

# Suppressing the charge-ordering transition in $\text{LiMn}_2\text{O}_4$ through substitution of Li by Mg

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The important electrode material  $\text{LiMn}_2\text{O}_4$  undergoes a first order structural phase transition near room temperature. This transition, known to affect electrode characteristics, was long thought to result from the Jahn–Teller nature of  $\text{Mn(III)}$ . However, Rodríguez-Carvajal and coworkers have recently established that with half-integral charge on Mn, what actually takes place at the transition is the crystallization of holes and electrons (charge ordering) in the crystal structure. Since the tendency to charge ordering is suppressed when charges on ions are *not* simple fractions, we have substituted Mg for Li to take Mn away from an average valence of 3.5. The transition is suppressed with as little as 4 atom% of Mg substitution for Li. The results suggest that the charge-ordering transition and Jahn–Teller distortions of the  $\text{Mn}^{\text{III}}\text{O}_6$  octahedra are distinct phenomena.

At sufficiently low densities, electrons in a uniform background of positive charges are sometimes found in ordered arrays. This discovery by Wigner<sup>1</sup> arises because the potential energy of interaction varies as the inverse average distance between electrons, while the kinetic energy varies only as the square of the inverse distance. At large distances (larger Wigner–Seitz radii or low densities) the kinetic energy is ineffectual in compensating the potential term and the formation of an ordered array of charges is favored.<sup>2</sup> In certain crystalline oxides, the necessary conditions of carrier density and conduction band width are met and the transition from nearly free electron behavior at high temperatures to localized and ordered carriers (real-space crystallization of the electrons and holes) at low temperatures have been experimentally realized. The first observation of this phenomenon was in  $\text{Fe}_3\text{O}_4$  by Verwey in a transition that now carries his name.<sup>3</sup>

The positive electrode material  $\text{LiMn}_2\text{O}_4$ , well studied because of its use in rechargeable Li-ion batteries, has been known to undergo a first order structural transition near room temperature.<sup>4</sup> In much of the literature, this transition has been discussed as arising from the Jahn–Teller nature of  $\text{Mn(III)}$ , and means of counteracting the transition have usually involved substituting Li for Mn, thereby increasing the oxidation state of Mn in  $\text{LiMn}_{2-x}\text{Li}_x\text{O}_4$ .<sup>5,6</sup> The transition within the Jahn–Teller scenario has been examined using X-ray diffraction<sup>7</sup> and by EXAFS.<sup>8</sup> The latter study suggests that even when the phase is cubic on average, the octahedra around  $\text{Mn(III)}$  are distorted. Sugiyama *et al.*<sup>9</sup> have studied the changes in the transition temperature on creating oxygen defects in the  $\text{LiMn}_2\text{O}_{4-\delta}$  structure. Their findings, analyzed within the Jahn–Teller framework, suggest that at low defect concentrations ( $\delta \approx 0.05$ ), the transition temperature goes through a minimum and then rises again to approach 290 K when  $\delta = 0.1$ . In this study, the substitutional series involved an increase in the amount of  $\text{Mn(III)}$  but the manner in which this was achieved makes interpretation a formidable task. Amatucci *et al.*<sup>10</sup> have studied the variation of the phase transition temperature in  $\text{Li}_x\text{Mn}_2\text{O}_{4-\delta}$  as a function of  $x$  and  $\delta$ , with emphasis on the electrochemical characteristics.

Shimakawa *et al.*<sup>11</sup> have, however, recognized the connection between  $\text{LiMn}_2\text{O}_4$  and the prototypic charge ordering spinel,  $\text{Fe}_3\text{O}_4$ , and pointed out that perhaps what is observed in  $\text{LiMn}_2\text{O}_4$  is a Verwey transition. The recent detailed structural work by Rodríguez-Carvajal and coworkers<sup>12</sup> using low temperature electron and neutron diffraction, the latter in conjunction with Rietveld refinement, has confirmed that in the low temperature phase, the structure (refined at 230 K) has  $Fddd$  symmetry and a  $3a \times 3a \times a$  supercell, where  $a$  refers to the cubic ( $Fd3m$ ) spinel cell parameter. Bond valence sum (BVS) calculations support a picture of charge ordering, with two classes of oxygen octahedra respectively surrounding  $\text{Mn(III)}$  and  $\text{Mn(IV)}$ . The  $\text{Mn(III)}$  octahedra are significantly distorted, as expected, while the  $\text{Mn(IV)}$  octahedra are not. This study by Rodríguez-Carvajal and coworkers is particularly important in the light of the considerable recent work on charge ordering in perovskite manganites associated with the phenomenon of giant magnetoresistance.<sup>13,14</sup>

Working within the assumption that it is not the amount of  $\text{Mn(III)}$  alone that leads to the structural transition, but the fact that  $\text{LiMn}_2\text{O}_4$  has half-integral valence leading to charge ordering,<sup>15</sup> we have substituted the similarly-sized  $\text{Mg}^{2+}$  ion into the  $\text{Li}^+$  sites in the hope that taking Mn away from a charge of 3.5 in *any* direction would suppress the transition. We find that with as little as 4 atom% of Mg substitution for Li, the transition is almost completely suppressed. The results are not only of technological significance, but also support the view that the transition indeed arises through the real-space ordering of holes and electrons.

