

Synthesis and Rietveld crystal structure refinement of mackinawite, tetragonal FeS

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Abstract

Mackinawite, tetragonal FeS, has been synthesised by reacting iron with Na₂S solutions. A Rietveld structure refinement of X-ray powder diffraction data, recorded using X-rays monochromated from synchrotron radiation with a wavelength of 0.6023 Å, has been performed. The structure has been refined in the tetragonal space group, *P4/nmm*, and has the following cell parameters: $a = 3.6735(4)$, $c = 5.0328(7)$ Å, $V = 67.914(24)$ Å³. Our refinement shows that the FeS₄ tetrahedron in mackinawite is almost perfectly regular, with a much smaller distortion than has been previously reported. An improved X-ray diffraction data set is provided.

KEYWORDS: mackinawite, Rietveld structure refinement, synthesis.

Introduction

The mineral mackinawite, first described by Evans *et al.* (1962, 1964), is identical to synthetic tetragonal iron monosulphide (Berner, 1962, 1964), an unnamed tetragonal iron sulphide mineral (Kuovo *et al.*, 1963) and the synthetic iron sulphide 'kansite' (Meyer *et al.*, 1958). The importance of this metastable (Davison, 1991) iron-sulphur phase is due to its role as precursor to the formation of pyrite in sedimentary and hydrothermal systems.

Mackinawite possesses a layer structure similar to that found in tetragonal PbO (litharge, space group *P4/nmm*), with Fe and S occupying the sites of O and Pb, respectively, in litharge. X-ray diffraction patterns from natural mackinawite (Kuovo *et al.*, 1963), and neutron (Bertaut *et al.*, 1965) and electron (Uda, 1968) diffraction analyses of synthetic mackinawite, support this interpretation.

A structural refinement of a natural crystal of mackinawite from Outukumpu, Finland (Taylor and Finger, 1970), shows that the structure may be thought of in terms of a distorted cubic close-packed array of S atoms with some of the tetrahedral interstices filled with Fe. Each metal atom is at the centre of a slightly distorted tetrahedron of S atoms. These tetrahedra share edges forming sheets of

tetrahedra which are stacked normal to the *c*-axis, with only weak van der Waals forces holding these sheets together. Mackinawite has been reported as both a metal-excess (Clark, 1966) and a sulphur deficient (Taylor and Finger, 1970) phase.

Tetragonal Fe_{1+x}Se and Fe_{1+x}Te, which share the anti-litharge structure found in mackinawite, are reported as metal-excess chalcogenides (Tsuji *et al.*, 1976); a compilation of data on these phases is given in Table 1.

In addition to the tetragonal iron chalcogenide phases, it is of interest to note that there exists a family of AB₂X₂ compounds (Hoffmann, 1988) having the ThCr₂Si₂-type structure consisting of B₂X₂²⁻ layers separated by A²⁺ layers. The bonding between A²⁺ and B₂X₂²⁻ layers appears largely ionic, but within each B₂X₂²⁻ layer there is not only B-X bonding, but also an indication of some metal-metal B-B bonding. These B₂X₂²⁻ layers share the same structure as the sheets of FeS₄ tetrahedra which make up mackinawite.

Several methods for synthesising mackinawite are described in the literature, including routes involving precipitation of Fe²⁺_(aq) by H₂S, reaction of metallic Fe with H₂S in solution (Berner, 1964), and electrochemical formation (Yamaguchi and Moori, 1972). Dry synthesis of mackinawite (Takeno *et al.*,

TABLE 1. Properties of iron chalcogenides with tetragonal-PbO structures (space group $P4/nmm$, $Z = 2$)

Iron chalcogenide	Fe_{1+x}S ($x = 0.00\text{--}0.07$)	Fe_{1+x}Se ($x = 0.05$)	Fe_{1+x}Te ($x = 0.11\text{--}0.25$)
Maximum temperature of stability	540 K (to NiAs-type)	731 K (to NiAs-type)	1200 K decomposes
Unit cell dimensions at 298 K (Å)	$a = 3.6795(8)$ $c = 5.030(2)$ $c/a = 1.3670(7)$	$a = 3.77$ $c = 5.52$ $c/a = 1.464$	$a = 3.83$ $c = 6.27$ $c/a = 1.637$
Density	4.28 g cm^{-3}	5.71 g cm^{-3}	6.85 g cm^{-3}
References	(1,2,3)	(4,5,6)	(7,8)

