

- COPPENS, P., PAULTER, D. & GRIFFIN, J. F. (1971). *J. Amer. Chem. Soc.* **93**, 1051–1058.
- COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451–2458.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756, 757–758.
- CRUICKSHANK, D. W. J. & ROLLETT, J. S. (1953). *Acta Cryst.* **6**, 705–707.
- FUKAMACHI, T. (1971). *Tech. Rep. ISSP*, **B**, No. 12.
- GÜDEL, H. V., LUDI, A., FISCHER, P. & HÄLG, W. (1970). *J. Chem. Phys.* **53**, 1917–1923.
- HASER, R., BROIN, C. E. DE & PIERROT, M. (1972). *Acta Cryst.* **B28**, 2530–2537.
- HASSEL, O. & SALVESEN, J. R. (1927). *Z. Phys. Chem.* **128**, 345–361.
- International Tables for X-ray Crystallography* (1959). Vol. II, Birmingham: Kynoch Press.
- IWATA, M. & SAITO, Y. (1972). To be published.
- KAMIMURA, H., KOIDE, S., SUGANO, S. & TANABE, Y. (1958). *J. Phys. Soc. Japan*, **13**, 464–473.
- KALMAN, B. L. & RICHARDSON, J. W. (1971). *J. Chem. Phys.* **55**, 4443–4456.
- KOBAYASHI, A., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* **B28**, 2709–2715.
- KOHN, J. A. & TOWNES, W. D. (1961). *Acta Cryst.* **14**, 617–621.
- KONNO, M., MARUMO, F. & SAITO, Y. (1973). *Acta Cryst.* **B29**, 739–744.
- KURIYAMA, X. & HOSOYA, X. (1963). *J. Phys. Soc. Japan*, **18**, 1315–1319.
- LONG, T. V., HERLINGER, A. W., EPSTEIN, E. F. & BERNAL, I. (1970). *Inorg. Chem.* **9**, 454–464.
- MATHIEWS, D. A. & STUCKY, G. D. (1971). *J. Amer. Chem. Soc.* **93**, 5954–5959.
- MEEK, D. W. & IBERS, J. A. (1970). *Inorg. Chem.* **9**, 465–470.
- MESSMER, G. G. & AMMA, E. L. (1968). *Acta Cryst.* **B24**, 417–422.
- MUTO, A., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* **B26**, 226–233.
- PALENIK, G. J. (1964). *Acta Cryst.* **17**, 360–367.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. Ithaca: Cornell Univ. Press.
- RAYMOND, K. N., CORFIELD, P. W. R. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 1362–1372.
- REED, J. W. & HARRIS, P. M. (1961). *J. Chem. Phys.* **35**, 1730–1737.
- SAKURAI, T. (1967). *X-ray Crystal Structure Analysis*. (In Japanese). Tokyo: Shokabo.
- SHULL, C. G. & YAMADA, Y. (1962). *J. Phys. Soc. Japan*, **17**, Supplement B-III, 1–6.
- TSUCHIYA, H., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* **B28**, 1935–1941.
- TSUCHIYA, H., MARUMO, F. & SAITO, Y. (1973). *Acta Cryst.* **B29**, In the press.
- UNICS (1967). Edited by T. SAKURAI, Crystallographic Society of Japan.
- VERSCHOOR, G. C. & KEULEN, E. (1971). *Acta Cryst.* **B27**, 134–145.
- WATSON, R. E. & FREEMAN, A. J. (1960). *Phys. Rev.* **120**, 1134–1141.
- WEISS, R. J. (1966). *X-ray Determination of Electron Distributions*. Amsterdam: North-Holland.
- WEISS, R. J. & FREEMAN, A. J. (1959). *J. Phys. Chem. Solids*, **10**, 147–161.

*Acta Cryst.* (1973). **B29**, 832

## The Crystal Structure of Barium Diferrite

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A new barium ferrite,  $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$ , has been synthesized hydrothermally. It is hexagonal, space group  $P6_3/m$ , with lattice dimensions  $a = 5.160$  and  $c = 13.811$  Å;  $Z = 2$ . The structure has been determined by the heavy-atom method and refined by least-squares methods using the block-diagonal approximation to a final  $R$  of 0.08. The hexagonal unit cell consists of six layers of large ions. There are two successive layers of three oxygen ions, but the third layer contains only one oxygen ion and one barium ion. Thus an open space is formed at the third level. The basal plane containing the barium ion is a mirror plane of the structure. Ferric ions are distributed equally into two different sites: one surrounded tetrahedrally and the other octahedrally by oxygen ions.

### Introduction

Because of the practical importance of  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$  as a permanent magnet (Went, Rathenau, Goter and van Oosterhaut, 1951, 1952), the system  $\text{BaO}-\text{Fe}_2\text{O}_3$  has been investigated by many workers (Goto & Takada, 1960; Batti, 1960; van Hook, 1964). The phase diagram of this system contained  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ ,  $\text{BaO} \cdot \text{Fe}_2\text{O}_3$  and  $2\text{BaO} \cdot \text{Fe}_2\text{O}_3$  ( $\text{BaFeO}_{2.5}$ ). Recently, a new metastable

compound,  $2\text{BaO} \cdot 3\text{Fe}_2\text{O}_3$ , has been reported (Shirk, 1970). These compounds were synthesized by either powder reactions or flux techniques, mostly at temperatures higher than 700°C.

Barium hexaferrite,  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ , has the magnetoplumbite structure (hexagonal,  $P6_3/mmc$ ) with cell dimensions  $a = 5.888$  and  $c = 23.22$  Å (Adelsköld, 1938). Barium monoferrite,  $\text{BaO} \cdot \text{Fe}_2\text{O}_3$ , is orthorhombic with  $a = 19.074$  Å,  $b = 5.372$  Å and  $c = 8.450$  Å, and has a

superstructure of hexagonal BaO·Al<sub>2</sub>O<sub>3</sub> (Do-Dihn, Bertaut and Chappert, 1969). According to Mori (1966) BaFeO<sub>x</sub> ( $x=2.5-3.0$ ) exists in various forms depending on the oxygen content  $x$ : a hexagonal phase similar to BaTiO<sub>3</sub>, and phases having structures of the perovskite type.

