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Antiferromagnetic Structure of Barium Strontium Tetraferrate(III), $BaSrFe_4O_8$

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Abstract

Neutron powder diffraction was used to determine the magnetic structure of $BaSrFe_4O_8$. Crystals of this compound are trigonal, $P\bar{3}1m$, with $a = 5{\cdot}4123$ (4), $c = 8{\cdot}0675$ (4) Å, $V = 204{\cdot}66$ (4) Å^3, $D_o = 4{\cdot}62$ (5), $D_c = 4{\cdot}67$ (2) Mg m^{-3} for $M_r = 576{\cdot}34$ and $Z = 1$. The magnetic structure is characterized by antiferromagnetic interactions between nearest-neighbour Fe^{3+} ions. The magnetic unit cell has the same periodicity as the crystallographic one, *i.e.* $\mathbf{k} = [0]$. The magnetic structure belongs to the irreducible representation Γ_1^g of the group $P\bar{3}1m$ with the magnetic moments parallel to the c axis of the crystallographic unit cell (A_z type). The Fe^{3+} magnetic moment in this compound is $4{\cdot}25 \pm 0{\cdot}1$ BM (1 BM $\equiv 9{\cdot}27 \times 10^{-24}$ JT^{-1}) at 293 K. The Néel temperature determined by neutron diffraction was found to be $T_N = 690 \pm 5$ K. Relationships between structural and magnetic properties are discussed.

Introduction

In the scope of a general study of the structural and magnetic properties of the compositions in the ternary system $BaO–SrO–Fe_2O_3$, we report here the neutron diffraction results obtained for $BaSrFe_4O_8$ which has a trigonal unit cell.

From a study of the phase-equilibrium diagram of $BaO–SrO–Fe_2O_3$ (Batti, 1962), it was concluded that a new stable compound with the composition $BaSrFe_4O_8$ may occur as a single phase above 1373 ± 10 K. It undergoes thermal transformation at about 1473 K and melts incongruently at 1513 ± 10 K. The crystal structure of this phase as determined by Meriani & Sloccari (1970) was shown to be orthorhombic, *Pnna*, $a = 5{\cdot}516$, $b = 8{\cdot}263$, $c = 9{\cdot}188$ Å and $Z = 2$.

Hexagonal $BaSrFe_4O_8$ was first reported by Kanamaru & Kiriyama (1964). An investigation by Lucchini, Minichelli & Meriani (1973) revealed that it exists in two allotropic forms: a high-temperature phase which has the previously mentioned orthorhombic structure, and the low-temperature phase, obtained at a temperature lower than 1453 K, having a hexagonal structure with $a = b = 5{\cdot}448$, $c = 8{\cdot}091$ Å; space group $P\bar{6}m2$ and $Z = 1$.

Table 1. *Reported crystallographic data for trigonal* $BaSrFe_4O_8$

Herrmann & Bacmann (1975), Cadée (1975)		Lucchini, Minichelli & Meriani (1973)	
Space group	$P\bar{3}1m$	Space group	$P\bar{6}m2$
Ba in 1(*a*)	000	Ba in 1(*a*)	000
Sr in 1(*b*)	$00\frac{1}{2}$	Sr in 1(*b*)	$00\frac{1}{2}$
Fe in 4(*h*)	$\frac{1}{3}\frac{2}{3}z$	Fe(1) in 2(*h*)	$\frac{1}{3}\frac{2}{3}z$
	$z^* = 0{\cdot}225$		$z = 0{\cdot}245$
O(1) in 2(*c*)	$\frac{1}{3}\frac{2}{3}0$	Fe(2) in 2(*i*)	$\frac{2}{3}\frac{1}{3}z$
O(2) in 6(*k*)	$x0z$		$z = 0{\cdot}255$
	$x^* = 0{\cdot}346$	O(1) in 1(*c*)	$\frac{1}{3}\frac{2}{3}0$
	$z^* = 0{\cdot}280$	O(2) in 1(*f*)	$\frac{2}{3}\frac{1}{3}\frac{1}{2}$
		O(3) in 6(*n*)	xyz
			$x = 0{\cdot}515$
			$y = 0{\cdot}485$
			$z = 0{\cdot}260$

* Values obtained by neutron diffraction (Herrmann & Bacmann, 1975).

