

## The Crystal Structure of Brownmillerite, $\text{Ca}_2\text{FeAlO}_5$

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The crystal structure of brownmillerite,  $\text{Ca}_2\text{FeAlO}_5$ , has been determined from single-crystal data collected with a Buerger-Supper-Pace-Picker automatic diffractometer. There are four  $\text{Ca}_2\text{FeAlO}_5$  formula units in an orthorhombic cell, space group  $Ibm2$  ( $C_{2v}^{22}$ ), with  $a=5.584$  (5),  $b=14.60$  (1),  $c=5.374$  (5) Å. Brownmillerite has sheets of corner-sharing [Fe, Al]-O octahedra (normal to  $b$ ) connected to single chains of (Al, Fe)-O tetrahedra that are parallel to the  $c$  axis. Average [Fe, Al]-O and (Al Fe)-O distances are 2.001 and 1.797 Å, respectively, both with  $\pm 0.015$  Å limits of error ( $=3\sigma$ ). The calcium ion is surrounded by an irregular array of seven oxygen ions with average Ca-O distance  $2.461 \pm 0.015$  Å. Refinement of site occupancy gave the distribution formula:  $\text{Ca}_2[\text{Fe}_{0.76}\text{Al}_{0.24}](\text{Al}_{0.76}\text{Fe}_{0.24})\text{O}_5$ .

### Introduction

Brownmillerite, the major constituent of the ferrite phase of Portland cement, was first described by Törnebohm (1897) and named 'celite'. Hanson, Brownmiller & Bogue (1928) reported that celite is  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  and that a solid-solution series extends to  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ . Numerous studies have been made to determine the maximum aluminum content in this series. Yamauchi (1937) and Swayze (1946) independently estimated the end-member to be near  $6\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  ( $x \simeq 1.36$  and  $1.33$  in  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ , respectively). Cirilli & Burdese (1951) and Malquori & Cirilli (1952) reported the limiting composition to be approximately  $\text{Ca}_2\text{Al}_{1.39}\text{Fe}_{0.61}\text{O}_5$ , whereas Newkirk & Thwaite (1958) reported it to be  $\text{Ca}_2\text{Al}_{1.41}\text{Fe}_{0.59}\text{O}_5$ .

Natural occurrences of brownmillerite are quite rare [see Hentschel (1964) and Bentor, Gross & Heller (1963) for localities and mineral associations].

The crystal structure of brownmillerite was suggested by Büssem (1937, 1938). *Imma* was thought to be the most probable space group with the basic structure consisting of layers of corner-sharing  $\text{AlO}_6$  octahedra alternating with layers of  $\text{FeO}_4$  tetrahedra.

The structure of end member  $\text{Ca}_2\text{Fe}_2\text{O}_5$  was solved by Bertaut, Blum & Sagnières (1959). The space group is *Pcmm* ( $D_{2h}^{16}$ ), and the atomic arrangement is similar to that proposed by Büssem (1937, 1938) with perovskite-like sheets of  $\text{FeO}_6$  octahedra (normal to  $\mathbf{b}$ ) sharing corners with chains of  $\text{FeO}_4$  tetrahedra that are parallel to  $\mathbf{a}$ . A refinement of this structure was carried out by Colville (1970) to verify the marked distortion of the oxygen octahedra and tetrahedra around the iron sites that had been reported by Grant (1969) as a result of Mössbauer studies (see Colville, 1970, for figures of the structural details).

Bertaut *et al.* (1959) concluded that  $\text{Ca}_2\text{FeAlO}_5$  crystallizes in space group *Pnma* rather than *Imma* and that reflections with  $h+k+l=(2n+1)$  were too weak to be observed. X-ray diffraction evidence that a structural change might occur was first presented by Newkirk & Thwaite (1958). A plot of cell parameters *versus* composition shows a change of slope near  $x=0.66$ . Smith (1962) gave a similar plot of the variation of cell constants and interplanar spacings with composition, with a change of slope near  $x=0.66$ . He also measured the intensities of  $h0l$  reflections with  $h+l=2n+1$  with increasing aluminum content and compared them with the intensity of the 103 reflection. These reflections decrease to zero at  $x=0.66$  (see Fig. 2 of Smith, 1962). Smith concluded that  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$  is not isostructural throughout the entire compositional range but exhibits a higher-order phase transition to space group *Imma* when  $x > 0.66$ . Results of a Mössbauer spectroscopic study of the  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$  ( $x \leq 1.0$ ) system confirm the existence of two phases, but they indicate that the transition is of the first order (Geller, Grant & Fullmer, 1970).

