Acta Cryst. (1957). **10**, 332

The Structure of Calcium Ferrite

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(*Received* 30 *August* 1956)

The crystal structure of $CaFe_2O_4$ has been determined from single-crystal studies. The crystal system is orthorhombic, the space group is $Pnam$–D_{2h}^{16}, and the unit cell dimensions are $a_0 = 9{\cdot}230$, $b_0 = 10{\cdot}705$, $c_0 = 3{\cdot}024$ Å. The coordination of oxygens around Fe is that of a distorted octahedron; around Ca there occurs a coordination of nine oxygens in a configuration first noted in $CaTi_2O_4$ and present also in CaV_2O_4, with which $CaFe_2O_4$ is isomorphous.

Introduction

The structure of $CaFe_2O_4$ has been unknown for a number of years, even though there have been several X-ray studies (Forestier, 1931; Hilpert & Wille, 1932; Kittel & Hüttig, 1934; Rudorff & Reuter, 1945; Burdese, 1952), mainly of powder diagrams. While the formula is the same as that for a spinel, $CaFe_2O_4$ does not have the spinel structure, although that statement is found in the literature (Kittel & Hüttig, 1934). The most recent work prior to this investigation, that of Burdese (1952) on a single crystal, gave an orthorhombic cell which is in approximate agreement with that reported here. No structure determination, however, was made by Burdese.

Toward the completion of this work, the authors have become aware of a preliminary report by Bertaut, Blum & Magnano (1955) on the structure of CaV_2O_4, wherein it is stated that $CaFe_2O_4$ is isomorphous with CaV_2O_4. Although the atomic parameters given for the vanadite are only approximate, the isomorphism is confirmed by the structure of the ferrite that we have found.

Unit cell, space group and powder pattern

Precession, rotation and Weissenberg photographs of a needle of $CaFe_2O_4$ showed the lattice to be orthorhombic and gave approximate values of the cell dimensions which were refined from powder data to be

$$a_0 = 9{\cdot}230 \pm 0{\cdot}012,\ \ b_0 = 10{\cdot}705 \pm 0{\cdot}014,$$
$$c_0 = 3{\cdot}024 \pm 0{\cdot}004 \text{ Å},$$

with the needle axis along c.

The space group is D_{2h}^{16}–$Pnam$, with $Z = 4$. The criteria governing absences are: $(h0l)$ only present with $h = 2n$, and $(0kl)$ only present with $k+l = 2n$. All atoms are in position

$$4(c):\ \ x, y, \tfrac{1}{4};\ \ \bar{x}, \bar{y}, \tfrac{3}{4};\ \ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{3}{4};\ \ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{4}\,.$$

The values of atomic parameters are as follows:

	x	y
Fe_{I}	0·433	0·610
Fe_{II}	0·420	0·108
Ca	0·756	0·654
O_{I}	0·208	0·162
O_{II}	0·115	0·477
O_{III}	0·521	0·784
O_{IV}	0·419	0·424

Interplanar spacings, relative intensities and Miller indices are given in Table 1 for the powder pattern of $CaFe_2O_4$.

Table 1. *Powder pattern of* $CaFe_2O_4$

(Cr $K\alpha$ radiation)

d (Å)	I	hkl
4·617	20	021 002
3·498	5	022
2·676	100	040 023
2·531	65	121 102
2·240	20	131
2·115	25	024 113
1·961	15	141
1·837	40	142 104
1·808	15	114
1·745	10	150 025
1·664	20	062
1·545	20	063
1·539	20	006
1·512	25*	161 144 200 125
1·458	15	162
1·411	8	036 064
1·374	8	163
1·335	20	046
1·326	10	081
1·314	25	240 223
1·280	10	027 164
1·247	10	173
1·230	8	224
1·215	2	181
1·202	2	117
1·181	10*	047 182 165 127

* Broad.

Experimental

The material used in this investigation was prepared by a method which is a modification of that used by Sosman & Merwin (1916). An equi-molar mixture of $CaCO_3$ and Fe_2O_3 was ground in a mortar, then transferred to a zircon crucible which was put into a furnace at 900° C. (in air) and rapidly heated to 1250° C., at which temperature the mixture became liquid; after 20 min. at 1250° C., the sample was solidified by cooling to 1200° C., held at that temperature for 20 min. and air quenched to room temperature. This treatment yielded a lump of calcium ferrite which was dark gray in color and iridescent. On breaking open the ingot many needles and bundles of needles were found surrounding an interior cavity. Some of the individual needles were quite satisfactory for single-crystal diffraction analysis. These were of the following approximate dimensions: 0·1–0·2 mm. in diameter and 1–2 mm. in length.

The single crystal X-ray data were obtained with Mo $K\alpha$ (zirconium filtered) radiation. Precession photographs were made about two different directions in the crystal. Weissenberg photographs were made for the equator and first, second and third layers, with the needle axis as rotation axis. Powder patterns for the bulk material and for needles only were obtained with Cr $K\alpha$ (vanadium filtered) radiation. Intensity measurements were made by visual comparison with calibrated intensities on a strip of film for both Weissenberg and powder data.

