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Structural Phase Transition and Nonstoichiometry of Li_2FeCl_4—Neutron Diffraction Studies

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Neutron powder diffraction studies have been performed on Li_2FeCl_4 at 298, 498, and 698 K. The resulting powder profiles were fitted by the Rietveld method to final R_I = 6.9, 3.2, and 4.0%, respectively. The orthorhombic room-temperature polymorph (RTM) Li_2FeCl_4 *oC*14 crystallizes in the $SnMn_2S_4$-type NaCl superstructure (space group *Cmmm*, $Z = 2$, a = 732.95(8), b = 1034.2(1), and c = 365.90(4) pm), the high-temperature form Li_2FeCl_4 *cF*56 in an inverse spinel structure (space group $Fd\bar{3}m$, $Z = 8$, a = 1043.64(1) pm at 498 K) with increasing Frenkel disorder of the lithium ions from the tetrahedral 8*a* lattice sites to the octahedral 16*c* interstitial sites with the increase in temperature. Li_2FeCl_4 RTM possesses a Li^+ ion deficiency as given by the formula $Li_{2-2x}Fe_{1+x}Cl_4$. Stoichiometric samples annealed at 373 K are two-phase containing Suzuki-type Li_6FeCl_8.

Introduction

Li_2FeCl_4 has been reported to crystallize in an inverse spinel structure (*1*). Both Lutz *et al.* (*2, 3*) and Kanno *et al.* (*4*) have independently established that this ternary lithium chloride exhibits very high lithium ion conductivity. Later it was revealed that spinel-type Li_2FeCl_4 is really a high-temperature polymorph which can be obtained as a metastable compound at ambient temperature (*5, 6*). For the crystal structure of the orthorhombic room-temperature form, which can be obtained by annealing below 370 K, Kanno *et al.* (*5*) suggested a spinel superstructure with 1 : 1 ordering at the octahedral sites from X-ray powder studies. However, some questions arise concerning their crystal structure determination due to the different structure exhibited by the related compound Li_2CoCl_4 (*7*) as well as in connection with the interpretation of the Mössbauer spectra of Li_2FeCl_4 (*6*). In order to ascertain the correct crystal structure of orthorhombic Li_2FeCl_4 we performed neutron powder diffraction measurements at ambient and elevated temperatures (*8*).

Experimental Methods

A polycrystalline sample of Li_2FeCl_4 was prepared by fusing stoichiometric amounts of the anhydrous binary chlorides in evacuated sealed borosilicate glass ampoules. The starting materials LiCl and $FeCl_2 \cdot 4H_2O$ were dried and dehydrated in a HCl stream at 680 K. Transformation to the orthorhombic polymorph was obtained by annealing the sample at 370 K for 3 months.

The neutron diffraction powder patterns of Li_2FeCl_4 were collected at 298, 498, and 698 K on the powder diffractometer D2B at the Institut Laue–Langevin in Grenoble (ILL). The sample was sealed in a quartz ampoule placed in a thin-walled vanadium can. The neutron wavelength was 159.4 (2)