The site occupancy of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in brownmillerite has been of interest since Büssem (1937, 1938) hypothesized that all  $\text{Fe}^{3+}$  ions were in the tetrahedral sites and all  $\text{Al}^{3+}$  ions were in the octahedral sites. Cirilli & Burdese (1951) and Malquori & Cirilli (1952) suggested a random distribution of the  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions in the two sites. Smith (1962) studied the relative intensities of the  $0k0$  reflections *versus* composition. He predicted that the  $\text{Al}^{3+}$  ions preferentially substitute in the tetrahedral sites until about half the tetrahedral sites are filled. Additional  $\text{Al}^{3+}$  ions are distributed equally in the two sites until, at  $\text{Ca}_2\text{AlFeO}_5$ ,  $\frac{3}{4}$  of the  $\text{Al}^{3+}$  ions are in the tetrahedral sites and  $\frac{1}{4}$  are in the octahedral sites. Results of Mössbauer spectroscopy indicate that the  $\text{Al}^{3+}$  ions are not restricted to the tetrahedral sites below  $x=0.50$  (Geller *et al.*, 1970); the distribution for  $\text{Ca}_2\text{Al}_{0.5}\text{Fe}_{1.5}\text{O}_5$  was found to be  $\text{Ca}_2[\text{Fe}_{0.90}\text{Al}_{0.10}](\text{Fe}_{0.60}\text{Al}_{0.40})\text{O}_5$  (throughout this paper

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[ ] and ( ) indicate octahedral and tetrahedral sites, respectively, when referring to formulae.

Although much has been written about brownmillerite, its structure has never been determined in detail. Indeed, when Grant, Geller, Wiedersich, Gouser & Fullmer (1968) found by Mössbauer spectroscopy that the magnetic structure of brownmillerite is different from that of  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , they based the determination of the magnetic space group ( $Ic'm'm'$ ) on the crystal space group  $Icmm$  proposed by Büssem (1937, 1938) and by Smith (1962). Results of the present analysis show that the most probable crystal space group of  $\text{Ca}_2\text{FeAlO}_5$  is  $Ibm2$  not  $Icmm$ . A separate report (Geller, Grant & Colville, 1971) demonstrates that the magnetic space group of  $\text{Ca}_2\text{FeAlO}_5$  is  $I_pbm'2'$  not  $Ic'm'm'$ .

The review of the crystal chemistry and magnetic structures of substituted  $\text{Ca}_2[\text{Fe}](\text{Fe})\text{O}_5$  by Geller, Grant & Gonsler (1971) was written in 1968.

### Experimental

A single crystal of  $\text{Ca}_2\text{AlFeO}_5$  was selected from the batch from which the single crystals were taken for the Mössbauer experiments (Grant *et al.*, 1968; Geller *et al.*, 1970). A sphere of diameter 0.33 mm was obtained using a sphere grinder (Schuyff & Hulscher, 1968; Crandall, 1970) similar to the one invented by Bond (1951) and mounted along the  $a$  axis. Weissenberg and precession photographs showed no evidence of twinning. Consistent with  $Icmm$  ( $D_{2h}^{28}$ ) or  $Ibm2$  ( $C_{2v}^{22}$ ), reflections  $hkl$  with  $h+k+l=2n+1$ , and  $0kl$  with  $k, l=2n+1$ , were absent.

Cell parameters were obtained from precession photographs. Cell parameters and other crystallographic data for brownmillerite are:

$$\begin{aligned} a &= 5.584 \text{ (5) \AA} & \text{F.W. } & 242.99 \\ b &= 14.60 \text{ (1) \AA} & \text{Volume } & 438.12 \text{ \AA}^3 \\ c &= 5.374 \text{ (5) \AA} & Z & = 4 \\ \rho_{\text{calc}} &= 3.68 \text{ g.cm}^{-3} & \mu(\text{Mo K}\alpha) & = 59.7 \text{ cm}^{-1}. \end{aligned}$$

Using Mo  $K\alpha$  radiation and Zr-Y balanced filters, 358 independent intensities were collected with a Buerger-Supper-Pace-Picker automated diffractometer from 8 levels about  $a$  in the range  $0.0 \leq \sin \theta \leq 0.5$ . The scan rate was  $2^\circ/\text{min}$ , and background counts were taken on each side of the peaks at  $\frac{1}{2}$  the total scan time. Intensities were corrected for absorption and Lorentz-polarization effects.

