

X-ray study of $K_6LiFe_{24}S_{26}Cl$, a djerfisherite-like compound¹

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Abstract

The X-ray powder diffraction pattern of a djerfisherite-like compound, $K_6LiFe_{24}S_{26}Cl$, recovered as one of the reaction products in a battery development program at Argonne National Laboratory, is similar to that of the mineral which occurs in meteorites and in terrestrial vein deposits. A structure of this compound, proposed on the basis of the X-ray data, was refined to an R of 0.06 using 38 $FeK\alpha/Mn$ reflection data. The cell is cubic, probable space group is $Pm\bar{3}m$ and $a = 10.358 \pm 0.005$ Å. The structure has clusters of eight edge-shared FeS_4 tetrahedra about the face-centers of the cube similar to that in pentlandite. Potassium, chlorine, and lithium atoms are distributed among these clusters.

Introduction

A research program is in progress at Argonne National Laboratory to develop rechargeable batteries for electrical-vehicle propulsion and for load-leveling applications (Nelson *et al.*, 1974). The electrochemical cells for these batteries have a molten-salt electrolyte of LiCl-KCl eutectic and operate at temperatures of 400–450°C. In one type, the negative electrode is a Li-Al alloy, and the positive electrode is FeS. Several new phases have been found in the positive electrodes (Martin *et al.*, 1974; Mrazek and Battles, 1975). One phase is a compound which gives an X-ray powder diffraction pattern that is similar to that of the mineral djerfisherite. Wet-chemical analysis of this compound, extracted from an electrode,² led to the formula, $K_{5.5}Li_{0.6}Fe_{24.0}S_{25.9}Cl_{1.0}$. It is cubic, primitive, with $a = 10.358 \pm 0.005$ Å. Djerfisherite, observed in two meteorites (Fuchs, 1966), was analyzed as $K_3(Na,Cu)(Fe,Ni)_{12}S_{14}$, with two formula units per unit cell and with $a = 10.34 \pm 0.01$ Å. Fuchs observed one weight percent chlorine, but the Commission on New Minerals of the International Mineralogical Association recommended that chlorine be excluded from this formula. El Goresy *et al.* (1968, 1971) have supported Fuchs' original observation

that chlorine was indeed present and not as a contaminant,

The first terrestrial occurrence of djerfisherite, $K_3Cu_3(Fe,Ni)_{11}S_{14}$ with $a = 10.41$ Å, was reported by Genkin *et al.* (1969). Dobrovol'skaya *et al.* (1975) have recognized three types of djerfisherite: (1) where iron is predominant (meteorites, skarns), (2) copper-containing (alkaline rocks), and (3) nickel-containing (kimberlites). Compositional data for some djerfisherite-type compounds found in various media are summarized in Table 1.

Experimental

The electrochemical preparation of a djerfisherite-type compound will be described by Mrazek and Battles (in preparation). A. E. Martin (1975) has described the out-of-cell preparation of this phase. It was produced by the reaction of Li_2FeS_2 with Fe in molten LiCl-KCl eutectic (58.2 mole percent LiCl-41.8 mole percent KCl) at 400–450°C. The X-ray powder diffraction patterns of the out-of-cell preparations have $a = 10.360 \pm 0.005$ Å, and they appear the same as that of the electrochemically produced material.

Crystallographic data for the electrochemically prepared phase were obtained using the Norelco powder camera of 114.6 mm diameter, and filtered $FeK\alpha$ radiation. Unit-cell parameters were derived by extrapolation of a_{hkl} vs. $\cos^2 \theta$, after correction for film shrinkage. Thirty-eight X-ray film intensities were recorded with a Leeds and Northrup densitome-

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² The details are reported by Mrazek and Battles (in preparation), Argonne National Laboratory. Mr. K. J. Jensen, Analytical Chemistry Laboratory, performed the chemical analysis.

