JOURNAL OF SOLID STATE CHEMISTRY **11**, 128–134 (1974)

Infinitely Adaptive Structures, $Ba_{1+x}Fe_2S_4$, in the Ba–Fe–S System

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Received November 21, 1973

X-ray and electron diffraction results are reported for compounds with compositions given by $Ba_{1+x}Fe_2S_4, 0.062 \leqslant x \leqslant 0.143$. The composition range is spanned by an infinite number of ordered phases, $Ba_pFe_{2q}S_{4q}$, p and q integers, with superstructures based on the NH_4CuMoS_4 structure type. The one-dimensional ordering of barium atoms in these structures is a function of temperature of preparation, and the system is thus a suitable model for the testing of current theories relating high temperature structures to periodic atomic thermal vibrations.

Introduction

The term *infinitely adaptive structures* has recently been proposed by J. S. Anderson to describe groups of crystalline materials for which "within certain composition limits, every possible composition can attain a unique, fully ordered structure, without defects arising from solid solution effects and with no biphasic coexisting ranges between successive structures" (*1*).

The first well-characterized samples were recognized by Bursill, Hyde, and Philp in the Ti–O and Cr–Ti–O systems (*2*). Their "swinging shear plane" families constitute a classic example of infinitely adaptive structures based on crystallographic shear in rutile. In fact, for all structural systems exhibiting crystallographic shear, there are compositional regions in which the *CS* plane rotates and produces an infinite number of ordered structures. From the author's laboratories there has been reported such a series of structures in the system $(Fe,Cr)_2O_3$–$(Ti,Zr)O_2$—these are related to the α-PbO_2 structure but may be considered to derive from rutile by crystallographic shear (*3*). In general, infinitely adaptive structures have been best characterized in oxide systems, although Anderson (*1*) has suggested that in chalcogenide systems the same structural principle applies, e.g., $Bi_{1-x}Te$, $0 \leqslant x \leqslant 0.1837$ (*4*).

In this paper evidence is presented for a continuum of ordered phases in the ternary system Ba–Fe–S. The compositions for the infinitely adaptive structures are given by $Ba_{1+x}Fe_2S_4$, with $0.062 \leqslant x \leqslant 0.143$. A single crystal X-ray structure determination coupled with electron diffraction data for one of the homologues, $Ba_5Fe_9S_{18}$ (*5*), has established the structural principle by which this series of phases may be considered as members of an homologous series $Ba_pFe_{2q}S_{4q}$ with p and q integers.

Structural Considerations

The structural basis of the infinitely adaptive series of ordered structures in the $Ba_{1+x}Fe_2S_4$ system has been elucidated from the structure of the phase with $x = 0.111$, solved by electron and single crystal X-ray diffraction methods (*5*). The structure determined for this phase, $Ba_5Fe_9S_{18}$, is shown in Fig. 1. The compound has tetragonal symmetry with $a = 7.776$, $c = 49.86$ Å, and contains infinite chains of edge-shared iron–sulphur tetrahedra $(FeS_{4/2})_n$ directed along the c axis, with the barium atoms packing between the chains. If the barium atoms packed

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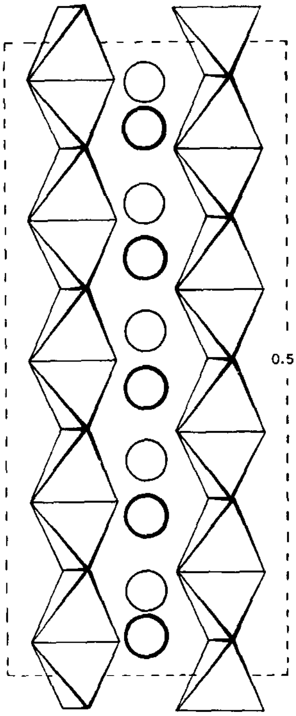


FIG. 1. The contents of a unit cell of $Ba_5Fe_9S_{18}$ viewed along [1$\bar{1}$0], showing packing of Ba atoms (open circles) between infinite chains of edge-shared iron–sulphur tetrahedra $(FeS_{4/2})_n$.

