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Refinement of Structures of the Composite Crystals $Ba_xFe_2S_4$ (x = 10/9 and 9/8) in a Four-Dimensional Formalism

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Abstract

The structures of the composite crystals of tetragonal columnar sulfide, $Ba_{10/9}Fe_2S_4$ ($M_r = 392{\cdot}55$) and $Ba_{9/8}Fe_2S_4$ ($M_r = 394{\cdot}46$), have been refined on the basis of a four-dimensional superspace group using the X-ray diffraction data collected by Grey [*Acta Cryst.* (1975), **B31**, 45–48] and Hoggins & Steinfink [*Acta Cryst.* (1977), **B33**, 673–678]. The crystals are composed of linear strings of edge-shared FeS_4 tetrahedra $(FeS_{4/2})_\infty$ and rows of Ba ions. R_F was 0·082 on a commensurate modulated structure model with 23 structural parameters using 212 reflections for $Ba_{10/9}Fe_2S_4$, and 0·153 with 33 parameters using 1083 reflections for $Ba_{9/8}Fe_2S_4$. The symmetry operations of the superspace group employed are $(0,0,0,0;\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2}) + x_1,x_2,x_3,x_4$; $-x_2,x_1,x_3,x_4$; $-x_1,x_2,\frac{1}{2}+x_3,x_4$; $x_2,x_1,\frac{1}{2}+x_3,x_4$; $-x_1,-x_2,x_3,x_4$; $x_2,-x_1,x_3,x_4$; $x_1,-x_2,\frac{1}{2}+x_3,x_4$; $-x_2,-x_1,\frac{1}{2}+x_3,x_4$, and the superspace group can be transformed into P^{I4bm}_{1ss} with a basis transformation. The unit cells and other crystal data are $a_1 = a_2 = 7{\cdot}776$, $a_3 = 5{\cdot}540$ Å, $\sigma = (0\,0\,10/9)$, $V = 334{\cdot}98$ Å^3, $D_x = 3{\cdot}89$ Mg m^{-3}, $Z = 2$ for $Ba_{10/9}Fe_2S_4$, and $a_1 = a_2 = 7{\cdot}776$, $a_3 = 5{\cdot}551$ Å, $\sigma = (0\,0\,9/8)$, $V = 334{\cdot}10$ Å^3, $D_x = 3{\cdot}90$ Mg m^{-3}, $Z = 2$ for $Ba_{9/8}Fe_2S_4$.

Introduction

Recently, it has become clear that some crystals consist of plural structural units, each with its own periodicity (Janner & Janssen, 1980; Makovicky & Hyde, 1981), and they are called composite crystals (Janner & Janssen, 1980). Layered ternary chalcogenides such as $(LaS)_{1\cdot2}CrS_2$ with composite crystal structures have attracted much interest (Kato, Kawada & Takahashi, 1977; Wiegers, Meetsma, van Smaalen, Haange, Wulff, Zeinstra, de Boer, Kuypers, van Tendeloo, van Landuyt, Amelinckx, Meerschaut, Rabu & Rouxel, 1989; Kato, 1990; Onoda, Kato, Gotoh & Oosawa, 1990). These crystal structures have been described as an interpenetration of two layered structures which alternate regularly through the crystal in spite of the misfit between their two-dimensional lattices. The description of such a total structure can be based on superspace-group theory (Janner & Janssen, 1980).

The present paper is concerned with columnar composite structures. Examples such as $Ba_xFe_2S_4$ (x = 10/9 and 9/8) (Grey, 1975; Hoggins & Steinfink, 1977) and $A_{1+x}Cr_2X_{4+x}$ (A = Eu, Sr, Ba, Pb; X = S, Se; $x = 0{\cdot}29$) (Brouwer & Jellinek, 1977; Brouwer, 1978) are found among the ternary chalcogenides.