## 1 Experimental

The spinel samples were prepared from  $\text{Li}_2\text{CO}_3$ ,  $\text{MgCO}_3$ , and manganese oxalate ( $\text{Mn}^{\text{II}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) taken in suitable stoichiometric amounts. Well-ground powders were pre-fired in air at 1023 K for 24 h. This was followed by regrinding, pelletising and firing in air for 12 h at 1073 K. The conditions used were identical for all the samples. Powder X-ray diffraction in the reflection ( $\theta$ – $2\theta$ ) geometry was recorded using  $\text{Cu-K}\alpha$  radiation on a Siemens D5005 diffractometer and treated using Rietveld analysis as implemented in the XND code.<sup>16</sup> Mn oxidation states were determined as

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follows: known amounts of the compounds dissolved in acidified, standard  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  solutions were titrated against standard dichromate solutions, with the end-points being determined potentiometrically. We believe the average valences presented here to be reproducible to  $\pm 0.01$ . The phase transition was followed by differential scanning calorimetry on a Perkin-Elmer DSC2C instrument using heating and cooling rates of  $20 \text{ K min}^{-1}$ .

## 2 Results and discussion

### 2.1 Structure

The ionic radii<sup>17</sup> of four-coordinate  $\text{Li}^+$  ( $0.59 \text{ \AA}$ ) and of  $\text{Mg}^{2+}$  ( $0.57 \text{ \AA}$ ) are very similar. Small substitutions of Mg for Li would be difficult to follow through variations in the lattice parameter. We have therefore examined four compositions of  $\text{Li}_{1-x}\text{Mg}_x\text{Mn}_2\text{O}_4$  viz.  $x=0$ ,  $x=0.05$ ,  $x=0.10$  and  $x=0.15$  by Rietveld refinement of the powder X-ray diffraction profiles. Measured and calculated diffraction patterns for the four phases are presented in Fig. 1. There was no evidence for any phase other than the cubic spinel in any of the samples. No evidence was found for any change in the symmetry of the phases for these substitutions, though there was a perceptible broadening of the patterns when  $x \neq 0$ . The origins of this broadening will be examined below. All the patterns could be refined to  $R_{\text{Bragg}}$  values of less than 5%.

Parts (a) and (b) of Fig. 2 display results from the analysis of the diffraction patterns. The variation of the  $a$  parameter with  $x$  shown in part (a) suggests that even with up to 15% substitution of Mg for Li, the changes in the lattice parameter are miniscule. The initial increase for a very small substitution ( $x=0.05$ ) possibly reflects two opposing effects. The first is the substitution of the smaller  $\text{Mg}^{2+}$  for  $\text{Li}^+$  which would tend to contract the unit cell. The second is the reduction of the Mn oxidation state which would tend to expand the unit cell. Using reported values for the "titrations" of the lattice parameter against Li content<sup>18</sup> and of the lattice parameter against oxygen content,<sup>4</sup> we can confirm that the  $x=0$  compound, with a lattice parameter of  $8.244(7)$ , is nearly perfectly stoichiometric.

