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Refinement of the Crystal Structure of Dicalcium Ferrite, $Ca_2Fe_2O_5$

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The crystal structure of dicalcium ferrite, $Ca_2Fe_2O_5$, has been refined with three-dimensional X-ray intensity data, collected with a Philips automatic, linear single crystal diffractometer, PAILRED. Least squares refinement of the structure yielded an R-value of 0.076. Dicalcium ferrite crystallizes in space group *Pnma* and least squares refinement of Guinier powder data yielded the following unit cell dimensions: $a = 5.4253 \pm 0.0005$ Å, $b = 14.7687 \pm 0.0017$ Å, and $c = 5.5980 \pm 0.0005$ Å.

In $Ca_2Fe_2O_5$, iron is both octahedrally and tetrahedrally coordinated by oxygen, and the crystal structure is built up from chains of alternating iron-oxygen octahedra and tetrahedra, running parallel to the b-axis, with calcium atoms in the holes between the polyhedra. The octahedra and tetrahedra are, however, considerably distorted, evidently to improve the coordination polyhedron of the nine oxygen atoms around each calcium. The iron-oxygen distances within the octahedron lie between 1.961 and 2.117 Å (*cf.* 2.066 Å in Fe_3O_4), while the tetrahedral distances Fe–O lie between 1.837 and 1.923 Å (*cf.* 1.876 in Fe_3O_4).

The crystal structure of dicalcium ferrite has been determined by Bertaut *et al.*[1] As a complement to an investigation of the crystal structures of compounds with the approximate formula $CaFe_4O_7$, it was considered desirable to have accurate information concerning the structures of the other known binary calcium ferrites, *i.e.* $Ca_2Fe_2O_5$ and $CaFe_2O_4$. Since the configuration of oxygen about iron in the latter compound is distorted octahedral,[2] it was suspected that the coordination in dicalcium ferrite was not as regular as had been reported.[1]

EXPERIMENTAL

Preparation. Dicalcium ferrite was prepared by intimately mixing finely ground powders of calcium oxalate and iron(III) oxalate and pressing the resulting mixture to a cylindrical pellet 13 mm in diameter and approximately 2 mm thick. The pellet was then heated to 1100°C for 3 h in a tube furnace, through which oxygen was passed. The sintered mass was crushed and single crystals were picked out.

The mixture of oxalates, which decomposes to give the oxides, reacts much more rapidly than a mixture of the oxides and is also more reactive than a mixture of calcium carbonate and iron(III) carbonate. The gas evolved during the thermal decomposition of the oxalates contains equal amounts of CO_2 and CO which entails a low oxygen partial pressure at 1100°C ($\log p_{O_2} = -12.418$).[3] This does not, however, cause any problems since, as Turkdogan [4] has shown, dicalcium ferrite is stable down to about $\log p_{O_2} = -13.60$.

X-Ray methods. The cell parameters were determined by means of a Guinier camera using Cu$K\alpha_1$-radiation with lead nitrate as an internal standard ($a_{Pb(NO_3)_2} = 7.8564$ Å at 21°C[5]).

The crystal fragments were plates of irregular shape with the *b*-axis perpendicular to the plate surface. A suitable single crystal was therefore first mounted in a Buerger precession camera with the *b*-axis precessing around the primary beam. In this way the directions of the other axes could be located and the crystal could then be mounted along the *a*-axis. The single crystal intensity data were collected with a Philips automatic, linear diffractometer, PAILRED, using Mo$K\alpha$-radiation and a LiF (200) monochromator. The layers for which $h = 0,1 \cdots 7$ were registered for $\sin\theta < 0.754$ which gave 987 independent reflections.

Since the crystal dimensions were about $0.16 \times 0.05 \times 0.16$ mm and the linear absorption coefficient for Mo$K\alpha$-radiation is 87.1 cm^{-1}, the intensities were corrected for absorption according to Coppens *et al.*[6] Nine planes were used to define the crystal and the volume was divided into 256 elements.

Computing methods. Lorentz and polarization corrections of the single crystal intensities were performed with the program DATAP1[10] and the absorption correction with the program DATAP2.[11] Since the diffractometer measured intensities of reflections with both positive and negative values of *l*, the mean values of the pairs $F(hkl)$ and $F(hk\bar{l})$ were calculated.[12] Least squares refinement of positional parameters, temperature factors and scale factors was performed with LALS,[11] difference electron density calculation with DRF [11] and calculation of interatomic distances and angles with DISTAN.[11] The atomic scattering factors for Ca, Fe, and O used in the calculations were those of Cromer and Waber.[13]

SYMMETRY AND CELL DIMENSIONS

Rotation and Weissenberg photographs, as well as the subsequent diffractometer data, indicated an orthorhombic symmetry. The observed conditions for reflection are: $hk0$: $h = 2n$; $0kl$: $k + l = 2n$, which give the possible space groups *Pnma* (No. 62) and $Pna2_1$ (No. 33),[7] in accordance with Bertaut.[1] Since Bertaut has exhibited the existence of a centre of symmetry by statistical methods, it was not considered necessary to take the non-centrosymmetrical space group, $Pna2_1$, into account.