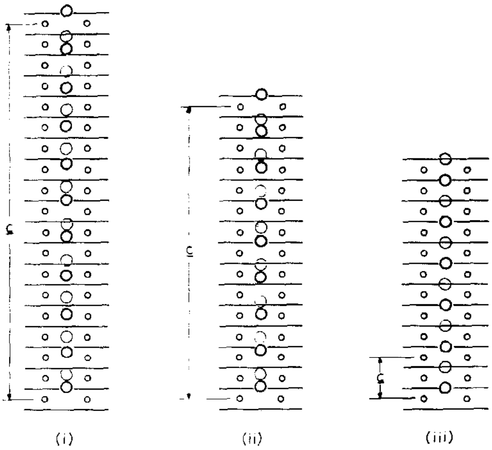
exactly in the (00*l*) planes containing the sulphur atoms, with Ba–Ba = 5.5 Å, the compound would have the stoichiometry $BaFe_2S_4$ and its structure would be of the $NH_4(Cu,Mo)_2S_4$ type, (*6*) (see Fig. 2 (iii)). Instead, the barium atoms pack more densely than the sulphur atoms so that Ba–Ba (along *c*) ≃ 5.0 Å. The periodicity of the structure is repeated every tenth barium (00*l*) layer, or every ninth iron or sulphur (00*l*) layer (Fig. 2 (i)), and the stoichiometry is given as

$$9 \times Fe_2S_4 + 10 \times Ba = Ba_5Fe_9S_{18}.$$

An homologous series of ordered phases based on the "out of phase" packing of barium and iron or sulphur atoms may be envisaged with stoichiometries given by

$$p \cdot Ba + q \cdot Fe_2S_4 \equiv Ba_pFe_{2q}S_{4q}$$

where *p* and *q* are integers. The X-ray diffraction patterns for these compounds will contain two sets of strong reflections—(*h k np*) due to the barium lattice and (*h k nq*) due to the iron plus sulphur lattice. The predicted structure of a homologue with $p = 8$, $q = 7$, for example, is shown in Fig. 2 (ii).



(i) (ii) (iii)

FIG. 2. Idealized representation of structures in the $Ba_{1+x}Fe_2S_4$ system showing (00*l*) layers of S atoms as black lines. The small circles represent Fe atoms and the large circles Ba atoms. (i) Structure of $Ba_5Fe_9S_{18}$; (ii) proposed structure for $Ba_4Fe_7S_{14}$; (iii) proposed structure for stoichiometric $BaFe_2S_4$; NH_4CuMoS_4 has this structure (*6*).

In theory, the entire composition range $Ba + \infty\, Fe_2S_4$ to $\infty Ba + Fe_2S_4$ may be continuously spanned by an infinite number of completely ordered structures $Ba_pFe_{2q}S_{4q}$. In practice the continuum of ordered structures will be limited to a narrow compositional range near $BaFe_2S_4$ owing to charge balance requirements, geometrical packing considerations, and limitations on long range ordering.

Experimental

Compositions $Ba_{1+x}Fe_2S_4$ were prepared by reacting mixtures of BaS, Fe and S in evacuated, sealed silica tubes. The mixtures were contained within graphite capsules to prevent reaction with the silica walls. The iron powder (Koch–Light—*ex* iron carbonyl) and sulphur (Koch–Light) were 99.9% pure. BaS was prepared from A.R. $BaCO_3$ by reduction in a H_2/H_2S mixture. Samples were equilibrated in a horizontal platinum-wound furnace at temperatures in the range 500–800°C, for periods of 1–5 days, then quenched

TABLE I

RESULTS OF SEALED TUBE EQUILIBRATION STUDIES IN THE Ba–Fe–S SYSTEM

Run No.	Starting composition BaS (mole)	Starting composition Fe (mole)	Starting composition S (mole)	Weight of sample	Temperature (°C)	Reaction time (days)	Products	Value of x in composition of $Ba_{1+x}Fe_2S_4$
1	1	2	3	0.30	820	2	$Ba_{1+x}Fe_2S_4 + BaFe_2S_3$	0.140
2	1	2	3	0.15	780	1	$Ba_{1+x}Fe_2S_4 + BaFe_2S_3$	0.143
3	1	2	4	0.30	787	1	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$ (pyrrhotite)	0.105
4	1	2	4	0.30	755	4	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$	0.091
5	1	2	3	0.30	755	4	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$	0.105
6	1	2	3	0.12	690	3	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$	0.114
7	1	2	3	0.30	690	2	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$	0.077
8	1	2	3	0.30	664	3	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S + FeS_2$	0.080
9	1	2	5	0.30	664	3	$Ba_{1+x}Fe_2S_4 + FeS_2$ (pyrite)	0.062
10	1	2	3	0.17	632	2	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$	0.077
11	1	2	3	0.30	563	4	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S + FeS_2$	0.095
12	1	2	3	0.30	700 540	1 +3	$Ba_{1+x}Fe_2S_4 + Fe_{1-y}S + FeS_2$	0.111

in water. Temperature stability to ±0.5°C was maintained with an Ether "Transitrol" potentiometric controller, and temperatures were measured with a Pt–13% Rh thermocouple, calibrated to an accuracy of ±1°C.

