La projection de l'empilement moléculaire sur le plan (xOz) est représentée sur la Fig. 4. Les chiffres romains (I à VII) inscrits dans les cycles benzéniques permettent de repérer les molécules correspondantes. La partie supérieure des molécules est dessinée en traits épais et la partie inférieure en traits fins.

L'empilement moléculaire, dans la structure de l'acétyl-I' benzoylferrocène, est déterminé par les forces de van der Waals provenant surtout des contacts C···C, C···H et H···H (Tableau 5). Le nombre important de courtes distances entre les atomes de la molécule I et ceux des molécules II, VI, IV, XI, XIV et surtout VII est assez remarquable, d'autant que certaines de ces distances (notées par un astérisque dans le Tableau 5) sont inférieures à la somme des rayons de van der Waals. Ceci dénote un empilement moléculaire extrêmement compact. Les contacts intermoléculaires les plus nombreux et les plus forts se font par l'intermédiaire des cycles benzéniques (*cf.* contacts entre les molécules I et VII; entre I et IV).

En comparant les Fig. 3(a) et 4, nous constatons que le fait d'amener le centre de gravité G(I) en coïncidence avec le centre de l'atome de fer entraîne le rapprochement des cycles benzéniques I et VII, I et XIV, II et IV *etc*.... Ceci conduit à penser que la torsion du noyau ferrocénique et, en particulier, le décalage des cycles pentadiéniques, est bien provoqué par les interactions intermoléculaires consécutives à le tendance des molécules organiques à s'empiler selon un assemblage le plus compact possible (Kitaigorodskii, 1961).

Nous tenons à remercier Monsieur le Professeur R. Dabard (Laboratoire de Chimie Organique E, Faculté des Sciences de Rennes) qui nous a suggéré cette étude et a préparé les cristaux d'acétyl-I' benzoylferrocène. Tous les calculs ont été réalisés au Centre de Calcul du C.N.R.S. à Paris à l'aide de programmes mis à notre disposition par Madame C. Pascard (Maître de Recherche au C.N.R.S., Gif-sur-Yvette) à qui nous exprimons notre vive reconnaissance.

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The Crystal Structure of Barium Monoferrite, $BaFe_2O_4$

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Single-crystal diffraction patterns of 'hexagonal barium monoferrite', $BaFe_2O_4$ have revealed that the crystals consist of twin components and the symmetry of the component crystal is orthorhombic. The unit cell contaning eight formula units has the dimensions: $a=19{\cdot}05$, $b=5{\cdot}390$ and $c=8{\cdot}448$ Å. The space group is $Bb2_1m$. Parametric relations were found between the unit cell above mentioned and the hexagonal lattice reported for barium monoaluminate, but the structure of $BaFe_2O_4$ cannot simply be regarded as a superstructure of $BaAl_2O_4$, except for the positions of the barium atoms. The key to the structure was obtained from characteristics of reflexions and the P_O function. Each iron atom is surrounded tetrahedrally by four oxygen atoms, while there are two kinds of barium atoms, one surrounded by seven and the other by eleven oxygen atoms. The arrangement of the atoms is not a close packed one.

Introduction

Most of the ferrites, $M^{2+}Fe_2^{3+}O_4^{2-}$, crystallize in the spinel structure which is characterized by the small size of the divalent metallic ions. These together with the ferric ions occupy the interstices in the close-packed framework formed by the oxygen ions. This will not be the case if the size of the divalent ions increases. For instance, calcium monoferrite assumes a different structure from that of spinel (Hill, Peiser & Rait, 1956; Decker & Kasper, 1957), in which the calcium ions tend to be eight- or ninefold coordinated and the iron ions are octahedrally surrounded by oxygen atoms. Several authors reported the crystal structure of strontium monoferrite (Hill, Peiser & Rait, 1956; Kanamaru & Kiriyama, 1964). Though the structure does not seem to be established, it is evident that it is different from the spinel structure.

The phase equilibrium of the two component system, $BaO–Fe_2O_3$, was extensively studied by Okazaki, Kubota & Mori (1955). They found barium monoferrite, $BaFe_2O_4$, as a distinct compound which was confirmed by several workers (Inoue & Iida, 1958; Lotgering, 1959; Goto & Takada, 1960). Okazaki, Mori & Kanamaru (1961) succeeded in preparing 'single crystals' of barium monoferrite and reported they are antiferromagnetic and the crystal structure is based on a unit cell having the dimensions $a=5{\cdot}51n$ and $c=8{\cdot}44$ Å, of approximately hexagonal symmetry. Glasser & Glasser (1963) reported from a powder diffraction study that it has the barium monoaluminate, $BaAl_2O_4$, structure.

Okazaki, Mori & Mitsuda (1963) showed that single crystals of barium monoferrite grown from melt were in fact twinned crystals consisting of three components (trilling), the c axis being the axis of twinning. They further found that the true symmetry of the crystal is orthorhombic and the unit cell has the dimensions $a_0=19{\cdot}05$, $b_0=5{\cdot}390$ and $c_0=8{\cdot}448$ Å. Kanamaru & Kiriyama (1964) and Do Dinh & Bertaut (1965) reported that they had found a phase having the same type of lattice as that of barium monoferrite in the solid solution represented by $BaFe_xAl_{2-x}O_4$ in the range $x>1{\cdot}8$.

Recently, Arlett, White & Robbins (1967) and Perrotta & Smith (1968) reported that barium monoaluminate assumes a superstructure (a doubling of the hexagonal a axis), though the crystal structure was not given.

In this paper, the results of an X-ray investigation on the mode of twinning and the crystal structure of artificially prepared crystals of barium monoferrite will be given. The structural relation between barium monoferrite and barium monoaluminate will also be discussed.

Experimental

Barium monoferrite was prepared by heating a mixture of barium carbonate and ferric oxide. The raw materials, in the stoichiometric ratio were intimately mixed and ground in a ball mill. After drying, they were made into pellets, which were fired at 1300°C for 4 hours.

