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Crystal Structures of $Ca_2Fe_{1\cdot43}Al_{0\cdot57}O_5$ and $Ca_2Fe_{1\cdot28}Al_{0\cdot72}O_5$*

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The crystal structures of $Ca_2Fe_{1\cdot43}Al_{0\cdot57}O_5$ and $Ca_2Fe_{1\cdot28}Al_{0\cdot72}O_5$ have been determined from single-crystal data obtained with a Buerger–Supper–Pace–Picker automatic diffractometer. Both are isostructural with brownmillerite, belonging to space group *Ibm*2 (C_{2v}^{22}). Lattice constants are $a=5\cdot588$ (5), $b=14\cdot61$ (2), $c=5\cdot380$ (5) Å and $a=5\cdot583$ (5), $b=14\cdot58$ (2), $c=5\cdot374$ (5) Å respectively. The distribution of the Al^{3+} ions in these crystals and in brownmillerite (Ca_2FeAlO_5), all synthesized under very similar conditions, is such that 75–76% of the Al^{3+} ions are in tetrahedral sites. The results give new information on the magnetic phase relations of the $Ca_2Fe_{2-x}Al_xO_5$ system.

Introduction

Crystals of $Ca_2Fe_2O_5$ have their Fe^{3+} ion moments directed along the crystallographic *c* axis (Gonser, Grant, Wiedersich & Geller, 1966; Corliss, Hastings, Kunnmann & Banks, 1966; Friedman, Shakad & Shtrikman, 1967; Takeda, Yamaguchi, Tomiyoshi, Sukase, Sugimoto & Watanabe, 1968); the most probable magnetic space group of $Ca_2Fe_2O_5$ is *Pcm'n'*. In brownmillerite, Ca_2FeAlO_5, the Fe^{3+} ion moments are aligned along the *a* axis (Grant, Geller, Wiedersich, Gonser & Fullmer, 1968); the most probable magnetic space group was thought to be *Ic'm'm'* because although the crystal structure had not been worked out in detail, *Icmm* was reported to be the most probable space group (Büssem, 1937, 1938; Smith, 1962).

A refinement of the structure of $Ca_2Fe_2O_5$ (Bertaut, Blum & Sagnières, 1959) was carried out (Colville, 1970) to verify the results of a Mössbauer spectroscopic study (Grant, 1969) which showed that the oxygen octahedra and tetrahedra about the Fe^{3+} ions must be considerably distorted. A determination of the crystal structure of brownmillerite (Colville & Geller, 1971) showed that its most probable space group is *Ibm*2. (In fact, *Icmm* would have required one unreasonably short tetrahedral cation–oxygen distance.) It was proposed (Geller, Grant & Colville, 1971) that the most probable magnetic space group for brownmillerite is $I_Pbm'2'$.

A Mössbauer spectroscopic investigation (Geller, Grant & Fullmer, 1970; see also Geller, Grant & Gonser, 1971) of intermediate compositions (that is, $0<x<1$ in $Ca_2Fe_{2-x}Al_xO_5$) showed that there is a range of composition and of temperature in which two magnetic structures occur simultaneously. In the papers thus far published (Geller *et al.*, 1970; Geller *et al.*, 1971) it was thought that these corresponded to the *Pcm'n'* of $Ca_2Fe_2O_5$ and (originally *Ic'm'm* but later) $I_Pbm'2'$ of Ca_2FeAlO_5. Thus we decided to refine the structure of $Ca_2Fe_{1\cdot28}Al_{0\cdot72}O_5$, expecting, at room temperature, to find about 70% of the $I_Pbm'2'$ structure and 30% of the *Pcm'n'* structure (Geller, Grant & Fullmer, 1970). We did not know the scale of the domains and so we tested both coherent ($I\sim|F|$) and incoherent ($I\sim|F|^2$) scattering models. We found that the best fit of $|F_c|$ *vs*. $|F_o|$ was obtained when the structure was refined purely in *Ibm*2. This now presented difficulties in the interpretation of the results obtained by Mössbauer spectroscopy.