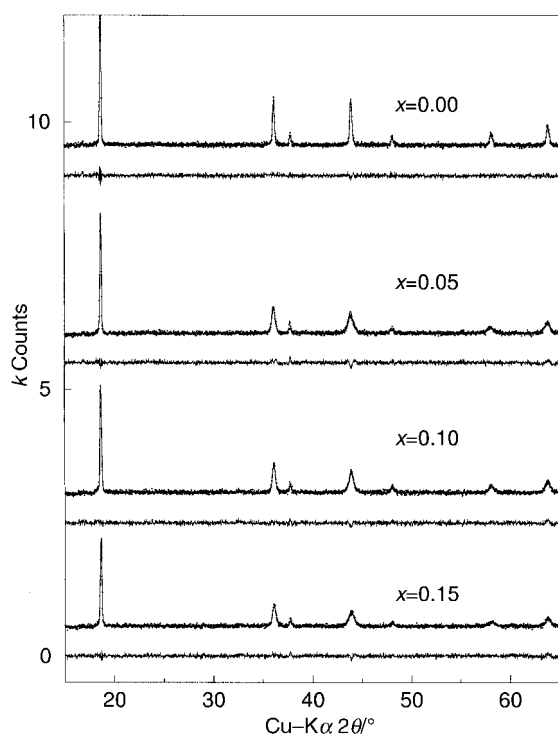


Fig. 1 Experimental (points) and Rietveld-fitted X-ray diffraction profiles of  $\text{Li}_{1-x}\text{Mg}_x\text{Mn}_2\text{O}_4$ . Difference profiles (between data and fit) are also displayed.

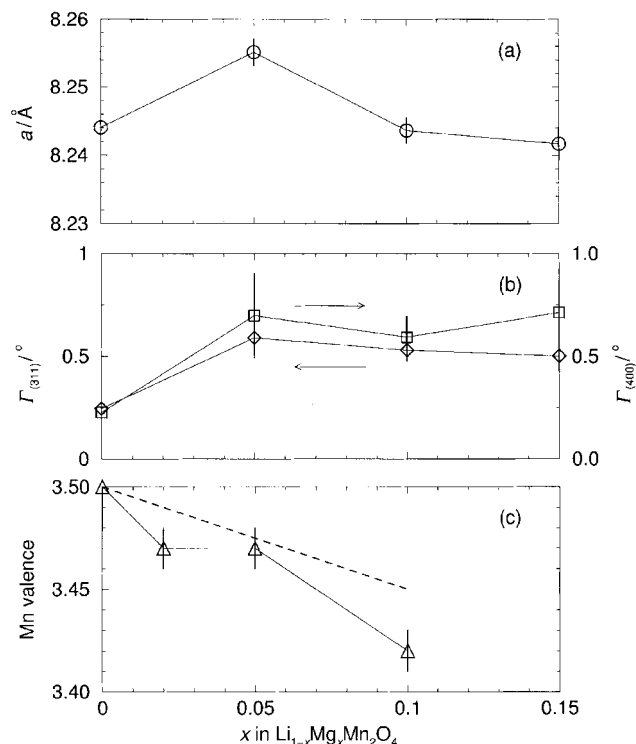


Fig. 2 (a) Evolution of the cubic cell parameter of  $\text{Li}_{1-x}\text{Mg}_x\text{Mn}_2\text{O}_4$  as a function of  $x$ . (b) Evolution of the diffraction full widths at half-maximum (FWHM) of the 311 and 400 reflections. (c) Evolution of the average Mn valence, as determined by potentiometric titrations. The dashed line corresponds to the values expected from the nominal stoichiometries.

Part (b) of the figure indicates the evolution of the linewidths of two of the reflections in the spinel structure, the 311 reflection appearing at a  $2\theta$  value of around  $36^\circ$  and the 400 reflection appearing at a  $2\theta$  value of around  $44^\circ$ . The peaks were separately refined as a sum of a Gaussian and a Lorentzian width and the sum of these is displayed. It is evident that the addition of Mg in place of Li results in a noticeably broader linewidth corresponding to decreased crystalline correlation or increased strain in the structure. The increase in the linewidth seems to occur for very small substitutions (less than 5 atom% Mg), after which it saturates. The only explanation that we are able to offer for this unusual behavior is that, even for very small substitutions, the  $\text{Mn}^{\text{III}}\text{O}_6$  octahedra are locally distorted and form structures that are averaged into what seems to be a cubic phase when probed by powder XRD. This notion gains credence from the EXAFS study of Yamaguchi *et al.*<sup>8</sup> who find evidence for distorted  $\text{Mn}^{\text{III}}\text{O}_6$  in  $\text{LiMn}_2\text{O}_4$  even at 300 K, a temperature which is above the charge-ordering transition temperature. Indeed, through an *in situ* electrochemical XRD study, Le Cras *et al.*<sup>19</sup> have demonstrated structural changes from cubic to tetragonal as soon as Li insertion commences in  $\text{LiMn}_{2-x}\text{Li}_x\text{O}_4$ . This suggests that Mg substitutions might pin local distortions, but in a manner that is crystallographically incoherent and therefore does not, for small Mg amounts, result in changes in the bulk crystal structure, but does manifest as a broadening of the X-ray Bragg peaks.