(1) Taylor and Finger (1970)
 (3) Vaughan and Craig (1978)
 (5) Grønvold and Westrum (1959)
 (7) Haraldsen *et al.* (1944)

(2) Lennie (1994)
 (4) Hagg and Kindstrom (1933)
 (6) Grønvold (1968)
 (8) Grønvold *et al.* (1954)

1982) requires addition of substantial quantities of Cu, Co or Ni; synthesis of mackinawite from elemental Fe and S has not been achieved.

A conflicting range of values is reported for the upper temperature limit of stability for mackinawite. Kuovo *et al.* (1963) report that a reconstructive transition from mackinawite to hexagonal pyrrhotite (FeS) occurs at 518 K, while Sarkar (1971) reports a temperature of between 493 to 498 K for the same transition. In contrast, stability limits in the much lower temperature range of 393 to 426 K have been reported (Takeno and Clark, 1967; Takeno, 1965*a,b*; Clark, 1966). These low breakdown temperatures of natural mackinawites may, however, involve addition of sulphur from surrounding minerals (Zoka *et al.*, 1972), and would not, therefore, be expected to be relevant to the closed system.

The Rietveld refinement and synthesis experiment described here forms part of a larger study (Lennie, 1994) which provides new information on the thermal stability of mackinawite, the expansion of the unit cell with temperature, and on solid-state transformations of this phase to both hexagonal pyrrhotite (Fe_{1-x}S) and to greigite (Fe_3S_4), the thiospinel of iron.

Experimental synthesis of mackinawite

Thirty cm^3 of a solution of Na_2S (20 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 200 cm^3 deionised water) was added slowly to 500 cm^3 of an 0.5 molar acetic acid/acetate buffer (pH = 4.6) in which approximately 4–5 g of finely divided iron wire (Roncraft, Sheffield) had been previously immersed. Dissolution of the iron wire by reaction

with the acetate buffer for 30 minutes or so evolved H_2 , providing a reducing environment. The Na_2S solution was then added slowly, and exceeded the capacity of the acetate buffer, increasing the pH to a value of approximately 6.5. This solution, containing the iron wire, was allowed to stand open to the atmosphere at room temperature for 24 hours.

The iron wool generated H_2 while dissolving, and this gas, trapped in the wool mat, floated the iron to the top of the solution. Mackinawite forming on the iron surface spalled off and dropped to the bottom of the flask giving good (but not entirely complete) separation of mackinawite from the iron.

After reaction, the iron wool was removed and the supernatant solution poured off. The mackinawite remaining was rinsed onto a 0.45 μm filter, then rinsed several times with deaerated deionised water while a water vacuum was applied to remove the solution. While still moist, the mackinawite was placed in U-shaped aluminium foil boats approximately 2 cm long. After crimping both ends of the foil, these were placed in borosilicate tubes previously sealed at one end using an $\text{O}_2\text{--CH}_4$ flame. These tubes were partially prefilled with enough acetone to completely cover the mackinawite contained in the aluminium boat. Surplus acetone was then removed from the tube.

A number of tubes of mackinawite prepared in this way were dried together in a flask for two hours under a vacuum of 10^{-2} mbar; acetone and water removed from the sample was condensed in a liquid N_2 cooled trap. When dry, the tubes were removed from the evacuated flask under an O_2 -free N_2 atmosphere, and individually sealed, under vacuum, using an O--CH_4 flame.