Table 1. Compositions of djerfisherite type compounds

Source	Formula*
Pena Blanca Spring (enstatite achondrite)	$K_{7.1}Na_{0.3}(Fe_{23.1}Ni_{0.3}Cu_{0.6})_{24.0}S_{26.2}Cl_{1.1}^+$ $K_{6.7}(Fe_{22.9}Ni_{0.6}Cu_{0.5})_{24.0}S_{25.1}Cl_{1.2}$
St. Marks (enstatite chondrite)	$K_{6.3}Na_{0.4}(Fe_{21.9}Ni_{0.7}Cu_{1.4})_{24.0}S_{24.6}Cl_{1.0}^+$ $K_{5.4}Na_{0.3}(Fe_{22.1}Ni_{0.3}Cu_{1.6})_{24.0}S_{25.6}Cl_{0.7}^{**}$
Toluca (iron meteorite)	$K_{6.2}(Fe_{21.8}Ni_{1.8}Cu_{0.4})_{24.0}S_{25.5}Cl_{1.1}^+$
Talnakh (ore deposit)	$K_{4.8}(Fe_{17.9}Ni_{0.6}Cu_{5.5})_{24.0}S_{24.0}^{++}$
Khimbiny (massif pegmatites)	$K_{5.6}Na_{0.6}Mg_{1.2}(Fe_{19.3}Cu_{4.7})_{24.0}S_{26.8}^{+*}$
Electrochemical cell	$K_{5.5}Li_{0.6}Fe_{24.0}S_{25.9}Cl_{1.0}^{***}$

*Compositions are referenced to the transition atom ratio of 24.0.
+El Goresy *et al.* (1968), electron micro-probe analysis.
**Fuchs (1966), electron micro-probe analysis.
++Genkin *et al.* (1969), micro-x-ray spectrographic analysis.
+Sokolova *et al.* (1971), chemical analysis; chlorine present, about 1.4 weight percent, Dmitrieva and Ilyukin (1975).
***Mrazek and Battles (in preparation), wet chemical analysis.

ter and converted to integrated values. Weak intensity data were collected after longer exposure, and then scaled and collated with the primary reflection data. On a scale of 0 to 100, 11 reflections were greater than 14, and 9 reflections recorded 0. An absorption correction was applied using $\mu R = 1.5$, for a sample in a 0.1 mm O.D. capillary.

Least-squares refinement on coordinates, scale factor, and thermal parameters was performed with a modification of the program of Busing *et al.* (1962). The program minimizes the function $\sum ||F_0|^2 - |F_c|^2|^2$ and permits refinement on overlapped X-ray powder diffraction data. The final refinement was carried out in space group $Pm\bar{3}m$, using atomic scattering factors for Fe^{2+} , K^{1+} , S^{2-} , Cl^{1-} and Li^{1+} from the *International Tables for Crystallography* (1962). Dispersion corrections were applied to all atoms except lithium (Cromer, 1965). The basic crystallographic data are shown in Table 2.

Structure determination

In view of the lack of sufficient data, trial structures for the electrochemical phase were established by modeling. Derived structures were based on the packing of FeS_4 tetrahedra. Of the various trial structures, the one based on the superstructure of sphalerite led to reasonable distances, and the atoms could be re-

ferred to the point positions of space group $Pm\bar{3}m$. This model, with the formula, $K_6LiFe_{24}S_{26}Cl$, was also in reasonable agreement with the chemical analysis, $K_{5.5}Li_{0.6}Fe_{24.0}S_{25.9}Cl_{1.0}$. The atom positions for this structure were used as a starting point in least-squares refinement. After adjustment of the scale factor, the least-squares on coordinates and temperature factors converged in four cycles to $R = 0.06$ using unit weights. The final coordinates are presented in Table 3. The interatomic distances are given in Table 4. Table 5 shows the calculated and observed X-ray powder pattern intensities. There is good overall agreement which indicates the correctness of the proposed model.

Although the refinement was made in space group $Pm\bar{3}m$, either space group $P\bar{4}3m$ or $P432$ is also possible. Further refinement in space groups of lower symmetry (and consequent increase in parameters) did not seem justified because of the low R -factor already obtained, the reasonable bond distances for this model, and the limited number of measured reflections. Figure 1 shows the forward half of the unit cell of $K_6LiFe_{24}S_{26}Cl$.

Discussion

The structure has 24 distorted tetrahedra. Each shares three edges with other tetrahedra forming a cluster of eight tetrahedra about the face-centers of the cube. The cluster is linked to other clusters by corner-sharing of a tetrahedron.