In our investigations of magnetic oxides and hydroxides, we prepared some new barium ferrites hydrothermally by heating ferric oxide in aqueous barium hydroxide solutions up to 300°C (Okamoto, Okamoto, Sekizawa & Ito, 1971). Among them, a new hexagonal barium diferrite, BaO·2Fe<sub>2</sub>O<sub>3</sub>, was found.

The present paper deals with the structure determination of BaO·2Fe<sub>2</sub>O<sub>3</sub>.

### Experimental

#### Sample preparation and chemical analyses

Three grams of nominally pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder (0.2  $\mu$  in mean particle diameter) and 60 ml of 0.5 M Ba(OH)<sub>2</sub> solution contained in a Teflon beaker were placed in a 500 ml autoclave together with 50 ml of distilled water. The autoclave was heated at a rate of about 200°C per hr, kept at 260°C for 16 hr, and finally air-cooled. Prior to the heating the autoclave was connected to a high pressure oxygen container, and filled with 10 kg cm<sup>-2</sup> of oxygen, in order to protect the specimen from reduction by hydrogen formed by a reaction between the stainless steel vessel and the water. The product was washed with very diluted HCl solution and then with distilled water until no Ba<sup>2+</sup> was detected in the supernatant liquid, and finally it was dried at about 50°C in air.

The crystals obtained were red hexagonal plates of 30  $\mu$  mean diameter. Standard wet chemical analyses showed that the product is composed of 30.7 wt% of BaO and 69.3 wt% of Fe<sub>2</sub>O<sub>3</sub>, and all iron ions in the structure are trivalent. This composition is very close to the calculated value for BaO·2Fe<sub>2</sub>O<sub>3</sub> (32.4 wt% of BaO and 67.6 wt% of Fe<sub>2</sub>O<sub>3</sub>).

#### Crystal data

The X-ray powder diffraction patterns were taken with Fe-filtered Co K $\alpha$  ( $\lambda=1.7902$  Å) radiation. Observed spacings, relative intensities and  $hkl$  indices are shown in Table 1.\* The hexagonal unit-cell dimensions were determined by least-squares calculations using eight suitable reflexions.

Weissenberg photographs indicated the hexagonal system. At an early stage, however, the Laue group

Table 1. Powder diffraction data for BaO·2Fe<sub>2</sub>O<sub>3</sub>

Intensities were measured using a Geiger counter diffractometer. Because of shape anisotropy of the sample, the effect of preferred orientation was unavoidable.

$d$ (Å)	$I/I_0$	$h k l$
6.90	45	0 0 2
4.26	60	1 0 1
3.46	70	0 0 4
3.21	60	1 0 3
2.73	95	1 0 4
2.58	35	1 1 0
2.350	20	1 0 5
2.303	100	0 0 6
2.252	8	1 1 3
2.207	8	2 0 1
2.069	20	1 1 4
2.012	8	2 0 3
1.877	25	2 0 4
1.806	40	1 0 7
1.727	65	0 0 8
1.677	6	2 1 1
1.587	8	2 1 3
1.518	12	2 1 4
1.491	8	3 0 0
1.480	8	2 0 7
1.453	8	1 0 9
1.435	40	1 1 8

( $6/m$  or  $6/mmm$ ) could not be uniquely assigned because the  $hkl$  and  $khl$  reflexions had nearly equal intensities. The only observed absences were  $00l$  with  $l$  odd, and the choice of space group was therefore among  $P6_3/m$ ,  $P6_3$  and  $P6_322$ . Only the first is centrosymmetric and this proved to be the correct space group in the subsequent structure determination.

The crystallographic data are:

Barium diferrite, BaO·2Fe<sub>2</sub>O<sub>3</sub>.

Hexagonal, space group  $P6_3/m$ . F.W. 472.7.

$a=5.160 \pm 0.003$ ,  $c=13.811 \pm 0.009$  Å,  $Z=2$ ,

$V=318.43 \pm 0.46$  Å<sup>3</sup>.

$D_x=4.93$  g cm<sup>-3</sup>,  $D_m=4.93$  g cm<sup>-3</sup> (by pycnometry).

#### Intensity measurements

A hexagonal, plate-like crystal of approximately 60  $\mu$  diameter and 10  $\mu$  thickness was mounted about the  $a$  axis and was used to obtain multiple-film Weissenberg photographs (layers 0 to 5), using Zr-filtered Mo K $\alpha$  radiation. The intensities were measured with a micro-photometer. Because of the small crystal size no absorption corrections were applied. After the Lorentz and polarization corrections were made, the intensities were put on a common scale using the equivalent reflexions from different layers. Intensity data for a total of 111 independent reflexions were collected.

#### Determination of the structure

The unit-cell composition is Ba<sub>2</sub>Fe<sub>8</sub>O<sub>14</sub>, and since there are twelve general positions in the space group, the barium, ferric and at least two oxygen ions must be on the special positions. On the basis of the approximate systematic absences of ( $h, h+3n, l$ ) reflexions with  $l$  odd, the barium ions were considered to be on the special

\* According to Erchak, Fankuchen & Ward (1946), a barium ferrite with composition BaO·2Fe<sub>2</sub>O<sub>3</sub> was formed by heating a mixture of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and BaCO<sub>3</sub>, with an atomic ratio of Fe/Ba=4, at 800°C in air. However, the powder patterns obtained by them differ from ours listed in Table 1. Furthermore, the BaO·2Fe<sub>2</sub>O<sub>3</sub> prepared by us decomposed into BaO·Fe<sub>2</sub>O<sub>3</sub> and BaO·6Fe<sub>2</sub>O<sub>3</sub> when heated above 650°C in air. The new hexagonal BaO·2Fe<sub>2</sub>O<sub>3</sub> is thus distinctly different from the BaO·2Fe<sub>2</sub>O<sub>3</sub> reported by Erchak *et al.*

positions 2(c) or 2(d) (*International Tables for X-ray Crystallography*, 1965). We located them on 2(d), since the choice is initially arbitrary. Approximate coordinates of the other ions were obtained from a three-dimensional Fourier map, which was calculated by using the phases based on the parameters of the barium ions. The ferric and oxygen ions were found to be on 4(e)[Fe(1)], 4(f)[Fe(2)], and 2(a)[O(1)], 12(i)[general positions, O(2)], respectively.

