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Neutron Diffraction Study of $Li_{1+x}(Li_{2x/3}Fe_{1-x}Sn_{1+x/3})O_4$, a Nonstoichiometric Ramsdellite and Its Transition to a Double Hexagonal Close Packed Structure for $x = 0$

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In the system $LiFeSnO_4$–Li_2SnO_3, a nonstoichiometric ramsdellite $Li_{1+x}(Li_{2x/3}Fe_{1-x}Sn_{1+x/3})O_4$ with a rather wide homogeneity range ($0 \leq x \leq 0.28$) has been isolated. Neutron diffraction study of the $|LiFeSnO_4|_{HT}$ ($x = 0$) and $Li_{1.42}Fe_{0.75}Sn_{1.08}O_4$ ($x = 0.25$) compounds has allowed us to locate lithium ions inside the tunnels of this structure. Li^+ ions are located in tetrahedral sites T_1 and T_2, but T_1 is preferentially occupied. The low temperature form of $LiFeSnO_4$, characterized by a double hexagonal packing of oxygens, has also been studied by neutron diffraction. The distribution of lithium and its influence on the stabilization of these structures are discussed.

Introduction

Most of the oxides which exhibit the MnO_2 ramsdellite structure (*1*) are characterized by empty tunnels. The only ramsdellite oxides in which the tunnels are partially occupied are the lithium titanate (*2, 3*) $Li_2Ti_3O_7$ (or $Li_t(Li_{0.29}Ti_{1.71})O_4$ with $t = 0.86$) and the ferrostannate $LiFeSnO_4$ (*4*), the latter being characterized by a transition ramsdellite $\rightleftharpoons$ double hexagonal (DH) close packed structure at 800°C. The X-ray diffraction study of these phases suggests a partial occupancy of the tunnels by the lithium ions. To verify this possibility and to determine the positions of lithium, a neutron diffraction study of $LiFeSnO_4$ has been undertaken. Moreover, from the previous results, it seems that the stability of the ramsdellite structure could be improved by introducing a greater amount of lithium in the ramsdellite tunnels. Thus we have also investigated the system $LiFeSnO_4$–Li_2SnO_3, which may lead to nonstoichiometric ramsdellites owing to the presence of an excess of lithium and to the similar sizes of the Li^+, Fe^{3+}, and Sn^{4+} ions.

Experimental

Synthesis

All the oxides were prepared from mixtures of Li_2CO_3, Fe_2O_3, and SnO_2. An excess of 5 mole% of Li_2CO_3 was always added with respect to the ideal formula to compensate for the small loss of Li_2O at high temperature. The mixture was first

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heated at 600°C, then decarbonated at 900°C, and finally heated at 1200°C for the synthesis of ramsdellites. Annealing the sample at 1300°C was necessary to obtain $Li_{1.42}Fe_{0.75}Sn_{1.08}O_4$ as a pure compound.

The low temperature form of $LiFeSnO_4$ was synthesized by annealing the ramsdellite form at 800°C.

X-ray Diffraction and Electron Microscopy

All the X-ray diffractograms of the samples were obtained with a Philips powder diffractometer using Cu$K\alpha$ radiation.

Electron diffraction micrographs were observed on microcrystals deposited on a carbon grid, using a JEOL 100 CX electron microscope.

Neutron Diffraction

Neutron diffraction patterns at room temperature were collected at the diffractometer D1B at the Laue–Langevin Institute (Grenoble) with a wavelength of 2.5186 Å from a pyrolytic graphite monochromator. The powdered samples were inserted in a standard vanadium can (ϕ 10 mm). The diffractometer has a 400-cell multidetector covering 80° in 2θ. For every sample, data were collected in two steps (low and high angles) of about 1 hr each.

Integrated intensities were obtained by fitting the shape of the Bragg peaks to Gaussians and the background to a first- or second-order polynomial (*5*). The neutron scattering lengths were taken from (*6*): −2.03(Li), 9.54(Fe), 6.228(Sn), and 5.805(O) (all values in fm).

