Acta Cryst. (1956). **9**, 981

The Crystal Structure of Calcium Ferrite and β Calcium Chromite

By Patricia M. Hill, H. S. Peiser and J. R. Rait

Research Department, Hadfields Limited, Sheffield 9, *England*

(*Received* 3 *June* 1956)

The present authors confirm Burdese's cell dimensions (a = 9·16±0·03, b = 10·67±0·03, c = 3·012±0·006 Å) for calcium ferrite, which is isomorphous with β calcium chromite and probably with strontium ferrite, but disprove his statement on the close-packed hexagonal arrangement of oxygen atoms. The space group is *Pnam.*

The solution of the still incompletely refined structure from Patterson synthesis, Fourier projection and three-dimensional Fourier section at $z = \frac{1}{4}$ is described. The residual disagreement factor, R, is 22%, this high value being partly due to pseudo-symmetry.

The crystal chemistry of the compound is briefly discussed in relation to some of its physical properties. The co-ordinations of Ca and Fe ions are normal.

Introduction

Although the X-ray powder pattern of calcium ferrite has been known for some time (A.S.T.M., 1950*a*), Malquori & Cirilli (1952) were first in reporting single-crystal data supplied to them privately by Burdese. These are quoted in Table 1, together with those obtained by the present authors for this compound and for β calcium chromite first described by Ford & Rees (1949).

The isomorphism of the two compounds suggests itself from these data alone and is confirmed by a comparison of the powder and single-crystal diagrams and Patterson syntheses. It was found from powder data that strontium ferrite appears to be another member of the isomorphous series, although it is stated in the literature (A.S.T.M., 1950*b*) to be hexagonal. Attempts to obtain single crystals have so far failed.

Experimental work

A plot of the falling rates in methylene iodide of crystals of calcium ferrite with similarly sized pieces of epidote, corundum, pyrite, magnetite and iron showed that the density of calcium ferrite could not be less than 4·8 g.cm.$^{-3}$. The calculated density for a crystal containing (Z =)4 molecules per unit cell is 4·88 g.cm.$^{-3}$. The possibility of Z being greater than 4 does not arise because the molecular volume (293 Å^3) is insufficient to accommodate twenty oxygen atoms even in a close-packed arrangement. From data for the equivalent positions in the space groups *Pnam* and *Pna*2_1 (deduced from systematic absences enumerated below) it is in fact immediately clear that Z must be divisible by 4.

Because of its hardness and the difficulty of obtaining untwinned crystals of a size suitable for X-ray diffraction studies, the single-crystal work was carried out on a relatively large crystal ($\mu R \sim 25$) of calcium ferrite elongated parallel to [001], which is the typical habit. This involved not only large corrections for absorption but also possible inaccuracies in the estimated intensities as a result of anomalous absorption effects which could not be entirely eliminated by averaging of measurements from equivalent reflexions. The crystals were not strongly magnetic and no electric effect was detected on heating from liquid-air to room temperature.

For calcium ferrite the following X-ray photographs were taken: (i) powder; (ii) [001] rotation using Co $K\alpha$; (iii) [100], [010] and [001] oscillation using Co $K\alpha$; and (iv) [001] Weissenberg (equatorial and equi-inclination for hk1 reflexions) using Cu $K\alpha$ radiation. For β calcium chromite [001] rotation and oscillation photographs were taken with Co $K\alpha$ radiation. Intensities were estimated visually on a scale from 1 to 200 by the double-film technique and averaged over the two sides of the films.

The intensities were corrected for absorption, polarization, the Lorentz effect and secondary ex-

Table 1. *Cell dimensions and symmetry*

Compound	Authors	Symmetry	a (Å)	b (Å)	c (Å)
$CaFe_2O_4$	Burdese	Orthorhombic	9·16	10·60	3·01
	Present authors	*Pnam*	9·16 ±0·03	10·67 ±0·03	3·012 ±0·006
$CaCr_2O_4$	Present authors	*Pnam*	9·07 ±0·02	10·61 ±0·03	2·99 ±0·04

tinction ($\varepsilon = 2\times10^{-4}$). The calculated F values were corrected for temperature ($B = 1\cdot4\times10^{-16}$ cm.^{2}) and the scattering factors of the Fe ions were adjusted to allow for the proximity of the K absorption edge of iron to the wavelength of the incident radiation.

