

## Structural Phase Transition and Nonstoichiometry of $\text{Li}_2\text{FeCl}_4$ —Neutron Diffraction Studies

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Received November 4, 1992; in revised form March 8, 1993; accepted March 11, 1993

Neutron powder diffraction studies have been performed on  $\text{Li}_2\text{FeCl}_4$  at 298, 498, and 698 K. The resulting powder profiles were fitted by the Rietveld method to final  $R_1 = 6.9, 3.2,$  and  $4.0\%$ , respectively. The orthorhombic room-temperature polymorph (RTM)  $\text{Li}_2\text{FeCl}_4$  *oC14* crystallizes in the  $\text{SnMn}_2\text{S}_4$ -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  $\text{Li}_2\text{FeCl}_4$  *cF56* in an inverse spinel structure (space group  $\text{Fd}\bar{3}m$ ,  $Z = 8$ ,  $a = 1043.64(1)$  pm at 498 K) with increasing Frenkel disorder of the lithium ions from the tetrahedral  $8a$  lattice sites to the octahedral  $16c$  interstitial sites with the increase in temperature.  $\text{Li}_2\text{FeCl}_4$  RTM possesses a  $\text{Li}^+$  ion deficiency as given by the formula  $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{Cl}_4$ . Stoichiometric samples annealed at 373 K are two-phase containing Suzuki-type  $\text{Li}_6\text{FeCl}_8$ . © 1993 Academic Press, Inc.

### Introduction

$\text{Li}_2\text{FeCl}_4$  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  $\text{Li}_2\text{FeCl}_4$  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  $\text{Li}_2\text{CoCl}_4$  (7) as well as in connection with the interpretation of the Mössbauer spectra of  $\text{Li}_2\text{FeCl}_4$  (6). In order

to ascertain the correct crystal structure of orthorhombic  $\text{Li}_2\text{FeCl}_4$  we performed neutron powder diffraction measurements at ambient and elevated temperatures (8).

### Experimental Methods

A polycrystalline sample of  $\text{Li}_2\text{FeCl}_4$  was prepared by fusing stoichiometric amounts of the anhydrous binary chlorides in evacuated sealed borosilicate glass ampoules. The starting materials  $\text{LiCl}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  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  $\text{Li}_2\text{FeCl}_4$  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)

