The Structure of Ba$_5$Fe$_9$S$_{18}$

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The crystal structure of Ba$_5$Fe$_9$S$_{18}$ has been determined by single-crystal X-ray analysis and refined to an R of 0·092, using visually estimated Cu $K\alpha$ data. The crystals are tetragonal, space group $P4/ncc$, $Z=4$, with $a=7\cdot776$ (3) and $c=49\cdot86$ (2) Å. The structure consists of chains of edge-shared iron–sulphur tetrahedra, (FeS$_{4/2}$)$_\infty$, directed along [001], with barium atoms packed between the chains. The barium atoms pack more densely than sulphur atoms along c and the periodicity of the structure is repeated every tenth barium (00l) layer or every ninth sulphur (00l) layer. Ba$_5$Fe$_9$S$_{18}$ is one homologue of a series of ordered phases Ba$_p$Fe$_{2q}$S$_{4q}$, p and q integers, for which the structures are based on this periodic 'out-of-phase' packing principle.

Introduction

As part of an investigation of the Ba–Fe–S system (Grey, Hong & Steinfink, 1971; Steinfink, Hong & Grey, 1972) we attempted to prepare the simple phase of composition BaFe$_2$S$_4$ by reacting mixtures of BaS + 2Fe + nS ($n=3$–5) in sealed silica tubes at temperatures in the range 500–850°C (Grey, 1974). X-ray diffraction studies of the products showed a predominantly single-phase barium iron sulphide in each case, together with minor amounts of pyrite or pyrrhotite, *i.e.* only one set of strong, sharp diffraction peaks attributable to a barium iron sulphide phase was observed for products prepared at different temperatures, although the peak positions changed markedly. Moreover, the shifts in peak positions were in opposite directions for some diffraction lines, suggesting a continuous *ordered* series of phases rather than classical solid solution behaviour. To investigate the system further, we selected a single crystal of one of the reaction products and carried out a crystal-structure analysis. From the structure solution, the formula of the barium iron sulphide was determined as Ba$_5$Fe$_9$S$_{18}$, a member of an homologous series of compounds Ba$_p$Fe$_{2q}$S$_{4q}$, with p and q integers (Grey, 1974).

Experimental

The stoichiometric mixture BaS:2Fe:4S was intimately mixed and packed into a graphite tube which was sealed within a silica tube at a pressure of 10^{-5} torr. The mixture was heated at 790°C for 20 h then quenched in liquid nitrogen. The reaction product consisted of aggregates of crystals in the form of large black shiny slabs. For the crystal-structure analysis, a large tabular crystal was selected and chipped into an approximately spherical shape, radius 0·05 mm. The symmetry and approximate unit-cell dimensions were determined by single-crystal methods using rotation and Weissenberg photographs. Ocillation photo-

graphs about the tetragonal c axis showed a long periodicity in this direction and an unusual intensity distribution whereby all the strong reflexions could be indexed on one or other of two subcells, with $c'=5\cdot0$ Å and $c''=5\cdot5$ Å as shown in Fig. 1. A periodicity of $c\simeq50$Å $=10\times c'=9\times c''$ was obtained by careful measurement of the oscillation photograph. This was confirmed by electron-diffraction results (Grey, 1974). The unit-cell parameters listed in Table 1 resulted from a least-squares refinement of powder data obtained with a Philips powder diffractometer fitted with a graphite monochromator, using Cu $K\alpha$ radiation. Silicon was used as an internal standard.

Table 1. *Crystallographic data for* Ba$_5$Fe$_9$S$_{18}$

Unit cell	Tetragonal
	$a=7\cdot776$ (3) Å
	$c=49\cdot86$ (2) Å
	$V=3014\cdot8$ Å^3
	$Z=4$
Formula weight	1766·4
Density (calculated)	3·89 g cm^{-3}
Systematic extinctions	$hk0$, $h+k\neq2n$
	$0kl$, $l\neq2n$
	hhl, $l\neq2n$
Space group	$P4/ncc$
Linear absorption coefficient for Cu $K\alpha$ radiation	952·7 cm^{-1}

