

Structure Refinement of the Spinel-Related Phases $\text{Li}_2\text{Mn}_2\text{O}_4$ and $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$

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The crystal structures of the lithium-rich and lithium-deficient spinel phases $\text{Li}_2[\text{Mn}_2]\text{O}_4$ and $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ have been determined by neutron-diffraction techniques. Structure refinements confirm earlier reports that the $[\text{Mn}_2]\text{O}_4$ framework of the $\text{Li}[\text{Mn}_2]\text{O}_4$ spinel remains intact during both lithium insertion and extraction, but demonstrate unequivocally that in $\text{Li}_2[\text{Mn}_2]\text{O}_4$ the Li^+ ions reside in face-shared tetrahedra and octahedra of the cubic-close-packed oxygen-anion array; in $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ the Li^+ ions are located randomly on only the tetrahedral sites of the spinel structure. © 1987 Academic Press, Inc.

Introduction

MnO_2 exists in nature as a number of different polymorphs, some of which are stabilized by small amounts of impurities (1). Recently, a novel polymorph, $\lambda\text{-MnO}_2$, with a structure characterized by the $[\text{B}_2]\text{X}_4$ framework of an $A_{\text{tet}}[\text{B}_2]_{\text{oct}}\text{X}_4$ spinel has been synthesized by lithium extraction from $\text{Li}[\text{Mn}_2]\text{O}_4$ (2). The interstitial space of $\lambda\text{-MnO}_2$ consists of a three-dimensional network of face-shared tetrahedra and octa-

hedra. An appreciable quantity of lithium can be inserted topochemically into the interstitial space with a simultaneous reduction of Mn^{4+} to Mn^{3+} in the crystal lattice, thereby rendering $\lambda\text{-MnO}_2$ an attractive candidate as a solid-solution electrode for a lithium battery and a possible alternative to heat-treated $\gamma\text{-MnO}_2$ (3).

The system $\text{Li}_{1\pm x}[\text{Mn}_2]\text{O}_4$ has been investigated previously in some detail (2,4–6). Lithium insertion into $\text{Li}[\text{Mn}_2]\text{O}_4$ is accompanied by a reduction of Mn^{4+} to Mn^{3+} . The increase in concentration of Mn^{3+} in the crystal lattice introduces a cooperative

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Jahn-Teller distortion at room temperature that lowers the crystal symmetry of $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ from cubic (space group = $\text{Fd}3\text{m}$) to tetragonal (space group = $\text{I}4_1/\text{amd}$). An initial structure determination with powder X-ray diffraction data has indicated, despite the low scattering power of X-rays by lithium, that in tetragonal $\text{Li}_2[\text{Mn}_2]\text{O}_4$ the Li^+ ions are almost randomly distributed over both the tetrahedral A-sites and interstitial octahedral sites of the spinel structure. In contrast, it was concluded from a subsequent neutron-diffraction study by Mosbah *et al.* that all the Li^+ ions in $\text{Li}_2[\text{Mn}_2]\text{O}_4$ are situated on octahedral sites, resulting in an ordered rocksalt structure (5).

Lithium extraction from the tetrahedral A-sites of $\text{Li}[\text{Mn}_2]\text{O}_4$ proceeds smoothly with a continuously decreasing "a" lattice parameter to $x \approx 0.5$ in $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ (6). A sudden decrease in the lattice parameter near this composition indicates a phase transition, the exact nature of which has not yet been established. Electrochemical extraction beyond the composition $\text{Li}_{0.5}[\text{Mn}_2]\text{O}_4$ has been shown to be difficult, even at low current rates (6). Evidence for stabilized spinel-related compositions $\text{A}_{0.5}[\text{B}_2]\text{X}_4$ has been established, for example, in $\text{Ga}_{0.5}[\text{Mo}_2]\text{S}_4$ in which the Mo ions dimerize along the $\langle 110 \rangle$ axes to form tetrahedral clusters (7). An ordering of the tetrahedral-site vacancies into one of the two A-site subarrays can be expected in the compositional range $0 < x \leq 0.5$.