We next decided to refine the structure of the crystal with formula $Ca_2Fe_{1\cdot40}Al_{0\cdot60}O_5$. Past investigations appeared to fix the transition from the primitive ortho-

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rhombic structure characteristic of $Ca_2Fe_2O_5$ to the body-centered orthorhombic structure characteristic of Ca_2FeAlO_5 at $0·60 < x < 0·66$ in $Ca_2Fe_{2-x}Al_xO_5$ (Smith, 1962; see also Newkirk & Thwaite, 1958). It was therefore somewhat surprising to find that refinement of the structure of $Ca_2Fe_{1·40}Al_{0·60}O_5$ in *Ibm*2 gave unequivocally better results than refinement in *Pcmn*. The question remained as to whether the compositions of these crystals were what they were thought to be. After this was checked, the results led to a better but not completely conclusive interpretation of the magnetic phase diagram (Geller *et al.*, 1970; Geller *et al.*, 1971).

Experimental

Single crystals of $Ca_2Fe_{2-x}Al_xO_5$, with $x=0·60$ and $x=0·72$, were ground into spheres (Bond, 1951; Schuyff & Hulscher, 1968; Crandall, 1970) and mounted along the crystallographic *a* axis for data collection. These crystals were from the same batches as those used for the Mössbauer experiments (Geller, Grant & Fullmer, 1970). The cell parameters, determined from Buerger precession camera photographs, and other crystal data are listed in Table 1.

Geller *et al.* (1970) estimated the nominal composition to be within $x = \pm 0·01$ by comparing powder photographs of these crystals with those of powder specimens prepared by solid state reaction. Electron microprobe analyses were made of the crystals actually used for the collection of intensity data; synthetic Al_2O_3 and $Ca_2Fe_2O_5$ were used as standards and the computer program *EMPADR* VII (Rucklidge & Gasparrini, 1969) for data reduction. This gave compositions of $Ca_2Fe_{1·43}Al_{0·57}O_5$ and $Ca_2Fe_{1·38}Al_{0·72}O_5$ for the two crystals, with estimated standard error in $x = \pm 0·03$.

For a crystal with $x=0·72$, 353 reflections were collected using a Buerger–Supper–Pace–Picker automated diffractometer, Mo $K\alpha$ radiation, Zr–Y balanced filters, and a scan rate of 2 deg. min^{-1}. Background counts were taken at $\frac{1}{6}$ the scan time on both sides of the peak for each filter. Relative $|F_o|^2$ were obtained from the intensities by application of the Lorentz–polarization–Tunell and absorption factors (Bond, 1959). For a crystal with $x=0·57$, 346 reflections were collected and $|F_o|^2$ obtained in the same manner as for the crystal with $x=0·72$.

Structure refinement

Refinement was carried out with the least-squares program of Busing, Martin & Levy (1962), modified by Ibers, Johnson, Ellison & Levy to include site occupancy refinement and the contribution from the imaginary parts of the scattering factors. The scattering factors were those of Tokonami (1965) for O^{2-}; those of Tomiie & Stam (1958) for Al^{3+} and Ca^{2+} and those of Watson & Freeman (1961) for Fe^{3+}. These were corrected for the real parts of anomalous dispersion (Cromer, 1965). With starting atomic positions of brownmillerite (Colville & Geller, 1971), refinement in space group *Ibm*2 led to an agreement index of 0·029; whereas, with starting atomic parameters from $Ca_2Fe_2O_5$ (Colville, 1970) and space group *Pcmn* an agreement index of 0·15 was obtained. Thus the most probable space group is *Ibm*2. Observed and calculated structure amplitudes are listed in Table 2. The site occupancy refinement gave a distribution formula of $Ca_2[Fe_{0·83}Al_{0·17}]\,(Fe_{0·45}Al_{0·55})O_5^*$ with standard error $\pm 0·01$.