Chemical analysis of the bulk material showed an excess of iron, and the presence of zirconium and silicon indicating some reaction with the crucible. Also, the presence of Fe_2O_3 and $ZrSiO_4$ could be detected in X-ray powder patterns for bulk material, but not for the patterns obtained from powdered needles.

The bulk material exhibited a weak ferromagnetism, due probably to Fe_2O_3. No ferromagnetism could be detected for clean needles of the calcium ferrite.

It was assumed that the needles investigated were free of the impurities in the bulk material, and in composition did correspond to the formula $CaFe_2O_4$.

No reliable experimental density could be obtained on the needles of $CaFe_2O_4$ because of their very small size and lack of a sufficient number of them. On the other hand, the density for lumps of the bulk material could be measured, but could not be taken as a reliable one for $CaFe_2O_4$ because of the presence of air pockets and impurities. That experimental density was 4·53 g.cm.$^{-3}$, while the X-ray density calculated for pure $CaFe_2O_4$ is 4·81 g.cm.$^{-3}$.

Determination of the structure

The systematic absences indicated space group $Pnam$–D_{2h}^{16} or $Pna2_1$–C_{2v}^{9}. Since the corrected intensities for the upper layers with l even (c axis as axis of rotation) are the same (except for normal decline) as the corresponding ones in the zero layer, and since all l-odd layers are alike similarly, the atoms must all lie on planes separated by one-half the cell dimension along c. Accordingly, $Pna2_1$ is ruled out and the proper space group for calcium ferrite is $Pnam$.

With the very short c dimension (3·024 Å), it seemed probable that all atoms would be resolved in a projection on (001). Consequently, it was decided to concentrate, at first, on the ($hk0$) Weissenberg data only. Intensity readings were made from three films of different exposure times with enough overlap of readable intensities to place all values on the same scale. These values were then corrected for Lorentz and polarization factors. An absolute intensity scale and a temperature factor ($B = 0{\cdot}49$ Å^2) were established by the method of Wilson (1942) and Harker (1948). From these, unitary structure factors were calculated.

The final structure was achieved by two different procedures. The first involved trial-and-error adjustment of parameters in the early stages, followed by the application of sign-determining relations for a limited set of reflections. This procedure became involved, for reasons to be discussed, and occasioned the second procedure which was based exclusively on the sign relationships. The latter process proved to be straightforward and quickly led to the same structure.

At the outset, approximate locations of metal atoms were obtained readily from an optical Patterson projection, made with Huggins masks. The metal atoms were in an almost regular hexagonal net which yielded a set of strong intensities that were in good agreement with the strongest intensities that were observed. In addition to general discrepancies for weaker reflections, the set of $hk0$ reflections with k odd, all relatively weak, were identically zero for this arrangement of metal atoms. Because of the simple nature of this arrangement, it seemed that trial-and-error methods would suffice to improve the structure to the point where Fourier methods could be employed. This did not prove to be the case. The placement of oxygens from spatial considerations and adjustment of metal parameters did give satisfactory intensity agreement for reflections other than those with k odd, but for these the agreement was poor. Accepting the signs as established for the other reflections, those for F_{hk0} with k odd were ascertained from inequality and equality relations, mainly the latter. A complication arose here in that systematic conflicts of sign occurred in the equality relations. These could be removed by assuming that the plane group was *pmg* rather than *pgg*. With the signs thus made available, the resulting projection gave many double or elongated peaks. A choice of one set of peak positions (related to the remaining peaks by a center of symmetry at the origin) corresponded to a reasonable atomic arrangement with improved intensity agreement, but the origin of this arrangement was not at a center of symmetry. Refinement procedures led to the projection shown in Fig. 1(a), which is truly centrosymmetric and with plane group *pgg* but with the center of symmetry displaced from the origin by $x = 0{\cdot}009$, $y = 0{\cdot}250$. The atomic parameters from this projection are within 0·002 of the final parameters given above.

The complications stemmed from the circumstance that the small deviations (from the highly symmetrical net of metal atoms) necessary to give improved in-

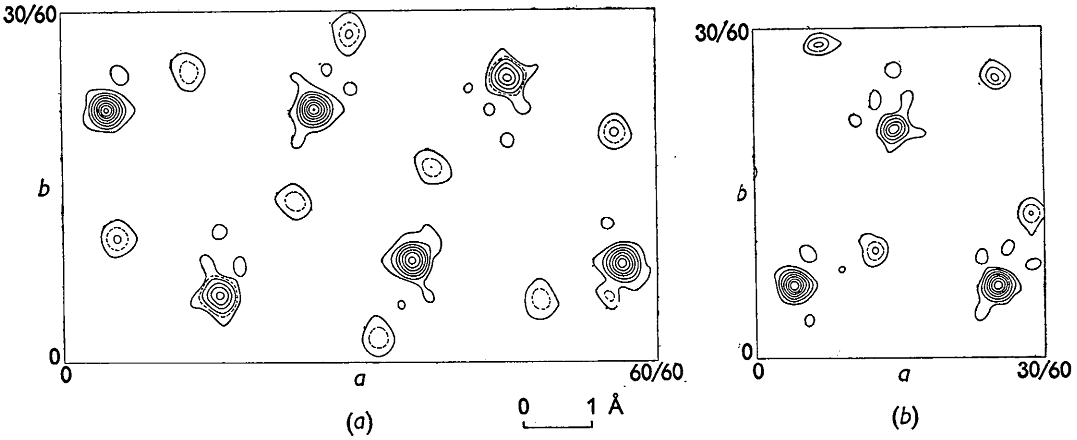

Fig. 1. Electron density for (001) projection of $CaFe_2O_4$ (*a*) with origin at the pseudo-center of symmetry, (*b*) with origin at a center of symmetry.