The purpose of determining the structures of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ and $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ with neutron diffraction data was therefore twofold:

- (i) to obtain more substantial evidence for the unusual coexistence of Li^+ ions in face-shared tetrahedra and octahedra of a cubic-close-packed oxygen array, thereby resolving previous contrasting reports on the location of the Li^+ ions in $\text{Li}_2[\text{Mn}_2]\text{O}_4$, and
- (ii) to search for structural features in ex-

tensively delithiated $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ samples, e.g., superlattice reflections due to Li^+ -ion ordering that could account for the phase transition that occurs at $\text{Li}_{\sim 0.5}[\text{Mn}_2]\text{O}_4$. A composition $\text{Li}_{\sim 0.3}[\text{Mn}_2]\text{O}_4$ was selected for structure analysis as delithiated samples $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ with $0.5 \leq x \leq 0.7$ tend to be two-phase: they consist of partially delithiated ($x < 0.5$) and extensively delithiated ($x > 0.5$) particles.

Experimental

$\text{Li}[\text{Mn}_2]\text{O}_4$ was prepared in air by solid state reaction of Li_2CO_3 (Alfa Products, 99.5%) and Mn_2O_3 (Koch Light, 98%) in the molar ratio 1 : 2. After calcining at 650°C for 12 hr, the sample was heated at 850°C for 24 hr. $\text{Li}_2[\text{Mn}_2]\text{O}_4$ was synthesized by chemical lithiation of $\text{Li}[\text{Mn}_2]\text{O}_4$ with an excess of *n*-butyl-lithium (Koch Light, 15w/w in hexane) in sodium-dried hexane at 50°C for several days under a nitrogen atmosphere. After reaction, the product was thoroughly washed with hexane, dried under vacuum, and stored under an argon atmosphere.

$\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ was prepared by a method described by Hunter (2). 13.2 g $\text{Li}[\text{Mn}_2]\text{O}_4$ in 350 ml water was reacted with 110 ml 4.5N H_2SO_4 until the solution reached pH = 1. The solution was stirred at room temperature for 6 hr.

The lithium concentration in the lithiated and delithiated spinel phases was obtained by atomic absorption spectroscopy. The compositions of the two compounds were determined by this method to be $\text{Li}_{2.05}[\text{Mn}_2]\text{O}_4$ and $\text{Li}_{0.26}[\text{Mn}_2]\text{O}_4$, respectively.

Approximately 7 g of sample was loaded into vanadium cans, 16 mm in diameter, and sealed with indium wire. Neutron-diffraction data were collected on the high-resolution powder diffractometer D1A at the Institut Laue Langevin, Grenoble, France. The neutron wavelengths used for data collection of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ and

$\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ were 1.3840 and 1.5082 Å, respectively.

Structures were refined with a profile-refinement program modified to describe peak shape by a Voigt function, which is a convolution of Gaussian and Lorentzian functions (8). The former function describes, to a good approximation, the constant-wavelength neutron-diffraction peak shape; the Lorentzian component to the peak shape arises because of particle-size effects. The Voigt function is particularly relevant to this work as intercalation and deintercalation of lithium with $\text{Li}[\text{Mn}_2]\text{O}_4$ are accompanied by a substantial reduction in particle size (9, 10).

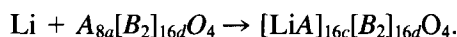
Neutron-scattering amplitudes used in the structure refinement were $b(\text{Li}) = -0.2030 \times 10^{-12}$ cm, $b(\text{Mn}) = -0.3730 \times 10^{-12}$ cm, and $b(\text{O}) = 0.5804 \times 10^{-12}$ cm (11). Initial unit-cell parameters were obtained from previously reported X-ray diffraction data for $\lambda\text{-MnO}_2$ and $\text{Li}_2[\text{Mn}_2]\text{O}_4$ (2, 4). During structure refinement, all parameters were refined simultaneously. In tetragonal $\text{Li}_2[\text{Mn}_2]\text{O}_4$, nine profile and six structural parameters were refined; in cubic $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ the number of refined profile and structural parameters were eight and four, respectively.

Results and Discussion

(a) $\text{Li}_2[\text{Mn}_2]\text{O}_4$

The structure of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ was refined with the space group $F4_1/\text{ddm}$, which defines a face-centered tetragonal cell equivalent to the smaller body-centered cell with space group $I4_1/\text{amd}$. For the sake of simplicity and consistency with cubic $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$, the site positions of the atoms are given, throughout this discussion, in terms of the aristotype cubic spinel space group, $\text{Fd}3\text{m}$. In this space group with the spinel notation, the tetrahedral *A*-type cations reside on the $8a$ sites, the octahedral