Thackeray *et al.*<sup>20</sup> have examined Li insertion in  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  electrochemically, following the open-circuit voltage as a function of composition, and by powder X-ray diffraction. They find that the XRD patterns can be indexed in a tetragonal ( $I4_1/amd$ ) unit cell when  $x$  exceeds 0.1, *i.e.* the average Mn valence decreases to less than 3.45. We expect the structural change from cubic to distorted (tetragonal in the first approximation) structures to become noticeable only for rather high Mg contents. While we have presented the analysis of

XRD patterns for relatively high substitutions (up to 15 atom%), the trends are expected to be valid for the much smaller substitutions that we have analyzed by calorimetry.

Potentiometric titrations permitted the average valence of manganese to be monitored as a function of Mg substitution in the Li site. The points with estimated error bars in Fig. 2(c) represent the experimental data, while the dashed line represents expected values, assuming Mg substitutes Li according to the nominal initial stoichiometries. The change in the oxidation state traces the expected value closely. Mg clearly does not substitute manganese in the present compounds, since in that case the Mn valence would increase.

## 2.2 The phase transition

In Fig. 3, cooling (solid) and heating (dashed) DSC traces of  $\text{Li}_{1-x}\text{Mg}_x\text{Mn}_2\text{O}_4$  are displayed for  $x=0,0.01\dots0.04$ . The transition on cooling in the pristine compounds takes place at around 275 K, as reported, while on heating it is found at 285 K. Except for the  $x=0.01$  composition, Mg substitution results in both the heating and cooling transitions being progressively pushed to lower temperatures, with smaller latent heats. When up to 5 atom% of Mg substitutes Li ( $x=0.05$ ), the transition can no longer be observed and the DSC trace (not shown) shows no change of slope that would signify a transition. The  $x=0.01$  sample shows unusual behavior in that, for this composition, the two transition temperatures are actually elevated. However, smaller substitutional steps are required in order to ensure that this is not an artifact. This implies better control over stoichiometry than has been possible in the present work.

We interpret the present data as suggesting that the ordering

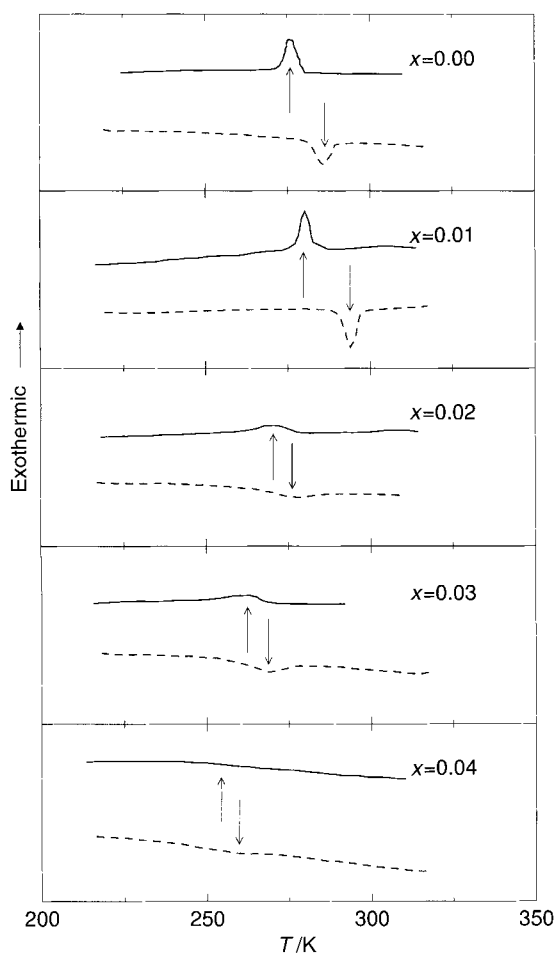


Fig. 3 DSC traces of  $\text{Li}_{1-x}\text{Mg}_x\text{Mn}_2\text{O}_4$  acquired on cooling (solid) and heating (dashed).