A refinement in space group  $Icmm$  ( $D_{2h}^{28}$ ) ( $c < a < b$ ) was attempted, using starting parameters from  $\text{Ca}_2\text{Fe}_2\text{O}_5$  (Colville, 1970) suitably modified for the special positions\* required in  $Icmm$  (see Smith, 1962, for a comparison of positions). Scattering factors were taken from Tokonami (1965) ( $\text{O}^{2-}$ ), from Tomiie & Stam (1958) ( $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$ ) and from Watson & Freeman (1961) ( $\text{Fe}^{3+}$ ); they were corrected for the real parts of anomalous dispersion (Cromer, 1965). The least-squares program used throughout this work is a modification of program *ORFLS* (Busing, Martin & Levy, 1962) by Ibers, Hamilton, Johnson, Ellison & Levy and includes contributions from the imaginary parts of the scattering factors. The agreement factor for  $Icmm$  was 0.19, indicating that this probably was not the correct space group. A refinement in space group  $Pcmm$  gave an agreement factor of 0.13; however, convergence was not achieved and large parameter interactions were observed.

\* However, the unreasonably short ( $\text{AlFe}$ )- $\text{O}(3)$  distance resulting from these positions made this space group seem unlikely.

Table 1. Calculated and observed amplitudes

h=0			h=1			h=1			h=2			h=2			h=3			h=4			h=4			h=5			h=5																	
k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>	k	l	F <sub>o</sub>						
0	0	41	39	3	0	60	59	18	3	40	40	18	0	1	38	34	5	5	14	14	7	2	20	20	4	0	7	2	1	5	36	35	6	3	63	63	7	3	41	41				
6	0	5	3	3	0	80	85	3	4	13	13	3	1	21	27	7	5	30	30	9	2	30	31	6	0	45	47	3	5	25	25	8	3	17	16	0	4	25	25					
10	0	201	228	5	0	80	85	3	4	13	13	3	1	21	27	7	5	30	30	11	2	34	33	8	0	71	73	5	5	13	12	10	3	18	18	2	4	38	37					
8	0	62	62	7	0	3	5	5	4	18	18	5	1	39	40	9	5	20	20	13	2	28	28	10	0	97	101	7	5	38	38	12	3	28	28	4	4	26	26					
12	0	67	68	9	0	38	38	7	4	23	23	7	1	50	52	11	5	15	16	15	2	28	28	10	0	97	101	7	5	38	38	12	3	28	28	4	4	26	26					
14	0	40	40	11	0	14	13	9	4	14	14	9	1	18	18	13	5	19	20	13	2	5	5	12	0	15	13	9	5	26	26	1	4	23	24	6	4	19	18					
16	0	56	55	13	0	35	34	11	4	13	13	11	1	17	18	7	6	34	34	17	2	40	40	14	0	7	4	11	5	30	30	3	4	50	49	5	4	37	36					
18	0	36	35	15	0	4	1	13	4	10	10	13	1	17	18	10	6	68	69	0	3	18	17	16	0	16	15	6	6	49	48	5	4	31	30	7	0	37	36					
20	0	70	67	17	0	31	31	15	4	14	13	15	1	34	35	4	6	12	6	3	3	37	36	1	1	50	49	2	6	24	24	7	4	31	30	7	0	37	36					
2	0	*181	225	19	0	2	2	17	4	15	15	17	1	9	9	6	6	32	31	4	3	93	95	3	1	5	5	4	6	21	20	9	4	34	35	k	1	F <sub>o</sub>	F <sub>c</sub>					
2	2	64	68	0	1	40	34	0	5	3	3	19	1	8	8	8	6	62	63	6	3	79	79	5	1	40	41	6	6	9	2	11	4	36	35	k	1	F <sub>o</sub>	F <sub>c</sub>					
4	2	44	44	2	1	28	27	2	5	30	31	0	2	*193	239	10	6	59	61	10	3	10	10	7	1	71	74	0	5	17	17	3	0	40	42	k	1	F <sub>o</sub>	F <sub>c</sub>					