The crystal structure of hexagonal $BaSrFe_4O_8$ was redetermined by Herrmann & Bacmann (1975) and be Cadée (1975). It was found that the compound crystallizes in the trigonal space group $P\bar{3}1m$, with $a = 5{\cdot}450$ (2), $c = 8{\cdot}101$ (3) Å and $Z = 1$. These results are in disagreement with the results of Lucchini *et al.* (1973) (Table 1).

We have studied $BaSrFe_4O_8$ by neutron diffraction to confirm the space group and determine the O parameters and the z parameter of the Fe atoms, needed for the determination of the magnetic structure which is the principal aim of this study.

Experimental

The sample of $BaSrFe_4O_8$ used for neutron diffraction was prepared using the ceramic sintering method. A stoichiometric powder mixture of $BaCO_3$, $SrCO_3$ and Fe_2O_3 was fired at 1173 K for 24 h. The resultant powder was pressed into pellets and heated again at 1373 K for 24 h, then left to cool slowly. X-ray diffraction measurements showed the sample with the required phase.

For the neutron diffraction measurements the material was contained in an aluminium furnace. The diagrams were taken at the ET-RR-1 research reactor

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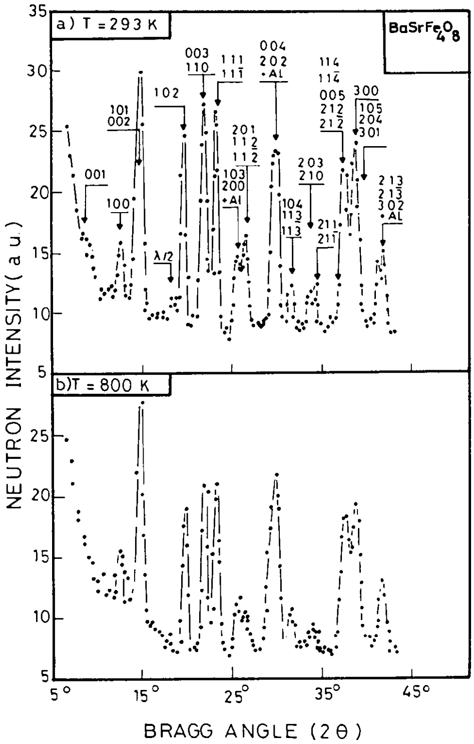

Fig. 1. Neutron diffraction patterns of $BaSrFe_4O_8$ at 800 and 293 K.

in Cairo on the powder diffractometer in steps of 10′ in 2θ with a neutron wavelength of 1·02 Å. The neutron diffraction patterns which were measured at 293 and 800 K are shown in Fig. 1.*

Neutron diffraction results

(*a*) *Crystal structure refinement*

Using the neutron diffraction data collected at 800 K we began by reinvestigating the crystal structure of the compound $BaSrFe_4O_8$ in an effort to clarify the discrepancy in the previous reports (see Table 1). Least-squares calculations were performed with a computer program which uses the total integrated intensities of individual peaks or groups of overlapping peaks.

Table 2. *Crystallographic parameters of* $BaSrFe_4O_8$ *obtained from the present neutron diffraction study*

The temperature factors were constrained to be isotropic. Standard deviations are in parentheses.

Ba sites 1(*a*)	000	$B = 0{\cdot}6\ (1)\ \text{Å}^2$
Sr sites 1(*b*)	$00\frac{1}{2}$	$B = 0{\cdot}5\ (1)$
Fe sites 4(*h*)	$\frac{1}{3}\frac{2}{3}z,\ z = 0{\cdot}224\ (2)$	$B = 0{\cdot}8\ (1)$
O(1) sites 2(*c*)	$\frac{1}{3}\frac{2}{3}0$	$B = 0{\cdot}3\ (1)$
O(2) sites 6(*k*)	$x0z,\ x = 0{\cdot}346\ (2),$ $z = 0{\cdot}297\ (2)$	$B = 0{\cdot}6\ (1)$