B-type cations on the $16d$ sites, and the oxygen anions on the $32e$ sites; the interstitial octahedra of the spinel structure are located at the $16c$ positions. An important feature of the spinel structure is that each $8a$ tetrahedron shares all four faces with empty $16c$ octahedra. It is thus easy to visualize that insertion of lithium ions into the spinel structure can lead to a cooperative displacement of the *A*-cations into octahedral sites ($16c$) and that this process leaves an ordered rocksalt structure after the addition of one lithium:



The manganese ions were constrained to the *B*-sites of the spinel structure during all stages of the refinement in keeping with previous data (4, 5). The following two models were used as a starting set to refine the structure of $\text{Li}_2[\text{Mn}_2]\text{O}_4$:

Model I. All $16c$ octahedral sites filled by lithium, and all $8a$ tetrahedral sites empty;

Model II. A random occupancy by lithium of both $8a$ tetrahedra and $16c$ octahedral sites, consistent with the stoichiometry $\text{Li}_2[\text{Mn}_2]\text{O}_4$.

Refinement of both models converged to a best fit between observed and calculated data that corresponded to occupancy of both $8a$ and $16c$ by lithium. Refinements with an isotropic temperature factor for lithium set arbitrarily at 1.0, 2.0, 3.0, and 4.0 Å² gave similar occupancy of both $8a$ and $16c$ sites. In particular, with $B = 2.0$ Å² the occupancies of the $8a$ and $16c$ sites were 0.43(5) and 0.79(2), respectively, which gives a stoichiometry $\text{Li}_{2.01}\text{Mn}_2\text{O}_4$; this is in good agreement with the stoichiometry $\text{Li}_{2.05}\text{Mn}_2\text{O}_4$ determined by chemical analysis. With $B = 4.0$ Å² the $8a$ -site occupancy increased to 0.52(6) and the $16c$ -site occupancy to 0.88(4), the latter still being significantly less than unity; in this case the sum of the occupancies is rather high, viz. 2.28(10). Attempts to constrain the lithium content to 2.0 and allowing the *B*

TABLE I
STRUCTURAL PARAMETERS OF $\text{Li}_{2.0}[\text{Mn}_2]\text{O}_4$

Space Group: $F4_1/ddm$; $a = 7.994(1) \text{ \AA}$, $c = 9.329(1) \text{ \AA}$						
Atom	Position ^a	x	y	z	$B(\text{\AA}^2)$	n
Li(1)	8a	0.1250	0.1250	0.1250	2.0	0.43(5)
Li(2)	16c	0.0000	0.0000	0.0000	2.0	0.79(3)
Mn	16d	0.5000	0.5000	0.5000	0.45(5)	1.0
O	32e	0.2589(2)	0.2589(2)	0.2530(2)	0.55(2)	1.0

Note. $R_N = 9.7\%$; $R_P = 20.2\%$; $R_{WP} = 19.5\%$; $R_E = 9.8\%$; $N - P + C = 2645$. Number of reflections used in the refinement = 158.

$$R_N = \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}} \quad R_{WP} = \left\{ \frac{\sum w [Y_{\text{obs}} - Y_{\text{calc}}]^2}{\sum w [Y_{\text{obs}}]^2} \right\}^{1/2}$$

$$R_P = \frac{\sum |I_{\text{obs}} - Y_{\text{calc}}|}{\sum Y_{\text{obs}}} \quad R_E = \left\{ \frac{N - P + C}{\sum w [Y_{\text{obs}}]^2} \right\}^{1/2}$$

where I = integrated Bragg intensity, Y = number of counts at angle 2θ , w = weights, and $N - P + C$ = number of observations - number of variables + number of constraints.

^a For the sake of simplicity and consistency with the data of $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$, the site positions of the cubic space group $Fd3m$ are used.

factors to vary resulted in a slow convergence toward the results of the unconstrained refinements. The R factors R_N and R_{WP} , as defined in Table I, for this model were 9.7 and 19.5%, respectively. Final profile and structural parameters are listed in Table I. The observed and calculated neutron-diffraction profiles for $\text{Li}_2[\text{Mn}_2]\text{O}_4$ are given in Fig. 1.