Single crystals were prepared by the Bridgman method. Barium monoferrite prepared in the above mentioned way was put in a conical platinum crucible and was melted and kept at about 1470°C for 2 hours in an oxygen atmosphere, followed by cooling slowly at a rate of 5 to 10°C per hour. This treatment yielded a lump of small crystals, which was confirmed to be barium monoferrite, $BaFe_2O_4$, by a chemical analysis.

The crystals are dark brown in colour and have a cleavage. It is difficult to cut out the crystal of suitable size for X-ray analysis because of brittleness. Therefore an effort was made to select suitable crystals by means of the Laue method. As has been reported earlier (Okazaki, Mori & Mitsuda, 1963), these crystals were found to be twinned. The crystal used for the X-ray work has approximate dimensions, $0{\cdot}2\times0{\cdot}5\times0{\cdot}1$ mm, the longest direction being along the b axis.

Oscillation photographs taken with the axis perpendicular to the cleavage plane as axis of rotation gave an identity period of 8·45 Å, which we shall call the c axis. A series of Weissenberg photographs about the same axis were taken with the Fe-filtered Co $K\alpha$ and Ni-filtered Cu $K\alpha$ radiations. The photographs of the even layer lines showed a splitting of the reflexions into two or three. There appeared a group of fairly strong reflexions – which we shall call main reflexions – and another group of rather faint reflexions as shown in Fig. 1(a).

If one ignores the splitting and considers only the main reflexions, these photographs could be interpreted by a hexagonal unit cell similar to that reported for barium monoaluminate (Wallmark & Westgren, 1937). The splitting of these reflexions indicates that the fragment is a twinned crystal consisting of three individuals with the c axis in common and mutually oriented at 120°, and the symmetry of each individual is not hexagonal but orthorhombic.

The faint reflexions are found to be satisfactorily indexed with the same orthorhombic unit cell. These correspond to the missing reflexions for the orthohexagonal lattice. A composite reciprocal lattice representation is given in Fig. 2(a).

Weissenberg photographs of the odd layer lines showed a peculiar pattern. An example of the photograph, $l=5$, is shown in Fig. 1(b). There can be seen grouping of reflexions, some in a form of a hexagon. It is found that these reflexions also lie on a composite reciprocal lattice layer if the length of a is doubled, as shown in Fig. 2(b).

These conclusions were confirmed by analysis of the powder diffraction patterns. Powder patterns were taken by an automatic recording diffractometer using Cu $K\alpha$, Fe $K\alpha$ and Co $K\alpha$ radiations, and also by a Guinier focusing camera with monochromatized Cu $K\alpha$ radiation. Strong reflexions corresponding to the main reflexions except $00l$ are split because of the deviation from hexagonal symmetry. The other reflexions observed are accounted for as the super-lattice lines of the pseudo-hexagonal sub-unit cell obtained by the main reflexions. All the reflexions were satisfactorily indexed based on the orthorhombic unit cell, $a_0=19{\cdot}05\pm0{\cdot}01$, $b_0=5{\cdot}390\pm0{\cdot}004$, $c_0=8{\cdot}448\pm0{\cdot}006$ Å, which can be taken as a superstructure of the pseudo-hexagonal unit cell $a_s=b_s=5{\cdot}473$, $c_s=8{\cdot}448$ Å, $\gamma_s=$