The columnar-compound series $Ba_xFe_2S_4$ ($1{\cdot}00 \le x \le 1{\cdot}142$) have been intensively investigated by X-ray diffraction (Grey, 1974, 1975; Hoggins & Steinfink, 1977; Boller, 1978; Swinnea & Steinfink, 1980, 1982*a*; Nakayama, Kosuge & Kachi, 1981), electron diffraction, electron microscopy (Nakayama, Kosuge & Kachi, 1980, 1982; Holladay & Eyring, 1986) and measurement of physical properties (Swinnea & Steinfink, 1982*b*). The crystal structures of $Ba_{10/9}Fe_2S_4$ (Grey, 1975) and $Ba_{9/8}Fe_2S_4$ (Hoggins & Steinfink, 1977) have been determined by a single-crystal X-ray analysis and refined with the superstructure model. The crystals are tetragonal with $a = 7{\cdot}776$ and $c = 49{\cdot}86$ Å for $Ba_{10/9}Fe_2S_4$, and $a = 7{\cdot}776$ and $c = 44{\cdot}41$ Å for $Ba_{9/8}Fe_2S_4$. Their structures consist of chains of edge-shared Fe–S tetrahedra, $(FeS_{4/2})_\infty$, along [001]; the Ba atoms are packed between the chains with a linear density of more than one atom within the basic period of the latter.

The diffraction intensity data of $Ba_{10/9}Fe_2S_4$ and $Ba_{9/8}Fe_2S_4$ seem to exhibit many absences not related to space-group extinctions. Diffractions which are very weak or absent can be indexed as higher-order

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Table 1. *Conditions of measurement and original analyses*

	$Ba_{10/9}Fe_2S_4$ (Grey, 1975)	$Ba_{9/8}Fe_2S_4$ (Hoggins & Steinfink, 1977)
Unit cell	Tetragonal	Tetragonal
a (Å)	7·776 (3)	7·7758 (10)
c (Å)	49·86 (2)	44·409 (8)
V (Å^3)	3014·8	2672·83
Z	18	16
M_r	392·55	394·46
D_x (g cm^{-3})	3·89	3·90
Systematic reflection conditions	$hk0$, $h+k=2n$ $0kl$, $l=2n$ hhl, $l=2n$	$hk0$, $h+k=2n$ $0kl$, $k+l=2n$ hhl, $l=2n$
Space group	$P4/ncc$	$P4/mnc$
Radiation	Cu $K\alpha$	Mo $K\alpha$
μ (cm^{-1})	952·7	121
Crystal shape	Sphere	Needle
Crystal size (mm)	$R=0·05$	0·05 × 0·08 × 0·18
μR or transmission factor	$\mu R=4·7$	0·162–0·560
Intensity estimation	Visual (integrated Weissenberg technique)	Diffractometer with Weissenberg geometry
Measured reflections (used in the original analysis)	212	1954
Number of parameters in the original analysis	45	47
Temperature factor	Isotropic	Isotropic (Fe and S), anisotropic (Ba)
R factor (original analysis)	$R=0·092$	$R(F)=0·29$, $R(F^2)=0·14$

satellites in the four-dimensional description as discussed by Hoggins & Steinfink (1977). This fact makes it possible to treat the structures as modulated ones with only lower-order modulations and thus to reduce the independent parameters to be refined. Moreover, the superspace-group approach allows a uniform treatment of the commensurate and incommensurate structures of this series and will lead to their better understanding. In this study the crystal structures of the columnar composite crystals $Ba_xFe_2S_4$ (x = 10/9 and 9/8) were reinvestigated using the X-ray diffraction data collected by Grey (1975) and by Hoggins & Steinfink (1977) in a four-dimensional formalism with the aid of a least-squares technique using the computer program *FMLSM* (Kato, 1990) based on the superspace-group approach for composite crystals (Janner & Janssen, 1980).

Single-crystal X-ray diffraction data

The crystallographic data for $Ba_{10/9}Fe_2S_4$ (Grey, 1975) and $Ba_{9/8}Fe_2S_4$ (Hoggins & Steinfink, 1977) are listed in Table 1. Both are considered to be commensurate composite crystals. All of the measured intensities of $Ba_{10/9}Fe_2S_4$ are used in the present structure refinement. In the case of $Ba_{9/8}Fe_2S_4$, 1161 reflections with $I > \sigma(I)$ remain in the present investigation.