The occupation of both 8a and 16c sites by lithium in $\text{Li}_2[\text{Mn}_2]\text{O}_4$ is evident from a comparison of the observed neutron-diffraction profile of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ (Fig. 2a) with the simulated profiles of the structures $\text{Li}_{8a}(\text{Li})_{16c}[\text{Mn}_2]_{16d}\text{O}_4$ (lithium in both tetrahedral and octahedral sites, Fig. 2b) and $(\text{Li}_2)_{16c}[\text{Mn}_2]_{16d}\text{O}_4$ (lithium in octahedral sites only, Fig. 2c). Although the profiles of

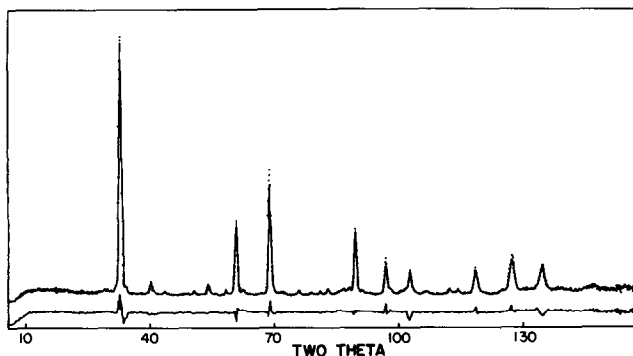


FIG. 1. The observed and calculated neutron diffraction powder patterns for $\text{Li}_2[\text{Mn}_2]\text{O}_4$. The difference between the observed and calculated profiles is plotted below on the same scale.

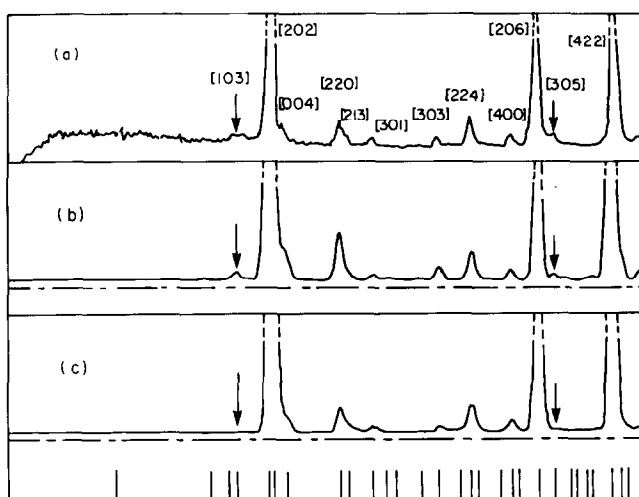


FIG. 2. A comparison of the observed neutron diffraction profile of (a) $\text{Li}_2[\text{Mn}_2]\text{O}_4$ with the simulated patterns of (b) $\text{Li}_{8a}(\text{Li})_{16c}[\text{Mn}_2]_{16d}\text{O}_4$ and (c) $(\text{Li}_2)_{16c}[\text{Mn}_2]_{16d}\text{O}_4$. The presence of the $[1\ 0\ 3]$ and $[3\ 0\ 5]$ reflections in the observed profile is indicative of lithium occupation of both tetrahedral sites (8a) and octahedral sites (16c).

the two simulated structures are similar, the presence of two weak reflections $[1\ 0\ 3]$ and $[3\ 0\ 5]$ in $\text{Li}_{8a}(\text{Li})_{16c}[\text{Mn}_2]\text{O}_4$, which are absent (or extremely weak) in $(\text{Li}_2)_{16c}[\text{Mn}_2]\text{O}_4$, serve to identify the correct model; the presence of these two reflections in the observed profile of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ (Fig. 2a) thus confirms the tetrahedral-site occupation by lithium.

The occupation of both 8a and 16c sites by lithium is also unequivocally confirmed by the difference Fourier map shown in Fig. 3. This map, which corresponds to a difference between observed and calculated structure factors based on the starting Model I (all 16c occupancy by lithium), is a section at height 0 perpendicular to $[1\ \bar{1}\ 0]$ that contains all possible occupied sites (8a, 16c, 16d, and 32e) in a spinel/rocksalt structure. Figure 3 clearly indicates appreciable negative scattering from the 8a sites along with a small positive contribution from the 16c sites. This negates the proposal of solely octahedral occupancy by lithium in $\text{Li}_2[\text{Mn}_2]\text{O}_4$ and, as a corollary, corroborates the evidence of partial occupancy of

both 8a (tetrahedral) and 16c (octahedral) sites by lithium obtained directly from profile refinement of the present data and intensity refinement of previous X-ray data (4).