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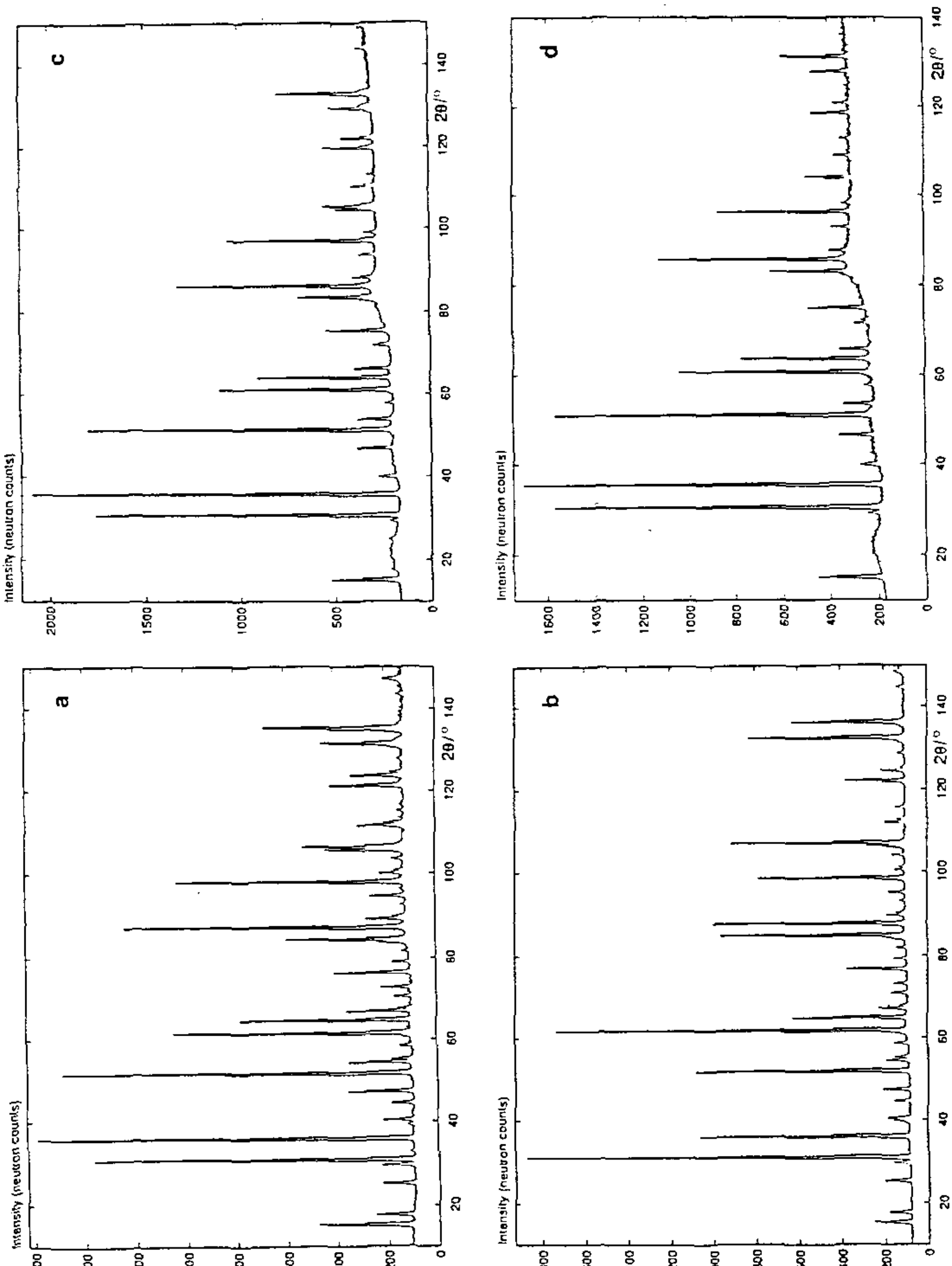
c
d
a
b
Intensity (neutron counts)
2θ/°

TABLE I

REFINED PROFILE PARAMETERS FOR Li_2FeCl_4 AT AMBIENT AND ELEVATED TEMPERATURES WITH E.S.D.'S IN PARENTHESES

	298 K	498 K	698 K
U (°²)	0.110(3)	0.060(9)	0.10(1)
V (°²)	−0.23(1)	−0.13(2)	−0.25(1)
W (°²)	0.273(7)	0.233(7)	0.267(7)
Asymmetry parameter	0.51(6)	0.67(9)	0.50(9)
Number of structural parameters refined	16	12	11

Note. 2Θ ranges (°) excluded from refinements due to extraneous peaks from the steel (a = 330 pm, $Im3m$) end cap of the sample holder: 39.0–41.0, 57.0–59.0, 71.0–73.2, 112.3–114.4, and 128.8–130.2.

pm. The measuring ranges (2Θ) used for structure refinement were 10–150°, the step width being 0.05°. The background was determined graphically. The structures were refined with the new Rietveld program PROFIL (*9*). The neutron scattering lengths used were b(Li) = −2.03, b(Fe) = 9.45, and b(Cl) = 9.5792 fm (*10*).

Results

The neutron diffraction patterns obtained, together with that of Li_6FeCl_8 (*8*), are shown in Fig. 1. Some Bragg peaks, for which the 2Θ ranges are given in Table I, are due to the sample holder, and are excluded from the structure refinement. The refinement converged to final R_{wp} = 12.4, 12.3, and 11.0% (expected 4.1, 3.0, and 3.4%, R_I = 6.9, 3.2, and 4.0%), based on 653, 417, and 322 observations, containing 159, 41, and 39 reflections and 637, 405, and 311 degrees of freedom for the 298, 498, and 698 K data, respectively. The final profile and structural parameters are given in Tables I and II, selected interatomic distances and angles in Table III.

The orthorhombic room-temperature polymorph (RTM) of Li_2FeCl_4 does not possess an ordered spinel superstructure (space group $Imma$) as reported by Kanno *et al.* (*5*). It is isostructural with Li_2CoCl_4 (*7*), crystallizing in an ordered NaCl superstructure (space group $Cmmm$, Z = 2, $SnMn_2S_4$ type (*11*)) with a unit cell (a = 732.95(8), b = 1034.2(1), and c = 365.90(4) pm) half as large as that assumed in (*5*). A detailed description of the $SnMn_2S_4$-type structure is given in (*7, 11, 12*).