Results and Discussion

Homogeneity Range, X-ray and Electron Diffraction Characterization of Ramsdellites

In the system $LiFeSnO_4$–Li_2SnO_3, the possibility of insertion of lithium in the tunnels of the ramsdellite structure is important since the limit Li_2SnO_3, which exhibits in fact a distorted sodium chloride structure, would correspond to the insertion of one Li^+ ion per formula MO_2 according to the formulation $Li_2(Li_{2/3}Sn_{4/3})O_4$. Thus, a nonstoichiometric ramsdellite $Li_{1+x}(Li_{2x/3}Fe_{1-x}Sn_{1+x/3})O_4$ with a rather wide homogeneity range, $0 \leq x \leq 0.28$, has been isolated.

TABLE I

LATTICE PARAMETER VARIATION IN THE RAMSDELLITE $Li_{1+x}(Li_{2x/3}Fe_{1-x}Sn_{1+x/3})O_4$ COMPOUNDS

Compound	a(Å)	b(Å)	c(Å)
$x = 0$	3.066(1)	5.066(1)	9.874(2)
$x = 0.10$	3.069(1)	5.078(2)	9.881(5)
$x = 0.18$	3.072(1)	5.101(2)	9.877(3)
$x = 0.25$	3.074(1)	5.116(5)	9.881(3)

The X-ray diffraction patterns of three compositions, $x = 0.1$, 0.18, and 0.25, were indexed in orthorhombic cells with very similar parameters (Table I). "a" and "c" are almost invariant with composition, whereas "b", which corresponds to the width of the tunnels, increases with x.

The electron diffraction study of these oxides has confirmed for most of the crystals the reflection conditions previously observed for the high temperature form of $LiFeSnO_4$, leading to the same space groups *Pmcn* or $P2_1cn$ (*4*). However, it must be pointed out that, for $x = 0.25$, the electron diffraction patterns of a small number of crystals exhibited either diffuse streaks or superstructure reflections. In both cases the lattice of the intense spots was that of ramsdellite. As an example, Fig. 1 shows electron diffraction patterns of the $(\bar{1}10)$ planes, characterized by superstructure reflections involving twice greater (Fig. 1a) or four times greater (Fig. 1b) a and b parameters.

Superstructure lines have never been ob-

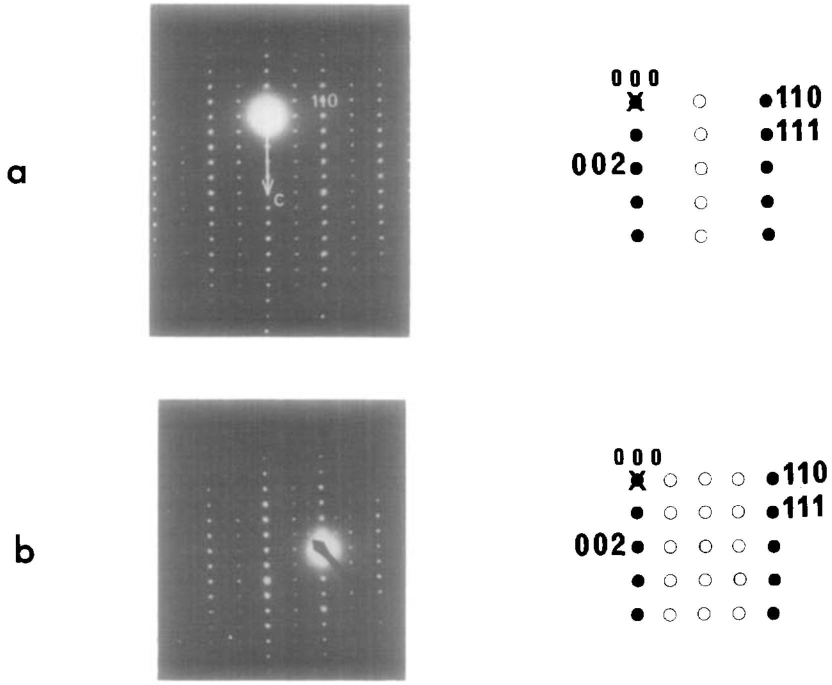

FIG. 1. Electron diffraction patterns of the ($\bar{1}10$) planes of $Li_{1.42}Fe_{0.75}Sn_{1.08}O_4$ ($x = 0.25$).

served in the X-ray patterns. These superstructure reflections could result either from a partial order of the cations in the octahedral sites, or from small distortions of the octahedral lattice. Whatever this phenomenon may be, it can be considered as a metastable state since by exposure to the electron beam, the superstructure reflections disappear leading to the classical ramsdellite cell.