6	2	46	44	4	1	*152	166	4	5	91	94	2	2	*110	110	2	2	27	20	3	7	17	18	12	3	43	44	11	1	15	15	2	5	30	29	5	0	6	7					
8	2	131	135	6	1	*110	118	6	5	66	68	4	2	27	20	3	7	17	18	12	3	43	44	11	1	15	15	2	5	30	29	5	0	6	7	5	0	37	36					
10	2	45	45	8	1	40	39	8	5	13	13	8	2	35	34	5	7	8	8	14	3	69	69	13	1	47	47	k	1	F <sub>o</sub>	F <sub>c</sub>	1	0	26	27	k	1	F <sub>o</sub>	F <sub>c</sub>					
12	2	32	32	10	1	62	63	10	5	30	30	8	2	*129	140	16	3	25	25	15	1	50	50	1	0	26	27	3	0	55	59	2	1	53	54	0	1	22	21					
14	2	41	42	12	1	80	82	12	5	48	48	10	2	78	81	15	4	27	26	16	3	51	50	2	0	27	26	5	4	37	37	17	1	9	7	5	0	46	47					
16	2	38	39	14	1	85	84	14	5	63	65	12	2	38	38	15	4	27	26	16	3	51	50	2	0	27	26	5	4	37	37	17	1	9	7	5	0	46	47					
18	2	42	41	16	1	46	46	1	6	20	20	14	2	26	25	k	1	F <sub>o</sub>	F <sub>c</sub>	5	4	27	26	16	3	51	50	2	0	27	26	16	3	51	50	2	0	27	26					
0	4	*162	169	18	1	44	43	3	6	17	17	16	2	35	35	k	1	F <sub>o</sub>	F <sub>c</sub>	7	4	20	20	4	2	29	26	9	0	16	17	10	1	0	33	33	4	0	13	12	1	2	29	27
2	4	82	83	20	1	20	20	5	6	12	11	18	2	46	46	3	0	*101	111	11	4	20	20	6	2	10	10	11	0	33	33	4	0	13	12	1	2	29	27					
4	4	26	28	1	2	11	13	7	6	11	11	1	3	52	51	5	0	68	71	11	4	42	42	8	2	51	50	13	0	9	9	6	0	16	17	5	2	35	34					
6	4	52	52	3	2	53	52	9	7	19	19	5	3	39	39	9	0	9	8	15	4	15	15	10	2	67	69	15	0	18	18	8	0	16	17	5	2	35	34					
8	4	105	107	5	2	22	21	11	6	18	18	5	3	39	39	9	0	9	8	15	4	15	15	10	2	67	69	15	0	18	18	8	0	16	17	5	2	35	34					
10	4	78	77	7	2	18	18	7	8	16	16	11	0	65	68	0	5	11	12	14	2	13	12	2	1	52	52	2	1	52	52	2	1	52	52	2	1	52	52					
12	4	28	28	9	2	10	10	2	7	30	33	9	3	24	27	13	0	12	11	0	5	33	33	16	2	21	16	8	1	1	38	38	7	2	48	46	7	2	48	46				
14	4	34	34	11	2	35	34	4	7	54	55	11	3	32	23	15	0	28	27	4	5	78	69	1	3	41	41	6	1	69	69	3	1	24	23	4	3	41	41					
16	4	29	29	13	2	5	4	6	7	54	55	11	3	32	23	15	0	28	27	4	5	78	69	1	3	41	41	6	1	69	69	3	1	24	23	4	3	41	41					
0	6	76	76	15	2	19	19	15	3	74	75	15	3	34	35	0	1	18	17	6	5	62	62	3	3	16	17	8	1	10	10	5	1	8	8	0	1	22	21					
2	6	42	44	17	2	3	3	17	3	13	14	2	1	24	22	10	5	14	14	7	3	54	54	12	1	22	21	10	1	22	21	9	1	55	55	0	1	22	21					
4	6	40	38	19	2	17	16	0	4	110	109	4	1	*128	136	12	5	33	33	9	3	22	22	14	1	59	59	14	1	59	59	14	1	59	59	14	1	59	59					
6	6	41	43	0	3	30	28	2	4	39	32	6	1	78	80	1	6	32	33	11	3	25	25	2	2	31	31	0	2	48	49	2	2	48	49	2	2	48	49					
8	6	55	55	0	3	39	37	4	0	*28	11	4	4	31	30	8	1	22	22	13	3	34	35	3	6	20	20	15	3	38	38	5	2	25	24	10	3	10	10					
10	6	53	54	4	3	*139	146	4	0	63	70	6	4	32	31	10	1	25	24	6	4	32	32	0	4	95	96	7	2	22	22	6	2	40	40	6	2	40	40					
12	6	17	16	6	3	86	85	6	0	30	31	8	4	77	75	12	1	59	61	7	6	32	32	0	4	95	96	7	2	22	22	6	2	40	40	6	2	40	40					
				8	3	35	35	8	0	113	117	10	4	54	53	14	1	69	69	8	4	23	21	11	2	55	56	10	2	76	76	10	2	76	76	10	2	76	76					
				10	3	53	53	10	0	57	59	12	4	17	16	16	1	36	36	8	4	23	21	11	2	55	56	10	2	76	76	10	2	76	76	10	2	76	76					
				12	3	71	72																																					