The Li_2FeCl_4 sample studied at 298 K was revealed to be two-phase. In addition to Li_2FeCl_4 $oC14$, small amounts of Suzuki-type Li_6FeCl_8 (*8, 13, 14*) were present. The neutron diffraction pattern of cubic Li_6FeCl_8 (with ordered Li^+ vacancies and Fe^{2+} ions in a LiCl matrix) is very similar to that of Li_2FeCl_4 RTM (see Fig. 1). The reflections from both almost coincide with each other, but they can be separated using the Rietveld method. Li_2FeCl_4 $oC14$ seems to be rather nonstoichiometric at ambient temperature, as shown by the better R values and thermal parameters if lithium deficiency is assumed according to the formula $Li_{2-2x}Fe_{1+x}Cl_4$ with x = 0.085(1) (see Table II).

The cubic high-temperature polymorph (HTM) of Li_2FeCl_4 crystallizes in the inverse spinel structure (space group $Fd\bar{3}m$, Z = 8) as known since 1975 (*1*), but with large Frenkel disorder of the lithium ions from the tetrahedral 8a sites to the octahedral 16c interstitial sites (see Table II). This behavior resembles that of other spinel-type ternary lithium chlorides $Li_2M^{II}Cl_4$ (M^{II} = Mg, V, Mn, Cd) (see, for example, (*15*)). The disorder increases with the increase in temperature, viz., from 40% Li on the interstitial position at 498 K to 70% at 698 K. Whereas the Li_2FeCl_4 sample studied was still biphasic even at 498 K, it was monophasic at 698 K.

Discussion

The transformation of Li_2FeCl_4 RTM with exclusively octahedrally coordinated lith-

FIG. 1. Neutron diffraction patterns of Li_2FeCl_4 RTM (298 K, a) and HTM (498 and 698 K, c and d) and of Suzuki-type Li_6FeCl_8 (*8, 16*) (b).

TABLE II

STRUCTURAL PARAMETERS OF Li_2FeCl_4 *oC*14 AND *cF*56 WITH E.S.D.'S IN PARENTHESES

Atom	Site	Occupation	*x*	*y*	*z*	$B_{iso}/10^4$ pm^2
		Li_2FeCl_4 *oC*14 (space group *Cmmm*, *Z* = 2, 298 K)				
Li	4*f*(2/*m*)	4	0.25	0.25	0.5	7.1(6)
Fe	2*a*(*mmm*)	2	0	0	0	1.26(8)
Cl(1)	4*h*(2*mm*)	4	0.2343(8)	0	0.5	1.13(6)
Cl(2)	4*i*(*m*2*m*)	4	0	0.2373(6)	0	1.40(7)
a = 732.95(8), *b* = 1034.2(1), and *c* = 365.90(4) pm						
R_{wp} = 12.6% (expected 4.1%), R_I = 6.7%						
		Refinement of the *oC*14 phase assuming composition $Li_{2-2x}Fe_{1+x}Cl_4$ (actually $Li_{1.83}Fe_{1.085}Cl_4$)				
Li	4*f*	3.66(2)	0.25	0.25	0.5	4.5(4)
Fe(2)	4*f*	0.17(1)	0.25	0.25	0.5	4.5(4)
Fe(1)	2*a*	2	0	0	0	1.30(6)
Cl(1)	4*h*	4	0.2345(8)	0	0.5	1.22(6)
Cl(2)	4*i*	4	0	0.2377(7)	0	1.45(7)
R_{wp} = 12.4% (expected 4.1%), R_I = 6.9%						
		Li_2FeCl_4 *cF*56 (space group $Fd\bar{3}m$, *Z* = 8) (498 K: first line; 698 K: second line)				
Li(1)	8*a*($\bar{4}$3*m*)	4.8(2)	0.125	0.125	0.125	4.4(6)
		2.4(2)	0.125	0.125	0.125	4.9(8)
Li(3)	16*c*($\bar{3}$*m*)	3.2(2)	0	0	0	4.4(6)
		5.6(2)	0	0	0	5.6(8)
Li(2)	16*d*($\bar{3}$*m*)	8	0.5	0.5	0.5	1.40(8)
		8	0.5	0.5	0.5	1.9(1)
Fe	16*d*	8	0.5	0.5	0.5	1.40(8)
		8	0.5	0.5	0.5	1.9(1)
Cl	32*e*(3*m*)	32	0.25665(6)	0.25665(6)	0.25665(6)	2.48(6)
			0.25581(9)	0.25581(9)	0.25581(9)	3.43(7)
a = 1043.64(1) and 1049.52(1) pm for 498 and 698 K, respectively						
R_{wp} = 12.3 and 11.0% (expected 3.0 and 3.4%), R_I = 3.2 and 4.0%						