For the $Ca_2Fe_{1·40}Al_{0·60}O_5$, the procedure was the same as that used for $Ca_2Fe_{1·28}Al_{0·72}O_5$. Refinement in space group *Pcmn* gave an agreement factor of 0·19, while refinement in space group *Ibm*2 gave an agreement factor of 0·032. The site refinement gave a distribution formula of $Ca_2[Fe_{0·83}Al_{0·17}]\,(Fe_{0·45}Al_{0·55})O_5$. The atomic positions are virtually the same as those of crystals with composition $x=0·72$. as all positional parameters are within the standard errors.

The atomic parameters are given in Table 3. Bond lengths and angles (Table 4) were calculated with the Busing, Martin & Levy (1964) *ORFFE* program. Standard errors include contributions from errors in the cell parameters.

Discussion

The results of this investigation show that both $Ca_2Fe_{1·43}Al_{0·57}O_5$ and $Ca_2Fe_{1·28}Al_{0·72}O_5$ are isostructural with brownmillerite (Colville & Geller, 1971). All belong to space group *Ibm*2. Because $Ca_2Fe_2O_5$ belongs to space group *Pcmn*, the transition† to the *Ibm*2 structure must occur at a composition between $Ca_2Fe_2O_5$ and $Ca_2Fe_{1·43}Al_{0·57}O_5$. In plots of chemical composition *vs.* cell parameters, Newkirk & Thwaite (1958) found changes in slope near $x=0·66$. Smith (1962) corroborated these results with similar plots. He also followed the decrease of intensities of $h0l$, $h+l=2n+1$, reflections with increasing aluminum con-

Table 1. *Crystal data for* $Ca_2Fe_{2-x}Al_xO_5$; $x=0·57$ *and* 0·72

	$x=0·57$	$x=0·72$		$x=0·57$	$x=0·72$
a	5·588 (5) Å	5·583 (5) Å	F.W.	254·54	251·08
b	14·61 (2)	14·58 (2)	Volume	439·23 $Å^3$	437·44 $Å^3$
c	5·380 (5)	5·374 (5)	*Z*	4	4
$\varrho_{cal.}$	3·85 g.cm^{-3}	3·82 g.cm^{-3}	μ_l (Mo $K\alpha$)	70·45 cm^{-1}	67·35 cm^{-1}
Space group	*Ibm*2	*Ibm*2	Crystal radius	0·111 mm	0·125 mm

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* Throughout this paper [ ] and ( ) refer to octahedral and tetrahedral sites respectively.

† Because *Pcmn* contains a symmetry element not in *Ibm*2 and *Ibm*2 contains a symmetry element not in *Pcmn*, neither is a subgroup of the other; thus the transition is first order.

tent. He concluded that crystals with $x \leq 0{\cdot}60$ belong to space group $Pcmn$ and those with $x \geq 0{\cdot}66$ belong to $Imma[\equiv Icmm]$. From the combined results, we must conclude that the transition must occur at a value of x near $0{\cdot}57 \pm 0{\cdot}03$, but surely at $x < 0{\cdot}60$.

The magnetic space groups of $Ca_2Fe_{1\cdot43}Al_{0\cdot57}O_5$ and Ca_2FeAlO_5 are different inasmuch as in the former the spins are parallel to the a axis, while in the latter they are parallel to the c axis. Assuming in all cases that the chemical and magnetic unit cells are the same (as they proved to be for $Ca_2Fe_2O_5$), the magnetic space groups are $I_Pb'm'2$ for $Ca_2Fe_{1\cdot43}Al_{0\cdot57}O_5$ (Geller, Grant & Colville, 1972) and $I_Pbm'2'$ for Ca_2FeAlO_5 (Geller, Grant & Colville, 1971).