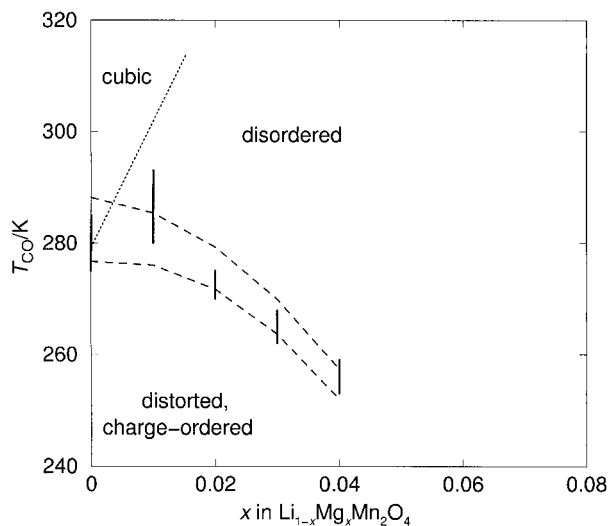
is destroyed completely. Such destruction of charge ordering can be very easily interpreted as the “melting” of the ordered array of holes (the charge crystal) due to a high concentration of defects, which in this case are electrons introduced at random by the Mg substitution. We reject the notion that the effect of Mg substitution is merely to “smear” the phase transition from one that is strongly first order to one that is second order or continuous. Such smearing would mean that the transition would continue to manifest itself, even for higher Mg amounts, albeit as a change of slope in the DSC trace rather than as peaks which arise from the latent heat. Additionally, the thermal hysteresis in the transition seems to be independent of the value of  $x$  suggesting that the transition remains first order throughout. If the effect of the Mg substitution were to smear the transition, the thermal hysteresis should also gradually vanish.

Assuming that the CO transition is an order–disorder transition that can be mapped on to some Ising model, the retention of the thermal hysteresis, even in the doped compounds, is in keeping with theories on the effects of impurities on first order transitions in 3D.<sup>21–23</sup> In systems where continuous symmetry is broken across the phase transition, such as Heisenberg magnets and ferroelectric materials, theory predicts on the other hand that impurities would smear the phase transition and make it progressively more second order.<sup>22</sup>

The effect of electron doping on the Verwey transition in  $\text{Fe}_3\text{O}_4$  has been examined in systems where F substitutes O.<sup>24</sup> The authors find for the compositions  $x=0.1$  and  $x=0.25$  in  $\text{Fe}_3\text{O}_{4-x}\text{F}_x$ , corresponding to Fe valence changes of 0.03 and 0.08 respectively, the main peak in the heat capacity is no longer observed, though the second peak is retained. This peak is claimed by the authors to correspond to a lowering of crystallographic symmetry to a compound that is not charge ordered. In the perovskite manganites, the studies on suppression of charge order through A-site substitution (keeping the Mn sublattice intact, as in the present work) are plagued by difficulties associated with oxygen non-stoichiometry and coexistence of phases.<sup>14</sup> A distinct difference between the title systems and the perovskite manganites is that in many of the manganite systems, charge ordering involves the simultaneous localization of itinerant electrons. This is also true for  $\text{Fe}_3\text{O}_4$ . In the present case, the high temperature state is already localised. The transition corresponds then to the crystallographic ordering of this localized state resulting in a semiconducting to semiconducting CO transition. This difference between these systems arises due to the distinctly different nature of the dominant magnetic interaction which, in the present systems, are antiferromagnetic, while  $\text{Fe}_3\text{O}_4$  and  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ <sup>14</sup> display para to ferrimagnetic and ferro to antiferromagnetic transitions, respectively.

## 3 Conclusions

Based on the evolution of the transition temperature and of the diffraction linewidths as a function of Mg substitution, we present a tentative  $T$ – $x$  diagram of electron-doped  $\text{LiMn}_2\text{O}_4$  in Fig. 4. If the transition is driven purely by cooperative Jahn–Teller effects, as was believed for some time, we see no reason why increasing the concentration of the Jahn–Teller active species in the structure should suppress the transition temperature. Judging from the thermal hysteresis which is indicated by vertical lines at the different  $x$  values, the transition retains its first order character until it vanishes. If there were segregation of the samples into Mg-rich and Mg-poor regions, we would expect to see no evolution in the transition temperature, though the signal itself would weaken. The structural details are complicated by the possibility of local distortions which are perhaps pinned to the substituent in some



**Fig. 4** Tentative phase diagram of the title system showing the suppression of charge ordering and the nature of the microstructure. The vertical lines at the different  $x$  values indicate the transition temperatures determined on heating (bottom of line) and cooling (top of line).

manner, resulting in the increased linewidth. Combining our analysis of the linewidth evolution and the previous work by other groups, mentioned in the earlier sections, we speculate that the boundary between the cubic phase and phases that are disordered (at least locally) exists very close to the pristine composition as indicated by the dotted line. Below the first order transition, the compounds are charge ordered and distorted. Even in the absence of charge ordering, the electrical conductivity of these compounds is low and they could be described for small doping at most temperatures as “Wigner glasses”, as suggested by Mott<sup>25</sup> for doped  $\text{Fe}_3\text{O}_4$  phases. The manner in which the first order region terminates without the thermal hysteresis being lost suggests the existence of a multicritical point in this diagram near  $x=0.04$  and 260 K.<sup>26</sup> This needs to be studied more closely, as do the electrochemical characteristics of the present compounds.

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