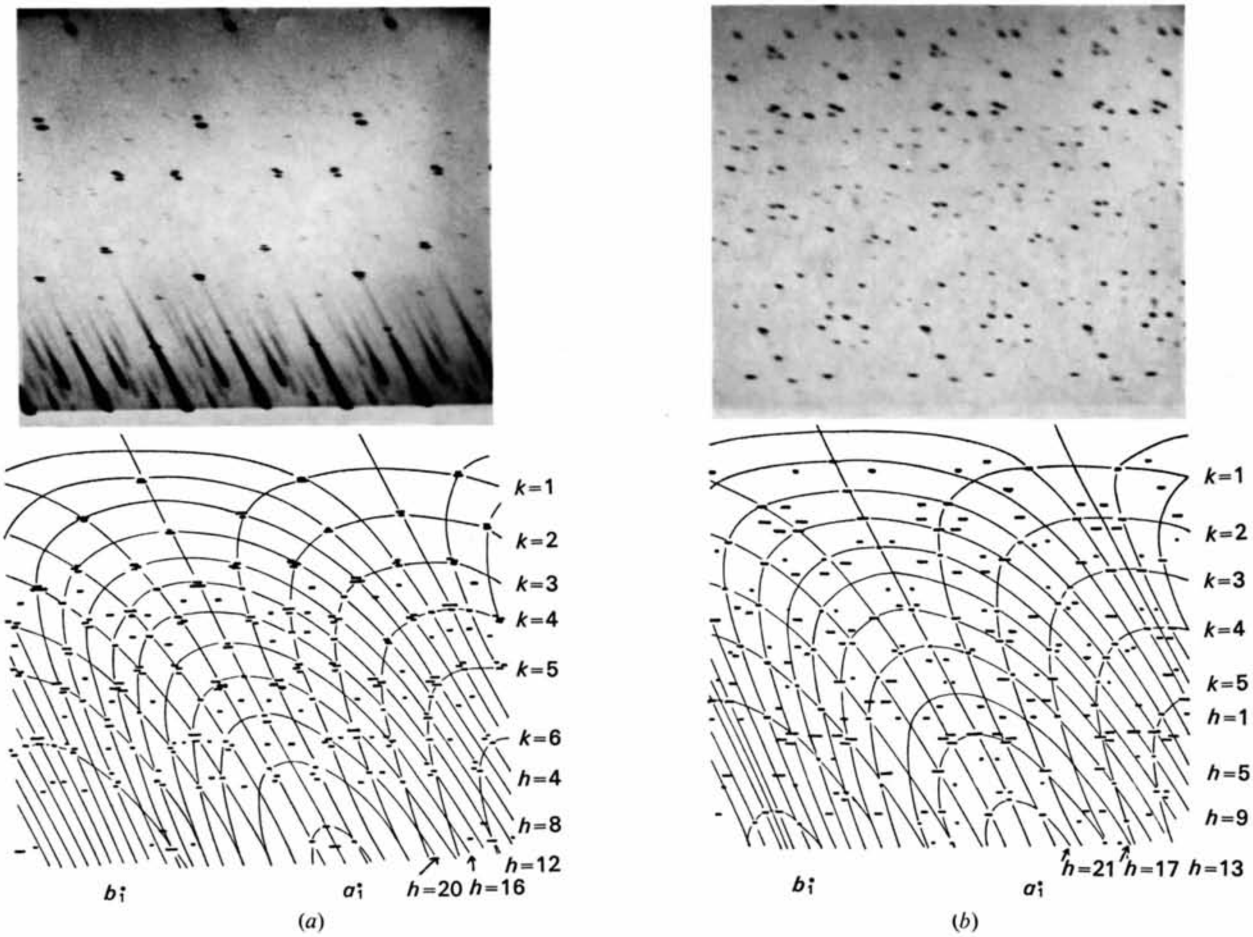

Fig. 1. Weissenberg photographs taken around the *c* axis. (*a*) Zero layer. (*b*) 5th layer.

121°. The following relations exist between the orthorhombic cell and the pseudo-hexagonal sub-unit cell, $a_0=2(a_s-b_s)$, $b_0=a_s+b_s$, $c_0=c_s$. The crystal under examination is found to be a single phase, and the possibility of segregation into two or more phases is definitely ruled out. Miller indices, observed and calculated interplanar spacings and relative intensities are given in Table 1 for the powder pattern. The orthorhombic cell contains eight chemical units of $BaFe_2O_4$. The calculated density, 4·79 g.cm^{-3}, agrees satisfactorily with the observed value, 4·70 g.cm^{-3}.

Systematic absences are hkl with $h+l$ odd and $0kl$ with k odd, and the corresponding space groups are $Bb2_1m$, $Bbm2$, $Bbmm$. For intensity data the $h0l$, $h1l$, $h2l$, $hk3$, $hk5$ reflexions were recorded on multiple film Weissenberg photographs using Fe-filtered Co $K\alpha$ and Ni-filtered Cu $K\alpha$ radiation. The intensities were estimated by visual comparison with the time exposure calibrated strips and were corrected for Lorentz and polarization factors in the usual way. The linear absorption coefficients were calculated to be $\mu=1230$, 1080 cm^{-1} for Cu $K\alpha$, Co $K\alpha$ radiation, respectively. Using these coefficients, an absorption correction was made by assuming cylindrical shape of the sample. An absolute intensity scale factor and an overall isotropic temperature factor ($B=2·0$ Å^2) were obtained by the method of Wilson (1942).

Determination of the structure

The main reflexions are characterized by h, l and $h/2+k$ all even. They could be indexed based on a pseudo-hexagonal unit cell derivable from the barium monoaluminate structure. The reflexions with h, l odd

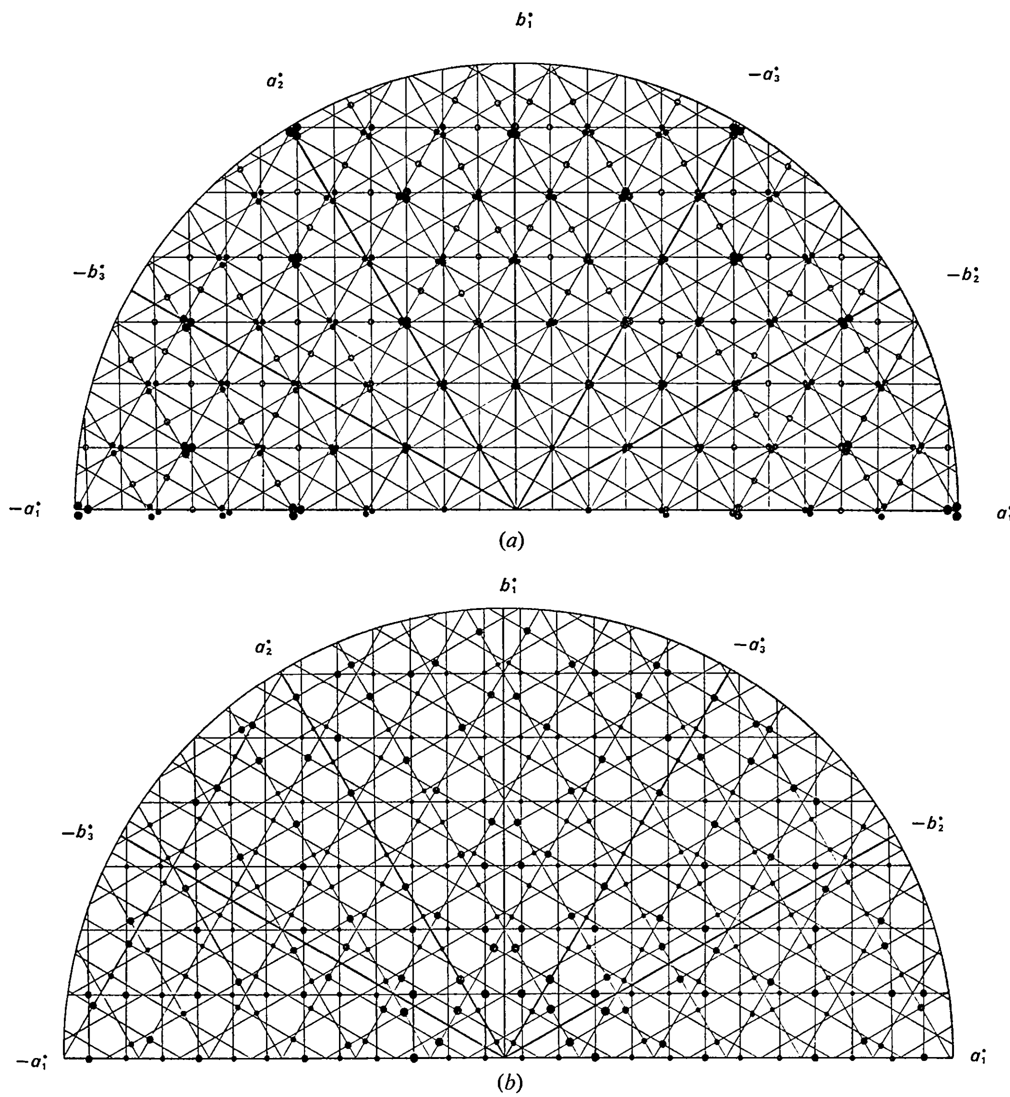

Fig. 2. Sections of twinned reciprocal lattice deduced from Weissenberg photographs. Three orientations required to index all reflexions. (a) Zero layer; open circles indicate the faint reflections. Reciprocal lattices are drawn only with h even. (b) 3rd layer; reciprocal lattices are drawn only with h odd.