The Guinier powder photograph was evaluated on a SAAB D21 computer with the program PEPP.[8] This program calculates, by the method of least squares, a function for the standard substance which correlates the glancing angles with the measured distances. From this function the $\sin^2\theta$-values for $Ca_2Fe_2O_5$ were calculated and the least squares refinement of the cell parameters was carried out on an IBM 360/65 computer using the program POWDER.[9] The following values were obtained: $a = 5.4253 \pm 0.0005$ Å, $b = 14.7687 \pm 0.0017$ Å, $c = 5.5980 \pm 0.0005$ Å, and $V = 448.5$ Å^3. Observed and calculated $\sin^2\theta$ values are listed in Table 1.

REFINEMENT

Since the magnitudes of the observed structure factors were comparable with those of Bertaut *et al.*,[1] it was considered appropriate to start with a calculation of structure factors based on the atomic coordinates published

Table 1. Guinier powder photograph of $Ca_2Fe_2O_5$. $\lambda(CuK\alpha_1) = 1.54051$ Å.

h k l	$10^5 \times \sin^2\theta$ obs	$10^5 \times \sin^2\theta$ calc	*F* calc	*I* obs
0 2 0	1089	1088	48	w
0 1 1	2166	2165	32	w
1 1 1	4181	4181	24	vw
0 3 1	4346	4342	67	s
0 4 0		4352	86	
1 2 1	4992	4997	9	vvw
1 3 1	6355	6357	50	m
0 0 2	7576	7573	233	vs
2 0 0	8058	8063	264	vs
1 4 1	8262	8262	202	vvs
0 5 1	8692	8694	91	s
1 0 2	9573	9589	47	vw
1 5 1	10690	10710	42	w
0 4 2	11915	11926	27	vw
2 3 1	12401	12405	60	m
1 6 1	13704	13702	98	s
2 0 2	15633	15637	257	vs
1 5 2	16390	16390	52	vw
2 2 2	16720	16725	82	w
0 8 0	17413	17410	259	s
2 6 0	17849	17856	55	vvw
0 3 3	19492	19488	133	m
1 8 1	21330	21319	70	vw
3 3 1	22473	22484	91	w
1 4 3	23408	23408	154	vs
0 5 3	23839	23840	91	vw
3 4 1	24391	24388	143	s
0 8 2	24979	24983	144	m
2 8 0	25470	25473	160	m
3 2 2	26807	26804	55	w
2 3 3	27543	27551	80	w
1 6 3	28847	28849	77	w
3 6 1	29832	29829	81	vw
0 0 4	30302	30293	123	w
1 10 1	31112	31112	70	vw
0 2 4	31377	31381	112	vw
2 5 3	31890	31904	83	vw
4 0 0	32234	32253	165	w
2 8 2	33026	33046	151	m
4 5 0	39069	39054	48	vvw
0 9 3		39074	23	
3 4 3	39541	39535	102	vw

by Bertaut. The subsequent comparison of the observed and calculated structure factors yielded an *R*-value of 0.12, and it was therefore decided to proceed directly with a least squares refinement. In the first three cycles of least-squares calculations positional parameters, isotropic temperature factors and an overall scale factor were refined. In the subsequent cycles the positional parameters were refined together with either separate scale factors for each layer or anisotropic temperature coefficients and an overall scale factor. Each

reflection was given a weight $w=\{a+|F_o|+c|F_o|^2+d|F_o|^3\}^{-1}$, according to Cruickshank,[14] with $a=15.0$, $c=0.25$, and $d=0.001$. In the last cycle of refinement the maximum shift was less than 1 % of the estimated standard deviations. The final R-value was 0.076. A difference electron density calculation provided a further check that the structure had been correctly described, the height of the largest peak in the difference map being one tenth of the height of an oxygen atom peak.

Table 2. Atomic coordinates, expressed as fractions of the cell edges, and standard deviations for $Ca_2Fe_2O_5$.

