

Crystal structure of Li_2FeS_2

R. J. Batchelor, F. W. B. Einstein, and C. H. W. Jones

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Rosamaria Fong and J. R. Dahn

Materials Science, Moli Energy Limited, 3958 Myrtle Street, Burnaby, British Columbia, Canada V5C 4-G2

(Received 4 June 1987)

The crystal structure of Li_2FeS_2 has space group $P\bar{3}m1$ with $a=3.902(1)$ Å, $c=6.294(2)$ Å, $U=83.00$ Å³, and $Z=1$. The structure refinement gives a final residual $R_f=0.043$ for 283 observations and nine variables (from single-crystal data using $\text{MoK}\alpha$ radiation $\lambda=0.71069$ Å). The structure consists of hexagonally-close-packed layers of sulfur with iron and lithium, equally and randomly, filling all of the tetrahedral interstices between the more separated pairs of sulfur layers. The remaining lithium atoms fill the octahedral interstices between the alternate, closer sulfur layers. To our knowledge this is the first ternary compound to have Fe(II) coordinated by sulfur atoms.

INTRODUCTION

Intercalation can be defined as the reversible insertion of guest atoms or molecules into a host solid such that the structure of the host is not changed significantly.¹ The crystal structure of a particular host often determines the number and nature of atoms which can be intercalated. Therefore, most studies of intercalation compounds begin with a good knowledge of the host structure. However, the crystal structure of Li_2FeS_2 has never been reported, although this compound has been actively studied²⁻⁷ and is claimed to be an intercalation compound by LeMehaute *et al.*²

Much of the early work on Li-Fe-S compounds was motivated by the search for rechargeable high-energy-density batteries. Both Li/FeS and Li/FeS₂ cells have been shown to have excellent reversibility at 450°C.^{3,4} Early studies of Li-Fe-S compounds focused on the determination of the equilibrium phases formed during the discharge and recharge of these cells. Through these studies some understanding of cell cycling mechanisms was obtained.

Early reports agreed on the existence of a single-phase compound, Li_2FeS_2 . Sharma,⁵ in his study of the equilibrium phase diagram for Li_2S -FeS system between 700 and 1600°C, identified Li_2FeS_2 as a phase which melted incongruently at 885 ± 5 °C. Martin³ reported the compositions of the phases within the Li_2S -FeS-FeS₂ triangle at 450°C, and determined that Li_2FeS_2 was one of the intermediate phases formed during charge and discharge of Li/FeS₂ and Li/FeS cells. Tomczuk *et al.*⁴ examined this phase by x-ray diffraction and indexed the powder pattern with a hexagonal cell with $a=3.90$ Å and $c=6.28$ Å. This result was identical to that reported by Melandres and Tani⁶ and Sharma.⁵

More recently, Brec *et al.*⁷ synthesized Li_2FeS_2 and studied it in lithium batteries at room temperature. They interpreted the cycling process as intercalation and identified three phases, two of which were reported to have hexagonal symmetry. The hexagonal phases were la-

beled as (1) γ -phase Li_xFeS_2 ($1.09 \leq x \leq 1.5$) and (2) ν -phase Li_xFeS_2 ($1.5 \leq x \leq 2$). Brec found that his x-ray powder data agreed with earlier work, but an observed ordering in the ($hk0$) planes led to a superstructure with a tenfold a parameter. Further investigations by infrared spectroscopy⁸ showed that the lithium atoms of Li_2FeS_2 occupied "octahedral" and "tetrahedral" sites. In addition, the FeS_2 "host" of these hexagonal phases was suggested to have the CdI_2 structure⁷ by analogy with Li_xTiS_2 .⁹

The powder x-ray pattern of samples of Li_2FeS_2 prepared in our laboratory showed lattice parameters in agreement with those previously reported (a tenfold superlattice in a was not observed), but the intensities of the peaks could not be fitted assuming the Fe and S atoms were in the CdI_2 structure. Rather, the model calculations suggested that the iron atoms were tetrahedrally coordinated by sulfur atoms, and a single-crystal-structure determination was therefore undertaken.