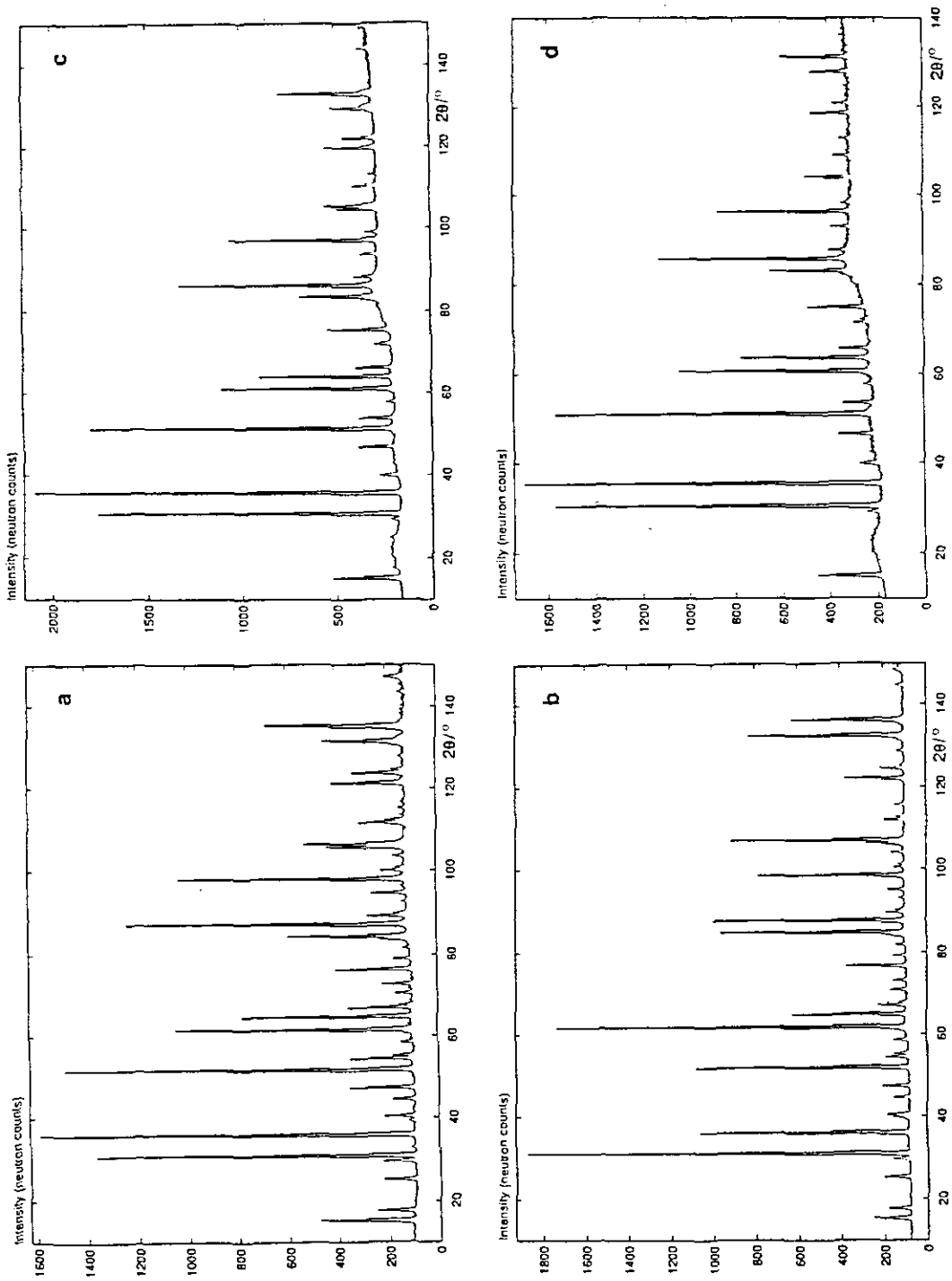


TABLE I  
REFINED PROFILE PARAMETERS FOR  $\text{Li}_2\text{FeCl}_4$  AT  
AMBIENT AND ELEVATED TEMPERATURES WITH  
E.S.D.'S IN PARENTHESES

	298 K	498 K	698 K
$U$ ( $^{\circ 2}$ )	0.110(3)	0.060(9)	0.10(1)
$V$ ( $^{\circ 2}$ )	-0.23(1)	-0.13(2)	-0.25(1)
$W$ ( $^{\circ 2}$ )	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.  $2\theta$  ranges ( $^{\circ}$ ) excluded from refinements due to extraneous peaks from the steel ( $a = 330$  pm,  $1m3m$ ) 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 ( $2\theta$ ) used for structure refinement were 10–150 $^{\circ}$ , the step width being 0.05 $^{\circ}$ . The background was determined graphically. The structures were refined with the new Rietveld program PROFIL (9). The neutron scattering lengths used were  $b(\text{Li}) = -2.03$ ,  $b(\text{Fe}) = 9.45$ , and  $b(\text{Cl}) = 9.5792$  fm (10).

## Results

The neutron diffraction patterns obtained, together with that of  $\text{Li}_6\text{FeCl}_8$  (8), are shown in Fig. 1. Some Bragg peaks, for which the  $2\theta$  ranges are given in Table I, are due to the sample holder, and are excluded from the structure refinement. The refinement converged to final  $R_{\text{wp}} = 12.4$ , 12.3, and 11.0% (expected 4.1, 3.0, and 3.4%,  $R_1 = 6.9$ , 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  $\text{Li}_2\text{FeCl}_4$  does not possess an ordered spinel superstructure (space group  $Imma$ ) as reported by Kanno *et al.*

(5). It is isostructural with  $\text{Li}_2\text{CoCl}_4$  (7), crystallizing in an ordered NaCl superstructure (space group  $Cmmm$ ,  $Z = 2$ ,  $\text{SnMn}_2\text{S}_4$  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  $\text{SnMn}_2\text{S}_4$ -type structure is given in (7, 11, 12).