Atom	Position	x	y	z
Ca	8*d*	0.4817(2)	0.1080(1)	0.0231(2)
Fe_1	4*a*	0	0	0
Fe_2	4*c*	−0.0541(2)	1/4	−0.0659(2)
O_1	8*d*	0.2623(7)	−0.0154(3)	0.2377(6)
O_2	8*d*	0.0224(8)	0.1406(3)	0.0715(6)
O_3	4*c*	0.5981(10)	1/4	−0.1243(8)

Table 3. Anisotropic temperature parameters β_{ij} and their standard deviations. The expression used is $\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	0.0089(3)	0.0011(0)	0.0066(2)	−0.0005(1)	0.0027(3)	0.0001(1)
Fe_1	0.0044(3)	0.0014(0)	0.0045(2)	0.0001(1)	−0.0002(3)	0.0002(1)
Fe_2	0.0053(3)	0.0010(0)	0.0055(2)	0	−0.0001(3)	0
O_1	0.0089(12)	0.0018(1)	0.0053(6)	−0.0001(5)	−0.0040(12)	0.0006(4)
O_2	0.0120(12)	0.0013(1)	0.0086(7)	0.0005(5)	0.0001(15)	0.0006(5)
O_3	0.0074(15)	0.0016(1)	0.0071(8)	0	−0.0013(18)	0

The atomic parameters obtained in the last cycle are given in Tables 2 and 3, and a comparison between observed and calculated structure factors is given in Table 4. Interatomic distances and angles, together with estimated standard deviations, are given in Table 5.

DISCUSSION OF THE STRUCTURE

The investigation has confirmed the main features of the structure proposed by Bertaut *et al.* The refinement shows, however, some extra details which the former study did not reveal. As Bertaut pointed out there are chains, parallel to the *b*-axis, of alternating iron-oxygen octahedra and tetrahedra (Fig. 1). These are, however, not regular but considerably distorted. In the octahedron the iron atom lies at the center of symmetry and there are four oxygen atoms in a plane inclined at an angle of 9.24° to the *a*-*c*-plane. The remaining two

Table 4. Observed and calculated structure factors. Non-observed reflections are indicated by a zero. The columns are k, F_o and F_c, respectively.