For the structure determination the crystal was aligned about one of the tetragonal a axes and intensity data for the levels 0kl–4kl were obtained by the integrated Weissenberg technique, using nickel-filtered copper radiation. The intensities were estimated visually using a calibrated film strip. Reduction to structure amplitudes and all subsequent computing was done by an Elliott 803 computer at the CSIRO Division of Mineral Chemistry with the programming system devised by Daly, Stephens & Wheatley (1963) and kindly made available by Dr P. J. Wheatley. A spherical absorption correction was applied, $\mu R=4\cdot7$, using data

taken from *International Tables for X-ray Crystallography* (1967).

Structure determination and refinement

A three-dimensional sharpened Patterson map showed that all the most prominent peaks lay on the Harker lines $00w$ and $0\frac{1}{2}w$, thus suggesting that the barium and iron atoms occupy special positions $8(e)$ and $4(c)$ of space group $P4/ncc$ (centrosymmetric setting, with origin at $\bar{1}$), *i.e.* the metals occur in strings directed along [001] at positions $(\frac{1}{4},\frac{1}{4},z)$ and $(\frac{1}{4},\frac{3}{4},z)$. In determining the metal-atom arrangement, use was made of the observed fact that all the strong reflexions could be indexed on one or other of two subcells with $c'=5\cdot0$ and $c''=5\cdot5$ Å. It has been pointed out (Binnie, Redman & Mallio, 1970) that numerous compounds containing infinite chains of edge-shared metal-sulphide tetrahedra have in common a $5\cdot5$ Å axis representing the periodicity of the chain ($=2\times$M–M). On this basis a model was constructed containing strings of edge-shared iron–sulphur tetrahedra with a repeat distance of $5\cdot5$ Å, and strings of barium atoms separated by $5\cdot0$ Å. The trial model thus contained iron atoms in position $8(e)$, with an average separation of $\frac{1}{2}\times5\cdot5$ Å $=2\cdot75$ Å and barium atoms in position $4(c)$, with an average separation of $5\cdot0$ Å. Values of z for the iron atoms were fixed by placing the first iron atom in the special position $4(b)$. The z coordinate for the first barium atom was determined from the Patterson map. Sulphur atoms were then arranged tetrahedrally around the iron atoms, with z coordinates halfway between those for the iron atoms and with x and y coordinates obtained from the Patterson map. From a structure-factor calculation for this approximate model a conventional R value of $0\cdot25$ was obtained. Least-squares refinement of atomic coordinates and isotropic thermal parameters reduced the R value to $0\cdot092$ for the 218 measured reflexions. Anisotropic temperature factors and anomalous dispersion corrections were not considered to be practical because of the relatively low number of reflexions.

The final positional and thermal parameters, with standard deviations, are listed in Table 2. In Table 3 are listed the final observed and calculated structure factors for all the observed reflexions. The bond lengths and angles are given in Table 4.

Table 2. *Final atomic parameters*

	x	y	z	$B(\text{Å}^2)$
Ba(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·0322 (4)	3·9 (10)
Ba(2)	$\frac{1}{4}$	$\frac{1}{4}$	0·1268 (4)	3·2 (4)
Ba(3)	$\frac{1}{4}$	$\frac{1}{4}$	0·2273 (3)	1·6 (2)
Ba(4)	$\frac{1}{4}$	$\frac{1}{4}$	0·3297 (3)	1·6 (2)
Ba(5)	$\frac{1}{4}$	$\frac{1}{4}$	0·4322 (3)	2·3 (3)
Fe(1)	$\frac{1}{4}$	$\frac{3}{4}$	0	2·1 (7)
Fe(2)	$\frac{1}{4}$	$\frac{3}{4}$	0·0535 (8)	3·0 (5)
Fe(3)	$\frac{1}{4}$	$\frac{3}{4}$	0·1097 (6)	2·9 (5)
Fe(4)	$\frac{1}{4}$	$\frac{3}{4}$	0·1653 (6)	2·8 (5)
Fe(5)	$\frac{1}{4}$	$\frac{3}{4}$	0·2209 (6)	2·4 (5)
S(1)	0·4358 (48)	0·8930 (51)	0·0282 (11)	1·6 (5)
S(2)	0·1400 (70)	0·9513 (70)	0·0816 (9)	2·6 (9)
S(3)	0·4403 (80)	0·8838 (85)	0·1358 (10)	3·1 (9)
S(4)	0·1010 (50)	0·9200 (50)	0·1917 (7)	2·0 (7)
S(5)	0·4100 (50)	0·9100	$\frac{1}{4}$	2·2 (9)