tensity agreement could be taken in two ways, corresponding to a choice of origin at a true center of symmetry or at a pseudo-center related to it by a translation of $y = \frac{1}{4}$. In point of fact, the latter choice was made. Consequently the signs of F_{hk0} with $k = 4n+2$ were systematically incorrect and led to the difficulties encountered in determining signs of F_{hk0} with k odd.

During the completion of the procedure outlined above, as the reason for the complications became evident, it was decided to undertake the other approach, using only direct methods throughout. There is a high fraction of unitary structure factors with large values among the reflections with k even; 50 out a total of 138 have values $> 0{\cdot}4$. The signs for all of these could be quickly established from the simplest inequality relationships (Harker & Kasper, 1948). The ones used almost exclusively were:

$$2U^2_{hk0} \leq 1+U_{2h,2k,0}\,,$$
$$4U^2_{hk0} \leq \{1+(-1)^{h+k}U_{2h,0,0}\}\,\{1+(-1)^{h+k}U_{0,2k,0}\}\,,$$
$$4U^2_{hk0} \leq \{1+(-1)^{h+k}U_{2h,0,0} + (-1)^{h+k}U_{0,2k,0}+U_{2h,2k,0}\}\,,$$
$$(U_{hk0}\pm U_{h'k'0})^2 \leq (1\pm U_{h+h',k+k',0})\,(1\pm U_{h-h',k-k',0})\,.$$

Many more signs could be determined for the smaller U_{hk0}'s from the last relationship above, but hardly any for those U_{hk0} where k is odd. The equality relationship in the simplest form (Cochran, 1952) was employed then; i.e.

$$s(hk0) = s(h'k'0)s(h+h',\, k+k',\, 0)$$
$$\text{for}\quad \bar{U} > 1/\sqrt{(nt)} \cong 0{\cdot}3\,,$$

where

$\bar{U}$ ≡ root mean square value of all unitary structure factors in the relation,
s ≡ sign,
n ≡ number of structure factors related by symmetry (4),
t ≡ number of independent terms used for the equality (3).

All possible relations satisfying the above conditions were tested for the U's of unknown sign, and only a small number were left uncertain. The first projection was quite satisfactory and the atomic parameters called for only a few sign changes. The next projection with these changes could not be refined. It is shown in Fig. 1(*b*) and the values of the parameters are the final ones given above. The agreement of calculated and observed structure factors (Table 2) is quite good, with $R = 0{\cdot}14$ (including unobserved reflections for which the calculated magnitude is greater than a value 20% below the limit of observation). The allocation of atoms to the planes $z = \frac{1}{4}$ or $\frac{3}{4}$ could be made unequivocally from spatial considerations with the knowledge of x and y parameters; it was confirmed by intensity comparisons for layers with l odd.

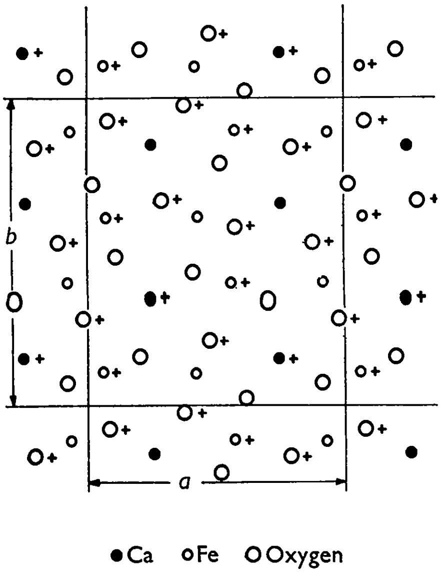

Fig. 2. Projection on (001) of the $CaFe_2O_4$ structure.