	0 K 0		22	12	12	9	0	5	17	0	0	14	30	30	5	28	28	15	12	-11
2	51	48	24	0	-5	10	16	17	18	9	9	15	0	7	6	15	14	16	17	-15
4	80	86				11	0	-4	19	0	5	16	0	2	7	35	-38	17	24	21
6	26	-29		0 K 7		12	15	-15	20	0	-3	17	0	1	8	145	151	18	20	18
8	240	259	1	23	-20	13	42	43	21	0	-5	18	22	20	9	15	18	19	22	-19
10	40	46	3	40	-38	14	14	13	22	31	28				10	71	74	20	15	-10
12	81	85	5	0	7	15	35	-35	23	0	4		1 K 10		11	0	-3	21	0	-8
14	42	-48	7	25	24	16	11	-10	24	23	21	0	0	-4	12	47	47	22	0	6
16	68	64	9	0	2	17	0	0	25	0	-1	1	0	3	13	26	26	23	21	-17
18	15	19	11	36	-36	18	8	9	26	12	10	2	0	-8	14	24	-21	24	11	-10
20	64	68	13	19	-19	19	0	-5	28	9	-8	3	33	37	15	21	-21	25	18	17
22	24	-25	15	0	9	20	7	-8				4	0	0	16	37	37	26	11	8
24	0	4	17	14	15	21	20	22		1 K 6		5	23	-25	17	0	5	27	0	-1
26	0	-3	19	14	-13	22	8	7	0	14	-14	6	0	-5	18	33	35	28	0	0
			21	20	-18	23	13	-14	1	49	45	7	8	-8	19	0	-5			
	0 K 1		23	0	-6	24	0	-4	2	0	-4	8	0	-1	20	44	46		2 K 6	
1	38	32				25	0	3	3	0	5	9	12	-13	21	16	16	0	48	45
3	64	-67		0 K 8		26	0	5	4	0	-5	10	8	-7	22	13	-12	1	9	-9
5	84	91	0	24	21	27	7	-7	5	19	20	11	27	28	23	0	-8	2	82	75
7	0	-3	2	57	57	28	0	-4	6	0	0	12	0	2	24	0	-2	3	26	25
9	45	45	4	0	7	29	10	8	7	55	-57	13	0	-6	25	0	2	4	0	8
11	17	-17	6	34	36				8	8	-9				26	0	6	5	21	-20
13	36	40	8	12	13		1 K 3		9	9	10		1 K 11		27	8	-6	6	39	38
15	0	-6	10	59	55	0	22	22	10	0	-2	0	15	17	28	33	30	7	9	8
17	25	28	12	0	5	1	0	-7	11	7	8	1	0	-3	29	9	7	8	29	29
19	0	-4	14	16	17	2	21	19	12	0	-3	2	14	16				9	11	-11
21	13	13	16	0	1	3	17	-12	13	36	35	3	0	0		2 K 3		10	74	76
23	9	-9	18	39	36	4	155	154	14	0	4	4	12	13	0	35	-31	11	18	19
25	14	14	20	0	3	5	0	1	15	35	-34	5	0	-3	1	0	9	12	8	9
			22	11	11	6	80	77	16	0	-2	6	14	16	2	27	25	13	10	-9
	0 K 2					7	0	3	17	9	-8	7	0	-1	3	90	-80	14	11	10
0	247	233		0 K 9		8	34	35	18	0	1	8	13	14	4	30	-28	15	0	8
2	0	0	1	20	-22	9	0	-2	19	0	-4	9	0	-4	5	83	83	16	0	4
4	33	-27	3	12	-13	10	26	-27	20	0	-2	10	12	13	6	15	14	17	12	-12
6	48	-50	5	0	-3	11	12	-10	21	33	28				7	0	3	18	51	46
8	136	144	7	33	37	12	67	65	22	0	4		2 K 0		8	23	-23	19	9	9
10	52	51	9	0	5	13	0	-4	23	11	-10	1	37	35	9	36	36	20	10	9
12	46	44	11	10	-12	14	65	63	24	0	1	2	17	-17	10	26	26	21	0	-3
14	37	-34	13	17	-18	15	0	0				3	11	-14	11	38	-35	22	9	7
16	45	44	15	25	25	16	48	43		1 K 7		4	32	-24	12	19	-18	23	0	8
18	34	36	17	14	14	17	0	2	0	32	-30	5	25	28	13	37	37	24	0	-6
20	51	56	19	0	0	18	23	-21	1	0	-9	6	48	-55	14	10	8	25	8	-8
22	11	-11				19	0	-4	2	59	57	7	40	-48	15	11	-8	26	18	17
24	0	5		0 K 10		20	12	11	3	0	3	8	158	160	16	14	-13			
26	10	9	0	9	6	21	0	-3	4	30	29	9	13	11	17	38	35		2 K 7	
			2	20	23	22	27	27	5	9	-13	10	33	36	18	17	17	0	0	-2
	0 K 3		4	0	3	23	0	-2	6	62	62	11	6	-8	19	11	-9	1	18	-16
1	26	23	6	16	19	24	38	35	7	0	6	12	42	49	20	9	-9	2	0	8
3	131	-133	8	0	6	25	0	3	8	18	-18	13	22	26	21	10	9	3	32	-30
5	94	91	10	20	23	26	0	-2	9	9	-8	14	31	-36	22	0	6	4	14	-15
7	44	-42	12	0	5	27	0	0	10	39	38	15	22	-28	23	18	-15	5	16	15
9	26	23	14	14	15	28	0	-1	11	0	-1	16	43	49	24	8	-7	6	0	3