EXPERIMENTAL PROCEDURE

Li_2FeS_2 was prepared by mixing stoichiometric amounts of Li_2S (Alfa, 99% pure), Fe (Spex, 99.9% pure), and natural FeS_2 (Teck Mining Corporation, with 0.2 at. % Cu, 0.1 at. % each Al and Ca, and trace amounts of Pb and Zn). The powders were mixed in a helium-filled glove box. The mixture was placed in a graphite tube within a quartz tube. Argon flow was maintained in the quartz tube while the sample was heated to 900°C, above the melting point of Li_2FeS_2 (885°C), for 16 h. After heating, the sample was allowed to cool over a period of 8 h to room temperature. The graphite tube was opened in the glove box and the product observed to be a grey lump which had clearly been molten.

Following heating, the weight of the sample was observed to have changed from 49.844 to 49.410 g. This weight loss corresponds to, at most, $\Delta x=0.167$ in $\text{Li}_{2-x}\text{FeS}_2$, assuming that the weight loss can be account-

TABLE I. Structure of Li_2FeS_2 .

Formula	Li_2FeS_2 —space group $P\bar{3}m1$
a	$=3.902(1) \text{ \AA}$
c	$=6.294(2) \text{ \AA}$
U	$=83.00 \text{ \AA}^3$
$\mu_{\text{Mo K}\alpha}$	$=54.58 \text{ cm}^{-1}$
d_c	$=2.678 \text{ g cm}^{-3}$
Z	$=1$
Formula weight:	133.85
Crystal dimensions:	$0.32 \times 0.23 \times 0.15 \text{ mm}^3$
Radiation, Mo $K\alpha$;	graphite monochromator; $\lambda = 0.71069 \text{ \AA}$
Transmission coefficients:	0.3875–0.5519
Scan mode:	θ – 2θ
Scan width:	$1.1 + 0.35 \tan\theta$ (deg)
Scan speeds:	0.97 – $5.49 \text{ deg min}^{-1}$ (dependent upon the intensity of a preliminary scan)
$2\theta(\text{max})$	$=90^\circ$
Reflections:	373; 283 [$\geq 2.5\sigma(I)$]
Refined variables:	9
R_f	$=0.043^a$
R_{wf}	$=0.066^b$
G	$=1.721^c$

^a $R_f = \sum(|F_o| - |F_c|) / \sum|F_o|$ for observed data [$I \geq 2.5\sigma(I)$].
^b $R_{wf} = \{\sum[w(|F_o| - |F_c|)^2] / \sum(wF_o^2)\}^{1/2}$ for observed data [$I \geq 2.5\sigma(I)$]; $w = [\sigma^2(F) + 0.001F^2]^{-1}$.
^c $G = \sum[w(|F_o| - |F_c|)^2] / (\text{degrees of freedom})$.

ed for by a loss of Li. Because the reaction was carried out under unsealed conditions, it is possible that the weight loss was due to sulfur evaporation. Powder x-ray diffraction showed the material to be single phase and the lattice parameters and intensities of the diffraction lines agreed well with those measured on the single crystal selected.

Li_2FeS_2 reacts rapidly with air, so all crystal selection was done within the glove box. Single crystals of Li_2FeS_2 were obtained by carefully breaking the sintered lump into small fragments. These fragments were viewed through the window of the glove box with a long-focal-length microscope. The crystal used was mounted in a 0.5-mm-diam glass capillary tube, sealed with epoxy in the glove box and subsequently flame sealed.

Diffraction data were measured on an Enraf-Nonius CAD-4F x-ray diffractometer, using a graphite monochromator. Background intensities were measured by extending each scan by 25% on either side of the predetermined scan angle. Two intensity standards were measured every hour (approximately after every 50

reflections). Both standards showed a small but systematic decrease in intensity ($\sim 8\%$) during the intensity-data collection.

The data were corrected analytically for absorption of x-rays.¹⁰ The calculated transmission factors ranged from 0.3875 to 0.5519. Intensity-scaling, Lorentz, and polarization corrections were applied. The intensity-weighted reciprocal lattice displayed the Laue symmetry $\bar{3}m$ with no systematic conditions, leading to a choice of six possible space groups: $P31m$, $P3m1$, $P\bar{3}1m$, $P\bar{3}m1$, $P321$, and $P312$. 447 measured data were merged ($R = 0.042$) to 373 independent data, of which 283, having intensities greater than 2.5σ , were considered observed and were used in the structure refinement. The crystal data, acquisition, and refinement details are summarized in Table I.