TABLE 2. Compositional analyses of synthetic FeS

1. ICP analysis of mackinawite dissolved in HCl

Element	wt.%	atom%
Fe	63.2	49.67
Ti	0.10	0.09
Mn	0.17	0.14
S (by difference)	36.53	50.10

2. X-ray fluorescence analysis of mackinawite

Element	wt.%
Cu	<0.001
Zn	0.005
Ni	0.023
Mn	0.39
Cr	0.034
Ti	0.16

Initial identification of mackinawite using X-ray powder diffraction was carried out using a Philips X-ray diffractometer, with Cu-K α X-rays generated at 40 kV and 20 mA. Samples were mixed with amyl acetate, spread on glass slides, and dried in air. The diffraction pattern of mackinawite showed broad peaks with the peak width at half peak height in the order of 0.5° 2 θ ; peak positions were consistent with previously reported diffraction patterns of mackinawite. The broad peak widths are due to the small particle size of the mackinawite crystallites.

A sample was prepared for compositional analysis by dissolving a weighed amount in hydrochloric acid. After the majority of sulphide had been removed (as H₂S) this solution was analysed by ICP spectrometry. A second sample of mackinawite powder was analysed by X-ray fluorescence to determine concentrations of impurities in the iron sulphide. The powder, pressed into a disc of boric acid at 5 tons applied pressure, was analysed using both Cr and Rh X-ray sources on a Philips PW 1450 XRF spectrometer. Both analyses are recorded in Table 2. The XRF analysis shows metallic impurities amounting to 0.61 wt.% in FeS. No fluorescence peaks due to Se were observed.

High-resolution powder diffraction

The synthetic mackinawite was further characterised by Rietveld structure refinement. High resolution powder diffraction data were recorded at Station 9.1 on the 5 Tesla wiggler beam line of the Daresbury

Laboratory Synchrotron Radiation Source. Monochromatic radiation of wavelength 0.6023 Å was selected from the channel-cut Si (111) monochromator, the radiation wavelength being calibrated from the positions of six reflections of a Si NBS 640b sample.

Mackinawite rapidly oxidises under ambient atmosphere conditions, and diffraction patterns were therefore collected from samples loaded directly from sealed borosilicate tubes under an inert atmosphere. This involved sealing the sample chamber of the diffractometer in a He-filled glove bag, breaking open the borosilicate sample vial, and loading mackinawite directly onto the aluminium flat plate sample holder (15 mm diameter, 1 mm deep) of the instrument. The sample chamber was continually purged with He during data collection. This mode of sample loading, and the limited amounts of sample available to us, necessarily compromised the quality of sample presentation within the diffractometer. The sample was not perfectly flat within the sample holder, and electrostatic effects meant that the sample could not be ground to as fine a powder as would normally be preferred. Nonetheless, data of sufficient quality for satisfactory Rietveld refinement were obtained.

Diffraction data were collected between 5 and 58° 2 θ ($d = 6.91$ to 0.622 Å) at steps of 0.01° 2 θ . Because mackinawite is extremely easily oxidized, the X-ray wavelength was selected to be above the Fe absorption edge to reduce photo-oxidation effects. No degradation of the sample was observed when held at room temperature in the He atmosphere; using a shorter X-ray wavelength also has the advantage of giving measurements of smaller interplanar spacings.

Results and discussion

The diffraction pattern showed mackinawite as the dominant phase, although some diffraction from α -Fe was observed. The regions 16.80–17.40°, 24.0–24.6°, and 29.5–30.1° 2 θ , containing the diffraction peaks from α -Fe, were thus excluded from the Rietveld refinement. The diffraction pattern used for the refinement is illustrated in Fig. 1.

The raw diffraction pattern was prepared for Rietveld refinement using the program MPREP, and refined using MPROF in the Powder Diffraction Program Library of Murray *et al.* (1990). The background was fitted with a polynomial curve; an overall scale factor, zeropoint, and preferred orientation factor (for orientation parallel to (001)) were also used. An asymmetric pseudo-Voigt line shape was employed. The structure proposed by Uda (1968) (space group $P4/nmm$) was used as a starting model. The refineable sample parameters were, therefore, restricted to cell edges,