The nature of the intermediate region in which it was believed that two magnetic structures coexisted will be discussed in detail elsewhere (Geller *et al.*, 1972). We give conclusions briefly here. There are now two possibilities for $Ca_2Fe_{1\cdot28}Al_{0\cdot72}O_5$ and other compositions lying between the boundaries of the pure $I_Pb'm'2$ and $I_Pbm'2'$ structures. One possibility is still the coexistence of the $I_Pb'm'2$ and $I_Pbm'2'$ structures and spin flipping as temperature is increased. In this case the system is more nearly analogous (but see Geller, *et al.*, 1972) to that of $CaFe_{2-x}Cr_xO_4$ investigated by Corliss, Hastings & Kunnmann (1967) than heretofore (Geller *et al.*, 1970) supposed. The other possibility is a continuous transition similar to that of $ErFeO_3$ (Grant & Geller,

Table 2. *Observed and calculated structure amplitudes for* $Ca_2Fe_{1\cdot28}Al_{0\cdot72}O_5$

The reflections marked with an asterisk were given low weights.

h=0

k	l	F_o	F_c
0	2	*149	234
2	2	12	12
6	0	13	6
4	2	51	55
8	0	*159	239
6	2	51	52
8	2	*122	143
10	0	61	59
0	4	151	166
2	4	83	83
10	2	43	43
4	4	27	27
12	0	74	75
12	2	40	40
8	4	103	106
14	0	43	44
10	4	78	76
14	2	43	44
16	0	58	59
12	4	33	31
0	6	75	70
2	6	47	47
4	6	40	36
16	2	43	44
6	6	45	44
14	4	39	37
18	0	32	31
8	6	55	51
18	2	38	38
10	6	57	54
16	4	31	30
20	0	72	71
12	6	19	19

h=1

k	l	F_o	F_c
1	0	22	21
0	1	48	45
3	0	57	63
2	1	29	28
4	1	*125	175
5	0	75	88
1	2	7	7
3	2	54	55
6	1	*96	115
7	0	2	2
5	2	24	23
0	3	36	34
2	3	44	44
8	1	49	49
7	2	21	20
9	0	40	41
4	3	*130	151
6	3	83	87
10	1	62	66
9	2	9	8
1	4	20	19
11	0	15	15
3	4	14	14
8	3	42	42
5	4	19	18
11	2	36	36
12	1	79	86
10	3	55	55
7	4	23	22
13	0	36	36
0	5	7	6
2	5	37	35
13	2	3	1
9	4	16	15
4	5	95	93
14	1	77	81
12	3	73	74
6	5	69	65
15	0	4	3
11	4	14	14
8	5	17	17
15	2	21	19
14	3	72	72
16	1	51	53
1	6	21	20
3	6	18	16
10	5	34	32
13	4	12	10
17	0	31	31
5	6	13	13
7	6	13	12
17	2	5	5
16	3	49	49
12	5	50	49
18	1	44	44
15	4	14	13
9	6	20	19
19	0	3	4
0	7	16	14
4	7	45	50
14	5	53	60
11	6	14	17
18	3	35	41
19	2	14	16
6	7	49	54
17	4	14	15
20	1	19	22

h=2

k	l	F_o	F_c
2	0	15	8
1	1	39	37
4	0	54	60
3	1	24	22
0	2	*163	244
5	1	45	45
2	2	83	90
6	0	35	36
4	2	28	25
7	1	55	55
8	0	*109	125
6	2	35	34
1	3	55	56
3	3	32	32
9	1	20	19
5	3	42	43
8	2	*122	143
10	0	57	58
7	3	56	57
0	4	105	108
2	4	37	34
11	1	16	15
10	2	77	80
4	4	27	26
12	0	34	32
9	3	33	33
6	4	33	34
12	2	44	43
13	1	39	38
8	4	74	75
1	5	31	32
11	3	25	25
3	5	13	13
14	0	33	32
5	5	16	16
10	4	53	53
14	2	27	27
15	1	38	36
7	5	32	31
13	3	38	38
16	0	37	37
12	4	20	20
9	5	24	22
0	6	83	83
2	6	54	53
4	6	9	6
16	2	38	37
15	3	36	36
17	1	10	9
6	6	33	33
11	5	15	16
14	4	32	32
18	0	46	46
8	6	58	58
18	2	44	44
13	5	21	21
17	3	16	16
1	7	15	16
10	6	57	57
19	1	9	8
3	7	16	17