– which we shall designate as 'odd reflexions' – appear on the powder patterns as super-lattice lines of the pseudo-hexagonal unit cell mentioned above. Because of the twinning, these 'odd reflexions' appear as satellites on oscillation photographs rotated about the *a* and *b* axis, and as spots arrayed in deformed hexagons on Weissenberg photographs rotated about the *c* axis. The reflexions with *h*, *l* even and $h/2+k$ odd are very weak or absent.

Since the pseudo-hexagonal sub-unit cell has nearly the same dimensions as those of barium monoaluminate, it was first assumed that the positions of the heavy atoms might be close to those of the barium and aluminum atoms in the barium monoaluminate structure. It was possible to assign positions for the eight barium atoms and sixteen iron atoms corresponding to the arrangement derivable from the barium monoaluminate structure from any of the three space groups $Bb2_1m$, $Bbm2$ and $Bbmm$. They are $0,0,0;\ \frac{1}{2},0,\frac{1}{2}+$

$$8\text{Ba}:\ \tfrac{1}{8},\tfrac{1}{4},0;\ \tfrac{3}{8},\tfrac{3}{4},0;\ \tfrac{5}{8},\tfrac{1}{4},0;\ \tfrac{7}{8},\tfrac{3}{4},0$$

$$16\text{Fe}:\ \tfrac{1}{24},\tfrac{3}{4},\pm\tfrac{1}{4};\ \tfrac{5}{24},\tfrac{3}{4},\pm\tfrac{1}{4};\ \tfrac{7}{24},\tfrac{1}{4},\pm\tfrac{1}{4};\ \tfrac{11}{24},\tfrac{1}{4},\pm\tfrac{1}{4}.$$

The calculated structure factors roughly agree with the observed ones for the main reflexions. However, this arrangement of atoms does not give any contribution to the 'odd reflexions'.

It was found that the 'odd reflexions' had maximum intensities with indices $h=6n+1$, when $l=4m+1$ and $h=6n+5$, when $l=4m+3$, where $n=0, 1, 2, 3$; $m=0, 1, 2$. Furthermore, it was found that the distributions of the intensities of these reflexions appearing on the Weissenberg photographs rotated about the *b* axis were almost the same for different *k*. Therefore, the intensities of the 'odd reflexions' can be represented by

$$I_{\text{obs}}\,(h,k,l\ \text{odd}) \propto \cos^2\left(\frac{\pi h}{6}+(-1)^{(l+1)/2}\cdot\frac{\pi}{6}\right).$$

It has been demonstrated that the P_E function, a Pat-

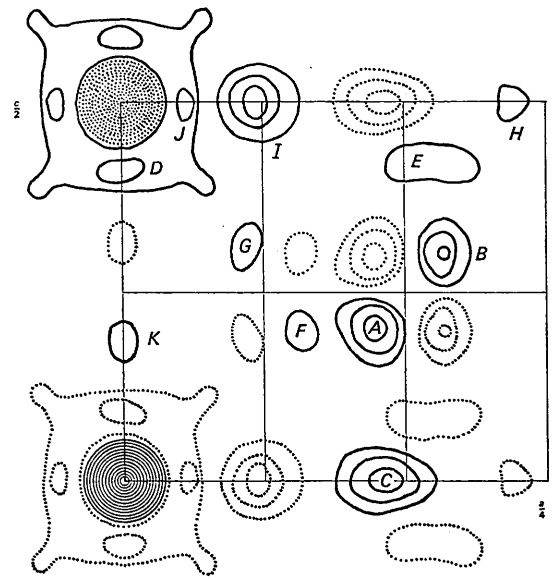

Fig. 3. Odd Patterson function projected on (010). Negative contours are dotted. *A*: Ba(I)–Fe(II), Ba(II)–Fe(I), Fe(I)–O(V), Fe(II)–O(IV). *B*: Ba(I)–Fe(I), Ba(II)–Fe(II), –Fe(I)–O(V), –Fe(II)–O(IV). *C*: Fe(I)–Fe(II), Ba(I)–O(V), Ba(II)–O(IV). *D*: Fe(I)–Fe(I), Fe(II)–Fe(II). *E*: Fe(I)–Fe(II). *F*: Ba(II)–Fe(II), –Ba(II)–Fe(I), Fe(I)–O(IV), –Fe(II)–O(V). *G*: Ba(I)–Fe(II), –Ba(I)–Fe(I). *H*: Ba(I)–Ba(II), Ba(I)–Ba(I), –Ba(II)–Ba(II). *I*: Fe(II)–Fe(II), –Fe(I)–Fe(I), Fe(I)–O(I), Fe(II)–O(III), Fe(I)–O(II), Fe(II)–O(II). *J*: Ba(I)–Ba(II). *K*: Fe(I)–O(IV), Fe(II)–O(V).

Table 1. *Powder pattern of* $BaFe_2O_4$

A Guinier focusing camera with monochromatized Cu $K\alpha$ radiation $\lambda=1{\cdot}5405$ Å was used.