The structural solution was obtained from the Patterson map. Refinement proceeded satisfactorily in the space group $P\bar{3}m1$. Full-matrix, least-squares refinement (which minimized $\sum[w(|F_o| - |F_c|)^2]$ for nine variable parameters (see Table II)) yielded a final residual

TABLE II. Atom positions in Li_2FeS_2 .

Atom	Occ.	x	y	z	U_{11} (\AA^2)	U_{33} (\AA^2)	U_{iso} (\AA^2)
Fe	0.533(4)	$\frac{1}{3}$	$\frac{2}{3}$	0.36775(16)	0.0174(4)	0.0221(5)	
S	1	$\frac{2}{3}$	$\frac{1}{3}$	0.24894(13)	0.0203(4)	0.0173(5)	
Li(1)	1	0	0	0			0.045(4)
Li(2)	(0.5) ^a	$\frac{1}{3}$	$\frac{2}{3}$	0.36775			

^aThe second lithium is disordered among the tetrahedral sites of layer II with the iron atoms. This Li was not included in the refinements, but is reflected in the greater than $\frac{1}{2}$ occupancy at the iron site.

$R_f = 0.043$, where $R_f = \sum(|F_0| - |F_c|) / \sum F_0$. (Here, in the usual way, F_0 and F_c are the observed and calculated structure factors of each Bragg reflection, respectively, and the summation runs over all reflections included in the structure refinement.) A weighting scheme (see Table II) was applied which kept $\langle \omega(|F_0| - |F_c|)^2 \rangle$ near constant as a function of $|F_0|$ and of $(\sin\theta)/\lambda$. The refinement was terminated when the maximum shift-over-error dropped below 0.01. The final difference map displayed a maximum peak of $1.6(2) e \text{ \AA}^{-3}$ and a minimum of $-0.9(2) e \text{ \AA}^{-3}$. Several maxima of this order occur near S and Fe along the threefold axis passing through these atoms. Minima occur at the Fe and S positions. These features are attributed to unresolved disorder and/or undetected long-range ordering of the structure.

The computations were performed on a MICROVAX-II computer using programs from the NRC-VAX Crystal Structure System.¹¹ Complex scattering factors for neutral atoms were used.¹² The final atomic coordinates, occupancies, anisotropic thermal parameters for Fe and S, and an isotropic temperature factor for Li are found in Table II.

DISCUSSION OF STRUCTURE

The structure of Li_2FeS_2 (see Fig. 1) is based on a hexagonal-close-packed (hcp) arrangement of sulfur atoms, which is distorted from ideal close packing by greater expansion in the a, b directions than in c . Furthermore, adjacent planes of sulfur atoms form a layer structure with alternate spacings between the sulfur planes of $3.133(2) \text{ \AA}$ (layer I) and $3.160(2) \text{ \AA}$ (layer II).

The lithium site (0,0,0) occupies a formally octahedral hole within layer I of the hcp lattice, point symmetry $\bar{3}m$. The Li-S distance is $2.7441(8) \text{ \AA}$. In our model, the iron and the remaining lithium atoms are equally disordered over all the formally tetrahedral holes within layer II. The refined occupancy for an iron atom only at this site is $0.533(4)$. This significant increase over half-iron-occupancy is attributed to half-lithium-occupancy, thus accounting for the empirical formula Li_2FeS_2 . Refinement of occupancy and/or thermal parameters of two atoms on a single site is, of course, indeterminate and was not attempted. Each atom in this position (point symmetry $3m$) is pseudotetrahedrally coordinated by sulfur with Fe-S distances of $2.4126(15) \text{ \AA}$ along the threefold axis and $2.3737(7) \text{ \AA}$ to the three "basal" sulfur atoms.