Table 2. *Observed and calculated structure factors*

hk0	F_o	F_c	hk0	F_o	F_c	hk0	F_o	F_c	hk0	F_o	F_c	hk0	F_o	F_c	hk0	F_o	F_c	hk0	F_o	F_c
2,0,0	63	64	25,3,0	8*	6	9,7,0	10*	8	22,10,0	10*	3	13,14,0	14*	9	11,18,0	14*	8	1,23,0	14*	1
4,0,0	10	13				10,7,0	11*	7	23,10,0	9*	4	14,14,0	28	28	12,18,0	17	15	2,23,0	14*	2
6,0,0	155	151	0,4,0	171	170	11,7,0	12*	2	24,10,0	6*	4	15,14,0	14*	10	13,18,0	14*	7	3,23,0	14*	8
8,0,0	44	40	1,4,0	25	26	12,7,0	15	17				16,14,0	14*	7	14,18,0	13	20	4,23,0	14*	2
10,0,0	13	18	2,4,0	22	17	13,7,0	13*	9	1,11,0	10*	5	17,14,0	13*	9	15,18,0	13*	13	5,23,0	14*	7
12,0,0	63	56	3,4,0	6*	2	14,7,0	19	24	2,11,0	10*	3	18,14,0	13*	1	16,18,0	12*	5	6,23,0	14*	3
14,0,0	23	28	4,4,0	7	9	15,7,0	14*	9	3,11,0	10*	5	19,14,0	12*	0	17,18,0	11*	0	7,23,0	13*	2
16,0,0	14	23	5,4,0	42	46	16,7,0	14*	7	4,11,0	19	18	20,14,0	11*	11	18,18,0	10*	7	8,23,0	13*	3
18,0,0	24	22	6,4,0	113	118	17,7,0	14*	8	5,11,0	18	10	21,14,0	9*	2	19,18,0	9*	6	9,23,0	13*	10
20,0,0	14*	15	7,4,0	26	25	18,7,0	14*	6	6,11,0	11*	4	22,14,0	8*	4	20,18,0	7*	8	10,23,0	12*	1
22,0,0	12	21	8,4,0	50	55	19,7,0	14*	7	7,11,0	11*	0							11,23,0	12*	5
24,0,0	10*	6	9,4,0	10*	2	20,7,0	21	16	8,11,0	12	16	1,15,0	12	7	1,19,0	14*	4	12,23,0	11*	2
			10,4,0	17	24	21,7,0	13*	7	9,11,0	12*	1	2,15,0	12*	1	2,19,0	14*	3	13,23,0	10*	3
1,1,0	5*	1	11,4,0	45	44	22,7,0	12*	10	10,11,0	12	11	3,15,0	12*	3	3,19,0	14*	2	14,23,0	9*	3
2,1,0	5*	3	12,4,0	56	51	23,7,0	10*	0	11,11,0	13*	7	4,15,0	22	14	4,19,0	14*	2	15,23,0	8*	7
3,1,0	24	19	13,4,0	12*	5	24,7,0	8*	3	12,11,0	13*	9	5,15,0	16	15	5,19,0	14*	5	16,23,0	6*	0
4,1,0	34	33	14,4,0	28	32				13,11,0	14*	0	6,15,0	13	11	6,19,0	14*	2			
5,1,0	22	18	15,4,0	13*	6	0,8,0	68	68	14,11,0	29	25	7,15,0	13*	2	7,19,0	14*	3	0,24,0	23	19
6,1,0	27	24	16,4,0	14	19	1,8,0	62	65	15,11,0	14*	0	8,15,0	13*	16	8,19,0	14*	1	1,24,0	14*	1
7,1,0	16	15	17,4,0	14*	14	2,8,0	35	35	16,11,0	14*	6	9,15,0	14*	8	9,19,0	14*	6	2,24,0	13*	8
8,1,0	8*	4	18,4,0	14	18	3,8,0	48	45	17,11,0	14*	5	10,15,0	14*	8	10,19,0	14*	3	3,24,0	13	8
9,1,0	31	32	19,4,0	14*	2	4,8,0	15	16	18,11,0	14*	5	11,15,0	14*	11	11,19,0	14*	10	4,24,0	13*	6
10,1,0	10*	10	20,4,0	14*	8	5,8,0	66	73	19,11,0	13*	0	12,15,0	14*	4	12,19,0	14*	4	5,24,0	13*	2
11,1,0	11	12	21,4,0	13*	1	6,8,0	40	51	20,11,0	18	17	13,15,0	14*	8	13,19,0	13*	12	6,24,0	18	18
12,1,0	33	26	22,4,0	12*	10	7,8,0	32	33	21,11,0	11*	1	14,15,0	14*	9	14,19,0	13*	10	7,24,0	13*	6
13,1,0	12*	3	23,4,0	11*	3	8,8,0	33	32	22,11,0	10*	4	15,15,0	14*	8	15,19,0	12*	10	8,24,0	12*	6
14,1,0	20	18	24,4,0	9*	6	9,8,0	11*	3	23,11,0	8*	5	16,15,0	14*	6	16,19,0	11*	1	9,24,0	16	17
15,1,0	22	20	25,4,0	7*	1	10,8,0	11*	9				17,15,0	13*	5	17,19,0	10*	10	10,24,0	11*	8
16,1,0	14	16				11,8,0	43	44	0,12,0	10*	6	18,15,0	12*	4	18,19,0	9*	0	11,24,0	11*	5