(*hkl*)	d_{obs}	d_{cal}	*I*	(*hkl*)	d_{obs}	d_{cal}	*I*
101	7·728	7·729	W	721	1·866	1·868	W
400	4·766	4·762	MW	10,10	1·792	1·796	WWW
210	4·691	4·691	M	820	1·779	1·785	WWW
111	4·425	4·423	MW	230	1·760	1·767	WWW
402	3·155	3·160	SS	105	1·682	1·683	WWW
212	3·134	3·140	SSS	614	1·671	1·672	MS
610	2·736	2·736	SS	024	1·661	1·662	MW
020	2·688	2·695	S	10,12	1·652	1·653	M
701	2·589	2·590	W	822	1·642	1·644	M
121	2·547	2·545	W	232	1·626	1·629	MS
113	2·473	2·474	W	115	1·607	1·607	WW
800	2·378	2·381	WWW	12,00	1·587	1·587	M
420	2·342	2·346	W	630	1·562	1·564	MS
711	2·336	2·336	W	12,20	1·367	1·368	M
612	2·296	2·296	M	040	1·348	1·348	MW
022	2·268	2·272	W	12,04	1·267	1·269	MW
004	2·111	2·112	M	634	1·255	1·257	M
513	2·088	2·088	WW	14,12		1·259	
802	2·074	2·074	M	10,32	1·246	1·250	MW
422	2·047	2·050	MS	442	1·237	1·239	MW
404	1·926	1·930	M				
214		1·926					

terson function synthesized using even terms alone will give the interatomic vectors arising from the averaged structure, while the P_O function, synthesized from odd terms, will give the vectors from the displaced structure (Sakurai, 1958; Qurashi, 1963). A three dimensional $P_O(u,v,w)$ function was synthesized. It showed up antisymmetric planes at $u=\frac{1}{4}$ and at $w=\frac{1}{4}$ as shown in Fig. 3.

Since displacements of heavy atoms from the averaged structure (sub-unit structure) should appear at $v=0$ and $\frac{1}{2}$, the other antisymmetric pairs which appear at $v=\frac{1}{3}$, $\frac{1}{6}$ must arise from the interactions between heavy atoms and oxygen atoms. As the approximate parameters of the heavy atoms are known, it is possible to assign those for the oxygen atoms. Now that the lattice translation along the b axis is 5·390 Å, the interatomic distances between the oxygen atoms would be too close if we admit the space groups *Bbmm* and *Bbm*2, because both of these two space groups have mirror planes perpendicular to the b axis. On the other hand, the space group $Bb2_1m$ has no mirror planes perpendicular to the b axis, and it allows the oxygen atoms to take any values for y. Moreover, a Patterson projection onto (001) synthesized using reflexions with $h/2+k$ odd alone definitely indicated atomic shifts along the b direction. Accordingly, the proper space group for barium monoferrite is determined to be $Bb2_1m$, which contains the following equivalent positions: $0,0,0;\ \frac{1}{2},0,\frac{1}{2}+8\ (b)$: $x,y,z;\ x,y,\bar{z};\ \bar{x},\frac{1}{2}+y,z;\ \bar{x},\frac{1}{2}+y,\bar{z}$,4 (a): $x,y,0;\ \bar{x},\frac{1}{2}+y,0$.

The peaks A and B near $\frac{1}{6},0,\frac{1}{4}$ in the P_O function were taken to be the antisymmetric pairs due to the displacements of barium and iron atoms from the averaged structure. The peak C at $\frac{1}{6},0,0$ was taken as arising from interactions between iron atoms. Coordinates of barium and iron atoms can, therefore, be taken as follows:

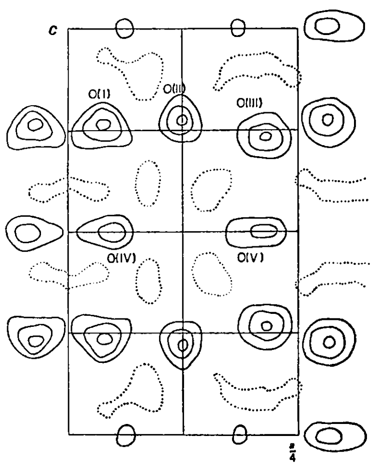

Fig. 4. Residual electron density projection on (010), showing oxygen atoms. The contributions of the barium and iron atoms have been subtracted. Contours are at intervals of 5 e.Å^{-2}, starting at 7 e.Å^{-2}. Negative contour is dotted.

$$8\text{Ba}:\ \tfrac{1}{8}+\Delta x_1,\tfrac{1}{4},0;\ \tfrac{3}{8}+\Delta x_2,\tfrac{3}{4},0 \text{ in } 4(a),$$
$$16\text{Fe}:\ \tfrac{1}{24},\tfrac{3}{4},\tfrac{1}{4}+\Delta z_1;\ \tfrac{5}{24},\tfrac{3}{4},\tfrac{1}{4}+\Delta z_2 \text{ in } 8(b)\,.$$

For simplicity, let us assume that $\Delta x_1=\Delta x_2=\Delta x$ and $\Delta z_1=\Delta z_2=\Delta z$. The absolute amplitudes of the structure factors calculated from the arrangement of heavy atoms mentioned above are represented as follows:

$$\begin{aligned}&|F_{\text{cal}}(h,k,l \text{ odd})|\\&=|-8f_{\text{Ba}}(\sin \pi h/4)\,(\sin 2\pi h\Delta x)-16f_{\text{Fe}}(\cos \pi h/4)\\&\times(\cos \pi h/6)\,(\sin \pi l/2)\,(\sin 2\pi l\Delta z)|\\&=4\sqrt{2}|f_{\text{Ba}}(\sin 2\pi h\Delta x)+2f_{\text{Fe}}(\sin \pi h/3)\,(\sin \pi l/2)\\&\times(\sin 2\pi l\Delta z)|\,,\end{aligned}$$

where $(\cos \pi h/4)\,(\cos \pi h/6)=(\sin \pi h/4)\,(\sin \pi h/3)$ for h odd. On the other hand, the observed amplitudes for h,l odd have the characteristics represented by

$$\begin{aligned}&|F_{\text{obs}}(h,k,l \text{ odd})|\\&=K|\cos\{\pi h/6+(-1)^{(l+1)/2}(\pi/6)\}|\\&=K|\tfrac{1}{2}(\sin \pi h/6)\,(\sin \pi l/2)+\sqrt{3}/2\,(\cos \pi h/6)|\\&=\tfrac{1}{2}K|(\sin \pi h/6)\,\{1+2\sqrt{3}\,(\sin \pi h/3)\,(\sin \pi l/2)\}|\,,\end{aligned}$$

where $\cos \pi h/6=2\,(\sin \pi h/6)\,(\sin \pi h/3)$ for h odd. Since the factor $\sin \pi h/6$ is equal to $\pm\frac{1}{2}$ for $h=6n+1$ and $6n+5$, the expression of the calculated structure factors agrees with that of the observed structure factors if Δx and Δz have the same sign. Thus, the mode of the displacements of the heavy atoms mentioned above was verified.