Symmetry

As discussed by Hoggins & Steinfink (1977), the diffraction patterns of $Ba_xFe_2S_4$ could be regarded as those of dual subsystems. The strong reflections of $Ba_{10/9}Fe_2S_4$ and $Ba_{9/8}Fe_2S_4$ can be indexed using two tetragonal unit cells with common a and different c: for the Fe_2S_4 part $a = 7·776$ and $c = 49·86/9 \simeq 44·41/8 \simeq 5·55$ Å; for the Ba part $a = 7·776$ and $c = 49·86/10 \simeq 44·41/9 \simeq 5·0$ Å. The subcell periodicities along **c** allow the use of the equation, $l = 9L + 10M$ or $l = 8L + 9M$, in order to index reflections with four integers $H(=h)$, $K(=k)$, L and M. Each reflection is expressed by

$$\mathbf{q} = H\mathbf{a}_1^* + K\mathbf{a}_2^* + L\mathbf{c}_1^* + M\mathbf{c}_2^*$$

where $\mathbf{a}_1^*$ and $\mathbf{a}_2^*$ are the reciprocal bases corresponding to **a** and **b**. $\mathbf{c}_1^*$ and $\mathbf{c}_2^*$ are reciprocal to **c** for the Fe_2S_4 part and the Ba part respectively (c_2^*/c_1^* = 10/9 or 9/8). The reciprocal base vectors of the Fe_2S_4 part and those of the Ba part are related to the minimal vector set in reciprocal space $\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*\} = \{\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}_1^*, \mathbf{c}_2^*\}$ through the following Z matrices (Janner & Janssen, 1980)

$$\text{Subsystem 1 }(Fe_2S_4)\quad Z^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

$$\text{Subsystem 2 (Ba)}\quad Z^2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The cell constants are $a_1 = a_2 = 7·776$ and $a_3 = 5·55$ Å, and the σ matrix is expressed as $(0\,0\,s)$ where s = 10/9 and 9/8 respectively for x = 10/9 and x = 9/8. The possible superspace group can be derived from the possible space groups of the subsystems. Excluding those which conflict with the known features of the structure, the symmetry operations of the probable space groups are

$$(0,0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})\ +x_1,x_2,x_3,x_4;\ -x_2,x_1,x_3,x_4;$$
$$-x_1,x_2,\tfrac{1}{2}+x_3,x_4;\ x_2,x_1,\tfrac{1}{2}+x_3,x_4;\ -x_1,-x_2,x_3,x_4;$$
$$x_2,-x_1,x_3,x_4;\ x_1,-x_2,\tfrac{1}{2}+x_3,x_4;\ -x_2,-x_1,\tfrac{1}{2}+x_3,x_4;$$
$$-x_1,-x_2,-x_3,-x_4;\ x_2,-x_1,-x_3,-x_4;$$
$$x_1,-x_2,\tfrac{1}{2}-x_3,-x_4;\ -x_2,-x_1,\tfrac{1}{2}-x_3,-x_4;$$
$$x_1,x_2,-x_3,-x_4;\ -x_2,x_1,-x_3,-x_4;$$
$$-x_1,x_2,\tfrac{1}{2}-x_3,-x_4;\ x_2,x_1,\tfrac{1}{2}-x_3,-x_4$$

or

$$+\ x_1,x_2,x_3,x_4;\ -x_2,x_1,x_3,x_4;\ -x_1,x_2,\tfrac{1}{2}+x_3,x_4;$$
$$x_2,x_1,\tfrac{1}{2}+x_3,x_4;\ -x_1,-x_2,x_3,x_4;\ x_2,-x_1,x_3,x_4;$$
$$x_1,-x_2,\tfrac{1}{2}+x_3,x_4;\ -x_2,-x_1,\tfrac{1}{2}+x_3,x_4.$$

If we choose another basis $\mathbf{a}_1'^* = \mathbf{a}_1^*$, $\mathbf{a}_2'^*, = \mathbf{a}_2^*$, $\mathbf{a}_3'^* = \mathbf{a}_3^*$ and $\mathbf{a}_4'^* = \mathbf{a}_4^* - \mathbf{a}_3^*$, the systematic reflection conditions on the new indices are reduced to $H'K'L'M'$: $H' + K' + L' = 2n$, $0K'L'M'$: $L' + M' = 2n$ ($K' + L' = 2n$) and $H'H'L'M'$: $M' = 2n$ ($L' = 2n$); $\sigma' = (0\,0\,s')$ where s' = 1/9 and 1/8 for x = 10/9 and