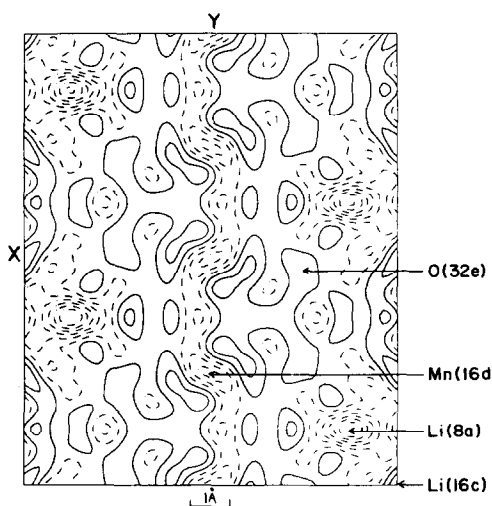


FIG. 3. The difference Fourier section of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ (Model I) at height 0 perpendicular to $[1\ 1\ 0]$ showing Li^+ occupation of both 8a and 16c sites of the spinel structure.

It is of interest to compare this result with the closely related systems $\text{Li}_{1+x}[\text{V}_2]\text{O}_4$ and $\text{Li}_{1+x}[\text{Ti}_2]\text{O}_4$ ($0 < x \leq 1$). In the system $\text{Li}_{1+x}[\text{V}_2]\text{O}_4$, electrochemical and powder X-ray diffraction data indicate that, at a composition $\text{Li}_{1.5}[\text{V}_2]\text{O}_4$, the Li^+ ions reside in both the tetrahedral (8a) and octahedral (16c) sites, which is consistent with the findings of the $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ system (12). For $x > 0.5$ the Li^+ ions in the tetrahedral sites are displaced into the remaining empty octahedra (16c) to yield rocksalt structure $(\text{Li}_2)_{16c}[\text{V}_2]_{16d}\text{O}_4$ in which the original $[\text{B}_2]\text{O}_4$ spinel framework is maintained. In the system $\text{Li}_{1+x}[\text{Ti}_2]\text{O}_4$, neutron-diffraction data of $\text{Li}_2[\text{Ti}_2]\text{O}_4$ show that, as in $\text{Li}_2[\text{V}_2]\text{O}_4$, the structure has a rocksalt configuration with the cations occupying all available octahedral sites (13); no structural information is available yet for intermediate compositions in the range $0 < x < 1$.

In the spinel structure the octahedral B-site cations are situated farthest from the tetrahedrally coordinated A-cations. This data thus shows that in $\text{Li}_2[\text{Mn}_2]\text{O}_4$ the inserted lithium ions occupy the 16c sites and that the electrostatic $\text{Mn}_{16d}^{3+}-\text{Li}^+$ interactions are still sufficiently strong to keep a fraction of the lithium ions on the 8a sites. The refined structure necessitates, therefore, the coexistence of lithium ions in face-shared tetrahedra and octahedra despite a very short $\text{Li}_{8a}^+-\text{Li}_{16c}^+$ interatomic distance of only 1.83 Å. This finding demonstrates the near equivalence in potential energy of the 8a and 16c sites at this composition, which is not surprising as the lithium ions in $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ ($0 \leq x \leq 1$) move through the 8a–16c network.

Coexistence of Li^+ ions on neighboring sites 16c and 8a would be stabilized by a relaxation of the ions from the center of site symmetry toward a site face adjacent to a vacant site. It follows that an octahedral-site Li^+ ion would only have one tetrahedral-site Li^+ -ion nearest neighbor and a tetrahedral-site Li^+ ion need have only one of

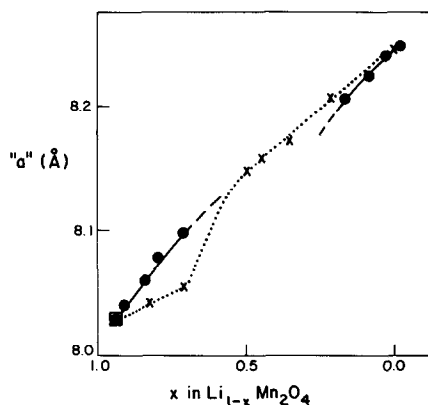


FIG. 4. Variation of the "a" lattice parameter of $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ ($0 < x < 1$) observed by acid treatment of $\text{Li}[\text{Mn}_2]\text{O}_4$. $x =$ our data, (●) after A. Mosbah *et al.* (5), (□) after J. C. Hunter (2).

its four nearest neighbor octahedral sites vacant. A maximum tetrahedral-site occupancy of 50% and octahedral-site occupancy of 75% could be achieved in an ordered system having only one of the two tetrahedral-site subarrays occupied. With disorder, a tetrahedral-site occupancy somewhat less than 50% must be anticipated; this prediction is consistent with observed tetrahedral- and octahedral-site occupancies of 43(5) and 79(3)%, respectively.