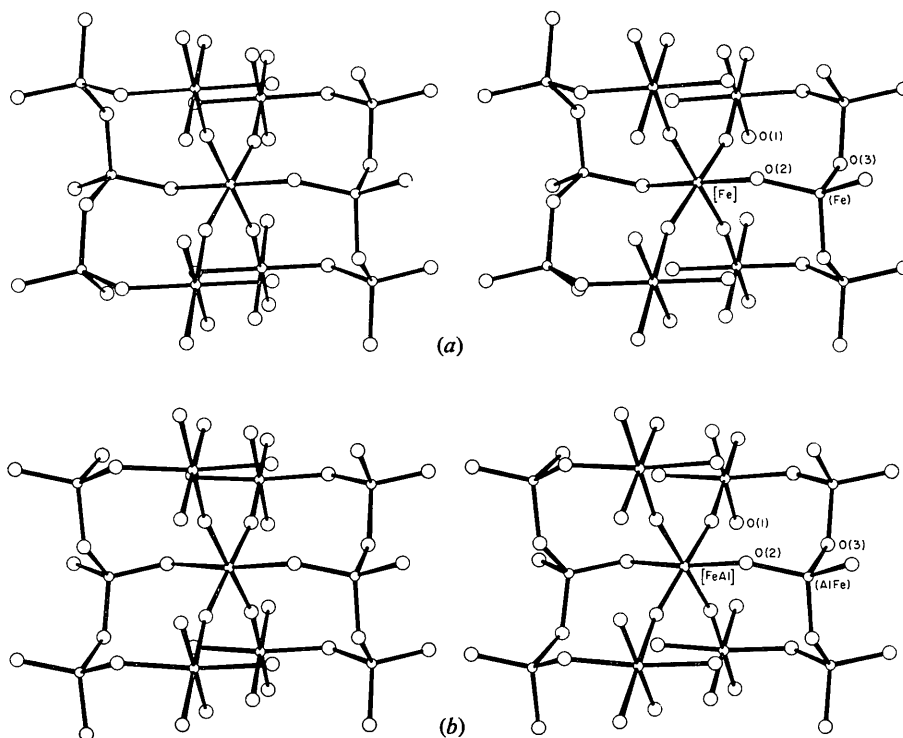


Fig. 1. Stereogram of (a)  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and (b)  $\text{Ca}_2\text{FeOAl}_5$  viewed approximately along [110].