17,1,0	14*	6	1,5,0	35	38	12,8,0	12	20	1,12,0	49	47	19,15,0	11*	10	19,19,0	13	14	12,24,0	10*	10
18,1,0	14*	7	2,5,0	25	14	13,8,0	16	14	2,12,0	41	38	20,15,0	10*	10				13,24,0	9*	11
19,1,0	14*	11	3,5,0	26	24	14,8,0	16	19	3,12,0	43	42	21,15,0	9*	3	0,20,0	14	17	14,24,0	8*	5
20,1,0	14*	9	4,5,0	7	3	15,8,0	14*	2	4,12,0	11	17	22,15,0	6*	2	1,20,0	14*	11	15,24,0	6*	6
21,1,0	13*	6	5,5,0	8	6	16,8,0	14*	13	5,12,0	64	65				2,20,0	14*	6			
22,1,0	12*	12	6,5,0	36	35	17,8,0	26	27	6,12,0	11*	0	0,16,0	29	30	3,20,0	32	34	1,25,0	13	9
23,1,0	11*	5	7,5,0	9*	2	18,8,0	14*	3	7,12,0	24	21	1,16,0	33	33	4,20,0	14*	10	2,25,0	13*	0
24,1,0	10*	4	8,5,0	9	9	19,8,0	14*	6	8,12,0	24	19	2,16,0	13	15	5,20,0	14	19	3,25,0	13*	0
25,1,0	8*	10	9,5,0	17	16	20,8,0	13*	9	9,12,0	31	29	3,16,0	52	49	6,20,0	17	19	4,25,0	13*	1
			10,5,0	10*	6	21,8,0	12*	4	10,12,0	13*	3	4,16,0	13	18	7,20,0	14*	7	5,25,0	12*	3
0,2,0	--	18	11,5,0	29	22	22,8,0	11*	7	11,12,0	63	55	5,16,0	37	38	8,20,0	14*	2	6,25,0	12*	5
1,2,0	29	26	12,5,0	16	16	23,8,0	10*	9	12,12,0	14*	1	6,16,0	13	14	9,20,0	22	24	7,25,0	12*	4
2,2,0	40	41	13,5,0	12*	7	24,8,0	8*	1	13,12,0	14*	1	7,16,0	13*	12	10,20,0	14*	10	8,25,0	11*	6
3,2,0	157	165	14,5,0	13*	5				14,12,0	14*	10	8,16,0	14	16	11,20,0	14	11	9,25,0	11*	2
4,2,0	74	66	15,5,0	13	10	1,9,0	11	13	15,12,0	14*	10	9,16,0	34	33	12,20,0	13*	13	10,25,0	10*	5
5,2,0	54	48	16,5,0	14*	0	2,9,0	32	24	16,12,0	14*	1	10,16,0	14*	5	13,20,0	13*	9	11,25,0	9*	4
6,2,0	27	25	17,5,0	24	22	3,9,0	10	8	17,12,0	21	26	11,16,0	26	29	14,20,0	12*	2	12,25,0	9*	5
7,2,0	33	37	18,5,0	14*	8	4,9,0	16	9	18,12,0	14*	3	12,16,0	14*	7	15,20,0	11*	15	13,25,0	7*	0
8,2,0	18	23	19,5,0	14*	6	5,9,0	9	8	19,12,0	13*	1	13,16,0	14*	6	16,20,0	11*	6			
9,2,0	77	86	20,5,0	14*	1	6,9,0	10*	1	20,12,0	12*	9	14,16,0	14*	8	17,20,0	9*	11	0,26,0	12*	16
10,2,0	10	9	21,5,0	13*	7	7,9,0	10*	3	21,12,0	11*	3	15,16,0	14*	11	18,20,0	8*	6	1,26,0	12*	5
11,2,0	21	27	22,5,0	12*	6	8,9,0	21	16	22,12,0	9*	2	16,16,0	13*	4				2,26,0	12*	2
12,2,0	11*	3	23,5,0	15	16	9,9,0	20	20	23,12,0	7*	9	17,16,0	14	18	1,21,0	14*	1	3,26,0	12*	17
13,2,0	32	32	24,5,0	9*	4	10,9,0	12*	4				18,16,0	12*	6	2,21,0	14*	2	4,26,0	12*	4
14,2,0	13*	11	25,5,0	7*	9	11,9,0	30	27	1,13,0	11*	1	19,16,0	11*	7	3,21,0	14*	1	5,26,0	11*	12
15,2,0	38	36				12,9,0	13*	1	2,13,0	11*	4	20,16,0	9*	2	4,21,0	14*	1	6,26,0	14	17
16,2,0	14*	2	0,6,0	33	24	13,9,0	13*	1	3,13,0	11*	10	21,16,0	8*	2	5,21,0	14*	1	7,26,0	11*	0
17,2,0	14*	16	1,6,0	40	35	14,9,0	14*	9	4,13,0	11*	2				6,21,0	14*	10	8,26,0	10*	6
18,2,0	14*	4	2,6,0	101	102	15,9,0	14*	6	5,13,0	11*	13	1,17,0	13	8	7,21,0	14	11	9,26,0	10*	8
19,2,0	14*	19	3,6,0	121	115	16,9,0	14*	0	6,13,0	12*	7	2,17,0	13*	1	8,21,0	14*	2	10,26,0	9*	6