h=3

k	l	F_o	F_c
1	0	3	2
0	1	19	19
3	0	106	118
2	1	24	23
4	1	*122	140
5	0	76	78
1	2	21	20
3	2	75	75
6	1	79	81
7	0	26	23
5	2	74	76
0	3	15	15
2	3	36	35
8	1	27	27
7	2	18	18
9	0	15	14
4	3	94	97
6	3	77	77
10	1	24	24
9	2	36	36
1	4	38	38
11	0	71	73
3	4	52	50
8	3	13	13
11	2	36	38
12	1	61	63
10	3	11	10
7	4	22	22
13	0	19	17
0	5	10	11
2	5	33	34
13	2	33	31
9	4	31	31
4	5	68	66
14	1	72	69
12	3	45	45
6	5	59	60
15	0	35	30
11	4	43	43
8	5	5	4
15	2	5	6
14	3	68	67
16	1	42	40
1	6	31	33
3	6	28	29
10	5	15	15
13	4	15	16
17	0	31	30
5	6	19	20
7	6	30	32
17	2	42	42
16	3	29	29
12	5	30	31
18	1	23	22
15	4	11	12
9	6	24	27

h=4

k	l	F_o	F_c
2	0	105	112
1	1	55	54
4	0	8	4
3	1	11	10
0	2	73	71
5	1	46	46
2	2	49	48
6	0	50	49
4	2	25	24
7	1	76	76
8	0	73	73
6	2	11	10
1	3	46	47
3	3	16	16
9	1	15	15
5	3	26	27
8	2	50	50
10	0	99	103
7	3	56	57
0	4	91	94
2	4	56	56
11	1	12	12
10	2	69	71
4	4	24	24
12	0	16	15
9	3	24	24
6	4	20	19
12	2	8	8
13	1	53	51
8	4	64	66
1	5	36	37
11	3	22	22
3	5	23	24
14	0	5	5
5	5	14	15
10	4	60	63
14	2	11	10
15	1	52	51
7	5	36	38
13	3	37	38
16	0	15	14
12	4	24	25
9	5	25	27
0	6	45	46
2	6	21	22
4	6	19	19
15	3	38	38
17	1	7	5
6	6	6	2
11	5	26	28

h=5

k	l	F_o	F_c
1	0	22	21
0	1	26	26
3	0	64	63
2	1	55	55
4	1	70	71
5	0	52	52
1	2	28	28
3	2	70	71
6	1	72	73
7	0	36	34
5	2	39	38
0	3	27	27
2	3	46	46
8	1	12	10
7	2	20	20
9	0	22	22
4	3	62	62
6	3	64	64
10	1	25	24
9	2	20	20
1	4	24	24
11	0	37	36
3	4	49	48
8	3	19	18
5	4	37	36
11	2	58	57
12	1	29	28
10	3	20	20
7	4	29	29
13	0	13	13
0	5	18	18
2	5	29	30
13	2	14	12
9	4	27	28
4	5	52	52
14	1	61	61
12	3	29	28
6	5	46	45
15	0	14	14
11	4	35	36
8	5	15	16

h=6

k	l	F_o	F_c
2	0	56	55
1	1	40	40
4	0	15	14
3	1	21	21
0	2	47	47
5	1	11	11
2	2	76	77
6	0	23	22
4	2	25	24
7	1	59	56
8	0	14	13
6	2	43	42
1	3	27	27
3	3	28	28
9	1	4	3
5	3	2	1
8	2	36	34
10	0	73	71
7	3	42	41
0	4	26	26
2	4	38	38
11	1	24	24
10	2	80	78
4	4	29	23
12	0	3	1
9	3	8	7
6	4	20	20
12	2	18	17

h=7

k	l	F_o	F_c
1	0	31	31
0	1	23	23
3	0	40	41
2	1	54	57
4	1	31	31
5	0	6	6
1	2	25	25
3	2	34	34
6	1	58	58
7	0	37	35
5	2	16	17
0	3	13	13
2	3	38	40
8	1	14	13
7	2	44	44
4	3	39	40