X-ray powder patterns were obtained using a Philips diffractometer fitted with a graphite monochromator, employing Cu$K\alpha$ radiation. Silicon was used as an internal standard for lattice parameter determination, and slow scan rates were employed so as to improve precision.

Results

The results of a number of sealed tube equilibrations involving different starting compositions and different temperatures are given in Table I. The barium/iron molar ration in the starting mixture was kept constant at 1:2, and the barium/sulphur molar ratio was varied in the range 1:4–1:6. This ensured that there was always a positive pressure of free sulphur in the reaction tube. For all runs carried out in the temperature range 540–820°C, X-ray identification of the quenched products showed the dominant phase to be $Ba_{1+x}Fe_2S_4$, with an X-ray powder pattern closely related to that for $Ba_5Fe_9S_{18}$ (*5*), i.e., $Ba_{1.111}Fe_2S_4$. With each change in reaction conditions the positions of the X-ray diffraction peaks for the resulting $Ba_{1+x}Fe_2S_4$ phase changed as shown for example in Fig. 3. However, in every instance the lines for $Ba_{1+x}Fe_2S_4$ could be indexed on a single unit cell and the observed diffraction peaks were of a sharpness comparable with those of the internal standard.

The composition(s) of the minor phase(s) in equilibrium with $Ba_{1+x}Fe_2S_4$ was a sensitive function of temperature and sulphur pressure. At temperatures around 800°C, the reaction product contained some $BaFe_2S_3$ (*7*). As the reaction temperature was lowered the equilibrium phase assemblage changed from $Ba_{1+x}Fe_2S_4 + BaFe_2S_3 + S$ to $Ba_{1+x}Fe_2S_4 + Fe_{1-y}S$ (pyrrhotite) + S, as shown in Table I. Finally, at temperatures below ca. 700°C, pyrite was detected in the reaction product. The ratio of pyrite to pyrrohtite increased with the amount of excess sulphur in the reaction mixture.

The stoichiometries of the $Ba_{1+x}Fe_2S_4$ phases were established from the X-ray characterization of the particular homologue $Ba_pFe_{2q}S_{4q}$, by careful indexing of the reflec-

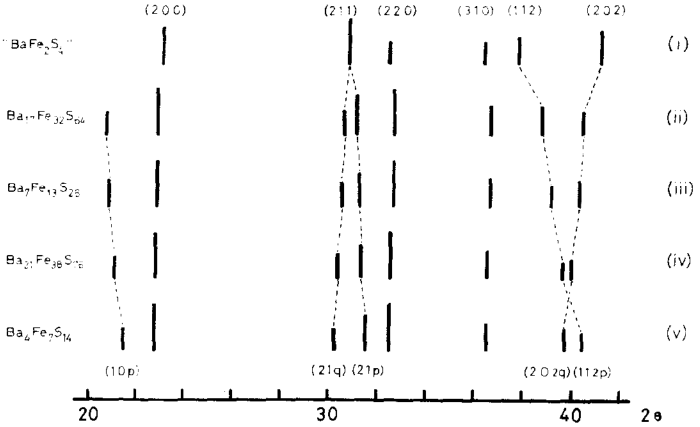


FIG. 3. Section of the powder diffraction data for compounds $Ba_{1+x}Fe_2S_4$. (i) Diffractogram for NH_4CuMoS_4 (Ref. (*6*)). The 2θ scale for this pattern has been displaced by $+1.0^\circ$, so the equivalent reflections may be more directly compared with those for $Ba_{1+x}Fe_2S_4$; (ii) $Ba_{1.062}Fe_2S_4, p = 17, q = 16$; (iii) $Ba_{1.077}Fe_2S_4, p = 14, q = 13$; (iv) $Ba_{1.105}Fe_2S_4, p = 21, q = 19$; (v) $Ba_{1.143}Fe_2S_4, p = 8, q = 7$.