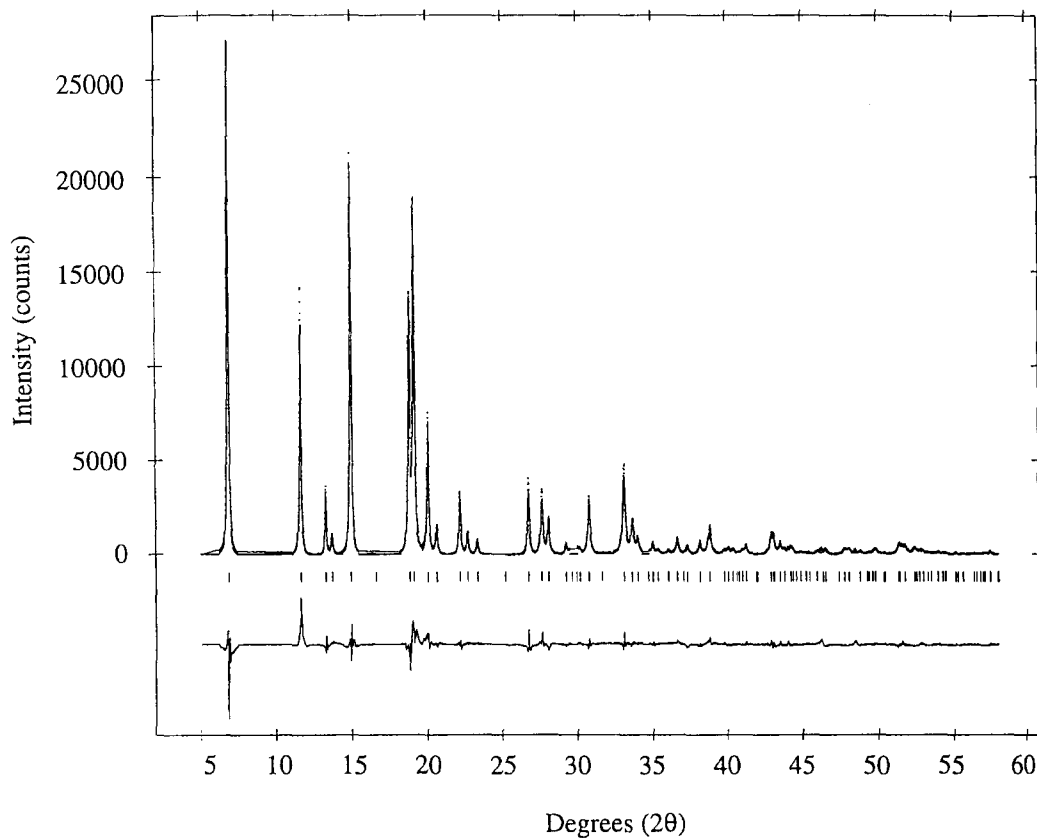


FIG. 1. X-ray diffraction (XRD) pattern of mackinawite obtained using synchrotron radiation. The difference between observed and Rietveld calculated intensities is shown below the XRD pattern.

TABLE 3. Refined structure parameters for synthetic mackinawite. Errors (σ) are in parentheses

Space group				
<i>P4/nmm</i> (No. 129) origin at $\bar{4}m2$				
Cell parameters				
(Rietveld)	<i>a</i> (Å)	3.6735(4)		
	<i>b</i> (Å)	3.6735(4)		
	<i>c</i> (Å)	5.0328(7)		
	<i>V</i> (Å ³)	67.914(24)		
Atomic positional parameters				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (iso)
Fe in 2(a):	0	0	0	0.41(2)
S in 2(c):	0	0.5	0.2602(3)	0.20(2)
The structure was refined with the following <i>R</i> factors:				
<i>R</i> _I = 9.15%	<i>R</i> _p = 12.42%	<i>R</i> _e = 4.39%		

isotropic temperature factors, and the *z*-coordinate of the S atom. The refinement converged to give the structural parameters and *R* factors summarised in Table 3, where

$$R_I = 100 \cdot \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}}$$

$$R_p = 100 \cdot \frac{\sum |Y_{\text{obs}} - Y_{\text{calc}}|}{\sum Y_{\text{obs}}}$$

$$R_e = 100 \cdot \left[\frac{\sum [N - P]}{\sum w \cdot Y_{\text{obs}}} \right]^{0.5}$$