Neutron Diffraction Study of the Ramsdellites: Structure Determination of $LiFeSnO_4$ *and* $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$

The aim of this work was to study the distribution of Li^+ in the different sites of the structure and to determine their positions with accuracy starting from the ideal ramsdellite framework (Fig. 2). Two phases were thus investigated: $LiFeSnO_4$ and $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$.

Structure calculations were made in the space group *Pmcn*, previously used for the X-ray structure determination of $LiFeSnO_4$, on 26 reflections, i.e., 32 *hkl* for $LiFeSnO_4$, and on 23 reflections, i.e., 30 *hkl* for $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$. The different ions were initially located in the 4(*c*) sites previously found for $LiFeSnO_4$ (*4*), so that

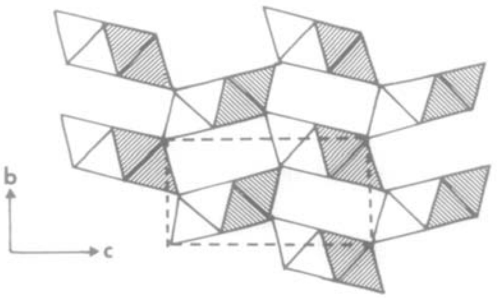

FIG. 2. Ideal ramsdellite structure projected onto (100) plane.

TABLE II

ATOMIC PARAMETERS OF HIGH TEMPERATURE COMPOUNDS $x = 0$ AND $x = 0.25$ DETERMINED BY NEUTRON DIFFRACTION (SPACE GROUP: *Pmcn*; 4(*c*) SITES: $\frac{1}{4}yz$)

	$LiFeSnO_4$ ($x = 0$)	$Li_{1.417}Fe_{0.75}Sn_{1.083}O_4$ ($x = 0.25$)
	$a = 3.066(1)$ Å	$a = 3.074(1)$ Å
	$b = 5.066(1)$ Å	$b = 5.116(5)$ Å
	$c = 9.874(2)$ Å	$c = 9.881(3)$ Å
T_1	$Li_{0.38}\square_{0.62}$	$Li_{0.625}\square_{0.375}$
y	0.935(6)	0.907(6)
z	0.466(3)	0.423(2)
B (Å^2)	3.7(5)	0.3(8)
T_2	$Li_{0.12}\square_{0.88}$	
y	0.972(25)	
z	0.605(4)	
B (Å^2)	0.2(18)	
O_c	$Fe_{0.50}Sn_{0.50}$	$Li_{0.083}Fe_{0.375}Sn_{0.542}$
y	0.9861(7)	0.9663(10)
z	0.1419(2)	0.1362(6)
B (Å^2)	0.03(3)	0.01(7)
O_1		
y	0.7076(5)	0.6602(14)
z	0.2828(3)	0.2704(6)
B (Å^2)	0.53(5)	0.46(11)
O_2		
y	0.2039(6)	0.2154(14)
z	−0.0394(4)	−0.0347(9)
B (Å^2)	0.69(6)	0.15(13)

the tunnels were only occupied by the lithium ions involving a statistical distribution of the metallic ions on the octahedral (Oc) sites corresponding, respectively, to $(FeSn)_{Oc}$ for $x = 0$ and $(Li_{0.17}Fe_{0.75}Sn_{1.08})_{Oc}$ for $x = 0.25$. Atomic positions and thermal parameters were refined. Then difference Fourier maps were calculated without Li^+ in the tunnels; they allowed the location of Li^+ in two tetrahedral sites, T_1 and T_2, for $LiFeSnO_4$ and in only the T_1 site for $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$. The Li^+ ions were then placed in these tetrahedral sites, and their atomic parameters, thermal parameters, and occupancy factors were successively refined. After a final refinement of all the atomic positions the discrepancy factors calculated on the intensities were $R = 0.015$ for $LiFeSnO_4$ and $R = 0.043$ for $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$. Decreasing the amount of lithium in the tunnels, led to a significant increase of R for both compounds. In the same way, distribution of Li^+ on two sites T_1 and T_2 for $Li_{1.25}(Li_{0.17}Fe_{0.15}Sn_{1.08})O_4$ produced a significant increase of the R factor.