For the O(2) oxygen atoms, however, two alternative assignments of the peaks were possible because two independent peaks were observed with equal peak values of  $10 \text{ e } \text{\AA}^{-3}$ : one on  $(ca.\frac{1}{3}, ca.\frac{1}{3}, ca.\frac{1}{2})$  (set I), and the other on  $(ca.\frac{1}{3}, ca.0, ca.\frac{1}{2})$  (set II). A disorder structure in which the O(2) oxygens statistically occupy the two sites with the same probability is improbable, because the fairly strong 111 and 113 reflexions can not be explained by such a structure. Thus, the oxygen atoms must be on either set I or set II. If O(2) is exactly on  $(\frac{1}{3}, \frac{1}{3}, z)$  (set I $^\circ$ ) or  $(\frac{1}{3}, 0, z)$  (set II $^\circ$ ), the two structures I $^\circ$  and II $^\circ$  are identical, and are related by a rotation of 180 $^\circ$  around the *a* axis:

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \quad (1)$$

where  $x_1, y_1$  and  $z_1$ , and  $x_2, y_2$  and  $z_2$  are the coordinates of the structures I $^\circ$  and II $^\circ$ , respectively. After refinement by the block-diagonal least-squares approximation beginning with structures I $^\circ$  and II $^\circ$  without change of indices, we obtained the corresponding structures I and II. These two structures were not exactly but approximately related to each other by the above transformation. In a strict sense, structures I and II are independent of each other when the *x* and *y* parameters of O(2) deviate from those in set I $^\circ$  or II $^\circ$  (see Appendix).

As can be seen from the Appendix, it is possible in principle to distinguish the correct structure. Unfortunately, however, we were not able to because of the small differences between the structure factors of structures I and II and of the insufficient accuracy of  $F_o$ . The *R* values of structures I and II after five cycles of refinement were 0.080 and 0.082, respectively.

The small differences between the structure factors of structures I and II arise from the following. Firstly, only the O(2) oxygen atoms are responsible for the differences since all the other atoms do not change by the above transformation; structures I and II excluding O(2) oxygens give the same structure factors. Secondly, the atomic coordinates of O(2) in structures I and II are close to those in the sets I $^\circ$  and II $^\circ$ , respectively, as mentioned previously. If the O(2) oxygen atoms are exactly on set I $^\circ$  or II $^\circ$ , we obtain

$$|F(hkl)_{I^\circ}| = |F(hkl)_{II^\circ}|. \quad (2)$$

Equation (2) shows that only the displacements of the atomic coordinates of O(2) from set I $^\circ$  or II $^\circ$  are responsible for the differences.

It should be noted that equation (2) is equivalent to the relation

$$|F(hkl)| = |F(khl)|$$

for both structures I $^\circ$  and II $^\circ$ . This relation shows that the Laue symmetry of structures I $^\circ$  and II $^\circ$  is enhanced from 6/*m* inherent in the space group  $P6_3/m$  to 6/*mmm*, as has been pointed out by Iwasaki (1972).

The final atomic parameters and the observed and calculated structure factors for structures I and II are listed in Tables 2 and 3, respectively. The differences between the atomic parameters of the two structures were found only with respect to the *x* and *y* coordinates of O(2). The other parameters were identical within one tenth of the standard deviations.

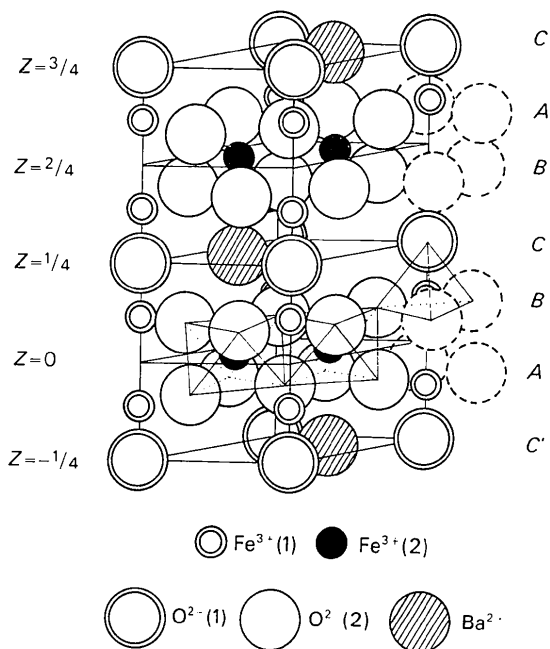
Table 2. Positional and thermal parameters