Table 3. *Parameters and standard errors for* $Ca_2Fe_{2-x}Al_xO_5$; $x = 0{\cdot}57$ *and* $0{\cdot}72$

Site		Ca 8(*c*)	[Fe Al] 4(*a*)	(Al Fe) 4(*b*)	O(1) 8(*c*)	O(2) 8(*c*)	O(3) 4(*b*)
x	(1)*	0·0270 (1)	0	0·9293 (2)	0·2533 (8)	0·0687 (6)	0·8668 (8)
	(2)	0·0270 (2)	0	0·9291 (2)	0·2525 (9)	0·0683 (6)	0·8653 (9)
y	(1)	0·1084 (1)	0	$\frac{1}{4}$	0·9856 (2)	0·1429 (2)	$\frac{1}{4}$
	(2)	0·1084 (1)	0	$\frac{1}{4}$	0·9859 (2)	0·1429 (3)	$\frac{1}{4}$
z	(1)	0·4910 (3)	0·0000	0·9516 (4)	0·2520 (8)	0·0269 (8)	0·6147 (9)
	(2)	0·4907 (3)	0·0000	0·9520 (4)	0·2503 (9)	0·0256 (9)	0·6133 (9)
β_{11}	(1)	0·0033 (2)†	0·0003 (3)	0·0024 (3)	0·0030 (7)	0·0037 (7)	0·0050 (12)
	(2)	0·0050 (2)	0·0018 (3)	0·0028 (4)	0·0030 (8)	0·0048 (8)	0·0077 (14)
β_{22}	(1)	0·0006 (1)	0·0007 (1)	0·0002 (1)	0·0008 (1)	0·0011 (1)	0·0006 (2)
	(2)	0·0008 (1)	0·0010 (1)	0·0004 (1)	0·0013 (1)	0·0014 (1)	0·0008 (2)
β_{33}	(1)	0·0084 (3)	0·0021 (4)	0·0026 (4)	0·0054 (9)	0·0088 (13)	0·0058 (16)
	(2)	0·0107 (2)	0·0051 (4)	0·0045 (5)	0·0093 (11)	0·0132 (15)	0·0060 (16)
β_{12}	(1)	0·0001 (1)	0·0000 (1)	0	−0·0001 (4)	0·0002 (2)	0
	(2)	0·0001 (1)	−0·0001 (1)	0	0·0001 (4)	0·0035 (3)	0
β_{13}	(1)	0·0001 (1)	0	−0·0002 (3)	−0·0013 (7)	−0·0007 (9)	−0·0002 (11)
	(2)	0·0001 (1)	0	−0·0001 (3)	0·0000 (1)	−0·0015 (10)	0·0007 (12)
β_{23}	(1)	−0·0001 (1)	0	0	−0·0004 (3)	0·0005 (3)	0
	(2)	0·0000 (1)	0	0	−0·0005 (4)	0·0006 (3)	0

* (1) is for $x = 0{\cdot}57$ and (2) is for $x = 0{\cdot}72$.

† Form of the temperature factor is: $T = \exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right]$.

Table 4. *Interatomic distances and angles in* $Ca_2Fe_{2-x}Al_xO_5$; $x=0{\cdot}57$ *and* $0{\cdot}72$