20,2,0	14*	6	4,6,0	52	52	17,9,0	39	29	7,13,0	12*	0	3,17,0	13*	2	9,21,0	14*	6	11,26,0	8*	12
21,2,0	13*	6	5,6,0	34	36	18,9,0	14*	6	8,13,0	12	8	4,17,0	13*	5	10,21,0	14*	5	12,26,0	6*	11
22,2,0	12*	1	6,6,0	25	24	19,9,0	14*	6	9,13,0	13	10	5,17,0	13*	3	11,21,0	13*	1			
23,2,0	11*	6	7,6,0	9*	5	20,9,0	13*	4	10,13,0	13	12	6,17,0	14*	13	12,21,0	13*	9	1,27,0	11*	3
24,2,0	10*	1	8,6,0	53	64	21,9,0	12*	4	11,13,0	25	22	7,17,0	14	3	13,21,0	12*	6	2,27,0	11*	2
25,2,0	8*	8	9,6,0	67	66	22,9,0	11*	1	12,13,0	14*	1	8,17,0	14*	1	14,21,0	11*	6	3,27,0	11*	2
			10,6,0	15	13	23,9,0	17	14	13,13,0	14*	1	9,17,0	14*	1	15,21,0	11*	6	4,27,0	10*	0
1,3,0	13	8	11,6,0	34	34	24,9,0	7*	5	14,13,0	14	9	10,17,0	14*	0	16,21,0	10*	5	5,27,0	10*	4
2,3,0	15	11	12,6,0	13	18				15,13,0	14*	1	11,17,0	14*	11	17,21,0	8*	1	6,27,0	10*	5
3,3,0	21	22	13,6,0	17	22	0,10,0	45	43	16,13,0	14*	3	12,17,0	14*	15	18,21,0	6*	6	7,27,0	9*	1
4,3,0	6*	5	14,6,0	31	34	1,10,0	19	22	17,13,0	25	22	13,17,0	14*	0				8,27,0	9*	2
5,3,0	7*	4	15,6,0	14	17	2,10,0	72	82	18,13,0	13*	3	14,17,0	14*	9	0,22,0	39	39	9,27,0	8*	6
6,3,0	30	25	16,6,0	14*	4	3,10,0	36	44	19,13,0	12*	2	15,17,0	13*	2	1,22,0	14*	1	10,27,0	7*	1
7,3,0	8*	2	17,6,0	14	14	4,10,0	42	47	20,13,0	11*	11	16,17,0	13*	5	2,22,0	14*	5			
8,3,0	33	30	18,6,0	14*	4	5,10,0	43	46	21,13,0	10*	2	17,17,0	12*	12	3,22,0	27	26	0,28,0	10*	13
9,3,0	15	11	19,6,0	14*	13	6,10,0	30	29	22,13,0	9*	4	18,17,0	11*	2	4,22,0	14*	0	1,28,0	10*	3
10,3,0	20	19	20,6,0	15	18	7,10,0	11*	2	23,13,0	11	15	19,17,0	10*	1	5,22,0	14*	4	2,28,0	9*	15
11,3,0	11*	6	21,6,0	13*	5	8,10,0	57	60				20,17,0	8*	5	6,22,0	29	28	3,28,0	9*	10
12,3,0	11	14	22,6,0	12*	2	9,10,0	12	19	0,14,0	41	41	21,17,0	6*	2	7,22,0	14*	0	4,28,0	9*	5
13,3,0	15	17	23,6,0	10*	9	10,10,0	12	12	1,14,0	21	21				8,22,0	14*	9	5,28,0	9*	2
14,3,0	29	22	24,6,0	9*	3	11,10,0	33	33	2,14,0	38	40	0,18,0	52	43	9,22,0	20	20	6,28,0	8*	11
15,3,0	26	19	25,6,0	6*	7	12,10,0	13*	14	3,14,0	12*	1	1,18,0	13*	5	10,22,0	13*	4	7,28,0	7*	4
16,3,0	14*	14				13,10,0	14*	4	4,14,0	32	31	2,18,0	14	20	11,22,0	13*	10	8,28,0	6*	12
17,3,0	14*	5	1,7,0	11	2	14,10,0	36	35	5,14,0	20	20	3,18,0	26	28	12,22,0	12*	12			
18,3,0	14*	11	2,7,0	26	24	15,10,0	14	14	6,14,0	34	36	4,18,0	14*	0	13,22,0	11*	6	1,29,0	8*	1
19,3,0	14	18	3,7,0	14	14	16,10,0	14*	0	7,14,0	13	20	5,18,0	14*	5	14,22,0	10*	8	2,29,0	8*	4
20,3,0	19	19	4,7,0	10	9	17,10,0	14	19	8,14,0	45	45	6,18,0	29	29	15,22,0	9*	8	3,29,0	7*	0
21,3,0	13*	10	5,7,0	10	18	18,10,0	14*	2	9,14,0	13	9	7,18,0	14*	10	16,22,0	8*	8	4,29,0	7*	0
22,3,0	12*	14	6,7,0	17	16	19,10,0	13*	3	10,14,0	14*	3	8,18,0	29	27	17,22,0	6*	4	5,29,0	6*	2
23,3,0	11*	2	7,7,0	9*	8	20,10,0	15	20	11,14,0	14	18	9,18,0	14	18						
24,3,0	10*	2	8,7,0	30	33	21,10,0	12*	4	12,14,0	14*	12	10,18,0	14*	4						