Determination of structure

There were only the following systematic absences on the Weissenberg photographs:

$hk0$'s ($h \le 11$; $k \le 13$): $h00$ when h odd, $0k0$ when k odd;

$hk1$'s ($h \le 11$; $k \le 13$): $h01$ when h odd; $0k1$ when k even ($k = 0$ not observable on Weissenberg but absent on oscillation photograph).

The space group therefore is either *Pnam* or *Pna*2_1. This conclusion, in conjunction with the very short c dimension (only slightly larger than an atomic diameter of a single oxygen atom), disproves the only other comment on the structure made by Malquori & Cirilli 'this compound crystallizes in the orthorhombic system with the O atoms so arranged as to form an almost hexagonal close-packed lattice'. No doubt these authors based their conclusion on the undisputed pseudo-hexagonal appearance of the [001]-zone reflexions (see weighted reciprocal lattice $l = 0$ in Fig. 1) coupled with the a- and b-axis dimensions, which so strikingly agree with 16 hexagonally close-packed oxygens for which these cell dimensions would be 9·15 and 10·56 Å compared with average observed values of 9·16 and 10·63 Å. The n glide perpendicular to the a axis, however, prevents the oxygens from being all at the same level with respect to the a–b plane.

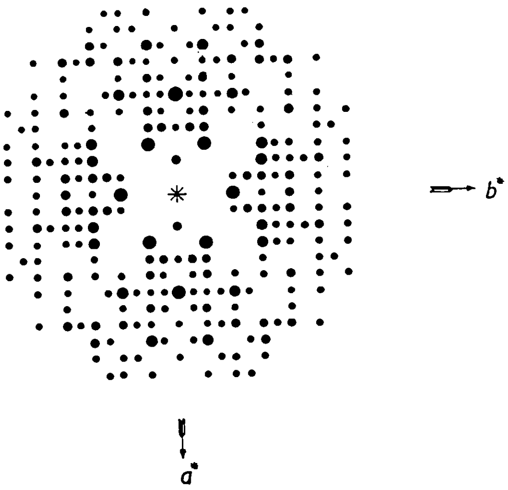


Fig. 1. Calcium ferrite weighted reciprocal lattice ($l = 0$). Area of each spot approximately proportional to structure amplitude. Very weak reflexions omitted.

An attempt to test for a centre of symmetry by a statistical method proved entirely inconclusive (the greater part of the $N(z)$ distribution lying well below that of a non-centrosymmetrical arrangement), presumably because the atoms are all in special positions (for *Pnam*) and the high pseudo symmetry causes many accidental absences. Similar cases quoted in the literature are those of eucryptite $LiAlSiO_4$ (Howells, Phillips & Rogers, 1950) and 9-paracarbethoxyphenyl-9-stibiafluorene, $C_{20}H_{12}O_2Sb$ (Hargreaves, 1955).