Refinement in  $Ibm2$  (standard orientation  $Ima2$ ), a non-centrosymmetric subgroup of  $Icmm$ , quickly led to an agreement factor of 0.027. The equation used for the weighting scheme had the form:

$$1/w = 1 + C/2[(F_{\text{obs}} - D) + |F_{\text{obs}} - D|] + A \exp \left[ -\frac{F_{\text{obs}}}{B} \right].$$

This gives the very low- and high-intensity reflections

slightly lower weight. With  $A = 5.0$ ,  $B = 6.0$ ,  $C = 0.02$  and  $D = 20.$ , this weighting gave

$$\left\{ \sum [w(F_{\text{obs}} - F_{\text{calc}})^2] / (N_o - N_v) \right\}^{1/2} = 1.02,$$

where  $w$  = weight,  $N_o$  = number of observations, and  $N_v$  = number of variables. The total number of variables, 44, included the  $\text{Fe}^{3+}$  occupancy of the octahedral site. The site refinement gave 0.76 (1)  $\text{Fe}^{3+}$  in the octahedral site, and results in a formula for brownmillerite of  $\text{Ca}_2[\text{Fe}_{0.76}\text{Al}_{0.24}](\text{Al}_{0.76}\text{Fe}_{0.24})\text{O}_5$ . Table 1 gives a comparison of calculated and observed amplitudes. Ten high-intensity reflections, marked with an asterisk, were given low weights (count rate exceeded  $4 \times 10^4$  counts/sec). One reflection, the 220, was weighted low because of intense, overlapping continuous radiation not eliminated by the Y filter.

### Discussion of the structure

The structure of brownmillerite is similar to that of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  in that it is composed of sheets of perovskite-like, corner-sharing octahedra perpendicular to the crystallographic  $b$  axis (centered at  $y = 0$  and  $\frac{1}{2}$ ) and connected to single chains of tetrahedra (centered at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ ) that are parallel to the  $c$  axis. Fig. 1 shows a stereogram of part of the  $\text{Ca}_2\text{FeAlO}_5$  structure and a stereogram of part of the  $\text{Ca}_2\text{Fe}_2\text{O}_5$  structure for comparison; these were generated using program ORTEP (Johnson, 1965). Of the point symmetries in brownmillerite (Table 2) and  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , only those of

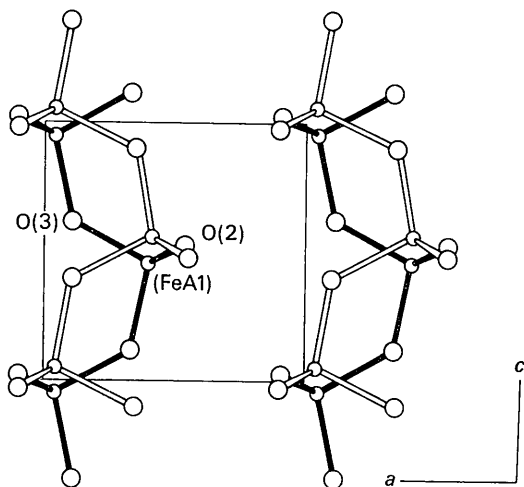


Fig. 2. Comparison of the single chain of tetrahedra centered at  $y = \frac{3}{4}$  in  $\text{Ca}_2\text{Fe}_2\text{O}_5$  (unshaded bonds) and  $\text{Ca}_2\text{FeAlO}_5$  (shaded bonds) viewed along the  $b$  axis. In each tetrahedron, O(2)1 is directly behind O(2).

the octahedral cation site at (0,0,0) are different, being  $\bar{1}$  in *Pcmm* and 2 in *Ibm2*. The main differences in the two structures are shown in Fig. 2. Whereas the single chains of tetrahedra at  $y = \frac{1}{4}$  are essentially the same in the two structures, the chains at  $y = \frac{3}{4}$  are related to these by  $\bar{1}$  in *Pcmm* and by 2 in *Ibm2*. The largest translation required in the structural transition is  $1.2 \text{ \AA}$  by O(3).

Interatomic distances and angles\* are listed in Table

\* Calculated with program *ORFFE* (Busing, Martin & Levy, 1964).