Table 2. *Comparison of R_F and wR_F for reflection data groups*

(*a*) $Ba_{10/9}Fe_2S_4$	*HK*00	*HKL*0 $L \neq 0$	*HK*0*M* $M \neq 0$	*HKLM* $L \neq 0$ and $M \neq 0$	Total
Number of reflections	17	56	79	60	212
R_F	0·060	0·090	0·081	0·094	0·082
wR_F	0·064	0·109	0·098	0·109	0·093
(*b*) $Ba_{9/8}Fe_2S_4$					
(i) For 1083 reflections with $I > \sigma(I)$					
Number of reflections	25	104	118	836	1083
R_F	0·042	0·070	0·063	0·302	0·153
wR_F	0·053	0·081	0·066	0·259	0·110
(ii) For 783 reflections with $\lvert L \rvert$ and/or $\lvert M \rvert$ less than 5					
Number of reflections	25	104	118	536	783
R_F	0·042	0·070	0·063	0·214	0·112
wR_F	0·053	0·081	0·066	0·206	0·094

9/8 respectively. Thus possible superspace groups can be transformed to $P^{I4/mbm}_{1\bar{1}ss}$ and P^{I4bm}_{1ss} as listed in the literature (de Wolff, Janssen & Janner, 1981; Yamamoto, Janssen, Janner & de Wolff, 1985).

In this study, the structure analysis was performed by using the former setting for ease in understanding the subsystem relation. The conditions for possible reflections are *HKLM*: $H + K + L + M = 2n$, 0*KLM*: $L = 2n$ ($K + M = 2n$) and *HHLM*: $L = 2n$ ($M = 2n$). They are satisified by all the main reflections of both subsystems but are only approximately fulfilled by satellite reflections on account of the commensurate nature of the lattice geometry.

Structure refinement

Refinement was performed on the basis of $|F|$ through a full-matrix least-squares refinement program *FMLSM* (Kato, 1990). As the crystals appear as sections for constant discrete values of the additional coordinate t in the commensurate cases, the integrals in the structure-factor formula should be replaced with summations (Kato & Onoda, 1991). In the present case, the edges of the integration domain are as follows: [0001] for subsystem 1 and [0010] for subsystem 2. Numbers of summation points are 9 (subsystem 1) and 10 (subsystem 2) for x = 10/9, and 8 (subsystem 1) and 9 (subsystem 2) for x = 9/8.

After some trials a model was established assuming the second set of symmetry operations mentioned above. The superspace group employed is equivalent to P^{I4bm}_{1ss}. The space groups of the basic structures of the two subsystems, the Fe_2S_4 and Ba parts, are *I*4*cm* and *I*4*mm*. Values of scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), and unit weights were assigned to all reflections. Besides one scaling factor, atomic coordinates and temperature factors, the Fourier amplitudes of the modulation functions were considered as structural parameters. As the atoms are located in special positions the modulation-function shapes are restricted as discussed previously (Onoda, Kato, Gotoh & Oosawa, 1990).

Table 3. *Atomic parameters with e.s.d.'s in parentheses*

$A_{\mathbf{k}}$ and $B_{\mathbf{k}}$ are the cosine and sine amplitudes of the Fourier series of the modulation function, where **k** is the modulation vector