The  $\text{Li}_2\text{FeCl}_4$  sample studied at 298 K was revealed to be two-phase. In addition to  $\text{Li}_2\text{FeCl}_4$  *oC14*, small amounts of Suzuki-type  $\text{Li}_6\text{FeCl}_8$  (8, 13, 14) were present. The neutron diffraction pattern of cubic  $\text{Li}_6\text{FeCl}_8$  (with ordered  $\text{Li}^+$  vacancies and  $\text{Fe}^{2+}$  ions in a  $\text{LiCl}$  matrix) is very similar to that of  $\text{Li}_2\text{FeCl}_4$  RTM (see Fig. 1). The reflections from both almost coincide with each other, but they can be separated using the Rietveld method.  $\text{Li}_2\text{FeCl}_4$  *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  $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{Cl}_4$  with  $x = 0.085(1)$  (see Table II).

The cubic high-temperature polymorph (HTM) of  $\text{Li}_2\text{FeCl}_4$  crystallizes in the inverse spinel structure (space group  $F\bar{d}3m$ ,  $Z = 8$ ) 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  $\text{Li}_2M^{\text{II}}\text{Cl}_4$  ( $M^{\text{II}} = \text{Mg, V, Mn, Cd}$ ) (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  $\text{Li}_2\text{FeCl}_4$  sample studied was still biphasic even at 498 K, it was monophasic at 698 K.

## Discussion

The transformation of  $\text{Li}_2\text{FeCl}_4$  RTM with exclusively octahedrally coordinated lith-

FIG. 1. Neutron diffraction patterns of  $\text{Li}_2\text{FeCl}_4$  RTM (298 K, a) and HTM (498 and 698 K, c and d) and of Suzuki-type  $\text{Li}_6\text{FeCl}_8$  (8, 16) (b).

TABLE II  
STRUCTURAL PARAMETERS OF  $\text{Li}_2\text{FeCl}_4$  *oC14* AND *cF56* WITH E.S.D.'S IN PARENTHESES

Atom	Site	Occupation	x	y	z	$B_{\text{iso}}/10^4 \text{ pm}^2$
$\text{Li}_2\text{FeCl}_4$ <i>oC14</i> (space group <i>Cmmm</i> , $Z = 2$ , 298 K)						
Li	$4f(2/m)$	4	0.25	0.25	0.5	7.1(6)
Fe	$2a(mmm)$	2	0	0	0	1.26(8)
Cl(1)	$4h(2mm)$	4	0.2343(8)	0	0.5	1.13(6)
Cl(2)	$4i(m2m)$	4	0	0.2373(6)	0	1.40(7)
$a = 732.95(8)$ , $b = 1034.2(1)$ , and $c = 365.90(4)$ pm						
$R_{\text{wp}} = 12.6\%$ (expected 4.1%), $R_1 = 6.7\%$						
Refinement of the <i>oC14</i> phase assuming composition $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{Cl}_4$ (actually $\text{Li}_{1.83}\text{Fe}_{1.085}\text{Cl}_4$ )						
Li	$4f$	3.66(2)	0.25	0.25	0.5	4.5(4)
Fe(2)	$4f$	0.17(1)	0.25	0.25	0.5	4.5(4)
Fe(1)	$2a$	2	0	0	0	1.30(6)
Cl(1)	$4h$	4	0.2345(8)	0	0.5	1.22(6)
Cl(2)	$4i$	4	0	0.2377(7)	0	1.45(7)
$R_{\text{wp}} = 12.4\%$ (expected 4.1%), $R_1 = 6.9\%$						
$\text{Li}_2\text{FeCl}_4$ <i>cF56</i> (space group $Fd\bar{3}m$ , $Z = 8$ ) (498 K: first line; 698 K: second line)						
Li(1)	$8a(\bar{4}3m)$	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)	$16c(\bar{3}m)$	3.2(2)	0	0	0	4.4(6)
		5.6(2)	0	0	0	5.6(8)
Li(2)	$16d(\bar{3}m)$	8	0.5	0.5	0.5	1.40(8)
		8	0.5	0.5	0.5	1.9(1)
Fe	$16d$	8	0.5	0.5	0.5	1.40(8)
		8	0.5	0.5	0.5	1.9(1)
Cl	$32e(3m)$	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						
$R_{\text{wp}} = 12.3$ and $11.0\%$ (expected 3.0 and 3.4%), $R_1 = 3.2$ and $4.0\%$						