3. The average [Fe, Al]-O and (Fe, Al)-O distances are  $2.001$  and  $1.797 \text{ \AA}$ , respectively. In  $\text{Ca}_2\text{Fe}_2\text{O}_5$  (Colville, 1970), the average [Fe]-O and (Fe)-O distances are  $2.016$  and  $1.878 \text{ \AA}$ , respectively. There is no aluminum isomorph of  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . The average [Al]-O and (Al)-O distances from three rare earth and yttrium aluminum garnets refined by Euler & Bruce (1965) are  $1.94$  and  $1.76 \text{ \AA}$ , respectively. Using these distances and those from  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , one may calculate approximate expected distances in brownmillerite with distribution formula  $\text{Ca}_2[\text{Fe}_{0.76}\text{Al}_{0.24}](\text{Fe}_{0.24}\text{Al}_{0.76})\text{O}_5$ . These are  $2.00$  and  $1.79 \text{ \AA}$  for [Fe, Al]-O and (Fe, Al)-O, respec-

Table 2. Parameters and standard deviations for brownmillerite,  $\text{Ca}_2\text{FeAlO}_5$

Site	Ca 8(c)	[Fe, Al] 4(a)	(Al, Fe) 4(b)	O(1) 8(c)	O(2) 8(c)	O(3) 4(b)
<i>x</i>	0.0273 (2)	0	0.9283	0.2523 (10)	0.0680 (7)	0.8607 (10)
<i>y</i>	0.1087 (1)	0	$\frac{1}{4}$	0.9861 (2)	0.1439 (3)	$\frac{1}{4}$
<i>z</i>	0.4920 (3)	0.0000	0.9533	0.2491 (10)	0.0246 (9)	0.6193 (11)
$\beta_{11}$	0.0045 (2)*	0.0015 (3)	0.0018 (4)	0.0027 (9)	0.0055 (9)	0.0036 (14)
$\beta_{22}$	0.0008 (1)	0.0011 (1)	0.0004 (1)	0.0011 (1)	0.0012 (2)	0.0008 (2)
$\beta_{33}$	0.0079 (3)	0.0029 (4)	0.0025 (6)	0.0069 (11)	0.0082 (15)	0.0074 (19)
$\beta_{12}$	0.0001 (1)	0.0000 (1)	0	-0.0005 (6)	0.0006 (3)	0
$\beta_{13}$	-0.0002 (3)	0	-0.0007 (4)	-0.0002 (8)	-0.0016 (11)	-0.0007 (13)
$\beta_{23}$	-0.0000 (1)	0	0	-0.0006 (4)	0.0008 (4)	0

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

Table 3. Interatomic distances and angles in  $\text{Ca}_2\text{FeAlO}_5$

(Al, Fe) tetrahedron				
(Al, Fe)-O(2)	(2)	1.764 (4)* $\text{\AA}$	O(2)-(Al, Fe)-O(2)1	121.3 (3)°
(Al, Fe)-O(3)		1.825 (6)	O(2)-(Al, Fe)-O(3)	(2) 107.6 (2)
(Al, Fe)-O(3)4†		1.836 (6)	O(2)-(Al, Fe)-O(3)4	(2) 106.3 (2)
Mean		1.797	O(3)-(Al, Fe)-O(3)4	107.0 (2)
			Mean	109.4
O(2)-O(2)1		3.075 (8)		
O(2)-O(3)	(2)	2.896 (6)		
O(2)-O(3)4	(2)	2.881 (6)		
O(3)-O(3)4		2.943 (5)		
[Fe, Al] octahedron				
[Fe, Al]-O(1)	(2)	1.945 (6)	O(1)-[Fe, Al]-O(2)	86.0 (1)
[Fe, Al]-O(1)	(2)	1.933 (6)	O(1)-[Fe, Al]-O(1)2	93.6 (3)
[Fe, Al]-O(2)	(2)	2.126 (4)	O(1)-[Fe, Al]-O(1)5	87.2 (1)
Mean		2.001	O(2)-[Fe, Al]-O(1)2	89.1 (1)
			O(2)-[Fe, Al]-O(1)3	93.9 (1)
O(1)-O(2)		2.778 (5)	O(2)-[Fe, Al]-O(1)5	91.1 (2)
O(1)-O(1)2		2.834 (12)	Mean	90.1
O(1)-O(1)5		2.674 (3)		
O(2)-O(1)2		2.856 (6)		
O(2)-O(1)3		2.966 (6)		
O(2)-O(1)5		2.897 (6)		
Calcium polyhedron				
Ca-O(1)1		2.532 (5)	Ca-O(1)5	2.559 (5) $\text{\AA}$
Ca-O(1)2		2.447 (5)	Ca-O(2)	2.560 (6)
Ca-O(1)3		2.472 (5)	Ca-O(2)5	2.313 (5)
Ca-O(3)		2.348 (3)	Mean	2.461
Cation-cation				
[Fe, Al]-[Fe, Al]5	3.857 (3)		[Fe, Al]-O(1)-[Fe, Al]	168.0 (2)°
[Fe, Al]-[Al, Fe]	3.652 (3)		[Fe, Al]-O(2)-[Al, Fe]	139.8 (2)
(Al, Fe)-(Al, Fe)4	3.329 (3)		(Al, Fe)-O(3)-(Al, Fe)	130.8 (3)

