) study was performed with a Philips CM30 electron microscope operating at 300kV. The HREM study was carried out with a Hitachi H9000NAR electron microscope operating at 300kV giving a point to point resolution of 1.8 Å.

The samples were gently ground in butanol then, microcrystals were deposited on a holey carbon film supported by a Cu grid. Image calculations were performed using MACTEMPAS and CRYSTALKIT programs[2].

FIGURE 1 Monoclinic stacking fault (See Color Plate IV).



X-RAY STUDY

As previously reported, a simulation made with the Diffax program[3] allowed to very well reproduce the experimental X-ray diffraction pattern, showing a statistical distribution of the stacking faults, at least for the low fault concentration corresponding to the samples under study. The occurrence of the stacking faults may be viewed as the insertion of a monoclinic cell between two blocks of orthorhombic symmetry (Fig. 1). This cell ($a \approx 5.53$Å, $b \approx 2.80$Å and $c \approx 5.30$Å) corresponds to a newly obtained monoclinic $LiMnO_2$ phase prepared by a topotactic deintercalation of α-$NaMnO_2$[4,5]. In order to confirm the XRD study conclusions, HREM experiments were performed.

HTEM STUDY

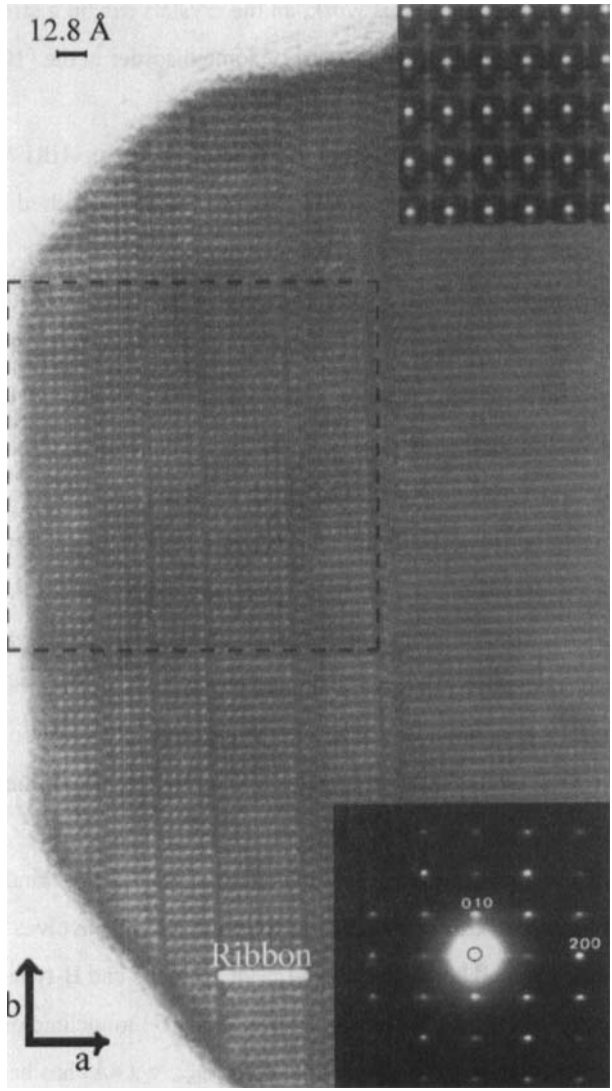


FIGURE 2 [001] HREM image of a faulted orthorhombic $LiMnO_2$ crystal. The LiO interlayer spacing appears as white dots. Calculated image is included as an inset (focus -70 nm and thickness 40 nm)

The ED study confirms the space group determined during the previous XRD experiment[1]. According to this work, all the crystals exhibit a streaking of the spots along a^* evidencing the existence of some disorder in the [100] direction (Fig. 2 bottom inset).

In order to understand the origin of this disorder an HREM study was performed. Fig. 2 represents an [001] HREM image of a faulted orthorhombic $LiMnO_2$ crystal. Calculated image is shown in the upper inset.

Due to a slight tilt of the crystal, the spacing between two LiO layers is imaged as white dot rows. The double MnO layers appear as dark contrast zones between two white dot rows. O-$LiMnO_2$ unit cell ribbons running along b are observed. Note that ribbons width is changing along a. This feature explains the spots streaking observed along a^*, in the [001] ED patterns.

In order to improve the observed contrast, specially in the thicker part of the crystal, the dotted part of figure 2 was processed. In the filtered image (see Fig. 3), six O-$LiMnO_2$ ribbons are observed. Depending on the way white dots rows of two successive ribbons are aligned or not, two kinds of boundaries can be described: A-type boundary where the white rows of one ribbon are translated by b/2 with respect to each other, and B-type where the white rows are aligned.