tions ($h\ k\ np$) and ($h\ k\ nq$) (see (Fig. 3)). The precision of measurement of the diffraction lines is ± 0.00007 in $\sin^2\theta$, giving a precision in the determination of x of ± 0.002. This limits the values of p and q that can be determined from X-ray diffraction data to numbers less than about 40. Homologues with higher values of p and q, i.e., with superstructures greater than ca. 200 Å, should be resolved by electron diffraction. Figure 4 is an electron diffraction pattern for a homologue close to $Ba_5Fe_9S_{18}$ in composition, in which the very large periodicity is reflected in the small "spacing anomalies" (*3*) between adjacent spots.

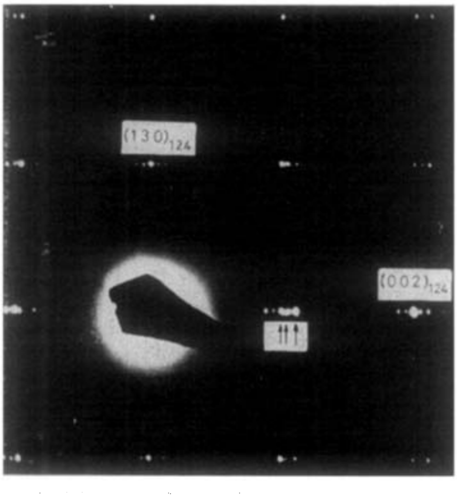


FIG. 4. Electron diffraction pattern for a $Ba_pFe_{2q}S_{4q}$ homologue with $p \simeq 10$, $q \simeq 9$, showing supercell spots along [00*l*]. Subscript (124) refers to the "$BaFe_2S_4$" subcell, e.g., as in NH_4CuMoS_4 (*6*). Arrows point to *d* spacing anomaly in the superstructure reflections indicating a very large *c* axis for a phase near to $Ba_{1.11}Fe_2S_4$ in composition.

Typical indexed powder diffraction data for a number of reaction products are given in Table II. The resulting calculated values of x in $Ba_{1+x}Fe_2S_4$ are listed in Table I. The composition of the $Ba_{1+x}Fe_2S_4$ phase was observed to be a sensitive function of both temperature of preparation and sulphur pressure. The effect of the latter is seen by comparing run 4 with run 5 and run 8 with run 9. These pairs of runs were conducted simultaneously and differ *only* in the amount of excess sulphur in the reaction mixture. The increase in excess sulphur gives an increase in the sulphur pressure in the sealed tube, and this results in a decrease in x for the equilibrium $Ba_{1+x}Fe_2S_4$ phase as shown in Table I. The same effect is obtained by increasing the total weight of the reaction mixture in the fixed-volume sealed tube, e.g., compare run 7 with run 6.

The effect of temperature is complicated by the corresponding temperature dependence of the sulphur pressure. Between 800°C and

TABLE II

X-RAY POWDER DIFFRACTION DATA

			$Ba_4Fe_7S_{14}$					$Ba_5Fe_9S_{18}$					$Ba_6Fe_{11}S_{22}$	
			$\sin^2\theta$					$\sin^2\theta$					$\sin^2\theta$	
h	k	l	calc.	obs.	h	k	l	calc.	obs.	h	k	l	calc.	obs.
0	1	8	0.03478	0.03482	0	1	10	0.03373	0.03368	0	1	12	0.03326	0.03327
0	2	0	0.03924	0.03924	0	2	0	0.03932	0.03927	0	2	0	0.03941	0.03941
1	2	7	0.06817	0.06817	1	2	9	0.06851	0.06852	1	2	11	0.06893	0.06880
1	2	8	0.07402	0.07395	1	2	10	0.07305	0.07304	1	2	12	0.07267	0.07263
2	2	0	0.07848	0.07846	2	2	0	0.07864	0.07859	2	2	0	0.07882	0.07877
0	0	16	0.09988	0.10000	1	3	0	0.09829	0.09828	0	0	24	0.09364	0.09381
1	3	0	0.09810	0.09817	0	3	10	0.11236	0.11231	1	3	0	0.09853	0.09854
0	3	8	0.11326	0.11335	0	2	18	0.11676	0.11681	0	3	12	0.11209	0.11203
1	1	16	0.11950	0.11974	2	3	10	0.15168	0.15160	1	1	24	0.11335	0.11336
0	2	14	0.11572	0.11558	0	4	0	0.15728	0.15722	0	2	22	0.11809	0.11800
0	2	16	0.13912	0.13924	1	3	18	0.17573	0.17607	0	2	24	0.13305	0.13319
2	3	8	0.15250	0.15254	1	4	10	0.19100	0.19100	2	3	12	0.15150	0.15167
0	4	0	0.15696	0.15690	2	4	0	0.19658	0.19673	0	4	0	0.15764	0.15779
1	3	14	0.17458	0.17441						1	3	22	0.17721	0.17714
1	4	8	0.19174	0.19182						2	4	0	0.19706	0.19707
2	4	0	0.19620	0.19617										