(b) $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$

Previous studies have shown that lithium can be extracted from $\text{Li}[\text{Mn}_2]\text{O}_4$ over the range $0 \leq x \leq 1$ (2, 5). Complete removal of lithium from $\text{Li}[\text{Mn}_2]\text{O}_4$ results in $\lambda\text{-MnO}_2$. A plot of our data of the "a" lattice parameter vs composition, x , in $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ shows a linear decrease in "a" to $x \approx 0.5$ (Fig. 4). At $x \approx 0.5$, "a" decreases sharply from 8.14 to ~ 8.05 Å and thereafter decreases more slowly to 8.03 Å at $\lambda\text{-MnO}_2$. Although no deviation from the cubic symmetry of space group $Fd3m$ has yet been detected over the entire range of delithiation, it has been proposed, because of the existence of the spinel-related phase

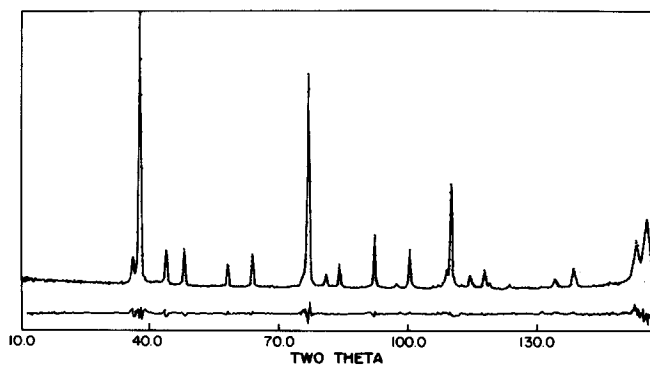


FIG. 5. The observed and calculated neutron diffraction powder patterns for $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$. The difference between the observed and calculated profiles is plotted below on the same scale.

$\text{Ga}_{0.5}[\text{Mo}_2]\text{S}_4$ with space group $F\bar{4}3m$ (7) that this abrupt change may result from lithium-ion ordering at the composition $\text{Li}_{0.5}[\text{Mn}_2]\text{O}_4$ (5, 14).

The neutron-diffraction pattern of $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ is given in Fig. 5. The refined lattice parameter of this compound is $8.0215(1) \text{ \AA}$ which, surprisingly, is less than the value of 8.03 \AA for $\text{Li}_{0.02}\text{MnO}_2$ reported by Hunter and Mosbah (2, 5). The absence in the diffraction profile of $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$ of any reflections $h\ 0\ 0$ ($h = 2n$) that are systematically absent in space group $Fd\bar{3}m$ (centrosymmetric), but present in $F\bar{4}3m$ (noncentrosymmetric) precludes the possibility of detecting any Li^+ -ion ordering equivalent to the Ga ordering in $\text{Ga}_{0.5}[\text{Mo}_2]\text{S}_4$. Structural models refined with

space group $F\bar{4}3m$ led to no improvement in the fit between the observed and calculated diffraction data. Refinement of the structure with space group $Fd\bar{3}m$ indicated that the lithium ions were distributed randomly with a site occupancy of 19% over all the tetrahedral $8a$ sites; attempts to refine these ions on the octahedral $16c$ sites led to a negative site occupancy. Final profile and structural parameters are listed in Table II. This result still leaves open the possibility of an order-disorder transition for the A-site vacancies at $x \approx 0.5$. A measurement for a sample with $0 < x < 0.5$ is needed to confirm whether the initial removal of Li^+ ions in the system $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ leaves the A-site vacancies ordered on one of the two A-site subarrays as x approaches 0.5.

TABLE II
STRUCTURAL PARAMETERS OF $\text{Li}_{0.2}[\text{Mn}_2]\text{O}_4$

Space Group: $Fd\bar{3}m$; $a = 8.0215(1) \text{ \AA}$						
Atom	Position	x	y	z	$B(\text{\AA}^2)$	n
Li	$8a$	0.1250	0.1250	0.1250	1.0	0.19(2)
Mn	$16d$	0.5000	0.5000	0.5000	0.44(2)	1.0
O	$32e$	0.2626(1)	0.2626(1)	0.2626(1)	0.76(1)	1.0

Note. $R_N = 4.8\%$; $R_P = 2.6\%$; $R_{WP} = 11.9\%$; $R_E = 6.2\%$; $N - P + C = 2427$. Number of reflections used in the refinement = 52. As defined in Table I.

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