Taking into account the XRD study conclusions, the two kinds of observed boundaries can be modeled as follows: A-type, involves the insertion of one monoclinic cell between two O-$LiMnO_2$ blocks and B-type corresponds to an orthorhombic $LiMnO_2$ cell sandwiched by two monoclinic ones. The possibility of two successive monoclinic cells (d_{theo} = 9.4Å) has been ruled out due to the observed distance between two ribbons (dobs = 13.4Å)

In order to confirm the proposed structure for the boundaries, calculated through-focus series of non faulted O-$LiMnO_2$ (see Fig. 4) and A-type boundary were performed .

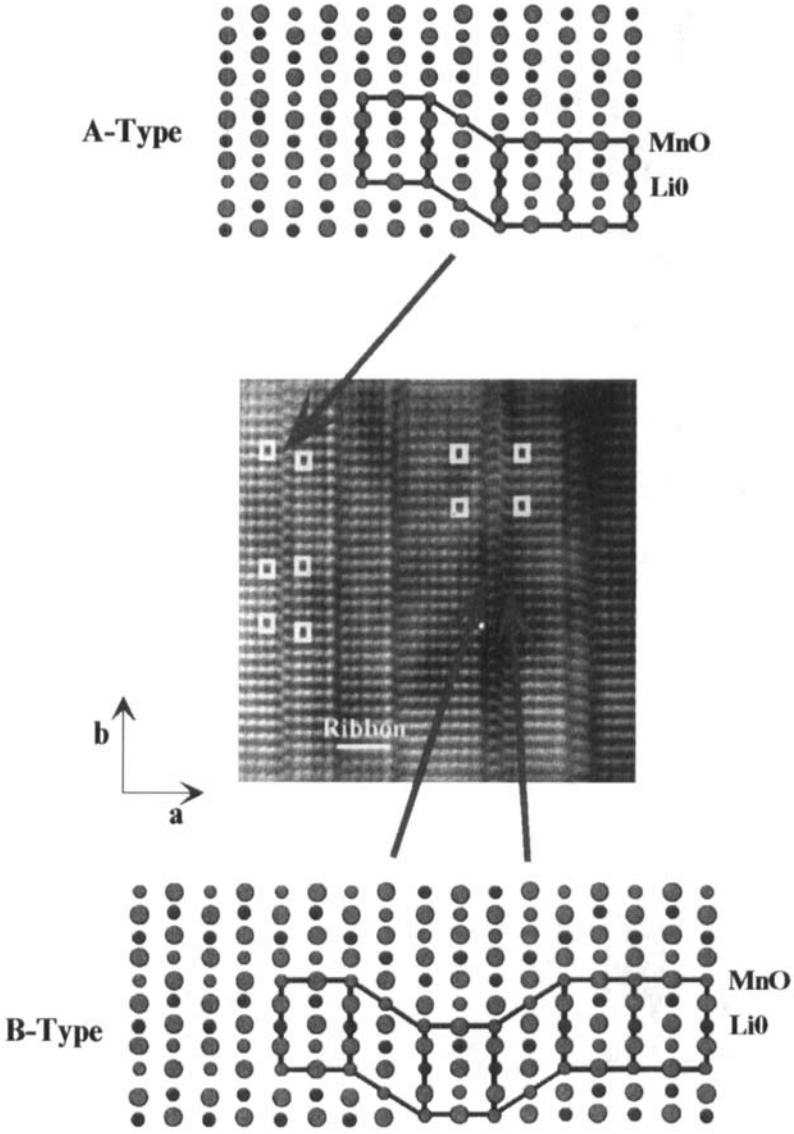


Figure 3 HREM filtered image with A- and B-type models for boundaries

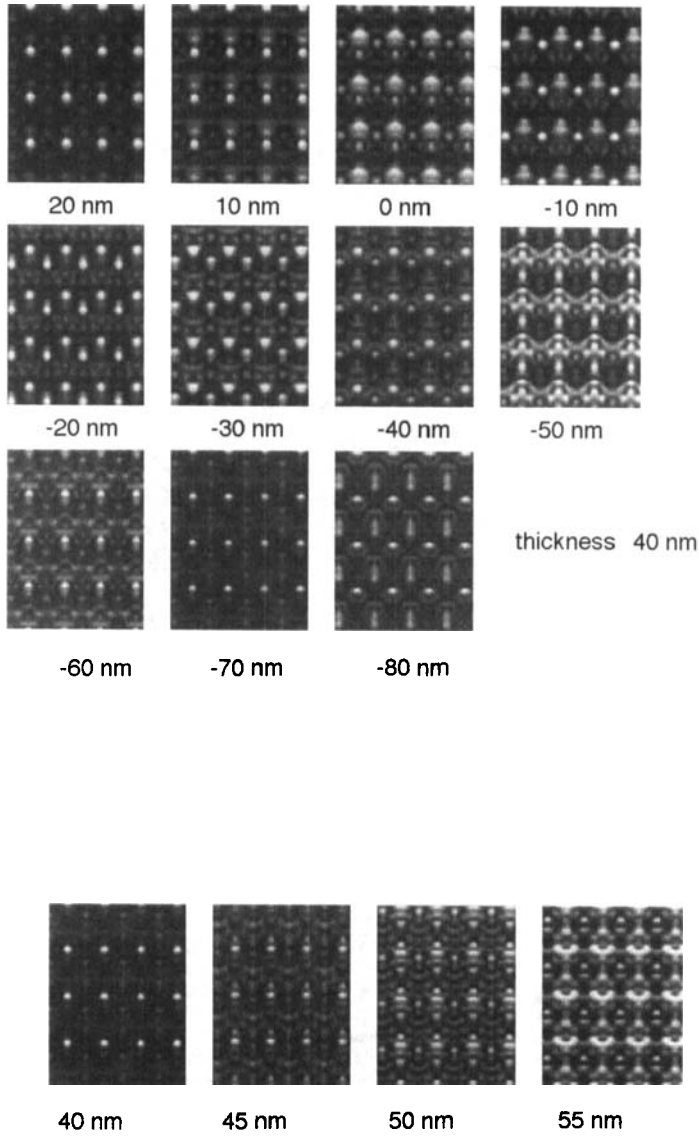


FIGURE 4 Through-focus series of O-$LiMnO_2$: focus step 10 nm, thickness 40 nm (upper images). Thickness influence: focus - 70 nm, thickness step=5 nm (lower images)

The experimental contrast observed at the level of the boundary fits quite well with the calculated one (see Fig. 5). In fact, the boundary contrast is built from three white dots (see black arrows) forming an obtuse angle (see yellow lines).