11	84	-79	16	0	4	29	0	-1	12	0	7	17	0	3	25	23	21	7	33	32
13	28	27							13	11	-11	18	26	29	26	0	8	8	0	-3
15	43	-38		0 K 11			1 K 4		14	49	48	19	0	-7	27	0	-1	9	15	14
17	31	28	1	19	-21	0	20	-18	15	0	3	20	56	61	28	0	-5	10	11	11
19	30	-29	3	0	-5	1	61	59	16	0	1	21	14	17				11	23	-22
21	0	5	5	11	-12	2	29	25	17	0	-5	22	11	-12		2 K 4		12	8	-8
23	31	-28	7	23	26	3	27	-24	18	27	24	23	11	-11	0	83	74	13	0	-6
25	23	22	9	0	-7	4	0	-5	19	0	0	24	0	5	1	22	17	14	0	0
			11	0	-8	5	56	57	20	9	-9	25	0	2	2	63	59	15	18	18
	0 K 4					6	20	21	21	0	-7	26	0	6	3	0	4	16	0	-5
0	140	123		1 K 1		7	73	-75	22	31	26	27	8	-7	4	20	-20	17	25	23
2	126	112	0	77	72	8	15	-15	24	9	7	28	48	41	5	0	1	18	10	8
4	0	8	1	28	24	9	19	18				29	8	8	6	0	4	19	0	-5
6	44	44	2	11	-9	10	15	14		1 K 8					7	18	-19	20	0	-2
8	76	74	3	43	-50	11	0	-4	0	0	4		2 K 1		8	55	52	21	13	-10
10	107	101	4	195	202	12	9	-9	1	19	19	0	0	-1	9	0	3	22	0	1
12	19	18	5	37	42	13	58	54	2	0	3	1	0	2	10	77	72	23	0	-1
14	0	0	6	89	98	14	11	11	3	33	33	2	14	13	11	0	3	24	0	-5
16	16	13	7	13	-15	15	51	-47	4	7	9	3	56	-60	12	15	13			
18	55	53	8	66	73	16	9	-9	5	14	-14	4	0	1	13	0	6		2 K 8	
20	25	23	9	22	23	17	0	1	6	0	5	5	29	27	14	0	-7	0	0	7
22	0	0	10	70	-70	18	0	6	7	24	-26	6	0	6	15	11	-9	1	13	-14
24	9	-9	11	23	-25	19	11	-8	8	0	3	7	23	-27	16	17	16	2	38	37
26	17	16	12	83	89	20	0	-8	9	0	-5	8	0	-4	17	0	-4	3	20	22
			13	14	16	21	38	33	10	0	-2	9	0	-6	18	56	49	4	0	-4
	0 K 5		14	63	73	22	0	5	11	26	26	10	12	11	19	0	-1	5	19	-20
1	0	-2	15	9	-10	23	21	-19	12	0	3	11	37	-38	20	32	28	6	22	21
3	81	-70	16	54	61	24	0	-4	13	8	9	12	0	-4	21	0	6	7	41	12
5	62	60	17	13	15	25	0	2	14	0	2	13	0	2	22	0	3	8	0	5
7	17	17	18	39	-43	26	0	3	15	12	-11	14	0	2	23	0	-1	9	15	-15
9	31	31	19	9	-10	27	14	-12	16	0	1	15	19	-22	24	0	-1	10	48	43
11	40	-40	20	21	22	28	8	-6	17	21	-18	16	0	-4	25	0	-3	11	16	17
13	21	21	21	0	5	29	16	14	18	0	-4	17	0	4	26	21	18	12	0	2
15	0	1	22	26	27				19	0	6	18	0	6	27	0	-3	13	15	-13
17	40	37	23	8	-7		1 K 5		20	0	-1	19	12	-14	28	22	20	14	14	13
19	13	-12	24	43	44	0	26	-26	21	16	13	20	0	-4				15	11	10
21	0	2	25	9	8	1	11	-12				21	0	-1		2 K 5		16	0	2
23	14	-14	26	11	-10	2	59	51		1 K 9		22	0	1	0	21	-22	17	14	-13
25	26	23	27	0	-3	3	0	8	0	8	-8	23	12	-13	1	0	-7	18	38	33
			28	0	4	4	81	76	1	0	-4	24	0	-3	2	36	32	19	10	9
	0 K 6		29	0	2	5	0	-7	2	35	37	25	0	6	3	76	-68	20	0	6
0	21	16				6	72	71	3	0	4	26	0	2	4	31	-28	21	0	-7
2	71	62		1 K 2		7	17	18	4	13	13	27	0	-3	5	38	37	22	13	12
4	23	-22	0	52	-47	8	0	-7	5	0	-2	28	0	-2	6	22	21			
6	28	26	1	30	31	9	0	2	6	34	38	29	0	1	7	0	2		2 K 9	
8	13	10	2	31	25	10	20	19	7	0	8				8	19	-19	0	17	16
10	76	76	3	28	-24	11	0	7	8	0	-4		2 K 2		9	9	9	1	20	-21
12	0	-3	4	28	-28	12	30	29	9	0	1	0	242	257	10	28	29	2	0	-7
14	12	10	5	51	52	13	0	-6	10	28	29	1	40	39	11	51	-51	3	14	-15
16	0	0	6	20	21	14	61	56	11	0	6	2	79	82	12	18	-19	4	0	3
18	60	53	7	50	-54	15	13	12	12	9	5	3	13	-12	13	0	1	5	0	-8
20	13	9	8	25	-28	16	18	17	13	0	-1	4	37	35	14	12	13	6	12	-13