I_{obs} and I_{calc} are the observed and calculated intensities for Bragg reflections, and Y_{obs} and Y_{calc} are the observed and calculated intensities at each point in the diffraction pattern. N is the number of points in the pattern, P the number of parameters refined ($[N - P] = 4165$ in this case), and w is the weight assigned to each step intensity. The relatively high values of R_I and R_p reflect the small deviations in sample height across the flat plate sample holder, which arose from the difficulties of sample loading.

TABLE 4. Bond distances and angles for synthetic mackinawite. Errors (σ) are in parentheses

Bond distances (Å)	
Fe-S	2.2558(9)
Fe-Fe	2.5976(3)
Bond angles (°)	
S-Fe-S	2 × 109.0251
	2 × 109.6947
Fe-Fe-Fe	4 × 90
Fe-S-Fe	2 × 70.3053
	2 × 109.0251

The agreement between the observed and calculated profiles in the Rietveld difference plot is illustrated in Fig. 1.

This structural analysis is consistent with previous reports of the structure of mackinawite; we were not able to refine vacancy occupancy or surplus Fe occupancy with any degree of significance. This refinement does not, therefore, provide any further

information on non-stoichiometry, either in terms of surplus Fe, or S-deficiency in the structure; a satisfactory refinement is achieved by assuming stoichiometric tetragonal FeS.

Comparing our refinement with the mackinawite structure of Uda (1968), we see that S is significantly displaced from $z = 0.25$. This has an impact on the resultant coordination environment (Table 4). Our refined structure shows that the FeS_4 tetrahedron is very nearly perfectly regular, with two S-Fe-S bond angles which deviate only very slightly from the ideal tetrahedral bond angle. Each S is bonded to four Fe in an asymmetric one-sided four-fold coordination with Fe-S-Fe bond angles of 70° and 109° , while the short Fe-Fe distance of 2.5976 Å (Fe in square planar coordination by Fe) confirms the importance of Fe-Fe metallic bonding within the (001) layers (Fig. 2).

A listing of the hkl Bragg reflections with associated interplanar spacings, and observed and calculated intensities obtained from this experiment, is given in Table 5. When compared with previously reported data for this mineral (Berner, 1964; Uda, 1968), this tabulation provides a more extensive range of experimental hkl intensity values, giving intensities of Bragg reflections out to 0.68 Å.