Atom	Position	Parameters		
		Structure I	Structure II	
Ba	2(d)	<i>x</i>	$\frac{2}{3}$	$\frac{2}{3}$
		<i>y</i>	$\frac{1}{3}$	$\frac{1}{3}$
		<i>z</i>	$\frac{1}{2}$	$\frac{1}{2}$
		<i>B</i>	0.30 (0.08)	0.30 (0.08)
Fe(1)	4(e)	<i>x</i>	0	0
		<i>y</i>	0	0
		<i>z</i>	0.1149 (0.0008)	0.1148 (0.0008)
		<i>B</i>	0.10 (0.12)	0.09 (0.12)
Fe(2)	4(f)	<i>x</i>	$\frac{1}{3}$	$\frac{1}{3}$
		<i>y</i>	$\frac{2}{3}$	$\frac{2}{3}$
		<i>z</i>	0.0089 (0.0008)	0.0089 (0.0008)
		<i>B</i>	0.31 (0.14)	0.31 (0.14)
O(1)	2(a)	<i>x</i>	0	0
		<i>y</i>	0	0
		<i>z</i>	$\frac{1}{2}$	$\frac{1}{2}$
		<i>B</i>	2.76 (1.51)	2.74 (1.50)
O(2)	12(i)	<i>x</i>	0.3435 (0.0076)	0.3307 (0.0082)
		<i>y</i>	0.3377 (0.0077)	0.0014 (0.0076)
		<i>z</i>	0.0790 (0.0024)	0.0790 (0.0024)
		<i>B</i>	1.09 (0.52)	1.14 (0.53)

Table 3. Observed and calculated structure factors

$$\Delta F_c = |F_c(\text{Structure I})| - |F_c(\text{Structure II})|.$$

hkl	F <sub>o</sub>	F <sub>c</sub> (Structure I)		F <sub>c</sub> (Structure II)		ΔF <sub>c</sub>	ΔF <sub>c</sub> /F <sub>o</sub>
		F <sub>c</sub>	σ <sub>F<sub>c</sub></sub>	F <sub>c</sub>	σ <sub>F<sub>c</sub></sub>		
001	57.73	74	41	1.13	66	55	+55.0
002	91	120	131	1.14	118	138	120.0
003	151	172	171	1.18	171	194	194.0
004	56	43	93	1.12	45	51	51.0
005	102	42	99	1.12	38	47	47.0
006	152	119	150	1.15	89	90	90.0
007	56	58	117	1.21	67	94	94.0
008	70	91	91	1.22	73	71	71.0
009	111	70	82	1.12	47	122	121.0
010	112	77	83	1.12	77	77	77.0
011	124	69	77	1.17	71	76	76.0
012	37	64	64	1.11	63	72	72.0
013	123	116	114	1.12	82	77	77.0
014	5	49	30	1.15	17	61	61.0
015	30	74	81	1.11	73	44	44.0
016	11	79	82	1.13	46	58	58.0
017	60	73	76	1.14	114	112	112.0
018	11	84	77	1.15	75	72	72.0
019	52	66	66	1.14	67	67	67.0
020	30	114	119	1.11	115	111	111.0
021	7	80	72	1.12	81	72	72.0
022	11	79	82	1.13	46	58	58.0
023	60	73	76	1.14	114	112	112.0
024	11	84	77	1.15	75	72	72.0
025	52	66	66	1.14	67	67	67.0
026	30	114	119	1.11	115	111	111.0
027	7	80	72	1.12	81	72	72.0
028	11	79	82	1.13	46	58	58.0
029	60	73	76	1.14	114	112	112.0
030	11	84	77	1.15	75	72	72.0
031	52	66	66	1.14	67	67	67.0
032	30	114	119	1.11	115	111	111.0
033	7	80	72	1.12	81	72	72.0
034	11	79	82	1.13	46	58	58.0
035	60	73	76	1.14	114	112	112.0
036	11	84	77	1.15	75	72	72.0
037	52	66	66	1.14	67	67	67.0
038	30	114	119	1.11	115	111	111.0
039	7	80	72	1.12	81	72	72.0
040	11	79	82	1.13	46	58	58.0
041	60	73	76	1.14	114	112	112.0
042	11	84	77	1.15	75	72	72.0
043	52	66	66	1.14	67	67	67.0
044	30	114	119	1.11	115	111	111.0
045	7	80	72	1.12	81	72	72.0
046	11	79	82	1.13	46	58	58.0
047	60	73	76	1.14	114	112	112.0
048	11	84	77	1.15	75	72	72.0
049	52	66	66	1.14	67	67	67.0
050	30	114	119	1.11	115	111	111.0
051	7	80	72	1.12	81	72	72.0
052	11	79	82	1.13	46	58	58.0
053	60	73	76	1.14	114	112	112.0
054	11	84	77	1.15	75	72	72.0
055	52	66	66	1.14	67	67	67.0
056	30	114	119	1.11	115	111	111.0
057	7	80	72	1.12	81	72	72.0
058	11	79	82	1.13	46	58	58.0
059	60	73	76	1.14	114	112	112.0
060	11	84	77	1.15	75	72	72.0
061	52	66	66	1.14	67	67	67.0
062	30	114	119	1.11	115	111	111.0
063	7	80	72	1.12	81	72	72.0
064	11	79	82	1.13	46	58	58.0
065	60	73	76	1.14	114	112	112.0
066	11	84	77	1.15	75	72	72.0
067	52	66	66	1.14	67	67	67.0
068	30	114	119	1.11	115	111	111.0
069	7	80	72	1.12	81	72	72.0
070	11	79	82	1.13	46	58	58.0
071	60	73	76	1.14	114	112	112.0
072	11	84	77	1.15	75	72	72.0
073	52	66	66	1.14	67	67	67.0
074	30	114	119	1.11	115	111	111.0
075	7	80	72	1.12	81	72	72.0
076	11	79	82	1.13	46	58	58.0
077	60	73	76	1.14	114	112	112.0
078	11	84	77	1.15	75	72	72.0
079	52	66	66	1.14	67	67	67.0
080	30	114	119	1.11	115	111	111.0
081	7	80	72	1.12	81	72	72.0
082	11	79	82	1.13	46	58	58.0
083	60	73	76	1.14	114	112	112.0
084	11	84	77	1.15	75	72	72.0
085	52	66	66	1.14	67	67	67.0
086	30	114	119	1.11	115	111	111.0
087	7	80	72	1.12	81	72	72.0
088	11	79	82	1.13	46	58	58.0
089	60	73	76	1.14	114	112	112.0
090	11	84	77	1.15	75	72	72.0
091	52	66	66	1.14	67	67	67.0
092	30	114	119	1.11	115	111	111.0
093	7	80	72	1.12	81	72	72.0
094	11	79	82	1.13	46	58	58.0
095	60	73	76	1.14	114	112	112.0
096	11	84	77	1.15	75	72	72.0
097	52	66	66	1.14	67	67	67.0
098	30	114	119	1.11	115	111	111.0
099	7	80	72	1.12	81	72	72.0
100	11	79	82	1.13	46	58	58.0
101	60	73	76	1.14	114	112	112.0
102	11	84	77	1.15	75	72	72.0
103	52	66	66	1.14	67	67	67.0
104	30	114	119	1.11	115	111	111.0
105	7	80	72	1.12	81	72	72.0
106	11	79	82	1.13	46	58	58.0
107	60	73	76	1.14	114	112	112.0
108	11	84	77	1.15	75	72	72.0
109	52	66	66	1.14	67	67	67.0
110	30	114	119	1.11	115	111	111.0
111	7	80	72	1.12	81	72	72.0
112	11	79	82	1.13	46	58	58.0
113	60	73	76	1.14	114	112	112.0
114	11	84	77	1.15	75	72	72.0
115	52	66	66	1.14	67	67	67.0
116	30	114	119	1.11	115	111	111.0
117	7	80	72	1.12	81	72	72.0
118	11	79	82	1.13	46	58	58.0
119	60	73	76	1.14	114	112	112.0
120	11	84	77	1.15	75	72	72.0
121	52	66	66	1.14	67	67	67.0
122	30	114	119	1.11	115	111	111.0
123	7	80	72	1.12	81	72	72.0
124	11	79	82	1.13	46	58	58.0
125	60	73	76	1.14	114	112	112.0
126	11	84	77	1.15	75	72	72.0
127	52	66	66	1.14	67	67	67.0
128	30	114	119	1.11	115	111	111.0
129	7	80	72	1.12	81	72	72.0
130	11	79	82	1.13	46	58	58.0
131	60	73	76	1.14	114	112	112.0
132	11	84	77	1.15	75	72	72.0
133	52	66	66	1.14	67	67	67.0
134	30	114	119	1.11	115	111	111.0
135	7	80	72	1.12	81	72	72.0