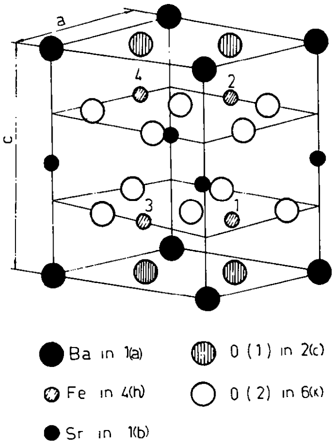

Fig. 2. The crystal structure of $BaSrFe_4O_8$.

The Fermi lengths used were (Bacon, 1972): Ba 5·2, Sr 6·9, Fe 9·6 and O 5·803 fm. It was realized that the nuclear intensities were not in accordance with space group $P\bar{6}m2$ given by Lucchini *et al.* (1973). The calculations in space group $P\bar{3}1m$ with 16 powder peaks containing 35 reflections gave a reliability factor $R = 0{\cdot}02$ where $R = \sum |I_o - I_c| / \sum I_o$. The final parameters are listed in Table 2.

Fig. 2 represents the structure of $BaSrFe_4O_8$. In this structure the Ba^{2+} ions are surrounded by 12 oxygen ions: six O(2) ions with interatomic distances Ba—O(2) = 3·041 (14) Å and six O(1) ions with distance Ba—O(1) = 3·124 (8) Å. The Sr^{2+} ions are surrounded by six oxygen ions O(2) forming an octahedron, with interatomic distance Sr—O(2) = 2·487 (13) Å. The Fe^{3+} ions are situated in tetrahedra of O^{2-} ions. These tetrahedra are arranged in parallel layers with every two tetrahedra sharing an O atom as a common corner. All the tetrahedra are similar and nearly ideal. Three distances Fe—O(2) are equal and have the value 1·866 (9) Å and the fourth distance, Fe—O(1) 1·807 (16) Å, is slightly shorter. The other meaningful interatomic distances as obtained from the parameters of Table 2 are: O(2)—O(2) = 3·067 (13), O(1)—O(1) = 3·124 (10), O(1)—O(2) = 2·979 (13), Ba–Sr = 4·038 (7), Fe–Fe = 3·124 (8), Ba–Fe = 3·609 (8), Sr–Fe = 3·836 (9) Å.

(*b*) *Magnetic structure*

The neutron diffraction pattern obtained at 293 K (Fig. 1) shows an enhancement of some of the nuclear intensities and does not show any new peaks resulting from the magnetic ordering. Thus, the magnetic unit

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* The numerical data corresponding to Fig. 1 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38111 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cell is identical to the crystallographic unit cell and the magnetic order is described by a propagation vector $\mathbf{k} = [0]$. The possible configurations and directions of the magnetic moments are strictly prescribed by symmetry; they must belong to one of the irreducible representations of the symmetry group of the paramagnetic phase (Landau & Lifshitz, 1969). In $BaSrFe_4O_8$ the space group is $P\bar{3}1m$ (D^1_{3d}). The propagation vector $\mathbf{k} = [0]$ is a point located at the origin of the Brillouin zone, and at this point the space group D^1_{3d} has four one-dimensional representations and two two-dimensional representations. The representation theory developed by Bertaut (1963, 1968) permits us to determine the possible configurations of the spin magnetic moment (**m**). Denoting the Fe^{3+} ions in the nuclear unit cell as:

$$\mathbf{m}_1 \text{ in } (\tfrac{1}{3}\tfrac{2}{3}z) \quad \mathbf{m}_2 \text{ in } (\tfrac{1}{3}\tfrac{2}{3}\bar{z})$$

$$\mathbf{m}_3 \text{ in } (\tfrac{2}{3}\tfrac{1}{3}z) \quad \mathbf{m}_4 \text{ in } (\tfrac{2}{3}\tfrac{1}{3}\bar{z})$$

there are four possible linear configurations:

$$\mathbf{F} = \mathbf{m}_1 + \mathbf{m}_2 + \mathbf{m}_3 + \mathbf{m}_4$$

$$\mathbf{A} = \mathbf{m}_1 - \mathbf{m}_2 - \mathbf{m}_3 + \mathbf{m}_4$$

$$\mathbf{C} = \mathbf{m}_1 + \mathbf{m}_2 - \mathbf{m}_3 - \mathbf{m}_4$$

$$\mathbf{G} = \mathbf{m}_1 - \mathbf{m}_2 + \mathbf{m}_3 - \mathbf{m}_4.$$

Investigation of the base vectors in the irreducible representations of the $P\bar{3}1m$ space group gives the modes reported in Table 3. In this table we notice that the magnetic modes along the *c* axis belong to the one-dimensional representations. The configuration **F** refers to ferromagnetic ordering which must be discarded on the grounds of other physical measurements. The absence of extra reflections in the neutron diffraction diagram eliminates the possibility of a complex-moment arrangement (Γ^g_3, Γ^u_3) and leaves only collinear antiferromagnetic modes. The systematic absence of the magnetic reflections of indices like *h*00 implies the absence of type **F** and **C** configurations. Also the configuration **G** can be ruled out owing to the absence of magnetic peaks of indices like *hhl*. The best fit to the neutron diffraction data corresponds, effectively, to an antiferromagnetic structure of A_z type, *i.e.* with the moment direction along the *c* axis and a moment value of 4·25 ± 0·2 BM for the Fe^{3+} ions at 293 K. The calculated intensities together with the observed magnetic intensities are given in Table 4. From the temperature dependence of the magnetic intensity of the reflection 101 it was possible to estimate the Néel temperature as $T_N = 690 \pm 5$ K.

The magnetic structure of $BaSrFe_4O_8$ is given in Fig. 3.

Table 3. *Irreducible representations of group* $P\bar{3}1m$ *and their associated magnetic modes for* $\mathbf{k} = [0]$

$\omega = \exp(2\pi i/3)$, $\omega^* = \exp(-2\pi i/3)$.

Γ_u	e	3	$2x$	$\bar{1}$	$4(h)$
Γ^g_1	1	1	1	1	A_z
Γ^g_2	1	1	$\bar{1}$	1	F_z
Γ^g_3	1 0	ω 0	0 1	1 0	$F_x F_y$
	0 1	0 ω^*	1 0	0 1	$A_x A_y$
Γ^u_1	1	1	1	$\bar{1}$	G_z
Γ^u_2	1	1	$\bar{1}$	$\bar{1}$	C_z
Γ^u_3	1 0	ω 0	0 1	$\bar{1}$ 0	$C_x C_y$
	0 1	0 ω^*	1 0	0 $\bar{1}$	$G_x G_y$

Table 4. *Comparison of calculated and observed magnetic intensities at* 293 K *for* $BaSrFe_4O_8$ (barns/*unit cell*; 1 barn ≡ 10^2 fm^2)

$h\,k\,l$	I_o	I_c*	
1 0 1	106·84	108·18	
1 0 2	4·48	5·32	
1 0 3	95·72	17·13	93·70
2 0 1		76·51	
2 0 2	6·02	5·26	
1 0 4	3·34	3·36	
2 0 3	110·66	23·22	110·76
2 1 1		43·77	
2 1 $\bar{1}$		43·77	
2 1 2	7·06	3·77	7·54
2 1 $\bar{2}$		3·77	

$R = \sum |I_o - I_c| / \sum I_o = 1{\cdot}7\%.$

* The form factor for Fe^{3+} ions is that given by Brockhouse, Corliss & Hasting (1955).

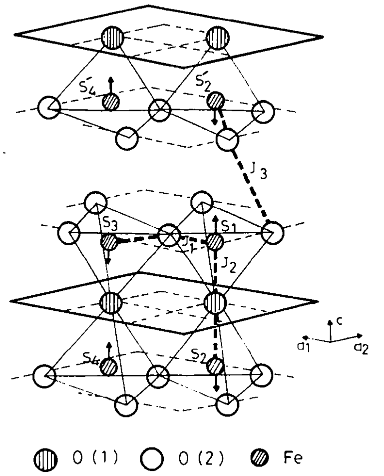

Fig. 3. The magnetic structure of $BaSrFe_4O_8$ at 293 K. Ba and Sr atoms are not shown.