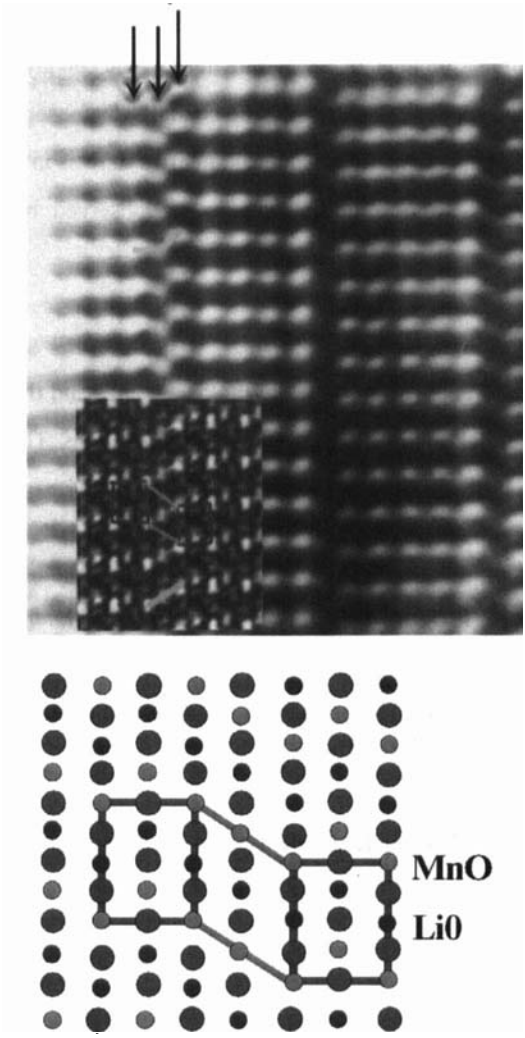


Figure 5 a) enlarged filtered image of the A-type boundary. Calculated image is showed as an inset (focus -70 nm and thickness 40 nm) ; b) schematic model of the A-type boundary. (See Color Plate V).

The slight differences observed between the calculated contrast and the experimental one, mainly concerning the value of this angle, may be attributed to some distortions in the connection between LiO and MnO layers.Most of the crystals studied exhibit these type of defects. In fact, crystals are built up from orthorhombic domains joined by one monoclinic cell layer. The size of the ribbons increases with the thickness of the crystal. This observation is consistent with the presence of a higher number of defects in the sample edge. Only in a few cases, are two successive b/2 shifts observed, but always at crystal edge.

CONCLUSION

This HREM study confirms completely the occurrence and the nature of the stacking fault model obtained from previous XRD studies. The presence of these faults do seem to be critical in obtaining high performance cathodic materials in lithium batteries[6].

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