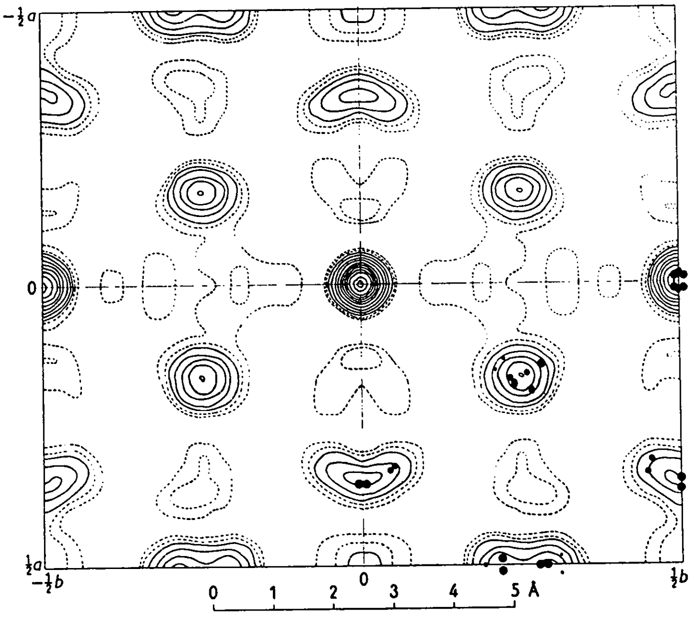


Fig. 2. Calcium ferrite [001] Patterson projection (0, 50 contours broken, remainder at hundreds) with metal–metal vectors (calculated from final metal co-ordinates) affecting the contours of one quadrant and shown as filled-in circles of weighted diameters.