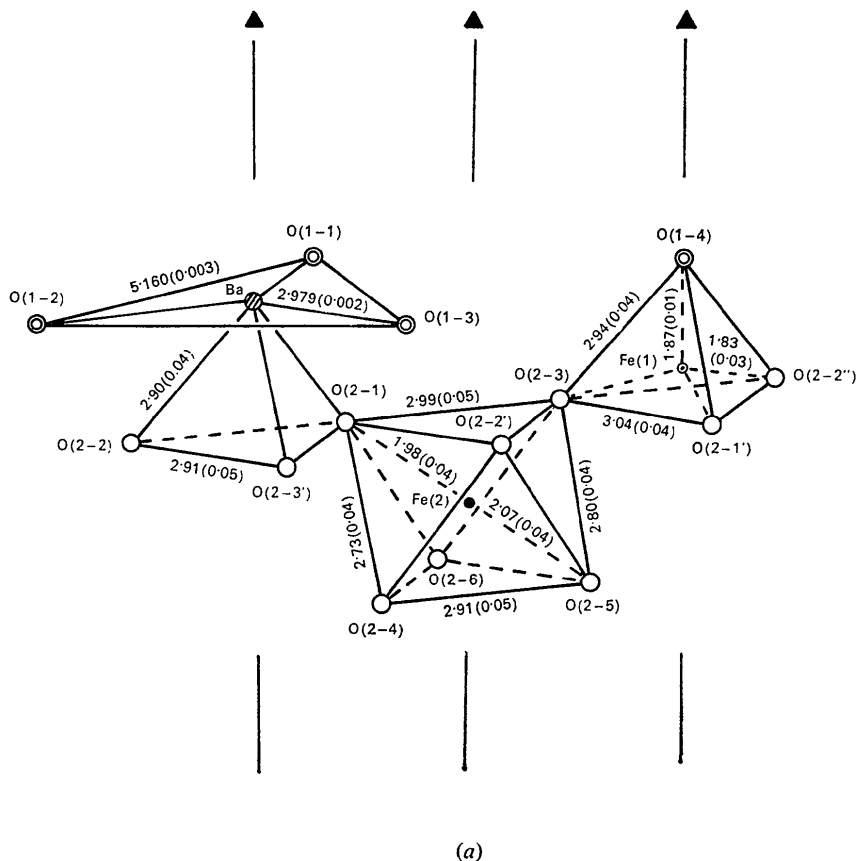

 Fig. 1. Crystal structure of  $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$  (structure I).