An alternate treatment of this disordered tetrahedral site using a scattering factor,

$$f = x f_{\text{Fe}} + (1 - x) f_{\text{Li}} \quad (1)$$

with x as a variable, where f_{Fe} and f_{Li} are the scattering factors of Fe and Li, respectively, was not attempted. This treatment suffers in that it implicitly assumes net full occupancy of the site with either Li or Fe and therefore constrains the refinement. On the other hand, our treatment described above suffers because it assumes that the angular dependencies of the Li and Fe scattering factors are the same. The difference in the angular dependence of these scattering factors is less than 20% throughout the

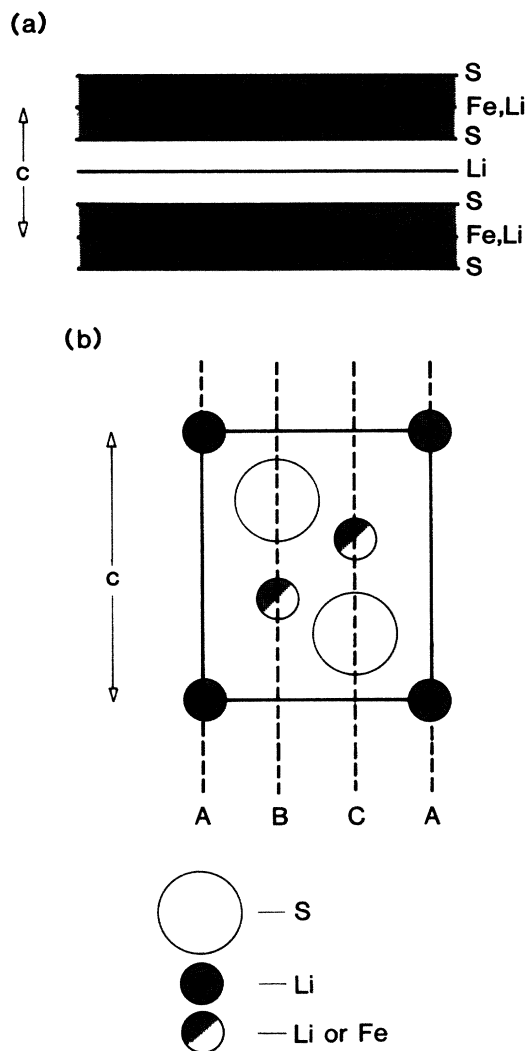


FIG. 1. (a) Schematic diagram of the layered Li_2FeS_2 structure. (b) (110) projection of the Li_2FeS_2 structure.

angular range of interest.¹² Therefore, because the effect of the lithium is small to begin with (three electrons for Li versus 26 for Fe), our approximate treatment is expected to give accurate results. Using Eq. (1), we get $x = 0.528$ with $f_{\text{Li}} = 3$, $f_{\text{Fe}} = 26$, and $f = (26)(0.533)$, or $x = 0.506$ with $f_{\text{Li}} = 2$, $f_{\text{Fe}} = 26$, and $f = (26)(0.533)$. Therefore our results are consistent with half-iron and half-lithium occupancy of each tetrahedral site within layer II.

A notable feature of the structure of Li_2FeS_2 is the full occupancy of all the tetrahedral holes in layer II. This is an unusual structural feature in that it imposes short M - M contacts, where $M = \text{Fe}$ or Li , of $2.8012(14) \text{ \AA}$. When projected into the (001) plane, these tetrahedral holes form a honeycomb lattice. Therefore, each iron site has three such interactions, which may be to either lithium or iron. Genuine occupational disorder between iron and lithium at this position may explain the evidence of more than a single iron environment in the ^{57}Fe Mössbauer spectrum of Li_2FeS_2 .⁶ Random distribution of Li and Fe over these positions would result in four different iron en-

vironments in the ratio 3:3:1:1. The Mössbauer spectrum, however, is not sufficiently well resolved to confirm this.

The iron in Li_2FeS_2 is formally Fe(II). While a variety of biological systems (such as ferredoxins) have Fe_4S_4 clusters with Fe atoms coordinated tetrahedrally by sulfur atoms,¹³ there are, however, to our knowledge, no ternary systems other than Li_2FeS_2 reported to have Fe(II) tetrahedrally coordinated by sulfur.