(*a*) $Ba_{10/9}Fe_2S_4$				
Subsystem 1	x (= x_1)	y (= x_2)	z (= x_3)	B (Å^2)
Fe				
Average	0·0	0·5	0·250 (6)	3·03 (19)
A_{0002}	0·0	0·0	0·020 (8)	0·0
B_{0002}	0·0	0·0	0·022 (8)	0·0
S				
Average	0·3372 (10)	0·8372	0·0	2·6 (3)
A_{0001}	0·0382 (15)	−0·0382	0·0	0·0
B_{0001}	−0·001 (8)	0·001	0·0	0·0
A_{0002}	0·003 (3)	0·003	−0·005 (11)	0·0
B_{0002}	−0·003 (7)	−0·003	−0·022 (5)	0·0
Subsystem 2	x (= x_1)	y (= x_2)	z (= x_4)	B_{eq} (Å^2)*
Ba				
Average	0·0	0·0	0·03 (2)	3·7 (3)
A_{0020}	0·0	0·0	0·033 (8)	0·2 (6)
B_{0020}	0·0	0·0	0·027 (6)	3·6 (5)
A_{0040}	0·0	0·0	0·048 (7)	0·0
B_{0040}	0·0	0·0	0·019 (8)	0·0
(*b*) $Ba_{9/8}Fe_2S_4$				
Subsystem 1	x (= x_1)	y (= x_2)	z (= x_3)	B (Å^2)
Fe				
Average	0·0	0·5	0·2395 (19)	1·05 (4)
A_{0002}	0·0	0·0	0·0032 (19)	0·0
B_{0002}	0·0	0·0	0·0102 (10)	0·0
S				
Average	0·3409 (3)	0·8409	0·0	1·10 (6)
A_{0001}	0·0323 (6)	−0·0323	0·0	0·0
B_{0001}	−0·004 (2)	0·004	0·0	0·0
A_{0002}	0·0002 (6)	0·0002	−0·012 (2)	0·0
B_{0002}	0·0005 (11)	0·0005	−0·0103 (19)	0·0
A_{0003}	0·003 (2)	−0·003	0·0	0·0
B_{0003}	0·0110 (10)	−0·0110	0·0	0·0
A_{0004}	0·0046 (8)	0·0046	0·006 (2)	0·0
B_{0004}	0·0016 (14)	0·0016	−0·006 (2)	0·0
Subsystem 2	x (= x_1)	y (= x_2)	z (= x_4)	B_{eq} (Å^2)†
Ba				
Average	0·0	0·0	−0·015 (11)	2·29 (7)
A_{0020}	0·0	0·0	0·025 (2)	1·21 (12)
B_{0020}	0·0	0·0	0·0378 (16)	−1·06 (16)
A_{0040}	0·0	0·0	0·0133 (14)	0·17 (14)
B_{0040}	0·0	0·0	0·0090 (15)	−0·72 (13)

* $B_{eq} = \frac{4}{3}[\beta_{11}a_1^2 + \beta_{22}a_2^2 + \beta_{33}a_3^2(\frac{9}{10})^2]$.

† $B_{eq} = \frac{4}{3}[\beta_{11}a_1^2 + \beta_{22}a_2^2 + \beta_{33}a_3^2(\frac{8}{9})^2]$.

For $Ba_{10/9}Fe_2S_4$, 212 independent structure factors observed by Grey (1975) were used. The structure model adopted was as follows. For subsystem 1 (Fe and S), an unmodulated isotropic temperature factor and displacive modulations up to the second order were assigned to each atom, while for subsystem 2 (Ba) displacive modulation up to the fourth order and modulations of anisotropic thermal parameters up to the second order were considered. The agreement was fairly good with 23 structural parameters:* R_F = 0·082 and wR_F = 0·093. R_F for *HK*00, *HKL*0, *HK*0*M* and *HKLM* ($L \neq 0$, $M \neq 0$)

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54068 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Selected interatomic distances* (Å)

(*a*) $Ba_{10/9}Fe_2S_4$

t	0	$\frac{1}{9}$	$\frac{2}{9}$	$\frac{3}{9}$	$\frac{4}{9}$	$\frac{5}{9}$
Fe—S$^{\rm i*}$	2·20 (5)	2·32 (6)	2·38 (6)	2·28 (7)	2·19 (6)	2·25 (6)
Fe—S$^{\rm ii*}$	2·32 (5)	2·32 (7)	2·26 (5)	2·24 (6)	2·30 (5)	2·33 (6)
Fe$^{\rm i}$—S$^{\rm iii*}$	2·33 (6)	2·29 (6)	2·24 (6)	2·27 (7)	2·32 (5)	2·32 (7)
Fe$^{\rm i}$—S$^{\rm ii*}$	2·25 (6)	2·37 (6)	2·34 (6)	2·22 (7)	2·20 (5)	2·32 (6)
Fe—Fe$^{\rm i}$	2·75 (4)	2·879 (19)	2·82 (3)	2·68 (3)	2·68 (3)	2·83 (3)
Fe$^{\rm i}$—Fe$^{\rm ii}$	2·83 (3)	2·88 (2)	2·75 (3)	2·656 (17)	2·75 (4)	2·88 (2)
Ba—S$^{\rm iv*}$				5·0 (2)	4·22 (10)	4·18 (7)
Ba—S$^{\rm v*}$	4·18 (7)	3·44 (15)	3·20 (5)	3·23 (7)	3·27 (7)	3·38 (3)
Ba—S$^{\rm vi*}$	3·38 (3)	3·23 (5)	3·17 (7)	3·15 (9)	3·40 (6)	3·28 (7)
Ba—S$^{\rm vii*}$	3·28 (7)	4·2 (2)	4·99 (10)			
Ba$^{\rm iii}$—S$^{\rm viii*}$				4·5 (2)	4·20 (5)	3·88 (17)
Ba$^{\rm iii}$—S$^{\rm ix*}$	3·88 (17)	3·19 (6)	3·26 (6)	3·21 (7)	3·35 (5)	3·29 (5)
Ba$^{\rm iii}$—S$^{\rm x*}$	3·29 (5)	3·23 (6)	3·09 (6)	3·33 (9)	3·29 (6)	3·6 (2)
Ba$^{\rm iii}$—S$^{\rm xi*}$	3·6 (2)	4·75 (17)	5·14 (12)			
Ba—Ba$^{\rm ii}$	4·38 (17)	4·9 (2)	5·22 (18)	4·84 (15)	5·55 (9)	4·38 (17)
Ba$^{\rm iii}$—Ba$^{\rm iv}$	4·34 (13)	5·41 (7)	4·79 (13)	5·3 (2)	5·0 (3)	4·34 (13)