ium ions to  $\text{Li}_2\text{FeCl}_4$  *cF56* with lithium ions on both tetrahedral and octahedral sites as established in this work differs from the order-disorder phase transitions of all other  $\text{Li}_2\text{M}^{\text{II}}\text{Cl}_4$  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  $\text{LiCl-FeCl}_2$ , especially with respect to the polymorphism and homogeneity ranges of  $\text{Li}_6\text{FeCl}_8$  (16) and  $\text{Li}_2\text{FeCl}_4$ , 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  $\text{Li}_{2-2x}\text{Fe}_{1+x}\text{Cl}_4$  RTM, iron ions are present at both the distorted octahedral sites  $2a$  (*mmm*) and  $4f$  ( $2/m$ ), and are randomly distributed among the lithium ions at the latter site (see Table II). These findings are supported by recent Mössbauer investigations (6), which resulted in the observation of two quadrupole doublets for the  $\text{Fe}^{2+}$  ions. The stronger sharp doublet (isomer shift  $1.15 \text{ mm s}^{-1}$  compared to iron, quadrupole splitting  $1.40 \text{ mm s}^{-1}$ , relative area 86%) can now be assigned to the  $\text{Fe}^{2+}$  ions on the position  $2a$ , the smaller relatively broad one ( $1.13$  and  $0.31 \text{ mm s}^{-1}$  and

TABLE III

SELECTED INTERATOMIC DISTANCES (pm) AND ANGLES ( $^\circ$ ) OF  $\text{Li}_2\text{FeCl}_4$  AT AMBIENT AND ELEVATED TEMPERATURES WITH E.S.D.'s IN PARENTHESES

$\text{Li}_{1.83}\text{Fe}_{1.085}\text{Cl}_4$ oC14 (298 K)			
$\text{MCl}_6$ octahedron <sup>a</sup>			
$2 \times M-\text{Cl}(1)$	258.80(4)	$1 \times \text{Cl}(1)-M-\text{Cl}(1)$	180.00
$4 \times M-\text{Cl}(2)$	259.25(4)	$4 \times \text{Cl}(1)-M-\text{Cl}(2)$	85.4(2)
		$4 \times \text{Cl}(1)-M-\text{Cl}(2)$	94.6(2)
		$2 \times \text{Cl}(2)-M-\text{Cl}(2)$	180.00
		$2 \times \text{Cl}(2)-M-\text{Cl}(2)$	89.77(1)
		$2 \times \text{Cl}(2)-M-\text{Cl}(2)$	90.23(1)
Fe(1) $\text{Cl}_6$ octahedron			
$4 \times \text{Fe}(1)-\text{Cl}(1)$	251.01(4)	$2 \times \text{Cl}(1)-\text{Fe}(1)-\text{Cl}(1)$	86.4(1)
$2 \times \text{Fe}(1)-\text{Cl}(2)$	245.81(4)	$2 \times \text{Cl}(1)-\text{Fe}(1)-\text{Cl}(1)$	93.6(1)
		$2 \times \text{Cl}(1)-\text{Fe}(1)-\text{Cl}(1)$	180.00
		$8 \times \text{Cl}(1)-\text{Fe}(1)-\text{Cl}(2)$	90.00
		$1 \times \text{Cl}(2)-\text{Fe}(1)-\text{Cl}(2)$	180.00
shortest Cl-Cl distances			
$\text{Cl}(1)-\text{Cl}(1)$	351.3(6)-380.7(6)		
$\text{Cl}(2)-\text{Cl}(2)$	365.9(1)-367.4(1)		
$\text{Li}_2\text{FeCl}_4$ cF56 (498 K)			
$\text{Li}(1)\text{Cl}_4$ tetrahedron			
$4 \times \text{Li}(1)-\text{Cl}$	237.98(7)	$6 \times \text{Cl}-\text{Li}(1)-\text{Cl}$	109.47(2)
$\text{Li}(3)\text{Cl}_6$ octahedron			
$6 \times \text{Li}(3)-\text{Cl}$	268.03(7)	$6 \times \text{Cl}-\text{Li}(3)-\text{Cl}$	87.07(2)
		$6 \times \text{Cl}-\text{Li}(3)-\text{Cl}$	92.93(2)
		$3 \times \text{Cl}-\text{Li}(3)-\text{Cl}$	180.00
$\text{MCl}_6$ octahedron <sup>b</sup>			
$6 \times M-\text{Cl}$	254.16(7)	$6 \times \text{Cl}-M-\text{Cl}$	86.83(2)
		$6 \times \text{Cl}-M-\text{Cl}$	93.17(2)
		$3 \times \text{Cl}-M-\text{Cl}$	180.00