			$Ba_7Fe_{13}S_{26}$					$Ba_{17}Fe_{32}S_{64}$					$Ba_{21}Fe_{38}S_{76}$	
			$\sin^2\theta$					$\sin^2\theta$					$\sin^2\theta$	
h	k	l	calc.	obs.	h	k	l	calc.	obs.	h	k	l	calc.	obs.
0	1	14	0.03290	0.03284	0	1	17	0.03251	0.03259	0	1	21	0.03385	0.03380
0	2	0	0.03954	0.03948	0	2	0	0.03966	0.03968	0	2	0	0.03930	0.03930
1	2	13	0.06927	0.06923	1	2	16	0.06960	0.06963	1	2	19	0.06865	0.06865
1	2	14	0.07244	0.07241	1	2	17	0.07218	0.07218	1	2	21	0.07298	0.07295
2	2	0	0.07908	0.07906	2	2	0	0.07932	0.07934	2	2	0	0.07861	0.07868
0	0	28	0.09208	0.09213	1	3	0	0.09915	0.09906	0	0	42	0.09540	0.09539
1	3	0	0.09885	0.09900	1	1	34	0.11023	0.11033	1	3	0	0.09826	0.09838
0	3	14	0.11198	0.11187	0	3	17	0.11184	0.11176	0	3	21	0.11228	0.11236
1	1	28	0.11185		0	2	32	0.11974	0.11991	1	1	42	0.11505	0.11508
0	2	26	0.11894	0.11889	2	3	17	0.15150	0.15148	0	2	38	0.11738	0.11726
0	2	28	0.13150	-	0	4	0	0.15864	0.15875	0	2	42	0.13470	0.13456
2	3	14	0.15152	0.15154	1	3	32	0.17923	0.17914	2	3	21	0.15159	0.15163
0	4	0	0.15818	0.15824	1	4	17	0.19116	0.19052	0	4	0	0.15721	0.15715
1	3	28	0.19093	0.19100	1	3	34	0.18955		2	2	42	0.17401	0.17390
1	4	14	0.19106		2	4	0	0.19830	0.19826	1	3	38	0.17634	0.17640
2	4	0	0.19770	0.19763						1	4	21	0.19090	0.19100
										2	4	0	0.19652	0.19680

about 680°C, decreasing the temperature is seen to decrease x and results in an approach towards the stoichiometric $BaFe_2S_4$ composition. However, below about 680°C further lowering of the reaction temperature reverses the above trend. This suggests that the sulphur pressure effect is dominant over the temperature effect at low temperatures. Considerably more detailed work with control of both sulphur pressure and of temperature would be required to obtain a full understanding of the thermodynamic properties of this complex region of the Ba–Fe–S system.

For the range of experimental conditions

TABLE III

CALCULATED LATTICE PARAMETERS[a] AND BOND LENGTHS[b] FOR SOME $Ba_{1+x}Fe_2S_4$ PHASES

x	Phase stoichiometry	a (Å)	c (Å)	Fe–Fe (Å)	Ba–Ba (Å)
0.143	$Ba_4Fe_7S_{14}$	7.783 (3)[c]	39.026 (18)	2.79	4.88
0.111	$Ba_5Fe_9S_{18}$	7.776 (3)	49.864 (20)	2.77	4.99
0.105	$Ba_{21}Fe_{38}S_{76}$	7.777 (3)	104.84 (6)	2.76	4.99
0.091	$Ba_6Fe_{11}S_{22}$	7.766 (3)	60.46 (3)	2.75	5.03
0.077	$Ba_7Fe_{13}S_{26}$	7.753 (3)	71.13 (3)	2.73	5.08
0.062	$Ba_{17}Fe_{32}S_{64}$	7.742 (3)	87.17 (4)	2.72	5.12

[a] Parameters calculated from least squares refinement of the data in Table II.