The value of Δz is estimated to be 0·05 from the peaks D at 0,0,0·40 and E at $\frac{1}{6}$,0,0·40. Since there were observed small peaks F and G near $\frac{1}{12},\frac{1}{2},\frac{1}{4}$, which would disappear if $\Delta x_1=\Delta x_2$ and $\Delta z_1=\Delta z_2$, it was suggested that these parameters had different values. Small peaks appeared at $u,\frac{1}{2},\frac{1}{2}$. It can be shown from the peak H at $\frac{1}{4},\frac{1}{2},\frac{1}{2}$ that $\Delta x_1<\Delta x_2$ and from the peak I at $\frac{1}{12},\frac{1}{2},\frac{1}{2}$ that $\Delta z_1<\Delta z_2$. We took tentatively the following values of Δx_1 etc. for the structure factor calculations: $\Delta x_1=0·004$, $\Delta x_2=0·005$, $\Delta z_1=0·04$, $\Delta z_2=0·05$. Using these parameter values for barium and iron, a Fourier projection $\varrho(x,z)$ was calculated, in which three oxygen atoms came out in the asymmetric unit. From peaks appearing at $0,\frac{1}{3},0$ and $\frac{1}{12},\frac{1}{6},\frac{1}{2}$ in the P_O function, it was suggested that the remaining two oxygen atoms were superimposed on two iron atoms in the same projection. Thus positions of the five oxygen atoms were taken as follows: 8 O(I): $\frac{1}{24},\frac{5}{12},\frac{1}{4}$, 8 O(II): $\frac{1}{8},\frac{11}{12},\frac{1}{4}$, 8 O(III): $\frac{5}{24},\frac{5}{12},\frac{1}{4}$ in 8(a) and 4 O(IV): $\frac{11}{24},\frac{1}{4},0$, 4 O(V): $\frac{7}{24},\frac{1}{4},0$ in 4(b). The residual disagreement factor

$$R_{\text{odd}}(h0l)=\sum ||F_o|-|F_c||/\sum |F_o|$$

was 28 % for the $h0l$ reflexions with h,l odd.

Refinement of positional parameters was proceeded by computing successive (F_o-F_c) syntheses projected on (010). After five cycles, the $R_{\text{odd}}(h0l)$ was reduced to 13 %. The positions of the oxygen atoms appeared on the (F_o-F_c) synthesis, where F_c's were the structure factors calculated with the barium and iron atoms alone is shown in Fig. 4. The Fourier projection $\varrho(x,z)$ is shown in Fig. 5. The atomic parameters were refined using 182 reflexions by the block-diagonal matrix least-squares method. The final atomic parameters are given in Table 2.

Table 2. *Atomic parameters*

4Ba(I) in 4(*a*)	0·1307	0·250	0
4Ba(II) in 4(*a*)	0·6173	0·227	0
8Fe(I) in 8(*b*)	0·0424	0·732	0·2776
8Fe(II) in 8(*b*)	0·2084	0·774	0·2913
8O(I) in 8(*b*)	0·037	0·403	0·243
8O(II) in 8(*b*)	0·123	0·917	0·225
8O(III) in 8(*b*)	0·209	0·417	0·281
4O(IV) in 4(*a*)	0·453	0·226	0
4O(V) in 4(*a*)	0·280	0·226	0

A comparison of the observed and calculated structure factors is listed in Table 3. The residual disagreement factors are 12% for 85 *h0l* reflexions and 16% for 97 *hkl* reflexions with *h*, *l* odd (including unobserved reflexions for which the calculated magnitude is greater than half of the minimum observable value). In all the calculations, the scattering factor curves employed were those given in *International Tables for X-ray Crystallography* (1962) except for O^{2-} for which the curve of Tokonami (1965) was used. The calculations of the Fourier series and structure factors were performed on an IBM 7074 computer.

Table 3. *Observed and calculated structure factors*

An asterisk indicates unobserved reflexions. The F_o values for these are given as $(1/\sqrt{2})\ F_{min}$.

h k l	Fo	Fc	h k l	Fo	Fc
2 0 0	24*	4	1 0 1	80	-88
4 0 0	183	-186	3 0 1	23*	-28
6 0 0	22*	-31	5 0 1	38	-33
8 0 0	182	159	7 0 1	182	163
10 0 0	20*	12	9 0 1	93	-84
12 0 0	486	-532	11 0 1	54	-39
14 0 0	19*	-15	13 0 1	103	99
16 0 0	94	62	15 0 1	94	90
18 0 0	32	26	17 0 1	64	-50
20 0 0	48	-41	19 0 1	104	-109
22 0 0	10*	-7	21 0 1	63	59
24 0 0	106	137	23 0 1	48	53
0 0 2	23	-31	1 0 3	45	43
2 0 2	23*	-13	3 0 3	52	-58
4 0 2	358	-480	5 0 3	141	165
6 0 2	21*	-26	7 0 3	55	-40
8 0 2	341	389	9 0 3	48	-52
10 0 2	20*	8	11 0 3	104	-119
12 0 2	48	19	13 0 3	52	24
14 0 2	19*	-4	15 0 3	98	102
16 0 2	218	200	17 0 3	107	-121
18 0 2	16*	19	19 0 3	28	-33
20 0 2	122	-127	21 0 3	49	48
0 0 4	638	620	23 0 3	59	79
2 0 4	41	37	1 0 5	126	-119
4 0 4	164	-184	3 0 5	20*	-5
6 0 4	20*	-20	5 0 5	122	-118
8 0 4	133	163	7 0 5	173	201
10 0 4	20*	-14	9 0 5	57	-64
12 0 4	298	-343	11 0 5	19*	20
14 0 4	19*	-30	13 0 5	94	115
16 0 4	79	75	15 0 5	50	59
18 0 4	14*	20	17 0 5	23	7
20 0 4	47	-50	19 0 5	119	-127
0 0 6	195	153	21 0 5	49	47
2 0 6	48	-44	1 0 7	67	62
4 0 6	225	-235	3 0 7	31	-23
6 0 6	19*	-14	5 0 7	119	121
8 0 6	165	199	7 0 7	63	-53
10 0 6	36	36	9 0 7	40	-39
12 0 6	113	-91	11 0 7	99	-97
14 0 6	15*	18	13 0 7	13*	-2
16 0 6	111	110	15 0 7	65	61
18 0 6	9*	15	17 0 7	90	-93
20 0 6	64	-69	1 0 9	62	-58
0 0 8	156	176	3 0 9	13*	-19
2 0 8	47	42	5 0 9	42	-44
4 0 8	164	-150	7 0 9	94	89
6 0 8	16*	-8	9 0 9	27	-20
8 0 8	130	133	11 0 9	8*	11
10 0 8	26	-25	13 0 9	59	63
12 0 8	98	-110			
14 0 8	33	-33			
16 0 8	78	71			
0 0 10	165	148			
2 0 10	26	-27			
4 0 10	76	-85			
6 0 10	8*	-7			
8 0 10	64	72			