*Indicates minimum observable amplitude for unobserved reflection.

The Fourier series and structure factor calculations were performed on an IBM computer. The former were made by the method of Wolontis (1955).

Discussion of the structure

A drawing of the final structure in projection on (001) is shown in Fig. 2. It is made up of layers of atoms at

$\frac{1}{4}$ and $\frac{3}{4}$ in z. Each iron atom is at the center of a distorted octahedron of oxygens (Fig. 3(*a*)) with Fe–O distances varying from 1·98 to 2·09 Å. Each calcium atom has eight oxygens surrounding it (Fig. 3(*b*)); it is at the center of a triangular prism of six oxygens with Ca–O distances 2·36–2·51 Å; one rectangular face of the prism is narrower than the other two, and oxygens out the centers of the two wider faces are at distances of 2·53–2·58 Å; a ninth oxygen out the center of the narrow face might be considered a neighbor of the calcium, but the distance to it is quite long (3·41 Å). A list of metal-oxygen distances is given in Table 3. Iron and calcium in $\mathrm{CaFe_2O_4}$ have the same kind of coordination as titanium and calcium in $\mathrm{CaTi_2O_4}$ (Bertaut & Blum, 1956), but the distortion from regular polyhedra is less in the titanate. These structures can be rationalized on the grounds that they provide expected octahedral coordination of oxygens about iron or titanium, and a higher coordination number (8 or 9) for calcium. The radius ratio, $R_{\mathrm{Ca}}/R_{\mathrm{O}}$, is $\sim 0{\cdot}75$, which is near the value (0·732) for transition from octahedral to higher coordination.

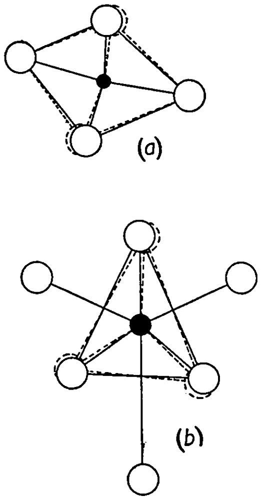

Fig. 3. Coordination (*a*) about Fe atom, (*b*) about Ca atom.

Table 3. *Metal–oxygen distances in* $\mathrm{CaFe_2O_4}$

Metal atom	Oxygen atom	No. of bonds	Bond length
$\mathrm{Fe_{I}}$	$\mathrm{O_{I}}$	2	2·07 Å
$\mathrm{Fe_{I}}$	$\mathrm{O_{III}}$	1	2·03
$\mathrm{Fe_{I}}$	$\mathrm{O_{IV}}$	1	2·00
$\mathrm{Fe_{I}}$	$\mathrm{O_{IV}}$	2	2·07
$\mathrm{Fe_{II}}$	$\mathrm{O_{I}}$	1	2·04
$\mathrm{Fe_{II}}$	$\mathrm{O_{II}}$	2	2·09
$\mathrm{Fe_{II}}$	$\mathrm{O_{II}}$	1	2·02
$\mathrm{Fe_{II}}$	$\mathrm{O_{III}}$	2	1·98
Ca	$\mathrm{O_{I}}$	2	2·51
Ca	$\mathrm{O_{I}}$	1	3·41
Ca	$\mathrm{O_{II}}$	2	2·38
Ca	$\mathrm{O_{III}}$	1	2·53
Ca	$\mathrm{O_{III}}$	1	2·58
Ca	$\mathrm{O_{IV}}$	2	2·37

It is interesting to consider the implications as to magnetic structure that follow from the crystal structure of calcium ferrite. It is established that in oxide systems, magnetic moments are aligned by an indirect effect involving an intervening oxide ion (superexchange). The effect is at its maximum for a cation–oxide ion–cation angle of 180°, and a minimum for 90°. Consequently, it is pertinent to consider nets formed by connections which involve large values of these angles. Such a network is given in Fig. 4. It can be seen that strong magnetic interactions would be expected to exist within thin sections normal to the y axis, but only very weak interactions would occur between the sections, where connection is made through angles of 99°. Since the moments of the two iron atoms on either side of an oxygen can be expected to be antiparallel to each other, one would expect the sections to be antiferromagnetic.

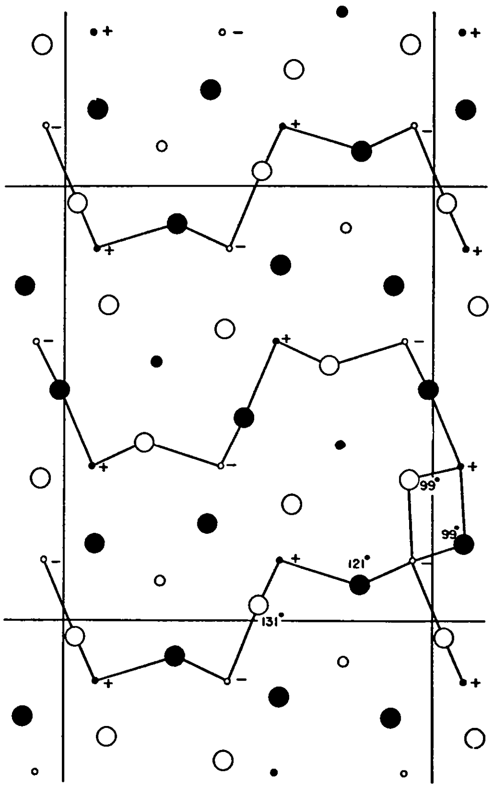

Fig. 4. Network of large Fe–O–Fe angles in $\mathrm{CaFe_2O_4}$.