Table 2. *Observed and calculated structure factors*

h	l \ k	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	0	-	S.A.	3.4(3.0)	S.A.	29.7($\overline{32.1}$)	S.A.	5.6($\overline{4.9}$)	S.A.	11.7(8.6)	S.A.	7.1(5.4)	S.A.	<1.2(.3)	S.A.
	1	S.A.	8.2($\overline{7.6}$)	S.A.	12.6(8.4)	S.A.	17.3(11.6)	S.A.	<1.2(0)	S.A.	9.8($\overline{5.0}$)	S.A.	<1.2(1.7)	S.A.	3.8(2.7)
1	0	S.A.	<2.6(.5)	5.9($\overline{4.0}$)	<2.6(1.5)	4.9($\overline{4.6}$)	9.3(6.2)	8.8(6.5)	2.7($\overline{2.6}$)	11.7(12.5)	2.4(1.5)	3.9($\overline{4.1}$)	<1.6($\overline{.3}$)	6.3($\overline{8.4}$)	<.6(0)
	1	S.A.	7.0(4.5)	20.3(18.9)	18.4($\overline{16.6}$)	13.0(11.3)	<1.9(1.7)	21.6($\overline{15.6}$)	10.0(8.0)	11.2($\overline{7.5}$)	8.2($\overline{5.5}$)	9.1(6.7)	<1.2(1.0)	9.8(11.1)	3.6(5.5)
2	0	12.1(12.3)	<2.5(1.0)	6.5(8.4)	<2.4($\overline{.7}$)	<2.7($\overline{2.4}$)	5.4($\overline{3.6}$)	16.0($\overline{20.0}$)	3.7(4.7)	6.7(6.0)	6.0(5.5)	12.1(13.9)	<1.4(.7)	5.6($\overline{7.2}$)	<.7($\overline{.5}$)
	1	20.3(19.1)	<1.8(2.4)	5.9(4.4)	7.8(6.5)	20.3($\overline{19.6}$)	3.5($\overline{4.7}$)	14.7($\overline{11.9}$)	2.4(3.3)	9.6(8.1)	<1.7(1.9)	9.7(9.5)	6.7($\overline{6.1}$)	-	-
3	0	S.A.	3.1($\overline{3.1}$)	21.5($\overline{30.6}$)	4.7($\overline{4.3}$)	<2.3(1.9)	4.8(4.2)	14.2(22.2)	2.6($\overline{2.3}$)	7.4(2.7)	<1.8(.3)	6.7($\overline{6.5}$)	<1.5(.2)	5.0($\overline{7.0}$)	1.4(1.5)
	1	S.A.	13.6($\overline{13.3}$)	6.5(5.6)	10.8(10.2)	<1.9($\overline{.9}$)	2.5($\overline{2.9}$)	7.7($\overline{6.6}$)	7.9($\overline{5.6}$)	<1.8(1.0)	6.5(6.3)	<1.4($\overline{1.3}$)	4.5(3.8)	-	-
4	0	3.0(3.4)	8.0($\overline{7.8}$)	9.9($\overline{13.2}$)	<2.3($\overline{1.7}$)	<2.2($\overline{1.4}$)	<2.1(.3)	7.4(10.8)	<1.9($\overline{1.7}$)	<1.9($\overline{1.9}$)	2.2(3.0)	7.1($\overline{7.1}$)	3.1(4.0)	1.9(4.2)	-
	1	26.0(23.3)	14.0($\overline{11.5}$)	6.1(6.3)	5.6($\overline{4.6}$)	16.0($\overline{19.4}$)	2.4(2.7)	9.6($\overline{11.6}$)	3.3($\overline{2.7}$)	8.9(7.7)	1.8($\overline{2.7}$)	8.7(9.8)	1.7(2.4)	-	-
5	0	S.A.	4.9($\overline{2.3}$)	9.0($\overline{7.8}$)	<2.1($\overline{2.0}$)	5.9($\overline{8.9}$)	<2.6(.8)	5.0(5.8)	<1.9($\overline{1.3}$)	9.1(13.3)	<1.6(.2)	6.5($\overline{8.2}$)	2.3($\overline{1.9}$)	6.1($\overline{10.5}$)	-
	1	S.A.	3.9(2.7)	17.0($\overline{17.4}$)	4.2($\overline{5.0}$)	<1.9($\overline{.5}$)	2.8(2.5)	7.7(6.6)	4.8(5.8)	2.8(3.4)	6.7($\overline{6.3}$)	5.3($\overline{4.8}$)	<.9(0)	-	-
6	0	27.4($\overline{28.2}$)	6.6(3.6)	5.9($\overline{5.1}$)	5.8(2.6)	15.7(22.1)	5.6($\overline{7.7}$)	4.1(4.5)	<1.7($\overline{1.2}$)	6.8($\overline{7.2}$)	<1.5(.6)	3.8($\overline{3.8}$)	<.8($\overline{2.3}$)	-	-
	1	8.7(7.4)	2.4(2.9)	6.4(5.0)	<1.8($\overline{1.1}$)	6.6($\overline{5.8}$)	8.8($\overline{9.6}$)	2.5($\overline{2.4}$)	2.0(3.4)	3.9(3.4)	5.6(5.4)	<.8(1.4)	2.9($\overline{4.7}$)	-	-
7	0	S.A.	4.4(2.4)	8.4($\overline{7.4}$)	<1.9($\overline{.2}$)	6.0(4.8)	<1.8(.3)	<1.7($\overline{1.6}$)	<1.7($\overline{1.6}$)	6.0($\overline{6.4}$)	<1.2(.6)	<.9(.7)	-	-	-
	1	S.A.	6.6($\overline{3.5}$)	12.4($\overline{10.5}$)	11.0(9.4)	6.5($\overline{6.1}$)	2.1(1.0)	9.3(9.9)	2.1($\overline{3.2}$)	8.9(11.5)	<2.7($\overline{.4}$)	4.9($\overline{7.4}$)	-	-	-
8	0	7.2($\overline{7.5}$)	<1.9(1.8)	4.7($\overline{4.3}$)	6.5(3.7)	8.7(9.3)	2.1(2.8)	9.0(10.9)	5.8($\overline{4.8}$)	4.8($\overline{5.5}$)	1.5($\overline{3.3}$)	5.5($\overline{10.5}$)	-	-	-
	1	10.9($\overline{10.5}$)	4.8($\overline{4.0}$)	<1.7(0)	<1.6(2.3)	7.3(7.5)	3.8(6.2)	5.3(4.3)	4.1($\overline{3.0}$)	3.1($\overline{3.2}$)	-	-	-	-	-
9	0	S.A.	6.0(5.1)	14.4(15.2)	2.0($\overline{2.2}$)	<1.5(0)	3.4($\overline{1.6}$)	8.2($\overline{11.2}$)	2.3(1.5)	<.8(.2)	-	-	-	-	-
	1	S.A.	<1.3(1.5)	7.9($\overline{8.6}$)	<2.2($\overline{.8}$)	<1.2(1.6)	<.9(0)	5.5(7.0)	3.7(3.9)	-	-	-	-	-	-
10	0	3.4($\overline{3.1}$)	<1.3($\overline{1.1}$)	<1.3(1.7)	3.7(1.4)	3.4(4.0)	1.2($\overline{2.5}$)	2.5($\overline{2.4}$)	1.3(2.1)	-	-	-	-	-	-
	1	10.4($\overline{12.4}$)	6.8(6.5)	2.9($\overline{3.5}$)	5.2(4.2)	5.5(6.8)	4.6($\overline{4.6}$)	4.5(6.9)	-	-	-	-	-	-	-
11	0	S.A.	<1.2(.2)	3.1(4.0)	<.8(1.1)	4.9(8.2)	3.2($\overline{2.5}$)	-	-	-	-	-	-	-	-
	1	S.A.	<.6($\overline{1.3}$)	3.6(5.2)	-	-	-	-	-	-	-	-	-	-	-