ium ions to Li_2FeCl_4 *cF*56 with lithium ions on both tetrahedral and octahedral sites as established in this work differs from the order–disorder phase transitions of all other $Li_2M^{II}Cl_4$ compounds. In the case of the latter, octahedral sites become more favorable for lithium ions with increasing temperature, which can be explained by the increasing Li–Cl distances due to the thermal expansion of the lattice.

The phase relationships of the system LiCl–$FeCl_2$, especially with respect to the polymorphism and homogeneity ranges of Li_6FeCl_8 (*16*) and Li_2FeCl_4, are obviously more complicated than that reported by Kanno *et al.* (*5*) and are far from being completely understood. Experimental studies are difficult because of the great similarity of the X-ray patterns of the phases present and the partial metastability of the respective high-temperature polymorphs at ambient temperature.

In the case of $Li_{2-2x}Fe_{1+x}Cl_4$ RTM, iron ions are present at both the distorted octahedral sites 2*a* (*mmm*) and 4*f* (2/*m*), and are randomly distributed among the lithium ions at the latter size (see Table II). These findings are supported by recent Mössbauer investigations (*6*), which resulted in the observation of two quadrupole doublets for the Fe^{2+} ions. The stronger sharp doublet (isomer shift 1.15 mm s^{-1} compared to iron, quadrupole splitting 1.40 mm s^{-1}, relative area 86%) can now be assigned to the Fe^{2+} ions on the position 2*a*, the smaller relatively broad one (1.13 and 0.31 mm s^{-1} and

TABLE III

SELECTED INTERATOMIC DISTANCES (pm) AND ANGLES (°) OF Li_2FeCl_4 AT AMBIENT AND ELEVATED TEMPERATURES WITH E.S.D.'S IN PARENTHESES

	$Li_{1.83}Fe_{1.085}Cl_4$ *oC*14 (298 K)		
MCl_6 octahedron[a]			
2× *M*–Cl(1)	258.80(4)	1× Cl(1)–*M*–Cl(1)	180.00
4× *M*–Cl(2)	259.25(4)	4× Cl(1)–*M*–Cl(2)	85.4(2)
		4× Cl(1)–*M*–Cl(2)	94.6(2)
		2× Cl(2)–*M*–Cl(2)	180.00
		2× Cl(2)–*M*–Cl(2)	89.77(1)
		2× Cl(2)–*M*–Cl(2)	90.23(1)
Fe(1)Cl_6 octahedron			
4× Fe(1)–Cl(1)	251.01(4)	2× Cl(1)–Fe(1)–Cl(1)	86.4(1)
2× Fe(1)–Cl(2)	245.81(4)	2× Cl(1)–Fe(1)–Cl(1)	93.6(1)
		2× Cl(1)–Fe(1)–Cl(1)	180.00
		8× Cl(1)–Fe(1)–Cl(2)	90.00
		1× Cl(2)–Fe(1)–Cl(2)	180.00
shortest Cl–Cl distances			
Cl(1)–Cl(1)	351.3(6)–380.7(6)		
Cl(2)–Cl(2)	365.9(1)–367.4(1)		
	Li_2FeCl_4 *cF*56 (498 K)		
Li(1)Cl_4 tetrahedron			
4× Li(1)–Cl	237.98(7)	6× Cl–Li(1)–Cl	109.47(2)
Li(3)Cl_6 octahedron			
6× Li(3)–Cl	268.03(7)	6× Cl–Li(3)–Cl	87.07(2)
		6× Cl–Li(3)–Cl	92.93(2)
		3× Cl–Li(3)–Cl	180.00
MCl_6 octahedron[b]			
6× *M*–Cl	254.16(7)	6× Cl–*M*–Cl	86.83(2)
		6× Cl–*M*–Cl	93.17(2)
		3× Cl–*M*–Cl	180.00

[a] *M* = Li, Fe(2) (4*f*).
[b] *M* = Li(2), Fe(16*d*).

14%) to the Fe^{2+} ions at the 4*f* site. The relative intensities of the two quadrupole doublets display the amounts of iron on these lattice sites. They are in nice agreement with the neutron diffraction results reported in this work (see Table II). The different quadrupole splittings of the 2*a*-site and the 4*f*-site iron ions correlate to the different distortion strengths of the corresponding $FeCl_6$ octahedra (see Table III).

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