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

† Symmetry transforms are numbered as follows: 1:  $x, \frac{1}{2} - y, z$ ; 2:  $\bar{x}, \bar{y}, z$ ; 3:  $\frac{1}{2} + x, \bar{y}, \frac{1}{2} + z$ ; 4:  $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$ ; 5:  $\frac{1}{2} - \bar{x}, y, \frac{1}{2} + z$ .

tively, and are in good agreement with the experimentally determined distances in brownmillerite.

Grant *et al.* (1968) report a distribution of  $\text{Ca}_2[\text{Fe}_{0.68}\text{Al}_{0.32}](\text{Fe}_{0.32}\text{Al}_{0.68})\text{O}_5$  for a powder specimen of brownmillerite quenched from 1290°C. Assuming the distribution corresponds to equilibrium at 1290°C, the enthalpy difference ( $H_t - H_o$ ) for the tetrahedral and octahedral sites is  $-0.20$  eV (e.g., see Grant, Wiedersich, Geller, Gonser & Espinosa, 1967). Using this value for  $\Delta H$ , and the distribution found by the X-ray diffraction analysis, the equilibrium temperature for the single-crystal material (furnace-cooled from  $\sim 1400^\circ\text{C}$ ) is found to be  $\sim 750^\circ\text{C}$ . This accounts for the difference in ion distribution found by Mössbauer spectroscopy for the powder specimen (Grant *et al.*, 1968) and that found for the single crystal by the structure analysis.

Table 4. *Parameters of vibration ellipsoids for  $\text{Ca}_2\text{FeAlO}_5$*

	Axis	Amplitude (r.m.s., Å)	Angles with crystallo- graphic axes (°)		
			<i>a</i>	<i>b</i>	<i>c</i>
Ca	1	0.084	18 (10)	108 (11)	93 (6)
	2	0.091	108 (10)	162 (11)	89 (10)
	3	0.107	86 (6)	90 (9)	4 (6)
[Fe, Al]	1	0.048	00 (2)	90 (2)	90
	2	0.065	90	90	0
	3	0.106	90 (2)	00 (2)	90
(Al, Fe)	1	0.054	36 (14)	90	54 (14)
	2	0.060	90	0	90
	3	0.063	126 (14)	90	36 (14)
O(1)	1	0.066	19 (17)	73 (16)	81 (12)
	2	0.100	74 (15)	119 (19)	146 (17)
	3	0.108	99 (14)	34 (14)	122 (17)
O(6)	1	0.093	139 (11)	64 (9)	120 (11)
	2	0.109	131 (11)	116 (26)	53 (23)
	3	0.113	88 (19)	39 (22)	52 (23)
O(3)	1	0.075	11 (20)	90	79 (21)
	2	0.093	90	0	90
	3	0.103	101 (20)	90	11 (21)

There is marked distortion of the oxygen octahedra and tetrahedra (Tables 3 and 4). The [Fe, Al]-O(2) distance is 2.13 Å compared with the other two [Fe, Al]-O distances of 1.945 and 1.933 Å. In the tetrahedra, the distortion is best seen by comparing O(2)-O(2)1 of 3.075 Å with the other three O-O distances, which average 2.91 Å. Both the octahedra and tetrahedra are elongated along the crystallographic *b* axis. The distortion particularly affects the magnitude and orientation of the principal axes of the thermal ellipsoid of vibration of the octahedral ion (Table 4). The vibration amplitude parallel to the largest principal axis, which exactly parallels the *b* axis, is roughly twice that of the others. (See Grant (1969), and Geller *et al.* (1971)

for results of an investigation of the nuclear electric field gradient in the system  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ ).

The calcium ion is surrounded by an irregular polyhedron of seven oxygen ions at distances ranging from 2.313 to 2.560 Å, with the mean distance of 2.461 Å.

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