Discussion and conclusion

The present neutron diffraction experiments confirm the space group of $BaSrFe_4O_8$ as $P\bar{3}1m$. The derived crystallographic parameters are very close to those reported earlier. The Fe^{3+} ions occupy one crystallographic site (4*h*), consistent with Mössbauer-effect measurements which give rise to simple six-line spectra at room temperature (Ravi & Jagannathan, 1980). The antiferromagnetic structure obtained at room temperature is characterized by an A_z-type configuration. This configuration can be explained by the negative exchange interactions, J_1 and J_2 (see Fig. 3), between the Fe atoms situated in two corner-sharing tetrahedra. The periodicity of the magnetic unit cell, *i.e.* the propagation vector $\mathbf{k}$, is determined by J_3 which is a superexchange interaction. This interaction is also negative as $\mathbf{k} = [0]$.

The results of neutron diffraction are in agreement with those of the Mössbauer effect. Both methods show that the magnetic moments of the Fe^{3+} ions are directed along the c axis of the unit cell, with a Néel temperature of about 690 K. This temperature is considerably lower than the 760 K obtained by Herrmann & Bacmann (1975). Cadée (1975) reported that his magnetic measurements carried out with a Faraday balance showed a Néel temperature higher than 1000 K. This unusually high value is inconsistent with our measurement of the disappearance of the magnetic contribution by neutron diffraction.

At room temperature the magnetic moment for the Fe^{3+} ion, 4·25 BM, is reduced by about 10% from the expected value for free Fe^{3+} (5 BM). This difference is probably due to the strong covalent character of the Fe^{3+}—O bond; but it seems that measurements of the electronic conductivity may confirm this.

The compound $BaSrFe_4O_8$ is isostructural with $BaCaFe_4O_8$ (Herrmann & Bacmann, 1971). The magnetic structures of the two compounds are very similar (Abbas, Mostafa & Fayek, 1982). From a structural point of view the substitution of strontium by calcium with smaller ionic radius may be expected to result in a decrease in the c value leaving the a value unchanged. The distance between the Fe^{3+} ions decreases, and this means that the magnetic interactions are stronger in the case of the Ca compound. Detailed data on the magnetic structure of $BaCaFe_4O_8$ are given elsewhere (Abbas *et al.*, 1982).

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On the Topotactic Dehydration $Ca_3(AsO_4)_2.11H_2O$ (Phaunouxite) → $Ca_3(AsO_4)_2.10H_2O$ (Rauenthalite), and the Structures of Both Minerals

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Abstract

Single crystals of the new mineral phaunouxite, $Ca_3(AsO_4)_2.11H_2O$ [a = 12·563 (7), b = 12·181 (6), c = 6·205 (4) Å, α = 88·94 (3), β = 91·67 (3), γ = 113·44 (4)°, V = 870·77 Å^3, M_r = 596·241, D_c = 2·274, D_m = 2·28 Mg m^{-3}, $F(000)$ = 600, μ(Mo $K\alpha$) = 4·8 mm^{-1}], form oriented intergrowths with rauenthalite, $Ca_3(AsO_4)_2.10H_2O$ [a = 12·564 (8), b = 12·169 (7), c = 6·195 (4) Å, α = 89·09 (3), β = 79·69 (3), γ = 118·58 (4)°, V = 812·65 Å^3, M_r = 578·226, D_c = 2·362, D_m = 2·36 Mg m^{-3}, $F(000)$ = 580, μ(Mo $K\alpha$) = 5·1 mm^{-1}], and dehydrate completely to that phase in dry air. The crystal structures of both minerals (space group $P\bar{1}$, Z = 2) were solved and least-squares-refined to R = 0·054 and 0·062, using 2715 and 1003 observed counter reflexions, respectively (Mo $K\alpha$ radiation). Isostructural (100) layers of

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