Table 4. Continued.

7	26	27
8	11	13
9	0	-3
10	0	-4
11	19	-19
12	0	5
13	25	-24
14	10	-9
15	16	16
16	0	6
17	0	7
	2 K 10	
0	16	17
1	0	-4
2	26	29
3	0	7
4	13	14
5	0	-6
6	22	25
7	0	4
8	13	13
9	0	-5
10	23	25
11	0	6
12	10	10
13	0	-4
14	15	16
	2 K 11	
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2	7	-9
3	0	-4
5	8	-7
6	9	-11
7	24	27
8	11	12
	3 K 1	
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2	11	13
3	84	-91
4	130	143
5	63	71
6	73	81
7	24	-26
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9	37	38
10	41	-41
11	53	-59
12	62	66
13	24	27
14	59	67
15	18	-21
16	41	46
17	27	31
18	25	-29
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21	9	8
22	24	27
23	15	-17
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25	16	20
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28	0	2
	3 K 2	
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4	33	-31
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6	44	45
7	37	-38
8	43	-45
9	0	5
10	34	36
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14	27	25
15	24	-25
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19	0	-2
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24	9	-9
25	0	1
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27	0	-5
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	3 K 3	
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1	0	-8
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3	30	-25
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5	15	16
6	79	73
7	16	15
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9	10	9
10	10	-9
11	16	-17
12	48	46
13	0	1
14	65	61
15	0	6
16	36	32
17	15	14
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19	0	-6
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21	0	-4
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23	0	-3
24	27	29
25	6	9
26	0	2
27	0	0
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5	27	26
6	32	32
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10	25	24
11	0	6
12	23	-22
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22	15	19
23	11	-11
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25	0	-3
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27	8	-7
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3	0	7
4	71	66
5	21	-21
6	62	62
7	26	27
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12	28	27
13	25	-23
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17	0	-5
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19	0	3
20	0	-1
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2	15	14
3	21	18
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5	0	5
6	17	18
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12	0	-4
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14	14	13
15	20	-20
16	0	-7
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3	16	14
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5	16	-16
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7	27	27
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11	10	11
12	17	16
13	16	-16
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16	12	10
17	0	-4
18	18	16
19	10	9
20	0	0
21	11	-12
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23	10	10
	3 K 8	
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3	26	26
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6	0	-1
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14	0	5
15	12	-11
16	0	3
17	19	-16
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19	0	3
20	0	1
21	12	11
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5	12	-13
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	3 K 11	
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1	0	-4
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6	13	14
7	0	6
8	11	12
	4 K 0	
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6	30	36
7	53	-62
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9	22	27
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17	9	8
18	33	38
19	6	-8
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22	0	-1
23	16	-16
24	7	-8
	4 K 1	
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2	11	11
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14	0	4
15	9	10
16	0	-8
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23	0	1
24	0	-4
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7	51	-55
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17	0	0
18	36	38
19	8	-8
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21	20	21
22	0	2
23	13	-13
	4 K 3	
0	38	-31
1	26	-23
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19	0	-6
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	4 K 4	
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7	17	-17
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13	10	9
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2	36	31
3	38	-34
4	42	-39
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7	23	23
8	23	-24
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14	10	9
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18	29	25
19	0	-2
20	14	-12
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2	36	31
3	37	33
4	0	3
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8	25	23
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14	0	1
15	8	8
16	12	11
17	19	-19
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2	13	12
3	30	-29
4	17	-16
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6	0	3
7	17	17
8	0	2
9	0	2
10	15	15
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13	15	-14
	4 K 8	
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4	15	16
5	23	-24
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7	15	14
8	19	19
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11	22	23
	4 K 9	
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3	12	-12
	5 K 1	
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17	26	31
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16	15	-16
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20	14	-15
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3	38	-35
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10	0	7
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17	16	16
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	5 K 4	
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3	0	1
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16	20	18
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7	16	-16
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10	0	3
11	18	21
12	0	-8
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16	0	-9
17	18	-18
	5 K 7	
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3	10	12
4	48	44
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8	16	16
9	15	-15
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11	0	5
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15	18	19
	5 K 8	
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2	0	-2
3	18	19
4	16	16
5	0	-5
6	0	7
7	18	-18
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9	0	0
10	11	-11
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12	0	6
	5 K 9	
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1	12	-14
	5 K 10	
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	6 K 0	
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2	47	53
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4	30	-33
5	27	31
6	23	28
7	51	-60
8	25	30
9	12	15
10	51	61
11	7	-6
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14	14	14
15	35	-41
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17	0	0
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19	8	-10
20	15	17
	6 K 1	
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2	23	22
3	0	1
4	9	-9
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13	14	-13
14	0	5
15	0	2
16	0	-8
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18	9	11
19	0	1
20	0	-7
	6 K 2	
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2	61	61
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4	0	1
5	18	18
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11	8	9
12	13	11
13	30	29
14	10	10
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19	0	-1
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2	32	27
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4	37	-33
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6	14	14
7	36	34
8	26	-25
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11	11	9
12	23	-22
13	9	-8
14	10	7
15	21	19
16	19	-17
17	0	0
18	25	24
19	13	12

Table 4. Continued.