(*b*) $Ba_{9/8}Fe_2S_4$

t	0	$\frac{1}{8}$	$\frac{2}{8}$	$\frac{3}{8}$	$\frac{4}{8}$
Fe—S$^{\rm i*}$	2·270 (16)	2·197 (19)	2·206 (13)	2·186 (15)	2·270 (16)
Fe—S$^{\rm ii*}$	2·24 (2)	2·34 (3)	2·28 (2)	2·28 (2)	2·24 (2)
Fe$^{\rm i}$—S$^{\rm iii*}$	2·222 (19)	2·391 (15)	2·219 (15)	2·313 (15)	2·222 (19)
Fe$^{\rm i}$—S$^{\rm ii*}$	2·259 (16)	2·179 (16)	2·198 (14)	2·220 (18)	2·259 (16)
Fe—Fe$^{\rm i}$	2·749 (7)	2·812 (6)	2·802 (7)	2·739 (6)	2·749 (7)
Fe$^{\rm i}$—Fe$^{\rm ii}$	2·782 (8)	2·820 (4)	2·769 (8)	2·731 (4)	2·782 (8)
Ba—S$^{\rm iv*}$				4·51 (4)	4·28 (5)
Ba—S$^{\rm v*}$	3·89 (9)	3·19 (3)	3·208 (18)	3·222 (12)	3·190 (14)
Ba—S$^{\rm vi*}$	3·284 (19)	3·32 (2)	3·126 (16)	3·37 (2)	3·39 (2)
Ba—S$^{\rm vii*}$	3·62 (7)	4·75 (9)			
Ba$^{\rm iii}$—S$^{\rm viii*}$				4·418 (19)	3·89 (9)
Ba$^{\rm iii}$—S$^{\rm ix*}$	3·43 (7)	3·168 (17)	3·238 (15)	3·183 (13)	3·284 (19)
Ba$^{\rm iii}$—S$^{\rm x*}$	3·368 (13)	3·18 (2)	3·23 (3)	3·388 (16)	3·62 (7)
Ba$^{\rm iii}$—S$^{\rm xi*}$	4·17 (10)	5·09 (3)			
Ba—Ba$^{\rm ii}$	4·54 (4)	5·11 (3)	5·066 (9)	5·15 (3)	4·55 (4)
Ba$^{\rm iii}$—Ba$^{\rm iv}$	4·86 (6)	5·11 (2)	5·15 (2)	4·88 (7)	4·54 (4)