Discussion

The structure of $Ba_5Fe_9S_{18}$ is illustrated in Figs. 2 and 3. It consists of chains of edge-shared iron–sulphur tetrahedra, $(FeS_{4/2})_\infty$, directed along [001] with barium atoms packed between the chains. The iron–iron separations along the chain vary between $2\cdot66$ and $2\cdot88$ Å with a mean value of $2\cdot77$ Å. Ther ion–sulphur tetrahedra all show considerable distortions, with Fe–S bond lengths varying between $2\cdot20$ and $2\cdot32$ Å and with S–Fe–S angles in the range 102 to 116°. The main bond-length variations and mean values for the FeS_4 tetrahedra are compared in Table 5 with equivalent values found in other compounds containing chains of edge-shared tetrahedra. The data in Table 5 show a correlation between the observed mean M–M and M–S bond lengths, and the formal oxidation state of iron. From $CsFeS_2$ (and $KFeS_2$), to $Ba_5Fe_9S_{18}$ to $Ba_7Fe_6S_{14}$ the formal valency assigned to the iron
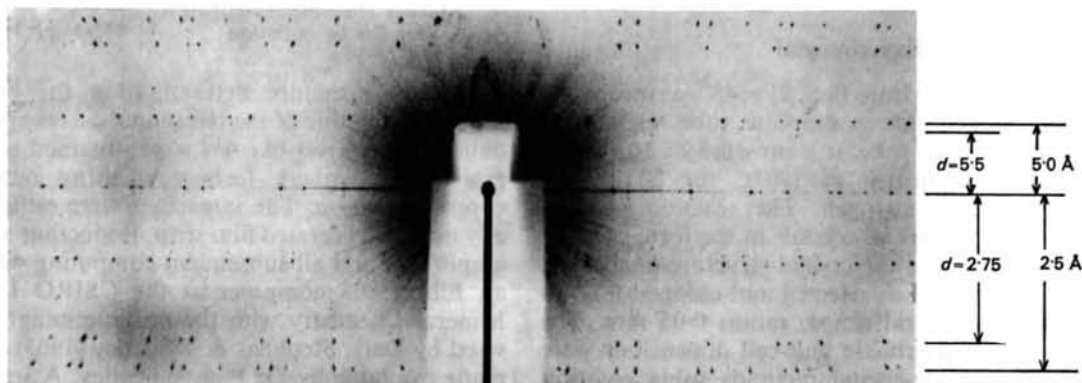

Fig. 1. Oscillation photograph with c as oscillation axis, showing pronounced subcells with $c'=5\cdot0$ and $c''=5\cdot5$ Å.

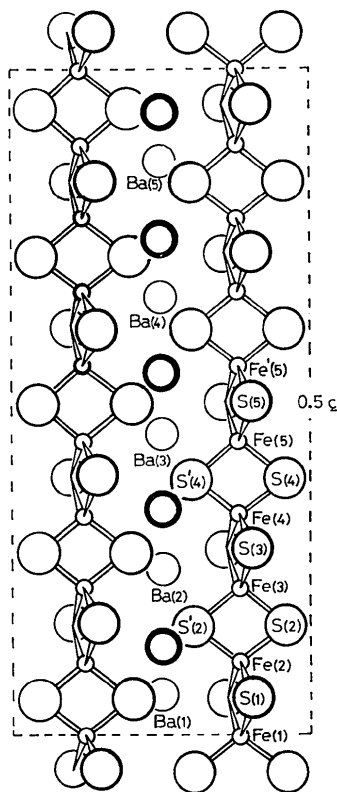## Table 3. *Observed and calculated structure factors*

Fig. 2. Contents of unit cell for Ba₅Fe₉S₁₈, viewed along [1̄1̄0].