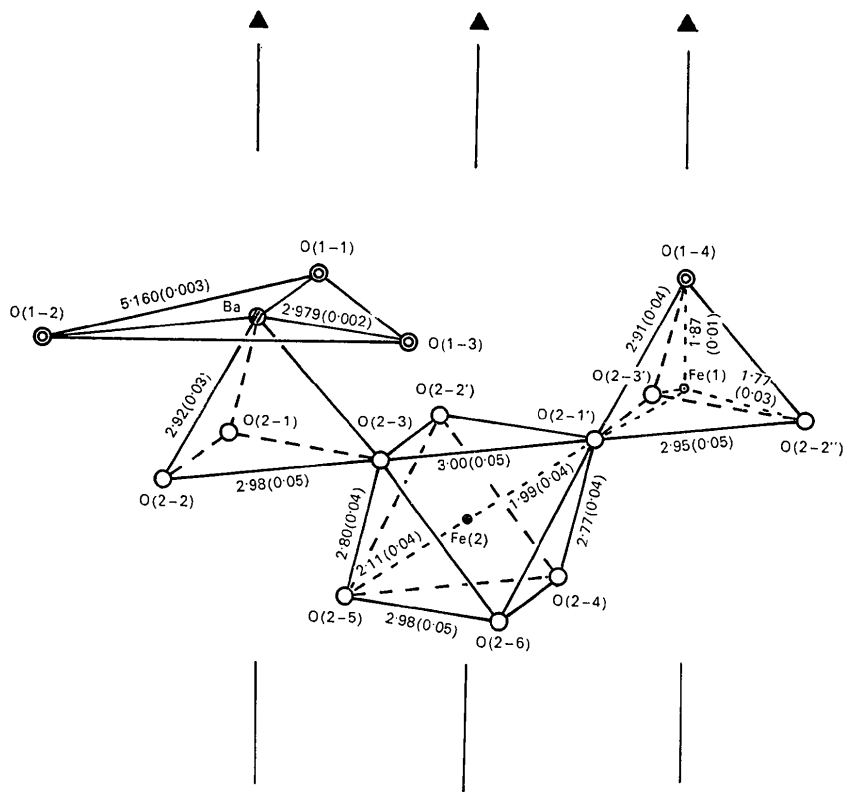
The scattering factors for  $\text{Fe}^{3+}$  were taken from *International Tables for X-ray Crystallography* (1962). The scattering factor curve for  $\text{O}^{2-}$  was that of Tokonami (1965). Since the scattering factors for  $\text{Ba}^{2+}$  were not directly available, they were obtained by extrapolation of those for the neutral Ba for the range  $\sin \theta/\lambda = 0-0.25$ . All calculations were carried out on a FACOM 270-30 computer, with the UNICS programs (Sakurai, Ito, Iwasaki, Watanabe and Fukuhara, 1967).

### Results and discussion

Although structures I and II are independent, the atomic configurations in the two structures are very similar. Structure I rotated by  $180^\circ$  about the  $a$  axis coincides with structure II within twice the standard deviations of the atomic parameters. The difference between the two structures is found only in the interatomic distances involving O(2), as discussed later.

Structure I is illustrated schematically in Fig. 1. The hexagonal unit cell is composed of six layers stacked along the  $c$  axis. If we denote the three successive layers at  $z = ca. -\frac{1}{12}$ ,  $ca. +\frac{1}{12}$  and  $+\frac{1}{4}$ , as  $A$ ,  $B$  and  $C$ , respectively, the packing scheme  $ABC$  is similar to that found in the f.c.c. lattice. Both  $A$  and  $B$  contain three


 Fig. 2. Interatomic distances for  $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$ . (a) Structure I.



(b)

Fig. 2 (cont.) (b) Structure II.

close-packed oxygen ions, whereas *C* contains only one oxygen and one barium ion. Thus, on the barium-oxygen mixed layer an open space is formed. The remaining three layers are related to the block *ABC* by the mirror plane through *C* and by the screw diad parallel to the *c* axis. Therefore, the overall stacking of the layers can conveniently be represented as *ABCBAC'*. The interlayer spacings are  $A-B=2.18$  and  $B-C=2.36$  Å.

Interatomic distances and angles are shown in Fig. 2 and Table 4. All the O-O distances forming the coordination polyhedra of metal ions in structures I and II fall within the range 2.73–3.04 Å, which is found in the close-packed oxygen framework, except for the O(1)–O(1) distance of 5.160(0.003) Å, which is equal to *a* in the Ba<sup>2+</sup> and O<sup>2-</sup> mixed layers. The Ba–O distances are 2.979(0.002) and 2.90(0.04) Å for structure I, and 2.979(0.002) and 2.92(0.03) Å for structure II, all of which are within the normal range.

Because of the open spaces, each barium ion is surrounded by nine oxygen ions instead of twelve. Similar configurations exist in the structures of BaO·Al<sub>2</sub>O<sub>3</sub> and BaO·Fe<sub>2</sub>O<sub>3</sub> (Wyckoff, 1965).

A remarkable feature of the structure is found in the distribution of ferric ions with equal concentrations on two cation sites. Four of the eight ferric ions, Fe(2), are surrounded octahedrally and the others, Fe(1),

Table 4. Interatomic angles

	Structure I	Structure II
(1) Tetrahedrally coordinated iron		
O(1-4)–Fe(1)–O(2-1')	105.7 (1.1)°	106.2 (1.2)°
O(2-1')–Fe(1)–O(2-2'')	112.9 (1.8)	112.5 (1.9)
(2) Octahedrally coordinated iron		
O(2-3)–Fe(2)–O(2-2')	98.1 (1.5)°	98.3 (1.6)°
O(2-3)–Fe(2)–O(2-4)	173.2 (1.5)	173.9 (1.5)
O(2-3)–Fe(2)–O(2-5)	87.5 (1.6)	86.2 (1.6)
O(2-3)–Fe(2)–O(2-6)	84.9 (1.4)	85.0 (1.4)
O(2-4)–Fe(2)–O(2-5)	89.1 (1.6)	90.1 (1.4)
(3) Barium and its surroundings		
O(1-1)–Ba–O(2-1)	60.1 (0.6)°	59.1 (0.8)°
O(1-1)–Ba–O(2-2)	89.6 (0.7)	120.5 (0.6)
O(1-1)–Ba–O(2-3')	120.3 (0.7)	—
O(1-1)–Ba–O(2-3)	—	90.4 (0.7)
O(2-1)–Ba–O(2-2)	60.2 (1.3)	61.4 (0.9)

tetrahedrally by oxygen ions. The octahedral Fe–O distances are 1.98(0.04) and 2.07(0.04) Å in structure I, and 1.99(0.04) and 2.11(0.04) Å in structure II. Apart from the slightly long distance of 2.11 Å found in structure II, these values agree with the normal value of  $2.01 \pm 0.08$  Å (*International Tables for X-ray Crystallography*, 1962).