Symmetry operation: (i) $-x_1, x_2, \frac{1}{2}+x_3, x_4$; (ii) $x_1, x_2, 1+x_3, 1+x_4$; (iii) $\frac{1}{2}+x_1, \frac{1}{2}+x_2, \frac{1}{2}+x_3, \frac{1}{2}+x_4$; (iv) $\frac{1}{2}+x_1, \frac{1}{2}+x_2, \frac{1}{2}+x_3, \frac{3}{2}+x_4$; (i*) $1-x_2, x_1, x_3, x_4$; $-1+x_2, x_1, \frac{1}{2}+x_3, x_4$; (ii*) $-1+x_2, 1-x_1, x_3, x_4$; $1-x_2, 1-x_1, \frac{1}{2}+x_3, x_4$; (iii*) $1-x_2, x_1, 1+x_3, x_4$; $-1+x_2, x_1, \frac{1}{2}+x_3, x_4$; (iv*) $x_1, -1+x_2, -1+x_3, x_4$; $1-x_2, x_1, -1+x_3, x_4$; $-x_1, 1-x_2, -1+x_3, x_4$; $-1+x_2, -x_1, -1+x_3, x_4$; (v*) $-x_1, -1+x_2, -\frac{1}{2}+x_3, x_4$; $-1+x_2, x_1, -\frac{1}{2}+x_3, x_4$; $x_1, 1-x_2, -\frac{1}{2}+x_3, x_4$; $1-x_2, -x_1, -\frac{1}{2}+x_3, x_4$; (vi*) $x_1, -1+x_2, x_3, x_4$; $1-x_2, x_1, x_3, x_4$; $-x_1, 1-x_2, x_3, x_4$; $-1+x_2, -x_1, x_3, x_4$; (vii*) $-x_1, -1+x_2, \frac{1}{2}+x_3, x_4$; $-1+x_2, x_1, \frac{1}{2}+x_3, x_4$; $x_1, 1-x_2, \frac{1}{2}+x_3, x_4$; $1-x_2, -x_1, \frac{1}{2}+x_3, x_4$; (viii*) $1-x_1, x_2, -\frac{1}{2}+x_3, x_4$; $x_2, x_1, -\frac{1}{2}+x_3, x_4$; $x_1, 1-x_2, -\frac{1}{2}+x_3, -1+x_4$; $1-x_2, 1-x_1, -\frac{1}{2}+x_3, x_4$; (ix*) x_1, x_2, x_3, x_4; $1-x_2, x_1, x_3, x_4$; $1-x_1, 1-x_2, x_3, x_4$; $x_2, 1-x_1, x_3, x_4$; (x*) $1-x_1, x_2, \frac{1}{2}+x_3, x_4$; $x_2, x_1, \frac{1}{2}+x_3, x_4$; $x_1, 1-x_2, \frac{1}{2}+x_3, x_4$; $1-x_2, 1-x_1, \frac{1}{2}+x_3, x_4$; (xi*) $x_1, x_2, 1+x_3, x_4$; $1-x_2, x_1, 1+x_3, x_4$; $1-x_1, 1-x_2, 1+x_3, x_4$; $x_2, 1-x_1, 1+x_3, x_4$.

are listed in Table 2. The final structural parameters are shown in Table 3.

For $Ba_{9/8}Fe_2S_4$, 78 reflections adjacent to the strong reflections of the Ba part ($l = 8n$, n integer) were omitted from the set of 1161 reflections with $I > \sigma(I)$ observed by Hoggins & Steinfink (1977) in order to avoid the influence of overlapping. Then a total of 1083 independent structure factors were used in the present refinement. After preliminary refinement, the structure model was set up with displacive modulations up to the second order for Fe and up to the fourth order for S and Ba. The anisotropic thermal parameters for Ba were modulated up to the fourth order, while the thermal parameters of Fe and S were isotropic and not modulated. The final R_F and wR_F values were 0·153 and 0·110 with 33 structural parameters. R_F for *HK*00, *HKL*0, *HK*0*M* and *HKLM* ($L \neq 0$, $M \neq 0$) and the final structure parameters are listed in Tables 2 and 3 respectively. The satellite reflections with both $|L|$ and $|M|$ greater than 4 may be omitted for evaluation of the agreement between observed and calculated structure factors, as the *n*th harmonic of the modulation is considered to contribute essentially to the intensity of satellites of order $M = n$. The values of R_F and wR_F for 783 reflections with $|L|$ and/or $|M|$ less than 5 are also shown in Table 2.

Discussion

The structure models are essentially the same as those proposed by Grey (1975) and Hoggins & Steinfink (1977). The basic structures consist of chains of edge-shared Fe–S tetrahedra, $(FeS_{4/2})_\infty$, directed along [001], with Ba atoms packed between the chains. The real structures are described as mutually displacive modulated structures. The maximum modulation displacements of Fe, S and Ba roughly estimated from the modulation amplitudes of Table 3 are about 0·1, 0·3 and 0·3 Å. They indicate that S and Ba are susceptible to modulation by each other. The three-dimensional coordinates of the atoms were calculated as sections for $t = 0$ [supplementary publication to Kato & Onoda (1991)], and parts of the structures are illustrated in Fig. 1 together with that of β-$BaFe_2S_4$ (Swinnea & Steinfink, 1980). The Ba–S coordination polyhedron changes periodically from a square antiprism with the coordination number 8 to a face-capped tetragonal prism with the coordination number 12 as reported by Hoggins & Steinfink (1977).