h k l	Fo	Fc	A	B	h k l	Fo	Fc	A	B
1 1 1	93	97	-97	-5	7 2 3	25	23	1	23
3 1 1	37	46	43	-16	9 2 3	64	68	42	-54
5 1 1	40	29	-25	16	11 2 3	110	112	112	4
7 1 1	126	113	-111	20	13 2 3	42	20	-10	17
9 1 1	79	79	-79	-2	15 2 3	72	88	-87	-16
11 1 1	58	45	42	-15	17 2 3	82	92	92	-5
13 1 1	115	129	129	-1	1 2 5	126	121	112	-47
15 1 1	72	77	-76	11	3 2 5	20	19	13	-14
17 1 1	54	57	-57	-1	5 2 5	83	90	65	62
19 1 1	63	75	74	-9	7 2 5	122	146	-139	-44
1 1 3	89	66	61	-26	9 2 5	48	51	51	0
3 1 3	21*	35	10	-34	11 2 5	55	30	-21	21
5 1 3	101	114	112	22	13 2 5	108	112	-107	34
7 1 3	45	34	21	27	15 2 5	55	60	-58	18
9 1 3	82	92	-91	-15	1 2 7	66	69	-69	-3
11 1 3	118	130	128	-20	3 2 7	49	44	18	40
13 1 3	60	32	31	4	5 2 7	76	75	-75	-11
15 1 3	60	61	-57	22	7 2 7	30	26	17	19
17 1 3	85	107	-107	-2	9 2 7	61	52	34	-39
19 1 3	32	25	23	-11	11 2 7	82	94	94	-4
1 1 5	112	133	-133	2					
3 1 5	31	35	35	1					
5 1 5	87	86	-85	6	1 3 1	50	84	73	41
7 1 5	131	146	-146	9	3 3 1	29	38	-20	32
9 1 5	54	49	-49	6	5 3 1	46	40	-5	-40
11 1 5	18*	22	-21	-7	7 3 1	73	80	62	-51
13 1 5	107	143	143	-4	9 3 1	60	62	61	4
15 1 5	59	61	-61	1	11 3 1	64	52	-22	47
17 1 5	16	8	-8	-1	13 3 1	89	103	-103	-8
1 1 7	63	63	60	-17	15 3 1	60	59	53	-25
3 1 7	19	27	16	-22	17 3 1	55	50	50	4
5 1 7	86	102	101	12	1 3 3	93	62	-62	2
7 1 7	38	46	43	16	3 3 3	56	73	-1	73
9 1 7	38	47	-46	-11	5 3 3	72	81	-77	-25
11 1 7	70	93	91	-15	7 3 3	55	37	-7	-37
13 1 7	29	9	6	6	9 3 3	82	81	72	38
1 1 9	38	49	-49	3	11 3 3	111	104	-103	17
					13 3 3	51	22	-17	14
					15 3 3	53	63	42	-48
1 2 1	63	83	66	-51	1 3 5	111	130	120	50
3 2 1	34	32	28	15	3 3 5	36	19	-19	-4
5 2 1	70	50	10	49	5 3 5	57	53	39	-35
7 2 1	118	121	-118	-25	7 3 5	86	96	85	-44
9 2 1	64	71	66	-26	9 3 5	42	43	39	-18
11 2 1	53	41	37	18	11 3 5	46	59	32	49
13 2 1	82	91	-85	33	13 3 5	104	126	-124	-18
15 2 1	75	81	-81	6	1 3 7	97	59	-59	-1
17 2 1	60	56	48	-29	3 3 7	56	53	-7	53
19 2 1	76	93	93	1	5 3 7	74	69	-68	-10
1 2 3	56	66	-63	-19	7 3 7	36	28	-22	-18
3 2 3	61	72	47	54	9 3 7	48	51	41	31
5 2 3	97	99	-98	-8					

Discussion of the structure

Each iron atom is at the centre of a distorted tetrahedron of oxygen atoms with the Fe–O distances ranging from 1·80 to 1·93 Å. These tetrahedra form a coordinated framework leaving cavities where the barium atoms are accommodated. This buildup principle is the same for the structure of barium monoaluminate which is known as the 'stuffed tridymite' type. However, in the structure of barium monoferrite the six-membered tetrahedra forming a ring have the conformation five-up and one-down, whereas in the structure of barium monoaluminate the conformation of the