The final atomic parameters of these oxides (Table II) are rather similar except for the T_2 site observed only in $LiFeSnO_4$, and the O_1 position which changes the size of the tunnel in the two oxides. The positions of the ions corresponding to the octahedral ramsdellite framework are very close to those observed by X-ray diffraction for $LiFeSnO_4$ (*4*), and give metal–oxygen distances close to those usually observed in oxides (Table III).

The results confirm unambiguously the presence of the lithium ions in the tunnels

TABLE III

INTERATOMIC DISTANCES (Å) IN $x = 0$ AND $x = 0.25$ COMPOUNDS (NEUTRON DIFFRACTION)

	$LiFeSnO_4$	$Li_{1.417}F_{0.75}Sn_{1.083}O_4$
$\lvert Li_1–O_1\rvert$	2.15	1.96
$\lvert Li_1–O_2\rvert \times 2$	2.06	2.13
$\lvert Li_1–O_2'\rvert$	1.83	1.98
$\lvert Li_2–O_1\rvert$	1.98	
$\lvert Li_2–O_2'\rvert$	2.17	
$\lvert Li_2–O_2\rvert \times 2$	2.15	
$\lvert M–O_1\rvert$	1.98	2.05
$\lvert M–O_1'\rvert \times 2$	2.04	2.05
$\lvert M–O_2\rvert$	2.10	2.12
$\lvert M–O_2'\rvert \times 2$	2.07	2.06
$\lvert M–M\rvert \times 2$	3.066	3.074
$\lvert M–M\rvert \times 2$	3.20	3.12
$\lvert Li–Li\rvert$		2.37
$\lvert Li_1–M\rvert$	2.75	2.85
$\lvert Li_1–M\rvert$	3.21	2.85
$\lvert Li_1–M\rvert \times 2$	2.94	2.79
$\lvert Li_2–M\rvert$	2.36	
$\lvert Li_2–M\rvert$	2.76	
$\lvert Li_2–M\rvert \times 2$	2.94	
$\lvert O_1–O_2\rvert \times 2$	2.89	2.86
$\lvert O_1–O_2'\rvert \times 2$	2.96	3.04
$\lvert O_1'–O_2\rvert \times 2$	2.73	2.72
$\lvert O_1'–O_1\rvert \times 2$	3.03	3.01
$\lvert O_2'–O_2\rvert \times 2$	2.69	2.77
$\lvert O_1'–O_1\rvert$	3.066	3.074
$\lvert O_2'–O_2\rvert$	3.066	3.074