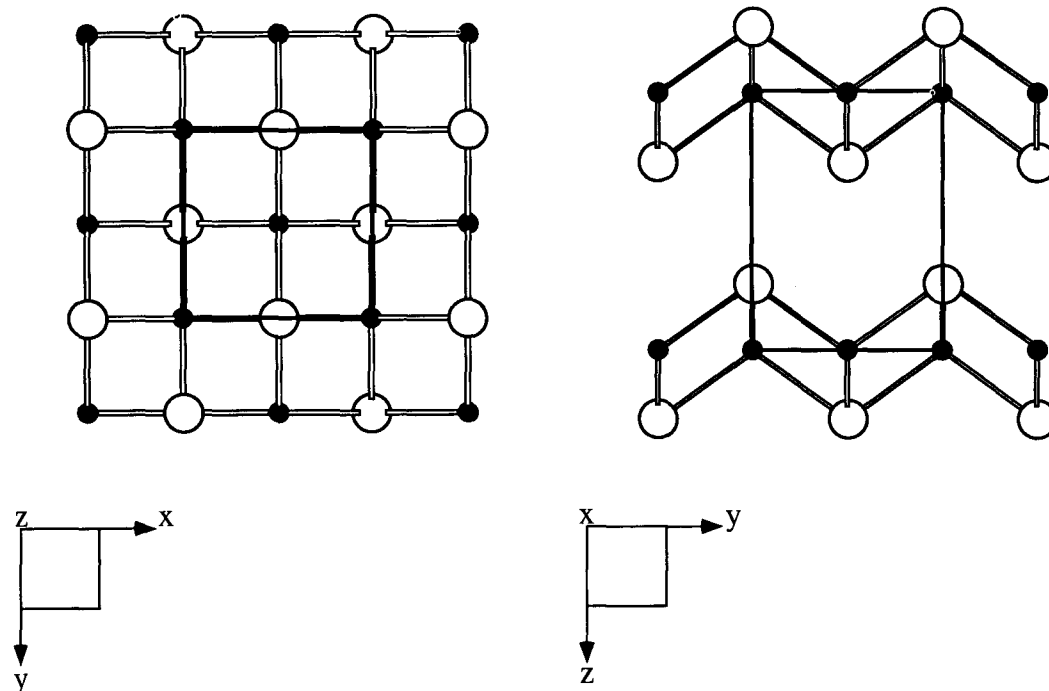


FIG. 2. Refined structure of mackinawite projected parallel to [001] (left) and [100] (right). Small filled spheres represent Fe atoms; large spheres represent S atoms. Fe-S bonds are shown, together with the outline of the unit cell. The structure comprises (001) sheets of edge-sharing FeS_4 tetrahedra, with van der Waals bonding between sheets.

TABLE 5. Powder diffraction pattern for mackinawite with intensities calculated using Rietveld refined parameters

<i>hkl</i>	<i>d</i> (Å)	<i>I</i> _{calc}	<i>I</i> _{obs}	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> _{calc}	<i>I</i> _{obs}
001	5.0328	100	100	402	0.8627	<1	<1
101	2.9672	38	50	215	0.8583	2	2
110	2.5976	8	8	314	0.8535	<1	1
002	2.5164	4	7	331	0.8533	2	2
111	2.3082	64	70	412	0.8399	<1	<1
102	2.0760	<1	<1	006	0.8388	<1	<1
200	1.8368	37	38	420	0.8214	4	5
112	1.8074	69	82	332	0.8187	4	5
201	1.7254	23	29	106	0.8178	<1	<1
003	1.6776	7	9	421	0.8107	3	3
211	1.5617	11	12	403	0.8056	2	2
103	1.5260	5	6	116	0.7982	4	4
202	1.4836	3	4	225	0.7956	1	1
212	1.3756	<1	<1	324	0.7918	<1	<1
220	1.2988	12	11	413	0.7869	1	1
004	1.2582	5	6	422	0.7809	<1	<1
221	1.2576	8	9	305	0.7776	1	1
203	1.2387	10	10	333	0.7694	1	2
104	1.1903	<1	<1	206	0.7630	<1	<1
301	1.1898	2	3	315	0.7607	3	4
213	1.1738	5	6	216	0.7471	<1	<1
310	1.1617	1	1	404	0.7418	3	2
222	1.1541	1	1	423	0.7377	2	3
114	1.1324	1	1	414	0.7271	<1	<1
311	1.1319	12	14	501	0.7270	<1	1
302	1.1011	<1	<1	431	0.7270	1	1
312	1.0547	23	26	510	0.7204	<1	<1
204	1.0380	10	12	007	0.7190	<1	<1
223	1.0270	5	6	325	0.7160	1	1
005	1.0066	1	1	334	0.7133	<1	<1
214	0.9989	<1	<1	511	0.7132	2	2
321	0.9986	3	4	107	0.7056	<1	<1
303	0.9891	1	2	502	0.7053	<1	<1
105	0.9708	1	2	432	0.7053	<1	<1
313	0.9550	4	6	226	0.7046	<1	<1
322	0.9444	<1	<1	117	0.6929	<1	<1
115	0.9386	4	4	512	0.6926	4	5
400	0.9184	3	4	306	0.6920	<1	<1
224	0.9037	6	8	424	0.6878	4	4
401	0.9035	2	3	316	0.6800	4	3
205	0.8827	1	2				
304	0.8775	<1	<1				
411	0.8773	2	2				
323	0.8708	2	2				
330	0.8659	<1	<1				

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