(Al, Fe) tetrahedron	$x=0{\cdot}57$	$x=0{\cdot}72$		$x=0{\cdot}57$	$x=0{\cdot}72$
(Al, Fe)–O(2) (2)	1·794 (4)	1·788 (4)*	O(2)–(Al, Fe)–O(2)1	121·3 (2)	121·6 (2)
(Al, Fe)–O(3)	1·846 (6)	1·855 (6)	O(2)–(Al, Fe)–O(3) (2)	107·7 (1)	107·5 (1)
(Al, Fe)–O(3)4†	1·873 (6)	1·858 (6)	O(2)–(Al, Fe)–O(3)4 (2)	106·1 (1)	106·3 (1)
			O(3)–(Al, Fe)–O(3)4	107·0 (2)	106·7 (1)
O(2)–O(2)1	3·130 (8)	3·121 (8)			
O(2)–O(3) (2)	2·939 (6)	2·937 (6)			
O(2)–O(3)4 (2)	2·932 (6)	2·919 (6)			
O(3)–O(3)4	2·991 (6)	2·980 (5)			
[Fe, Al] octahedron					
[Fe, Al]–O(1) (2)	1·971 (5)	1·959 (5)	O(1)–Fe, Al–O(2)	85·9 (1)	85·9 (1)
[Fe, Al]–O(1)3 (2)	1·930 (5)	1·937 (5)	O(1)–Fe, Al–O(1)2	93·1 (1)	93·3 (1)
[Fe, Al]–O(2) (2)	2·128 (5)	2·123 (4)	O(1)–Fe, Al–O(1)5	87·2 (1)	87·2 (1)
			O(2)–Fe, Al–O(1)2	88·7 (1)	89·0 (1)
			O(2)–Fe, Al–O(1)3	93·9 (1)	93·9 (1)
			O(2)–Fe, Al–O(1)5	91·4 (1)	92·2 (1)
O(1)–O(2)	2·795 (5)	2·786 (5)			
O(1)–O(1)1	2·862 (9)	2·849 (10)			
O(1)–O(1)5	2·690 (4)	2·687 (3)			
O(2)–O(1)2	2·869 (6)	2·863 (6)			
O(2)–O(1)3	2·970 (6)	2·971 (6)			
O(2)–O(1)5	2·908 (5)	2·904 (5)			
Ca polyhedron					
Ca–O(1)	2·544 (4)	2·538 (4)	Ca–O(2)	2·568 (5)	2·560 (5)
Ca–O(1)2	2·448 (4)	2·448 (5)	Ca–O(2)5	2·323 (4)	2·322 (4)
Ca–O(1)5	2·588 (4)	2·579 (4)	Ca–O(3)	2·350 (3)	2·347 (4)
Ca–O(1)3	2·489 (4)	2·489 (4)			
Cation–cation					
[Fe, Al]–[Fe, Al]5	3·878 (3)	3·875 (3)	[Fe, Al]–O(1)–[Fe, Al]	167·0 (2)	167·9 (2)
[Fe, Al]–(Al, Fe)	3·683 (3)	3·675 (2)	[Fe, Al]–O(2)–(Al, Fe)	138·0 (2)	139·9 (2)
(Al, Fe)–(Al, Fe)	3·354 (3)	3·350 (3)	(Al, Fe)–O(3)–(Al, Fe)	128·4 (2)	128·9 (3)

* Frequency of occurrence, distance (Å) or angle (°), (estimated standard error).

† Symmetry transforms are numbered as follows:

$1: x, \frac{1}{2}-x, z;\quad 2: \bar{x}, \bar{y}, z;\quad 3: \frac{1}{2}+x, y, \frac{1}{2}+z;\quad 4: \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z;\quad 5: \frac{1}{2}-x, y, \frac{1}{2}+z.$

1969) from $I_Pb'm'2$ to $I_Pbm'2'$ with increasing temperature. In this case, there is a fourth magnetic structure with magnetic space group C_Pm' involved and it is this structure* that exists in the intermediate region, which in accord with the $ErFeO_3$ case may be called a 'spin reorientation' region (with respect both to temperature and composition).

As mentioned earlier the analogous parameter values for the two crystals reported here do not differ significantly; thus the interatomic distances and angles of the two do not differ significantly. However, the mean cation–oxygen distances are in accord with the aluminum contents (Table 5).

Table 5. *Mean cation–oxygen distances* (Å) *in* $Ca_2Fe_{2-x}Al_xO_5$

x	Tetrahedral	Octahedral	Ca^{2+}
0·00	1·878	2·016	2·480
0·57	1·827	2·010	2·473
0·72	1·822	2·007	2·469
1·00	1·797	2·001	2·461

Estimated standard errors are 0·005.