One may speculate as to why calcium ferrite does not occur with the same structure as calcium titanate, where the coordination figures are more regular. In the titanate structure the number of Ti–O–Ti connections with large included angle is only half that of Fe–O–Fe connections in the ferrite. It may be that the stronger Fe–O–Fe magnetic interaction would favor the structure enabling more such connections to be made at the expense of regularity of atomic arrangement.

We are very grateful to Mr R. M. Waterstrat, who took the X-ray photographs used in this study, to Mr R. Habermann, who directed the calculations made on IBM equipment, and to Dr Howard T. Evans for helpful comments.

References

Bertaut, E. F. & Blum, P. (1956). *Acta Cryst.* **9**, 121.
Bertaut, E. F., Blum, P. & Magnano, G. (1955). *C. R. Acad. Sci., Paris*, **241**, 757.
Burdese, A. (1952). *Ric. Sci.* **22**, 259.
Cochran, W. (1952). *Acta Cryst.* **5**, 65.
Forestier, H. (1931). *C. R. Acad. Sci., Paris*, **192**, 842.
Harker, D. (1948). *Amer. Min.* **33**, 764.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Hilpert, S. & Wille, A. (1932). *Z. phys. Chem.* B, **18**, 291.
Kittel, H. & Hüttig, G. F. (1934). *Z. anorg. Chem.* **217**, 193.
Rudorff, W. & Reuter, B. (1945). *Z. anorg. Chem.* **253**, 177.
Sosman, R. B. & Merwin, H. E. (1916). *J. Wash. Acad. Sci.* **6**, 532.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.
Wolontis, V. M. (1955). *Acta Cryst.* **8**, 86.

Acta Cryst. (1957). **10**, 337

The Unit Cell of Orthorhombic Pentacalcium Trialuminate, $5CaO.3Al_2O_3$

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(*Received* 12 *November* 1956 *and in revised form* 24 *December* 1956)

The orthorhombic form of $5CaO.3Al_2O_3$ has been found to belong to space group $C222_1\text{–}D_2^5$, 4 formula units per unit cell of $a = 10{\cdot}975$, $b = 11{\cdot}250$, $c = 10{\cdot}284$ Å (probable error $\pm0{\cdot}005$ Å). Single crystals were investigated with copper radiation. Density 3·03–3·06 g.cm.$^{-3}$. Optical constants: colourless, non-pleochroic, biaxial negative $2V = 88{\cdot}5\pm0{\cdot}8°$, $\alpha = 1{\cdot}680\pm0{\cdot}001$, $\beta = 1{\cdot}682 \pm0{\cdot}001$, $\gamma = 1{\cdot}685\pm0{\cdot}001$, $\gamma-\alpha = 0{\cdot}005$. Acute bisectrix ($X$) perpendicular to cleavage face (001), obtuse bisectrix (Z) parallel to crystallographic a axis.

The similarity of the X-ray powder pattern to that of gehlenite, $2CaO.Al_2O_3.SiO_2$, is pointed out.

Introduction

Over forty years ago, Shepherd, Rankin & Wright (1909) reported a stable and an unstable form of $5CaO.3Al_2O_3$ with distinct optical characteristics. The structure of the stable form has been determined by Büssem & Eitel (1936) by single-crystal methods; the unit cell is cubic, $a = 11{\cdot}95$ Å. The measured density of 2·69 g.cm.$^{-3}$ did not agree with that calculated on the basis of a composition of $5CaO.3Al_2O_3$ and to bring the calculated density in line with the measured, the formula $12CaO.7Al_2O_3$ was suggested. It was then necessary to assume that two excess oxygens out of a total of 66 must be statistically distributed over the unit cell.

Lagerquist, Wallmark & Westgren (1937) subsequently suggested a slightly different alternative structure, with vacancies in aluminium locations. Their formula, $9CaO.5Al_2O_3$, as with $5CaO.3Al_2O_3$, does not allow an integral number of molecules to fit into the measured unit cell.

Dyckerhoff (1924) investigated laboratory melts and thought that the unstable form of $5CaO.3Al_2O_3$ might be found in high-alumina cement. This was further investigated by Sundius (1939), who found in certain high-alumina cements a needle- or lath-shaped pleochroic mineral which had optical properties similar to unstable $5CaO.3Al_2O_3$, as described by Shepherd *et al.* (1909); (Rankin & Wright (1915*a*, *b*) give more details). Henceforth in the literature this pleochroic cement mineral has been referred to as 'unstable $5CaO.3Al_2O_3$', although Sundius himself had observed that there is an appreciable amount of SiO_2 and Fe_2O_3 present.

Parker (1954), as a result of phase equilibrium studies in the system $CaO\text{–}Al_2O_3\text{–}MgO\text{–}SiO_2$, has demonstrated that the blue pleochroic mineral found in high-alumina cements is not unstable $5CaO.3Al_2O_3$ but a quaternary compound with a probable formula $6CaO.4Al_2O_3.(Mg,Fe)O.SiO_2$. Recently single crystals of an orthorhombic form of $5CaO.3Al_2O_3$ were prepared by Welch using the high-temperature microscope device (Welch, 1954).

There is obviously a very great possibility of confusion because the name 'unstable $5CaO.3Al_2O_3$' has been applied to different phases. Moreover, the orthorhombic $5CaO.3Al_2O_3$, although closely resembling Rankin & Wright's unstable compound, may prove