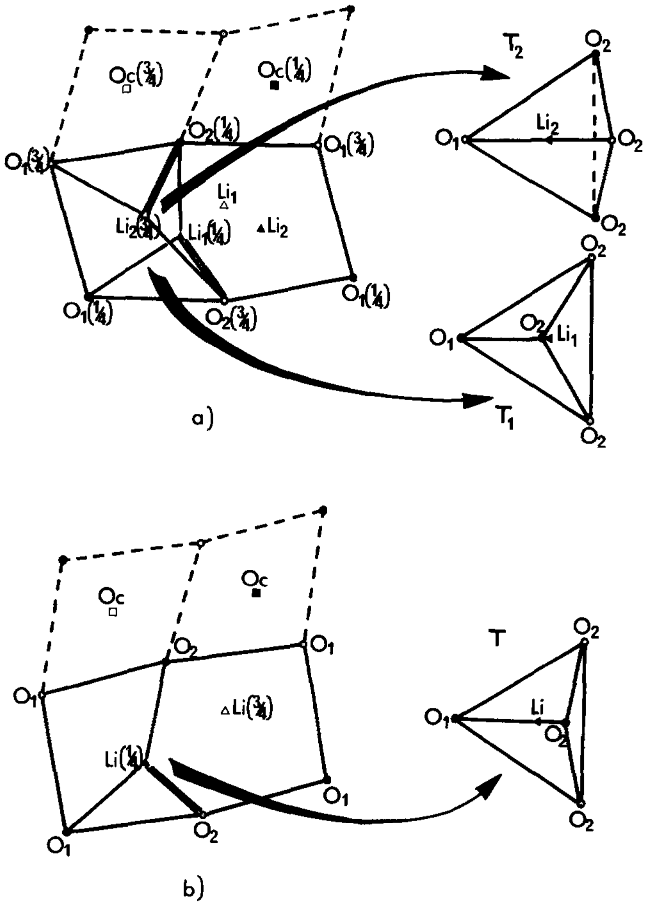

FIG. 3. Tunnel projection onto (100) plane and lithium sites of the ramsdellite-type compounds: (a) $x = 0$; (b) $x = 0.25$.

of the ramsdellite structure, and the possibility of localization of Li^+ in two types of tetrahedral sites, T_1 and T_2, as previously proposed by Morosin and Mikkelsen (*3*) for $Li_2Ti_3O_7$. However, it is clear that the distribution of Li^+ on these sites is not statistical as observed by these authors for $Li_2Ti_3O_7$. A preferential occupancy of the T_1 sites by Li^+ is observed, which seems to increase with the lithium amount: 76% of the Li^+ ions are located in the T_1 sites for $LiFeSnO_4$, and 100% of the Li^+ ions of the tunnels occupy the T_1 sites for $Li_{1.25}(Fe_{0.75}Li_{0.17}Sn_{1.08})O_4$. This behavior can easily be explained by considering the projection of the tunnel section on (100) and the projection of the tetrahedra on the octahedral faces of the ramsdellite framework (Fig. 3). In $LiFeSnO_4$ (Fig. 3a), the T_2 tetrahedron appears considerably distorted compared to the T_1 tetrahedron. In $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$ (Fig. 3b), the displacement of O_1 relative to $LiFeSnO_4$ changes the geometry of the tunnel slightly (Fig. 3b) and involves a displacement of the center of the T_1 tetrahedron compared to $LiFeSnO_4$. This results in longer T_1–T_1 distances (2.37 Å) which allow an occupancy factor of these sites by Li^+ greater than 50%. In $LiFeSnO_4$ the short T_1–T_1 distances (1.80

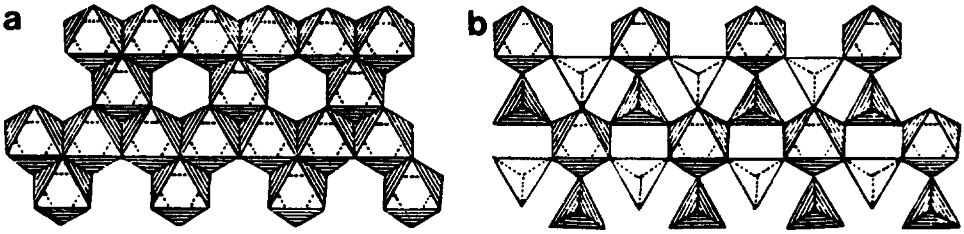

FIG. 4. Kagome layer (a) and mixed layer (b) in double-hexagonal $LiFeSnO_4$ (low temperature form).

Å) do not allow an occupancy factor of T_1 greater than 50%.