	6 K 4			3	18	-13	8	38	37	2	11	10	2	11	13	8	0	5		7 K 5			
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1	0	9		5	0	-3	10	28	28				4	0	2	10	11	11	1	15	-13		
2	25	21		6	11	10	11	22	23		7 K 1		5	0	-10	11	23	-23	2	19	16		
3	26	22		7	19	20	12	23	24	0	9	-8	6	10	10	12	16	17	3	11	-9		
4	0	6		8	0	-8	13	8	-7	1	0	-7	7	0	5	13	0	-1	4	46	43		
5	14	-13		9	12	-11	14	0	-1	2	42	41	8	13	-15	14	39	37	5	0	-4		
6	0	1		10	27	28	15	0	7	3	38	-40	9	12	-14	15	0	5	6	24	24		
7	18	-17		11	12	-12				4	29	31	10	0	7				7	15	18		
8	37	37		12	15	-15		6 K 7		5	23	26	11	17	17		7 K 4		8	17	18		
9	0	-8		13	18	-16	0	0	8	6	53	60	12	0	-4	0	44	-34	9	0	-1		
10	35	33		14	0	1	1	12	-11	7	11	11	13	0	-3	1	14	-11					
11	17	16		15	0	7	2	0	3	8	0	-1	14	0	8	2	14	13		7 K 6			
12	20	18		16	14	-12	3	15	-14	9	9	10	15	0	4	3	26	26	0	27	-23		
13	0	1		17	0	9	4	17	-16	10	16	16	16	0	-6	4	0	-2	1	0	-1		
14	0	-3					5	10	6	11	28	-30				5	17	-17	2	12	11		
15	0	-9			6 K 6		6	0	-6	12	10	11		7 K 3		6	16	17	3	24	22		
16	18	17		0	59	47	7	20	20	13	0	3	0	0	-1	7	0	2	4	0	4		
17	18	-15		1	0	-3	8	0	4	14	43	51	1	0	-6	8	25	-25	5	11	-10		
18	28	25		2	33	25	9	0	6	15	0	0	2	31	28	9	20	-21	6	17	18		
				3	34	30	10	11	11	16	7	9	3	31	-28	10	11	9	7	0	-3		
	6 K 5			4	32	28							4	37	35	11	23	22					
0	0	-6		5	22	-21		6 K 8			7 K 2		5	16	16	12	0	-8		7 K 7			
1	27	-22		6	10	13	0	23	21	0	23	-20	6	45	42	13	0	-6	-2	0	3		
2	30	24		7	0	2	1	0	-6	1	11	-10	7	13	13				3	0	6		

Table 5. Bond distances and angles, together with their standard deviations, in $Ca_2Fe_2O_5$. The number in parentheses after the atom symbol denotes:

(1)	x	y	z	(5)	$1-x$	$\bar{y}$	$\bar{z}$	(9)	x	$\frac{1}{2}-y$	z
(2)	$\frac{1}{2}-x$	$\bar{y}$	$-\frac{1}{2}+z$	(6)	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$	(10)	$-1+x$	y	z
(3)	$\bar{x}$	$\bar{y}$	$\bar{z}$	(7)	$1+x$	y	z	(11)	$-\frac{1}{2}+x$	y	$-\frac{1}{2}-z$
(4)	$-\frac{1}{2}+x$	y	$\frac{1}{2}-z$	(8)	$\frac{1}{2}+x$	y	$-\frac{1}{2}-z$				

Distances (Å)

Ca – O_1(5)	2.436(4)	Fe_1 – O_1(1)	1.961(4)
Ca – O_1(2)	2.484(4)	Fe_1 – O_1(2)	1.968(4)
Ca – O_1(1)	2.486(4)	Fe_1 – O_2(1)	2.118(4)
Ca – O_1(6)	2.725(4)		
Ca – O_2(6)	2.331(4)	Fe_2 – O_3(1)	1.837(4)
Ca – O_2(1)	2.555(4)	Fe_2 – O_3(10)	1.915(5)
Ca – O_2(7)	2.982(4)	Fe_2 – O_3(11)	1.921(5)
Ca – O_2(8)	3.370(4)		
Ca – O_3(1)	2.342(3)		

Angles (°)