Table 4. *Selected bond lengths (Å) and angles (°) for Ba₅Fe₉S₁₈*

Fe(1) tetrahedron		Fe(2) tetrahedron		Fe(3) tetrahedron		Fe(4) tetrahedron		Fe(5) tetrahedron	
Iron–sulphur									
Fe(1)–S(1) (×4)	2·29 (4)	Fe(2)–S(1) (×2)	2·21 (5)	Fe(3)–S(2) (×2)	2·27 (5)	Fe(4)–S(3) (×2)	2·32 (6)	Fe(5)–S(4) (×2)	2·27 (5)
		Fe(2)–S(2) (×2)	2·26 (5)	Fe(3)–S(3) (×2)	2·22 (6)	Fe(4)–S(4) (×2)	2·20 (5)	Fe(5)–S(5) (×2)	2·27 (5)
S(1)–S'(1) (×2)	3·65 (6)	S(1)—S'(1)	3·65 (6)	S(2)—S'(2)	3·61 (8)	S(3)—S'(3)	3·61 (8)	S(4)—S'(4)	3·52 (8)
S(1)–S''(1)(×4)	3·81 (6)	S(2)—S'(2)	3·57 (7)	S(3)—S'(3)	3·57 (8)	S(4)—S'(4)	3·52 (8)	S(5)—S'(5)	3·52 (8)
		S(1)—S(2) (×2)	3·54 (7)	S(2)—S(3) (×2)	3·60 (8)	S(3)—S(4) (×2)	3·84 (8)	S(4)—S(5) (×2)	3·76 (6)
		S(1)—S'(2) (×2)	3·81 (7)	S(2)—S'(3) (×2)	3·79 (8)	S(3)—S'(4) (×2)	3·65 (8)	S(4)—S'(5) (×2)	3·86 (7)
S(1)—Fe(1)-S'(1)	105·0	S(1)—Fe(2)-S(2)	104·3	S(2)—Fe(3)-S(3)	106·8	S(3)—Fe(4)-S(4)	116·4	S(4)—Fe(5)-S(5)	111·3
S(1)—Fe(1)-S''(1)	112·6	S(1)—Fe(2)-S'(1)	110·9	S(2)—Fe(3)-S'(2)	103·9	S(3)—Fe(4)-S'(3)	102·0	S(4)—Fe(5)-S'(4)	101·0
		S'(1)—Fe(2)-S(2)	116·7	S'(2)—Fe(3)-S(3)	115·4	S'(3)—Fe(4)-S(4)	107·9	S'(4)—Fe(5)-S(5)	116·2
		S(2)—Fe(2)-S'(2)	104·2	S(3)—Fe(3)-S'(3)	108·7	S(4)—Fe(4)-S'(4)	106·6	S(5)—Fe(5)-S'(5)	108·0
Iron–iron									
Fe(1)—Fe(2)	2·66 (2)	Fe(2)—Fe(3)	2·79 (2)	Fe(3)—Fe(4)	2·76 (2)	Fe(4)—Fe(5)	2·76 (2)	Fe(5)—Fe'(5)	2·88 (2)
Barium–sulphur									
Ba(1)–S(1) (×4)	3·14 (5)	Ba(2)–S(2) (×4)	3·34 (5)	Ba(3)–S(4) (×4)	3·32 (5)	Ba(4)–S(3) (×4)	3·13 (5)	Ba(5)–S(1) (×4)	3·33 (5)
Ba(1)–S(2) (×4)	3·48 (5)	Ba(2)–S(3) (×4)	3·25 (6)	Ba(3)–S(5) (×4)	3·11 (5)	Ba(4)–S(4) (×4)	3·21 (5)	Ba(5)–S(2) (×4)	3·48 (5)