The compound, $BaFe_2S_3$ (Hong and Steinfink, 1972), also has a structure in which a tetrahedron shares three edges with neighboring tetrahedra. However, these are pairs of tetrahedra linked by edge-sharing to other pairs forming an infinite chain of tetrahedra. Pentlandite, $(Fe,Ni)_9S_8$ (Lindqvist *et al.*, 1936; Hall and Stewart, 1973), not only has three

Table 2. Crystallographic data for $K_6LiFe_{24}S_{26}Cl$

System	Cubic
Space Group _o	$Pm\bar{3}m$, $P\bar{4}3m$ or $P432$
Unit Cell (Å)	$10.358 \pm .005$ Å
Volume (Å ³)	1111.3
Molecule/cell	1
Formula Weight	2450.99
Density g/cm ³ (calculated)	3.66
(measured)*	3.7

*Mrazek and Battles (in preparation).

Table 3. $K_6LiFe_{24}S_{26}Cl$, point positions, positional coordinates and isotropic temperature factors*

Atom	M	X	Y	Z	B
Fe	24m	0.3683(8)	0.3683(8)	0.1310(8)	1.6
S(1)	12h	0.247(2)	0.500	0.0	1.0
S(2)	8g	0.226(2)	0.226(2)	0.226(2)	1.0
S(3)	6f	0.251(2)	0.500	0.500	1.7
K	6e	0.296(2)	0.0	0.0	2.5
Li	1b	0.500	0.500	0.500	1.2
Cl	1a	0.000	0.000	0.000	1.2

*Estimated standard errors indicated in parenthesis in terms of last significant figures.

edge-sharing tetrahedra, but also has a cluster of eight tetrahedra about the face-centers of the unit cell. The metal-to-metal array forms a primitive cube 2.52 Å on edge. This is on the order of the metal-to-metal separation in pure iron. In $K_6LiFe_{24}S_{26}Cl$, the iron-to-iron separation forms a near cube which is about 2.71 on edge. The compound, $K_6LiFe_{24}S_{26}Cl$, can be derived from pentlandite by the appropriate removal and replacement of atoms other than the common cluster of tetrahedra. Genkin *et al.* (1969) interpreted the presence of relict pentlandite in Talnakh djerfisherite as an indication of djerfisherite genesis by replacement of pentlandite.

Potassium, chlorine, and lithium occupy sites between the tetrahedral clusters. Potassium is bonded

Table 4. Selected interatomic distances and angles in $K_6LiFe_{24}S_{26}Cl$ *

Atoms	Distances	Atoms	Distances
Fe-S(1)	2.30(1) x2	Fe-Fe	2.71(2)
Fe-S(2)	2.30(2)	Fe-Fe	2.73(2) x2
Fe-S(3)	2.30(1)		
K-S(1)	3.32(2) x4	Cl-K	3.07(2) x6
K-S(2)	3.39(2) x4	Li-S(3)	2.58(2) x6

Atoms	Angles
S(1)-Fe-S(1)	107.5(6)
S(3)-Fe-S(1)	107.0(5) x2
S(2)-Fe-S(1)	106.4(7) x2
S(2)-Fe-S(3)	121.9(8)

*Distances in Å and angles in degrees, with standard errors indicated in parentheses in terms of last significant figures.

Table 5. X-ray powder diffraction data for $K_6LiFe_{24}S_{26}Cl$ *

hkl	d(calc)Å	d(obs)Å	I(calc)**	I(obs)
100	10.358	10.36	40.3	45.0
110	7.324	7.34	28.8	32.0
111	5.980	5.99	44.0	45.0
200	5.179	-	0.1	0.0
210	4.633	-	0.0	0.0
211	4.229	-	0.1	0.0
220	3.662	-	0.4	0.0
300,221	3.453	3.452	8.8	10.0
310	3.276	3.275	23.2	21.0
311	3.123	3.126	37.2	35.0
222	2.990	2.990	72.6	75.0
320	2.873	2.876	6.6	7.4
321	2.768	2.769	2.1	2.0
400	2.590	-	1.0	0.0
410,322	2.512	2.512	11.4	12.0
330,411	2.442	2.438	2.8	3.0
331	2.376	2.376	47.3	45.0
420	2.316	2.315	2.9	3.7
421	2.260	2.261	1.0	1.5
332	2.208	2.205	1.6	2.5
422	2.115	-	0.3	0.0
430,500	2.072	2.071	10.8	10.0
510,431	2.032	2.031	5.6	6.0
511,333	1.994	1.992	13.2	13.0
520,432	1.924	1.923	5.0	5.5
521	1.891	-	0.8	0.0
440	1.831	1.831	100.0	100.0
441,522	1.803	1.802	4.4	4.9
530,433	1.776	1.775	8.4	8.7
531	1.751	1.751	8.2	8.3
600,422	1.726	1.726	2.6	2.5
610	1.703	-	0.0	0.0
611,532	1.680	1.679	1.1	0.5
620	1.638	-	0.0	0.0
621,540,443	1.618	1.619	2.9	2.9
541	1.598	1.598	2.7	2.7
533	1.580	1.579	2.4	2.5
622	1.562	1.561	17.4	17.0