O_1(1) – Fe_1(1) – O_1(2)	92.53(3)	O_3(1) – Fe_2(1) – O_3(9)	123.19(24)
O_1(1) – Fe_1(1) – O_2(1)	86.80(16)	O_3(1) – Fe_2(1) – O_3(10)	107.11(14)
O_1(2) – Fe_1(1) – O_2(1)	89.41(16)	O_2(1) – Fe_2(1) – O_3(11)	106.30(14)
		O_3(10) – Fe_2(1) – O_3(11)	105.62(15)

atoms lie on a line tilted 11.31° to the *b*-axis or 3.30° to the normal of the plane containing the four oxygen atoms ($O_1(1)-O_1(4)$). These four atoms lie in pairs at distances of 1.961 Å and 1.968 Å, respectively, while the remaining two oxygen atoms are situated at a distance of 2.118 Å from the central iron atom. This means that the octahedra are considerably elongated in the *b*-direction. The tetrahedra, on the other hand, in which the iron atoms lie in the mirror planes, are correspondingly compressed in the *b*-direction. The two iron-oxygen distances in the mirror plane are not significantly different from each other (1.915 and 1.921 Å), while the other two oxygen atoms are much closer to the iron atom, 1.837 Å (see Table 5). The iron-oxygen distances may be compared with those found in Fe_3O_4 (Table 7).

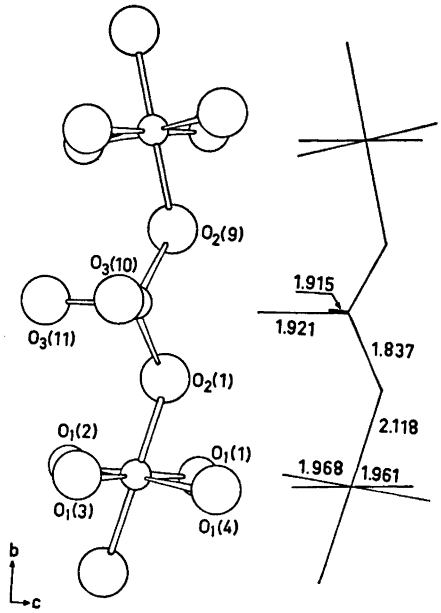

Fig. 1. The chain of iron-oxygen octahedra and tetrahedra. The small circles represent iron atoms. The iron-oxygen distances (in Å) are indicated. The oxygen atoms are denoted in accordance to Table 5.

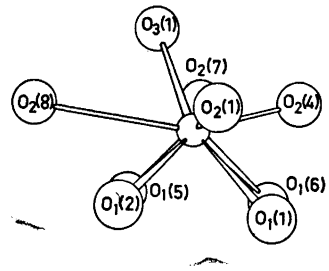

Fig. 2. The coordination of oxygen around calcium. The oxygen atoms are denoted in accordance to Table 5.

Table 6. Distances less than 4.0 Å between oxygen atoms. Symbols are explained in Table 5.

$O_1(1)-O_1(2)$	2.839	$O_1(1)-O_2(3)$	3.602
$O_1(1)-O_1(3)$	3.733	$O_2(1)-O_2(4)$	3.370
$O_1(1)-O_1(4)$	2.716	$O_2(1)-O_2(9)$	3.231
$O_1(1)-O_1(5)$	3.923	$O_2(1)-O_3(1)$	3.683
$O_1(1)-O_2(1)$	2.806	$O_2(1)-O_3(6)$	3.516
$O_1(1)-O_2(4)$	2.906	$O_2(1)-O_3(10)$	3.018
$O_1(1)-O_2(5)$	2.966	$O_2(1)-O_3(11)$	3.007
$O_1(1)-O_2(12)$	2.876	$O_3(1)-O_3(4)$	3.056

Table 7. Comparison of Fe – O distances for octahedral and tetrahedral coordination.

Compound	Octahedral coordination	Tetrahedral coordination	Reference
Generally	1.89 – 2.15 (± 0.08)	1.86 (± 0.06)	15, 16
Fe_3O_4	2.066	1.876	17
FeO	2.147		18
$CaFe_2O_4$	1.98 – 2.09		2
$Ca_2Fe_2O_5$	1.965, 2.118	1.837, 1.918	This work

The coordination of oxygen around calcium is not very regular. There are, however, features which deserve some attention. The oxygen polyhedron may be regarded as being a square antiprism in which a ninth oxygen atom ($O_3(1)$ in Fig. 2) has forced three of the four adjacent oxygen atoms ($O_2(1)$, $O_2(7)$, and $O_2(8)$ in Fig. 2) to move away from each other. The oxygen atom, $O_2(8)$, which is closest to the ninth oxygen atom, $O_3(1)$, is that which is most remote from the calcium atom (see Table 5). The distances between adjacent oxygen atoms are listed in Table 6.

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