[b] Calculated on the basis that the Fe and Ba atoms pack uniformly along the c axis.

[c] The numbers in parentheses are standard deviations.

studied, the observed range in x for the $Ba_{1+x}Fe_2S_4$ phases was $0.062 \leqslant x \leqslant 0.143$ (Table I). Lattice parameters for a number of phases within this range were calculated from least squares refinement of the diffraction data. The results are listed in Table III. The tetragonal a axis shows a smooth expansion with increasing x in $Ba_{1+x}Fe_2S_4$, i.e., the increased density of packing of barium atoms along the c axis is reflected in an expanding of the atomic packing in the basal phase. Also listed in Table III are calculated ideal values of Ba–Ba and Fe–Fe distances, assuming that these atoms are uniformly spaced along the c axis, i.e., Ba–Ba $= c/p$, Fe–Fe $= c/2q$. With increasing deviations from the stoichiometric "$BaFe_2S_4$" composition, the Ba–Ba separation decreases and the Fe–Fe (and S–S) separation increases. Plots of the calculated Ba–Ba and Fe–Fe bond lengths vs compositional x were linear, and extrapolations to $x = 0$ gave Ba–Ba $= 5.30$ Å and Fe–Fe $= 2.67$ Å for the stoichiometric $BaFe_2S_4$.

Discussion

The results presented in the present paper are of an exploratory nature. A complete definition of this complex phase region requires a considerable amount of careful preparative work involving long annealing times at a large number of temperatures, coupled with detailed electron diffraction and X-ray diffraction studies. However, the preliminary results have established the general principles—that in the Ba–Fe–S system the composition range $Ba_{1.062}Fe_2S_4$–$Ba_{1.143}Fe_2S_4$ is spanned by a continuous series of ordered phases with superstructures related to the NH_4CuMoS_4 structure type. No intervening two-phase regions were observed, and the system thus constitutes an example of an infinitely adaptive system according to Anderson's definition (*1*). The compositions are very sensitively dependent on both temperature and pressure. Approach to the ideal $BaFe_2S_4$ stoichiometry is aided by both lowering the reaction temperature and by increasing the excess sulphur pressure. The results suggest that stoichiometric $BaFe_2S_4$, containing only ferric iron, may be synthesized hydrothermally.

One can formally balance the nonintegral oxidation state of iron in the barium excess compositions, $Ba_{1+x}Fe_2S_4$, by invoking mixtures of ferrous and ferric iron, e.g., $Ba_{1.143}Fe_2S_4 \equiv Ba_4Fe_7S_{14} \equiv Ba_4(Fe_6^{3+}Fe^{2+})S_{14}$ and $Ba_{1.059}Fe_2S_4 \equiv Ba_9Fe_{17}S_{34} \equiv Ba_9(Fe_{16}^{3+}Fe^{2+})S_{34}$, i.e., the ratio of ferrous to ferric iron increases with increasing x in $Ba_{1+x}Fe_2S_4$, corresponding to increasing temperature of preparation. However, in Mössbauer studies on some $Ba_{1+x}Fe_2S_4$ compounds it has not been possible to identify separate ferrous and ferric iron peaks. This is consistent with the Mössbauer results for numerous other iron–sulphur compounds and is most probably due to the distribution of electrons in a wide electronic conduction band formed by the broad overlap of the sulphur orbitals with the antibonding metal *d* orbitals.

The system $Ba_{1+x}Fe_2S_4$ presents an excellent model system for testing current theories which postulate that quenched high-temperature structures represent frozen "quantum states" of the periodic thermal vibrations of the atoms. For a series of $Ba_{1+x}Fe_2S_4$ compounds, prepared at the same sulphur pressure, the periodicity of packing of the barium atoms along *c* should only be a function of the temperature of preparation, to which the periodic thermal motion of the barium atoms is directly related. This structural series could be approximated as a one-dimensional system involving only the periodic ordering of chains of barium atoms with temperature.

Acknowledgment

The author expresses his gratitude to Dr. J. G. Allpress for the electron diffraction results.

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