The Fe–O distances along the *c* axis in the Fe(1) tetrahedra are 1.87(0.01) Å and are the same for structures I and II, whereas those forming the basis of the

tetrahedra are 1.83(0.03) Å in structure I, and 1.77(0.03) Å in structure II. The latter value is somewhat short, although not exceptional (Table 5).

It should be noted that the pairs of tetrahedra along the *c* axis share a corner with a linear Fe–O–Fe bond, whereas each octahedron shares edges with the adjacent three octahedra forming pseudo-hexagonal layers of octahedra. According to Pauling (1960), the shared edges of coordinated octahedra about cations with large charges are expected to be shortened as a result of the distortion caused by the repulsion between the cations. This is proved experimentally for some ionic crystals. Such shortening of the O–O distance is observed in structure I, but not in structure II: the O–O distances in the coordinated octahedra of structure I are 2.73(0.04) Å for the shared edge and 2.80(0.04), 2.91(0.05) and 2.99(0.05) Å for the unshared edges, whereas those of structure II are 2.80(0.04) Å for the shared edge and 2.77(0.04), 2.98(0.05) and 3.00(0.05) Å for the unshared edges. Although the differences between structures I and II are too small to be statistically significant, the above considerations suggest that structure I is more likely than structure II.

There is a group of ferrimagnetic compounds composed of BaO, MO (M=divalent metal ions which can occur in the spinel structure) and Fe<sub>2</sub>O<sub>3</sub>. The compounds possess closely related hexagonal crystal structures (Jonker, Wijn & Braun, 1956, 1957). Among these a BaO.2Fe<sub>2</sub>O<sub>3</sub> block occurs in the so-called *Y* structure having the composition Ba<sub>2</sub>M<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>. This block (so-called *T* block) is composed of two close-packed oxygen layers and two close-packed oxygen-barium mixed layers, and clearly differs from the BaO.2Fe<sub>2</sub>O<sub>3</sub> structure presented in this paper.

BaO.2Fe<sub>2</sub>O<sub>3</sub> is antiferromagnetic and the chemical and magnetic properties will be reported elsewhere.

The authors wish to express their thanks to Dr H. Iwasaki for his helpful suggestions and critical discussions, which have contributed greatly to the final results. The authors are also grateful to Dr H. Sekizawa for his interest in this subject.

## APPENDIX

### Differences between structures I and II

Structures I and II are different only in the atomic coordinates of O(2) (Table 2). Although structure I rotated by 180° about the *a* axis coincides approximately

with structure II, the two structures are not equivalent, but either of the two is correct and the other incorrect, as shown below.

Let us first assume that I is the correct structure corresponding to the observed structure factors  $|F_o(hkl)|$ . It should be noted that the rotation of 180° about the *a* axis is not a symmetry operation of the space group *P*6<sub>3</sub>/*m*. Therefore, if we denote the structure obtained from I by the above rotation as structure I', the structure factors of I and I' are, in general, not equal to each other,

$$|F(hkl)|_{I'} \neq |F(hkl)|_I \quad (\text{A-1})$$

but

$$|F(hkl)|_{I'} = |F(khl)|_I. \quad (\text{A-2})$$

Equation (A-1) shows that we can distinguish, at least in principle, the correct structure I from the rotated structure I' on the basis of  $|F_o(hkl)|$ ;  $|F_o(hkl)|$  should be closer to  $|F(hkl)|_I$  than to  $|F(hkl)|_{I'}$ . It is also evident that structure II, which is obtained by fitting  $|F_o(hkl)|$  to  $|F(hkl)|_{I'}$  by least-squares calculations, must be incorrect because structure I' does not correspond to  $|F_o(hkl)|$  but to  $|F_o(khl)|$ .

An analogous situation exists if we initially assume that II is the correct structure.

## References

- ADELSKÖLD, V. (1938). *Ark. Kemi Min. Geol.* **12A**, No. 29, 1–9.  
 BARTH, T. F. W. (1935). *J. Chem. Phys.* **3**, 323–325.  
 BATTI, P. (1960). *Ann. Chim. Roma* **50**, 1461–1478.  
 BERTAUT, E. F., BLUM, P. & SAGNIÈRES, A. (1959). *Acta Cryst.* **12**, 149–159.  
 BIRCHALL, T., GREENWOOD, N. N. & REID, A. F. (1969). *J. Chem. Soc. (A)*, pp. 2382–2398.  
 DO-DIHN, C., BERTAUT, E. F. & CHAPPERT, J. (1969). *J. Phys.* **30**, 566–578.  
 ERCHAK, M., FANKUCHEN, I. & WARD, R. (1946). *J. Amer. Chem. Soc.* **68**, 2085–2093.  
 EULER, F. & BRUCE, J. A. (1965). *Acta Cryst.* **19**, 971–978.  
 GOTO, Y. & TAKADA, T. (1960). *J. Amer. Cer. Soc.* **43**, 150–153.  
 HOOK, H. J. VAN (1964). *J. Amer. Ceram. Soc.* **47**, 579–581.  
*International Tables for X-ray Crystallography* (1965). Vol. I. Birmingham: Kynoch Press.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 IWASAKI, H. (1972). *Acta Cryst.* **A28**, 253–260.  
 JONKER, G. H., WIJN, H. P. J. & BRAUN, P. B. (1956, 1957). *Philips Tech. Rev.* **18**, 145–180.  
 MORI, S. (1966). *J. Amer. Ceram. Soc.* **49**, 600–605.