<sup>a</sup>  $M = \text{Li}, \text{Fe}(2)$  (4f).

<sup>b</sup>  $M = \text{Li}(2), \text{Fe}(16d)$ .

14%) to the  $\text{Fe}^{2+}$  ions at the 4f 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 2a-site and the 4f-site iron ions correlate to the different distortion strengths of the corresponding  $\text{FeCl}_6$  octahedra (see Table III).

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

## References

1. C. J. J. VAN LOON AND J. DEJONG, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **31**, 2549 (1975).
2. H. D. LUTZ, H. HAEUSELER, AND W. SCHMIDT, German Patent 2,838,924 (1980); *Chem. Abstr.* **93** 75769m.
3. H. D. LUTZ, W. SCHMIDT, AND H. HAEUSELER, *J. Phys. Chem. Solids* **42**, 287 (1981).
4. R. KANNO, Y. TAKEDA, AND O. YAMAMOTO, *Mater. Res. Bull.* **16**, 999 (1981).
5. R. KANNO, Y. TAKEDA, A. TAKAHASHI, O. YAMAMOTO, R. SUYAMA, AND S. KUME, *J. Solid State Chem.* **72**, 363 (1988).
6. H. D. LUTZ, A. PFITZNER, W. SCHMIDT, E. RIEDEL, AND D. PRICK, *Z. Naturforsch. A. Phys. Sci.* **44**, 756 (1989).
7. M. SCHNEIDER, H. D. LUTZ, AND J. K. COCKCROFT, *Z. Kristallogr.* **203**, 183 (1993).
8. A. PFITZNER, Doctoral Thesis, University of Siegen (1991).
9. J. K. COCKCROFT, "PROFIL," Version 4.05, Institut Laue-Langevin, Grenoble, France (1991).
10. L. KOESTER AND H. RAUCH, "Summary of Neutron Scattering Lengths," IAEA Contract 2517/RB (1983).
11. M. WINTENBERGER AND J. C. JUMAS, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **36**, 993 (1980).
12. H. D. LUTZ, M. SCHNEIDER, P. KUSKE, AND H. J. STEINER, *Z. Anorg. Allg. Chem.* **592**, 106 (1991).
13. R. KANNO, Y. TAKEDA, M. MORI, AND O. YAMAMOTO, *Chem. Lett.* (7), 1465 (1987).
14. H. D. LUTZ, P. KUSKE, AND K. WUSSOW, *Z. Anorg. Allg. Chem.* **553**, 172 (1987).
15. H. J. STEINER AND H. D. LUTZ, *J. Solid State Chem.* **99**, 1 (1992).
16. E. RIEDEL, D. PRICK, A. PFITZNER, AND H. D. LUTZ, *Z. Anorg. Allg. Chem.* **619**, 901 (1993).