It is noteworthy that the M–M distances between the metallic ions of the edge-sharing octahedra are rather large (3.07 to 3.20 Å) compared to the $(Li)_{T_1}$–$(M)_{Oc}$ distances (2.69 to 2.91 Å) and especially to the $(Li)_{T_2}$–$(M)_{Oc}$ distances of $LiFeSnO_4$ (2.36 Å) and to the $(Li)_{T_1}$–$(Li)_{T_1}$ distances of the tunnels in $Li_{1.25}(Li_{0.17}Fe_{0.75}Sn_{1.08})O_4$ (2.37 Å). Thus, it appears that the very short Li–M or Li–Li distances (2.36 Å) do not influence the stability of the structure probably because the electrostatic repulsion between the Li^+ and M ions is weak owing to the low charge of Li^+. Such distances and even shorter Li–Li distances have indeed already been observed in other ternary lithium oxides, e.g., in Li_8SnO_6 ($d|Li_1$–$Sn|$ = 2.46 Å) (*7*), in Li_5TlO_4 ($d|Li_2$–$Li_5|$ = 2.29 Å, $d|Li_3$–$Li_4|$ = 2.36 Å) (*8*), or in Li_8CoO_6 ($d|Li'$–$Li'''|$ = 2.14 Å) (*9*). In this respect, it is interesting to compare these metal–metal distances with those of the low temperature form of $LiFeSnO_4$ (DH) which have been found to be rather short. For this reason the localization of lithium in DH $LiFeSnO_4$ has been studied by neutron diffraction.

DH $LiFeSnO_4$: Localization of Lithium by Neutron Diffraction

The structure of DH $LiFeSnO_4$ has already been studied by X-ray diffraction: it is based on double hexagonal close packing of oxygen atoms which can be described as double layers of polyhedra, i.e., layers of tetrahedra and octahedra (T_I, T_{II}, and Oc_I) and octahedral layers (Oc_{II}) as shown in Fig. 4. Determination of the structure was made on 24 reflections, i.e., 32 *hkl*, starting from the atomic positions previously obtained by X-ray diffraction. Atomic parameters, thermal factors, and cationic distribution were successively refined, lowering the discrepancy factor to $R = 0.019$. The final atomic parameters (Table IV) are very close to those observed by X-ray diffraction. The cationic distribution is also confirmed, leading to the formula

$$(Li_{0.56}Fe_{0.44})_{T_1}(Li)_{T_2}(Sn)_{Oc_1}(SnLi_{0.44}Fe_{1.56})_{Oc_2}O_8.$$

Thus, it is confirmed that the T_{II} tetrahedra, which share their edges with three Oc_{II} octahedra forming $(T_{II}(Oc_{II})_3)$ blocks (Fig. 5) are only occupied by Li^+ ions in order to minimize the electrostatic repulsions. From the interatomic distances (Table V) it appears that the $(M)_{Oc}$–$(M)_{Oc}$ distances (2.99 to 3.17 Å) of the edge-sharing octahedra are somewhat shorter than those observed in the ramsdellite form. The shortest M–M distances observed in this structure involve, like for the ramsdellite form, the presence of lithium ions, since they correspond to the $(Li)_{T_2}$–$(M)_{Oc_2}$ distances belonging to the $(T_{II}(Oc_{II})_3)$ blocks. However, they are longer (2.71 Å) than those observed in the high temperature ramsdellite form.

These results are in agreement with the

TABLE IV

ATOMIC PARAMETERS OF DH $LiFeSnO_4$ ($x = 0$) DETERMINED BY NEUTRON DIFFRACTION (SPACE GROUP: $P6_3mc$; CELL PARAMETERS: $a = 6.012(1)$ Å, $c = 9.776(2)$ Å)

Atoms	Site	*x*	*y*	*z*	*B* (Å²)
$[Li, Fe]_{T_1}$	2(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	−0.095(4)	0.97(23)
$[Li]_{T_2}$	2(*a*)	0	0	0.502(4)	2.80(72)
$[Sn]_{Oc_1}$	2(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	0.4862(15)	0.05(13)
$[Li, Fe, Sn]_{Oc_2}$	6(*c*)	0.1675(15)	−0.1675(15)	0.214(9)	0.63(6)
O_1	2(*a*)	0	0	0.3145(17)	0.13(14)
O_2	2(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	0.1076(9)	0.33(14)
O_3	6(*c*)	0.4808(7)	−0.4808(7)	0.3464(15)	0.94(6)
O_4	6(*c*)	0.1737(16)	−0.1737(16)	0.6036(10)	0.15(5)

reversible transition observed between the two structures which can be considered as two semi-ordered cationic distributions. Both structures, DH and ramsdellite, are stabilized by the presence of Li^+ ions, owing to the ability of this low charged cation to permit short Li–Li or Li–*M* distances. Moreover the stability of the structure does not seem to be affected by the Li–*M* or Li–Li distances. On the other hand, the presence of an excess of Li^+ in the ramsdellite structure increases its stability by decreasing the mean cationic charge on the octahedral sites.