Le Mehaute *et al.*² have shown that most of the lithium

can be removed from Li_2FeS_2 by electrochemical methods, and claimed that the host structure is only slightly changed. Preliminary *in situ* studies in our laboratory show that the Bragg peaks of $\text{Li}_{2-x}\text{FeS}_2$ become very broad as x increases towards $x \approx 1$. The question as to whether this lithiated material is an intercalation host remains unsettled and will be addressed by us in further research.

-
- ¹W. R. McKinnon and R. R. Haering, in *Modern Aspects of Electrochemistry*, edited by Ralph E. White and J. O'M. Bockris (Plenum, New York, 1983), Vol. 15, p. 235.
- ²A. LeMeHaute, R. Brec, A. Dugast, and J. Rouxel, *Solid State Ionics* **3/4**, 185 (1981).
- ³A. E. Martin, Argonne National Laboratory Report No. ANL-78-94, 1980 (unpublished), p. 167.
- ⁴Z. Tomczuk, B. Tani, N. C. Otto, M. F. Roche, and D. R. Vissers, *J. Electrochem. Soc.* **129**, 926 (1982).
- ⁵R. A. Sharma, *J. Electrochem. Soc.* **123**, 448 (1976).
- ⁶C. A. Melandres and B. Tani, *J. Phys. Chem.* **82**, 2850 (1978).
- ⁷R. Brec and A. Dugast, *Mater. Res. Bull.* **15**, 619 (1980).
- ⁸P. Gard, C. Sourisseau, G. Ouvrard, and R. Brec, *Solid State*

Ionics **20**, 231 (1986).

- ⁹J. R. Dahn, W. R. McKinnon, R. R. Haering, W. J. L. Buyers, and B. M. Powell, *Can. J. Phys.* **58**, 207 (1980).
- ¹⁰J. DeMeulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014 (1965).
- ¹¹E. J. Gabe, A. C. Larson, F. L. Lee, and Y. LePage, NRC VAX Crystal Structure System, National Research Council, Ottawa, 1984 (unpublished).
- ¹²*International Tables for X-ray Crystallography* (Kynoch, Birmingham, England, 1974), Vol. IV, Tables 2.2B and 2.3.1.
- ¹³F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed. (Wiley, New York, 1972), p. 872.

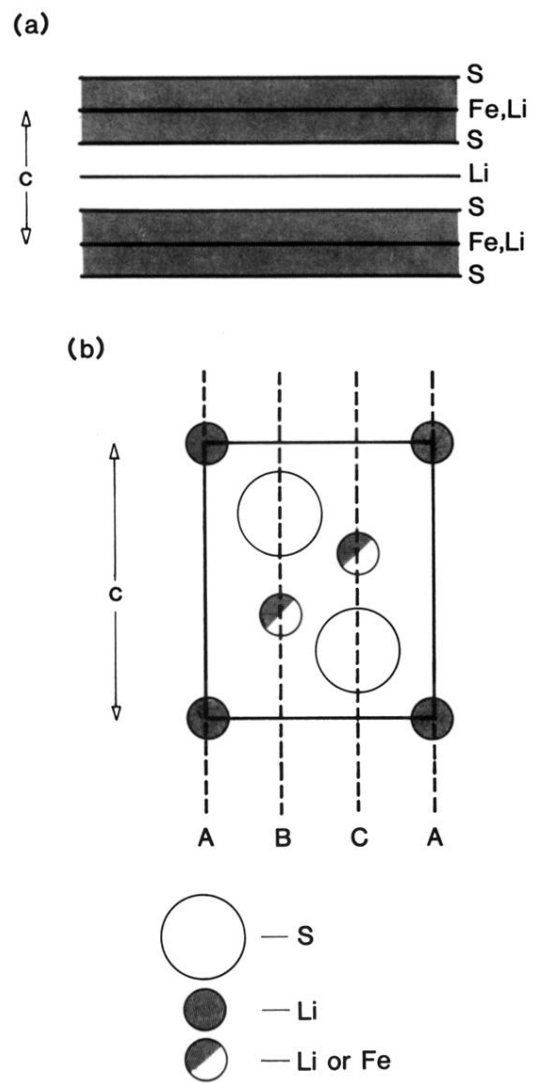


FIG. 1. (a) Schematic diagram of the layered Li_2FeS_2 structure. (b) (110) projection of the Li_2FeS_2 structure.