*Relative intensities, $FeK\alpha$ filtered radiation.
**Absorption corrected $\mu R = 1.5$.

to eight sulfurs and to one chlorine, resulting in an average value of K-S = 3.36 Å and K-Cl = 3.07 Å. Although the K-S distance appears reasonable for this coordination, the K-Cl value may be somewhat low. Lithium is surrounded by an octahedral array of sulfur atoms. The Li-S distance of 2.58 Å is also reasonable for this coordination.

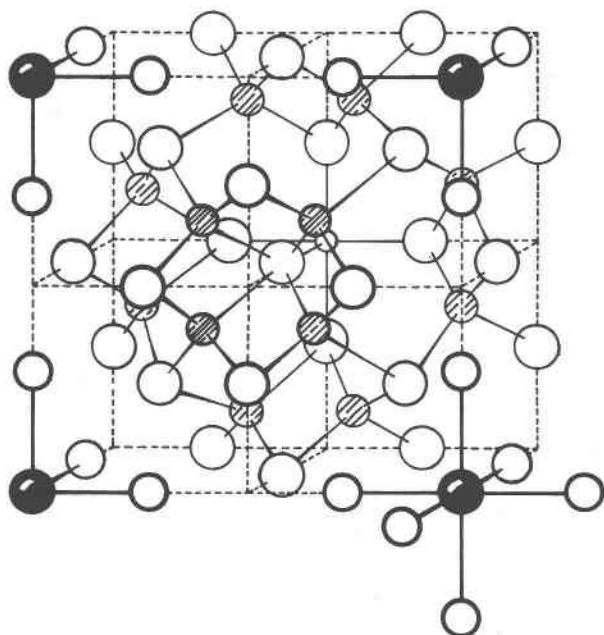


Fig. 1. The forward half of the unit cell of $K_6LiFe_{24}S_{26}Cl$. Large shaded circles are chlorine atoms, connected to open medium circles which are potassium atoms. Large open circles are sulfur atoms. Shaded small circles are iron atoms. The very small open circle is the lithium atom.

Discussion³

Electrochemically prepared $K_6LiFe_{24}S_{26}Cl$ can be considered as a superstructure of sphalerite with relationships to tetrahedrite (Wuensch, 1964) and pentlandite. These compounds are cubic with cells about 10 Å. They have, respectively, primitive, body-centered, and face-centered lattices. Their asymmetric unit or subcell of about 5 Å can be related to the sphalerite-type arrangement with either three or four tetrahedral units.

The structure analysis was based on the formula $K_6LiFe_{24}S_{26}Cl$. If electrical neutrality is maintained and the usual valence states are present, then 23 Fe^{2+} could be randomly distributed about the 24 available sites. However, if the stoichiometry is as proposed, then this could indicate an average charge of 1.91 for the iron atom (assuming S^{2-}). The basis for this

³ After this paper was submitted the author received information on the work of Dmitrieva (1976), and Dmitrieva and Ilyukhin (1975) on the crystal structure of Khibiny djerfisherite, $a = 10.465 \pm .001$ Å. Their structure differs from this study in that it contains magnesium instead of lithium and has a statistical distribution of iron with copper instead of iron only at sites. Although sodium was reported, its location in the structure was not established. Nevertheless, their overall structural details are in reasonable agreement with this study.

would have to depend on further analyses, especially electrical and magnetic measurements.

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