Interatomic distances calculated from the parameters of Table 3 are listed in Table 4. The calculation procedure for distances is the same as used in Kato (1990) and the calculation program is included in the supplementary materials of Kato & Onoda (1991). The variation in the Fe—Fe separation along the chain is not large, while the Ba—Ba distances along [001] vary remarkably. The FeS_4 tetrahedra show considerable distortions with Fe—S bond lengths varying between 2·18 and 2·39 Å. Some of the Ba—S distances are shown in Fig. 1. Modulation introduced in the thermal parameters of Ba is considered to correspond to the variation of the coordination state and the bond length around Ba. Although a smaller number of parameters are used in the present refinement in the four-dimensional formalism than in the three-dimensional superstructure model, the distances are in fair agreement with the values obtained in the original analysis (Grey, 1975; Hoggins & Steinfink, 1977).

Nakayama, Kosuge & Kachi (1982) investigated $Ba_xFe_2S_4$ ($1{\cdot}0 \leq x \leq 1{\cdot}15$), prepared under various conditions, using electron diffraction and described the result as follows. Although the composite crystal structure of $Ba_xFe_2S_4$ as a member of the infinitely adaptive series is incommensurate in general, the displacive modulation somehow 'locks in' the commensurate superstructures of $Ba_{i+1}(Fe_2S_4)_i$ or $Ba_{2j+1}(Fe_2S_4)_{2j-1}$. The highest-symmetry three-dimensional space groups for the various values of the integers i or j are: i even, $P4/mnc$; i odd, $P4/mcc$; j even or odd, $I4/m$ as derived by Hoggins & Steinfink (1977). In the superspace, however, all these structures would have the same superspace-group symmetry and would be described with the same set of parameters. It is only s in $\sigma = (00s)$ that varies with varying x in $Ba_xFe_2S_4$, probably $s = x$ as a rule. The present structure refinements showed that this is true at least for two cases of $i = 8$ and 9. $Ba_xFe_2S_4$ is an example of a series of compounds which may be understood systematically using the superspace-group approach.

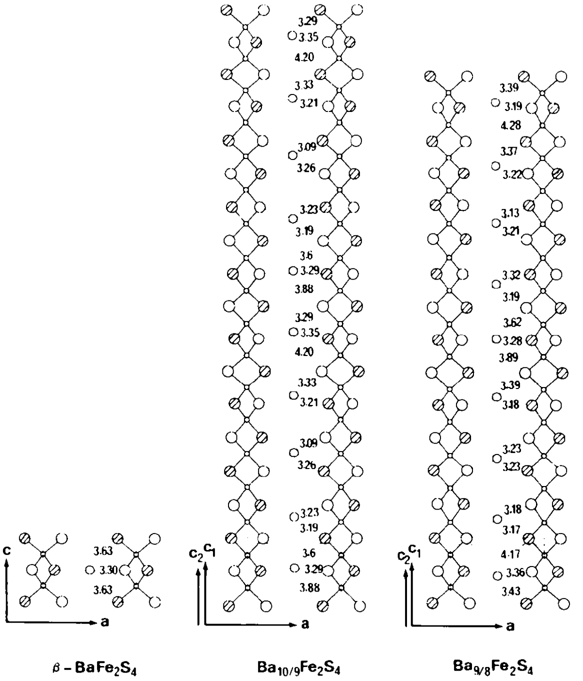

Fig. 1. Bounded projection ($0{\cdot}25 < y \leq 0{\cdot}75$) of the supercell. Small and medium circles represent Fe and Ba atoms at $y = \frac{1}{2}$, and open and hatched large circles represent S atoms at $y \simeq 0{\cdot}34$ and $\simeq 0{\cdot}66$ respectively. The calculated Ba—S distances (Å) are shown together; their repetition manner depends on odd- or even-numbered i in $Ba_{i+1}(Fe_2S_4)_i$.

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