TABLE V

INTERATOMIC DISTANCES (Å) IN DH $LiFeSnO_4$ (NEUTRON DIFFRACTION)

$\lvert T_1–O_2 \rvert$	× 1	1.98	$\lvert O_1–O_3 \rvert$	× 6	3.03
$\lvert T_1–O_3 \rvert$	× 3	2.02	$\lvert O_1–O_4 \rvert$	× 3	3.36
$\lvert T_2–O_1 \rvert$	× 1	1.84	$\lvert O_1–O_4 \rvert$	× 3	2.74
$\lvert T_2–O_4 \rvert$	× 3	2.06	$\lvert O_2–O_3 \rvert$	× 3	2.80
			$\lvert O_2–O_3 \rvert$	× 3	3.20
$\lvert Oc_1–O_3 \rvert$	× 3	2.06	$\lvert O_2–O_4 \rvert$	× 6	3.01
$\lvert Oc_1–O_4 \rvert$	× 3	2.02	$\lvert O_3–O_3 \rvert$	× 2	2.66
$\lvert Oc_2–O_1 \rvert$	× 1	2.00	$\lvert O_3–O_4 \rvert$	× 2	2.98
$\lvert Oc_2–O_2 \rvert$	× 1	2.02	$\lvert O_3–O_4 \rvert$	× 2	2.99
$\lvert Oc_2–O_3 \rvert$	× 2	2.09	$\lvert O_4–O_4 \rvert$	× 2	3.13
$\lvert Oc_2–O_4 \rvert$	× 2	2.08	$\lvert O_4–O_4 \rvert$	× 2	2.88
$\lvert Oc_2–Oc_2 \rvert$	× 2	2.99	$\lvert T_2–Oc_2 \rvert$	× 3	2.71
$\lvert Oc_2–Oc_2 \rvert$	× 2	3.02			
$\lvert Oc_1–Oc_2 \rvert$	× 3	3.17			
$\lvert Oc_1–Oc_2 \rvert$	× 6	3.74			

Conclusion

These results confirm that the high temperature form of $LiFeSnO_4$ exhibits the ramsdellite type; thus, one must rule out for this phase the Ca_2SnO_4 structure recently proposed by A. Watanabe *et al.* (*10*). Moreover, a rather wide homogeneity range occurs, owing to the presence of an excess of lithium.

It appears that the presence of lithium is of importance for the stabilization of

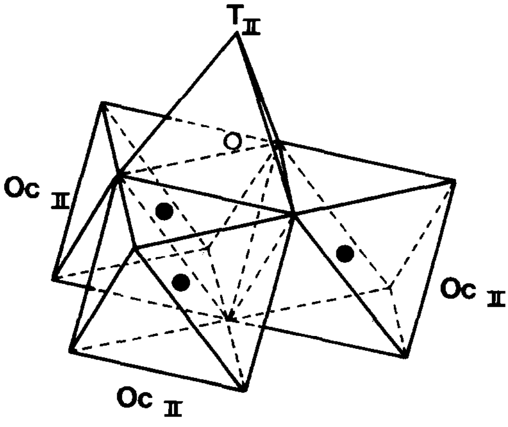

FIG. 5. $T_{II}(Oc_{II})_3$ blocks in DH $LiFeSnO_4$.

the ramsdellite as well as for the DH $LiFeSnO_4$-type structure, owing to its low charge. The maximum amount of Li^+ in the ramsdellite tunnels, which corresponds to 62% of the available sites, is the greatest which has ever been observed. Stabilization of the structure by decreasing the charge in the octahedral framework, or by forming more covalent bonds in the lattice, will be investigated.

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