The crystalline specimens of $Ca_2Fe_{2-x}Al_xO_5$, $x=0{\cdot}57$, $0{\cdot}72$, $1{\cdot}00$ were prepared under very nearly the same conditions (Geller, Grant & Fullmer, 1970; Grant *et al.*, 1968). The structure analyses indicate that in all cases, the fraction, f_t, of Al^{3+} ions in tetrahedral sites is 0·75–0·76.* If 0·76 is assumed to be the value for all specimens with $x \geq 0{\cdot}57$ prepared in this same manner, then when the tetrahedral sites are filled with Al^{3+} ions, x will be 1·32. At higher temperatures, a lower percentage of Al^{3+} ions go into tetrahedral sites (Colville & Geller, 1971); for brownmillerite quenched from 1290°C, $f_t=0{\cdot}68$. If we assume that this is constant for all specimens quenched from 1290°C, the tetrahedral sites will be filled with Al^{3+} ions when $x=1{\cdot}47$. The maximum attainable Al^{3+} ion content appears to be within this range, that is, 1·32–1·47 (see discussion and references in Geller, Grant & Gonser, 1971). It would seem that temperature and the filling of the tetrahedral sites with Al^{3+} ions determine the maximum Al^{3+} ion content.

The recent appearance of a paper entitled *Refinement of the Crystal Structure of Dicalcium Ferrite* $Ca_2Fe_2O_5$,

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* It should be realized that in a sense there are an infinite number of structures in this region; the spin directions presumably change with each infinitesimal change in temperature or composition.

* This is much different from the aluminum substituted yttrium iron garnet system (Geller, Williams, Sherwood & Espinosa, 1964) in which f_t for Al^{3+} decreases continuously until the end-member $Y_3Al_2Al_3O_{12}$ is reached.

by Berggren (1971) has been called to our attention. This paper contains no essentially new conclusion relative to the Colville (1970) paper.

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The Crystal Structure of Clopidol (3,5-Dichloro-2,6-Dimethyl-4-Pyridinol)

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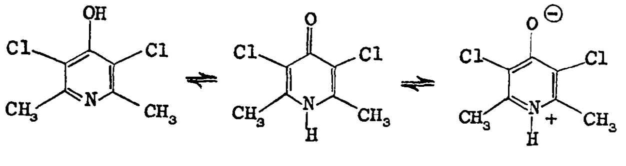
Clopidol (3,5-dichloro-2,6-dimethyl-4-pyridinol), $C_7H_7Cl_2NO$, is a commercially successful anticoccidial. The crystal and molecular structure of this heterocycle have been determined by single-crystal X-ray diffraction methods. Clopidol crystallizes (usually with twinning) in space group $P2_1/m$ with $a = 6\cdot795 \pm 0\cdot009$, $b = 6\cdot932 \pm 0\cdot013$, $c = 8\cdot746 \pm 0\cdot015$ Å, $\beta = 103\cdot56 \pm 0\cdot07°$, and $Z = 2$. X-ray intensity data were gathered on a Picker automatic four-circle diffractometer (Mo $K\alpha$ radiation) using both the θ–2θ and ω scan techniques. The crystal structure was solved from the Patterson function and refined by full-matrix least-squares methods assuming anisotropic temperature factors for the nonhydrogen atoms. The final R values were $R_1 = 4\cdot4$ and $R_2 = 3\cdot5$ % for the 421 reflections above background. The molecules are situated on the crystallographic mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$, and form infinite hydrogen-bonded chains in the **a** direction. From the bond lengths and the location of the nonmethyl hydrogen atom, clopidol is shown to exist as the pyridone tautomer in the crystalline state.

3,5-Dichloro-2,6-dimethyl-4-pyridinol, or clopidol, is the active ingredient in a commercially sucessful anticoccidial* used to control coccidiosis in chickens. Since clopidol is in principle able to exist in forms (I)-(III) and because the nature of the hydrogen-bonding system in the crystalline state was not known, a three-dimensional X-ray diffraction study of its crystal structure was undertaken.



(I) (II) (III)

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