Table 5. Tetrahedral Fe–O distances in various ferrites

Fe–O distance	Ferrite	Reference
1.90–1.94 Å	BaO.6Fe <sub>2</sub> O <sub>3</sub>	Townes, Fang & Perrotta (1967)
1.83–1.93	Bi <sub>2</sub> Fe <sub>4</sub> O <sub>9</sub>	Niizeki & Wachi (1968)
1.87–1.91	Inverse spinel ferrites	
1.86–1.88	2CaO.Fe <sub>2</sub> O <sub>3</sub>	Bertaut, Blum & Sagnières (1959)
1.861–1.875	R <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> (R: rare earth elements)	Euler & Bruce (1965)
1.79–2.18	β-NaFeO <sub>2</sub>	Birchall, Greenwood & Reid (1969)
1.73	KFeO <sub>2</sub>	Barth (1935)
1.60–1.63	BaO.Fe <sub>2</sub> O <sub>3</sub>	Do-Dihn, Bertaut & Chappert (1969)

NIIZEKI, N. & WACHI, M. (1968). *Z. Krystallogr.* **127**, 173–187.  
 OKAMOTO, S., OKAMOTO, S. I., SEKIZAWA, H. & ITO, T. (1971). *Proc. Intern. Conf. Ferrites, Kyoto, Japan*, pp. 168–170. Univ. of Tokyo Press.  
 PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.  
 SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* **43**, 62–69.

SHIRK, B. T. (1970). *Mater. Res. Bull.* **5**, 771–778.  
 TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.  
 TOWNES, W. D., FANG, J. H. & PERROTTA, A. J. (1967). *Z. Krystallogr.* **125**, 437–449.  
 WENT, J. J., RATHENAU, G. W., GORTER, E. W. & VAN OOSTERHOUT, G. W. (1951, 1952). *Philips Tech. Rev.* **13**, 194–208.  
 WYCKOFF, R. W. G. (1965). *Crystal Structures*, Vol. 3, p. 113. New York: Interscience.

*Acta Cryst.* (1973). **B29**, 838

## The Molecular and Crystal Structure of *N*-( $\beta$ -D-Ribofuranosyl)imidazole

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*N*-( $\beta$ -D-Ribofuranosyl)imidazole crystallizes from an ethanol-ether solution with two molecules per unit cell and space group  $P2_1$ . The unit-cell dimensions are  $a = 5.190$  (1),  $b = 7.775$  (1),  $c = 11.198$  (2) Å and  $\beta = 92.49$  (2)°. Diffractometer data with Mo  $K\alpha$  radiation ( $2\theta \leq 60^\circ$ ) at room temperature were collected, the structure solved and refined to weighted and unweighted  $R$  values of 0.04 and 0.03 respectively. The ribose ring may be described as C(3')-*endo*-C(2')-*endo* with C(3') and C(2') 0.604 and 0.055 Å from the plane defined by C(1'), O(1') and C(4'). The glycosidic torsion angle defined by O(1')-C(1')-N(1)-C(2) is  $-97.8^\circ$  and thus in the *syn* conformation. The torsion angle for the C(5')-C(4') bond is described as *gauche-trans* with  $\varphi_{OO} = +64.3$  and  $\varphi_{OC} = +180.4^\circ$ . The crystal structure is fixed by a system of three hydrogen bonds which link each molecule to six neighbouring molecules. The final difference electron-density map has significant features in the expected locations for  $\sigma$ -bonding electrons between carbon atoms and lone-pair electrons in the vicinity of the imidazole nitrogen N(3) and ribose oxygen atom O(5').

### Introduction

The anomeric effect is a well established phenomenon in carbohydrate chemistry (for a recent review see: Zefirov & Shekhtman, 1971). Comparison of crystal-structure studies of several pyranose-ring-containing carbohydrates has provided evidence for carbon-oxygen bond shortening in the region of the anomeric carbon atom C(1) (Berman, Chu & Jeffrey, 1967). When an electronegative atom is substituted at the anomeric carbon atom of a pyranose ring there is considerable stabilization of the axial anomer over that of the equatorial (Lemieux & Chü, 1958; Angyal, 1969). The reason for this stabilization is uncertain, but dipole-dipole attraction or repulsion forces may contribute to this effect. However if a positively charged group is substituted on the anomeric carbon atom, the equatorial anomer becomes the more stable conformation and this observation has been termed the reverse anomeric effect (Lemieux & Morgan, 1965). These authors report a  $1C$  chair conformation for *N*-(tetra-*O*-acetyl- $\alpha$ -D-glucopyranosyl)-4-methylpyridinium bromide rather than the more common  $C1$  chair. An X-ray crystallographic study of this compound (James, 1969) has shown that the conformation of this molecule in the crystals is the  $2.5B$  with the acetyl groups on C(2) and C(3) in a quasi-

axial orientation and the 4-methylpyridinium moiety in a quasi-equatorial position.

It is certain that this reverse anomeric effect plays an

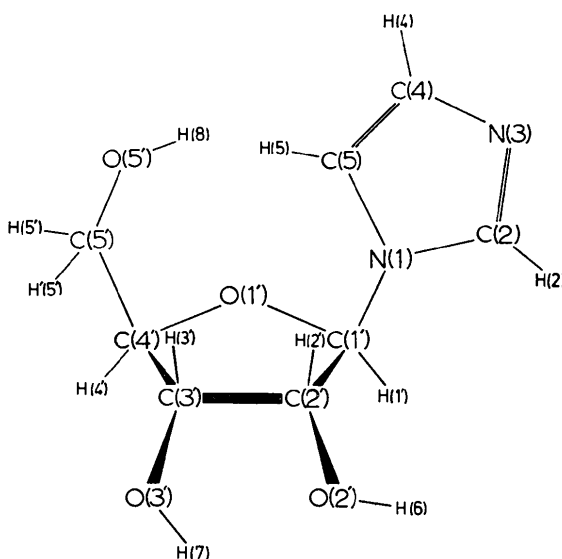


Fig. 1. Atomic numbering scheme for *N*-( $\beta$ -D-ribofuranosyl)imidazole used in this structure analysis.