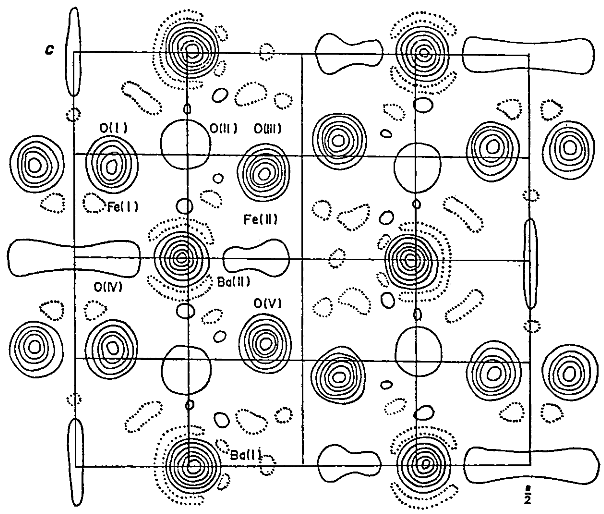

Fig. 5. Electron density projection on (010). Contours are at intervals of 10 e.Å^{-2} except around the barium atoms, where they are at intervals of 20 e.Å^{-2}, starting at 7 e.Å^{-2}. The negative contour is dotted.

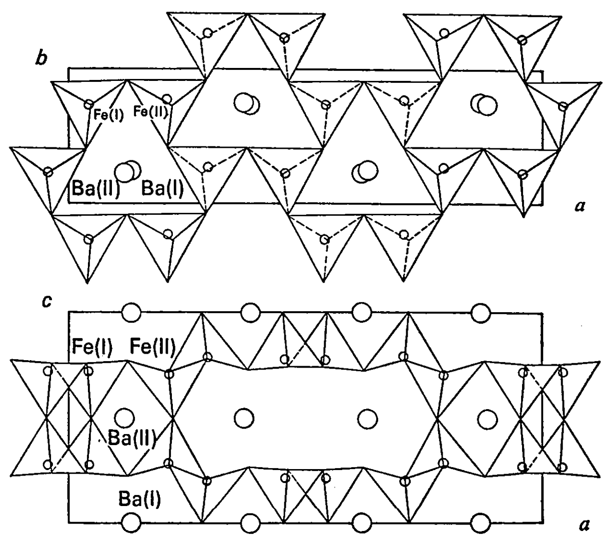

Fig. 6. Projection of the structure on (001) and (010) showing the arrangement of oxygen tetrahedra surrounding iron atoms.

six tetrahedra is one-up and one-down. The structure is shown in Fig. 6. Because there is a mirror plane passing through the barium atoms and the oxygen atoms situated at the apexes of tetrahedra, the FeO_4 tetrahedra in one layer are superposed with those in the adjoining layer as a mirror image of the former, whereas in the structure of barium monoaluminate the AlO_4 tetrahedra are twisted by about 60° relative to one another around the c axis. There are two kinds of barium atoms which are non-equivalent. Ba(I) is surrounded by seven oxygen atoms with the Ba–O distances ranging from 2·62 to 2·94 Å, and Ba(II) is surrounded by eleven oxygen atoms at distances ranging from 2·74 to 3·34 Å. A list of the metal-to-oxygen distances is given in Table 4. Though the structure is rather complicated, it is found that the electrostatic valency rule is nearly satisfied.

Table 4. *Metal–oxygen distances in* $BaFe_2O_4$

	No. of bonds	Bond length
Fe(I)—O(I)	1	1·88 Å
Fe(I)—O(I′)	1	1·80
Fe(I)—O(II)	1	1·88
Fe(I)—O(IV)	1	1·88
Fe(II)–O(II)	1	1·89
Fe(II)–O(III)	1	1·93
Fe(II)–O(III′)	1	1·86
Fe(II)–O(V)	1	1·80
Ba(I)—O(I)	2	2·84
Ba(I)—O(II)	2	2·62
Ba(I)—O(III)	2	2·94
Ba(I)—O(V)	1	2·85
Ba(II)–O(I)	2	2·82
Ba(II)–O(II)	2	2·86
Ba(II)–O(III)	2	2·74
Ba(II)–O(IV)	1	3·00
Ba(II)–O(IV′)	1	3·01
Ba(II)–O(IV″)	1	3·13
Ba(II)–O(V)	1	3·33
Ba(II)–O(V′)	1	3·34

Okazaki, Mori & Kanamaru (1961) found that the $1/\chi - T$ curve is well described by the Curie–Weiss law, $\chi = C/(T+\theta)$, where $C = 3{\cdot}75 \times 10^{-3}$ e.m.u./g.°C, $\theta =$ 200°K. It is suggested that this compound is an antiferromagnetic substance. The effective number of Bohr magnetons calculated from the observed Curie constant C is 2·17. This value is far less than the value expected for $S=\frac{5}{2}$. The rather distorted oxygen tetrahedra as found in this structure would give a strong crystalline field to the Fe^{3+} ions so that the $3d$-electrons would take the low spin states, $(d\gamma)^4(d\varepsilon)^1$. The deviation of the observed effective number of Bohr magneton from the value for $S=\frac{1}{2}$ may imply that the orbital angular momentum for $d\varepsilon$ is not perfectly quenched.

It has been shown that in oxide systems, magnetic moments are aligned by the super-exchange interaction through the intervening oxygen ions, and the effect is at its maximum for a cation–oxygen ion–cation angle of 180° and a minimum for 90°. In the structure of barium monoferrite, all the Fe^{3+} ions are found in pairs parallel to the c axis. These pairs have an intervening oxygen ion with an angle 174° for Fe^{3+}(I)–O^{2-}(IV)–Fe^{3+}(I′) and with an angle 158° for Fe^{3+}(II)–O^{2-}(V)–Fe^{3+}(II′). Further, parallel to the (001) plane all the Fe^{3+} ions are found to form hexagons. In these hexagons, too, the Fe^{3+} ions have an intervening oxygen ion with an angle 122° for Fe^{3+}(I)–O^{2-}(I)–Fe^{3+}(I″), with an angle 115° for Fe^{3+}(I)–O^{2-}(II)–Fe^{3+}(II) and with an angle 116° for Fe^{3+}(II)–O^{2-}(III)–Fe^{3+}(II″). These situations may favor, below the Néel temperature, the moments of the two iron ions on either side of an oxygen ion to be antiparallel to each other by super-exchange interation.

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