Table 5. *Comparison of bond lengths* (Å) *for some compounds containing chains of edge-shared tetrahedra*

|	$KFeS_2{}^a$	$CsFeS_2{}^a$	$NH_4CuMoS_4{}^b$	$Ba_5Fe_9S_{18}$	$Ba_7Fe_6S_{14}{}^c$
M–M (range)	2·70	2·62 and 2·81	2·70	2·66 to 2·88	2·75 and 2·83
M–M (average)	2·70	2·71	2·70	2·77	2·79
M–S (range)	2·18–2·29	2·18–2·28	2·19–2·31	2·20–2·32	2·24–2·36
M–S (average)	2·23	2·23	2·19 (Mo) 2·31 (Cu)	2·26	2·30
S–S (range)	3·32–3·50	3·44–3·85	3·60–3·86	3·52–3·86	3·60–3·89
S–S (average)	3·39	3·70	3·67	3·76	3·75
Formal charge on Fe	3·00	3·00		2·89	2·33

References
a Bronger (1968). *b* Binnie, Redman & Mallio (1970). *c* Grey, Hong & Steinfink (1971): this compound has groups of three edge-shared tetrahedra which are linked into chains by coiner sharing.

atoms decreases from 3·0 to 2·89 to 2·33, while the bond lengths are observed to increase in this order.

Each of the five independent barium atoms coordinates to eight sulphur atoms at Ba–S distances between 3·11 and 3·48 Å. The next shortest Ba–S distances are all greater than 4 Å. The barium atoms are situated on the fourfold axis of flattened square-antiprisms of sulphur (Fig. 3). The mean of the Ba–S bond lengths is 3·28 Å, which agrees closely with the sum of the ionic radii for Ba^{2+} and S^{2-}, 3·26 Å (Shannon & Prewitt, 1969).

The structure of $Ba_5Fe_9S_{18}$ may be considered as a superstructure based on the NH_4CuMoS_4 structure type. In the latter compound, the ammonium ions lie in the (00*l*) planes of sulphur atoms and their repeat distance along [001] equals the S–S repeat distance of 5·4 Å. However, in $Ba_5Fe_9S_{18}$ the barium atoms pack more densely than ammonium so that the Ba–Ba repeat distance along $[001] \simeq 5·0$ Å is considerably shorter than the S–S repeat $\simeq 5·5$ Å. The structure is repeated along [001] after every tenth barium atom or after every ninth sulphur or iron layer (containing 4S and 2Fe respectively, see Fig. 2) and the stoichiometry is given as

$$10Ba + 9Fe_2S_4 = Ba_{10}Fe_{18}S_{36} = 2Ba_5Fe_9S_{18}.$$
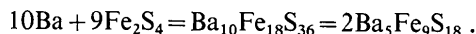
This basic structural principle of periodic out-of-phase packing of barium and sulphur atoms may be extended to postulate series of ordered phases with general stoichiometries given by

$$pBa + qFe_2S_4 \equiv Ba_pFe_{2q}S_{4q}$$
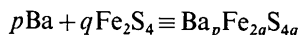
where *p* and *q* are integers. The structures of such a series of compounds will consist of infinite chains of edge-shared tetrahedra $(FeS_{4/2})_\infty$ with different packing densities of barium atoms between the chains. In practice we have indeed prepared and characterized a
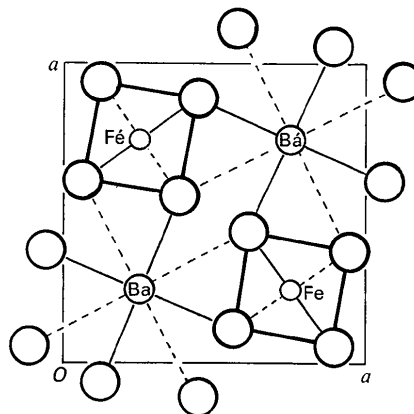

Fig. 3. Projection of unit cell for $Ba_5Fe_9S_{18}$ down [001], showing sulphur coordination around barium and iron atoms.

number of these phases in the composition range $Ba_{1+x}Fe_2S_4$, $0·062 \le x \le 0·143$ (Grey, 1974).

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