Figures in brackets: Calculated structure factors.
S.A.: Space-group absences.
-: sin θ equal to 0 or greater than 0·985.

Using F^2 values for the $hk0$ reflexions, a Patterson synthesis was prepared (Fig. 2) from which the following approximate metal-ion positions could be unequivocally derived: (30°, 45°, –), (150°, 45°, –), (90°, 135°, –). From packing considerations alone, the Ca ions could be shown to lie in the position corresponding to the third set of co-ordinates, that is on or near the glide plane. The approximate metal co-ordinates are such that they would give zero structure-amplitude contributions for $hk0$ (k odd) reflexions. The observed intensities for these is indeed very small (cf. Fig. 1 or Table 2), but it is nevertheless apparent that a few of them are too strong to be solely due to oxygens. This is borne out by the observation that the pseudo-halving is less pronounced at high angles than for low-angle reflexions.

Refinement was now difficult:

1. The Patterson could be excellently explained by several distortions from the pseudo-symmetrical metal positions. There are, in fact, three possible co-ordinates (differing only in the y parameter) for each of the three metal positions. Several non-equivalent combinations of these explain the Patterson very satisfactorily.
2. Fourier projections could only be constructed from $hk0$ (k even) reflexions, for which alone the signs could be determined (apart from one arbitrarily chosen sign of a k-odd reflexion). Marked elongation of Fourier peaks across pseudo-symmetry lines could not be detected.
3. Consideration of the Patterson for k-odd reflexions alone as arising, to a first approximation, from the four oxygen ions did not provide four sets of possible oxygen parameters, even when the $(F_o^2 - F_c^2)$ for k-even reflexions were added.
4. The 'error Patterson' (as under (3)) similarly could not be explained by distortion of the metal-ion positions alone.
5. Minimizing $\Sigma|F_o - F_c|$ for $h00$ and $0k0$ reflexions by adjusting metal-ion co-ordinates seemed at first to give striking and conclusive results; these, however, were not confirmed by other $hk0$ intensities nor were oxygen positions derived (from packing) which agreed with the complete observed intensity data.
6. Significant progress was made only when possible metal-ion shifts were separately considered, using full ($hk0$) data. Departure of the x or the y values from the quoted approximate co-ordinates of any one of the three ions produces possible distortions, only few of

which are equivalent. Finally one metal arrangement was found to be outstandingly the best near to the following co-ordinates: Fe_I (31°, 38°), Fe_{II} (155°, 40°) and Ca (90°, 126°). If the space group were *Pnam* there were now two possible sets of oxygen positions (from packing considerations) depending on whether the Ca ion was on the same level as Fe_I or Fe_{II} (in the x and y positive cell quadrant nearest the origin). Only for the latter arrangement was a much improved agreement obtained when the oxygen structure factors were added. The *hk*1 reflexions agreed well only with the Ca on the same level as Fe_{II}.

The good quality of the fit for the *hk*1 data in itself confirms the space group as *Pnam* rather than $Pna2_1$. The great strength of the 002 reflexion (not given in Table 2) also suggests *Pnam* to be correct. The short c cell edge, moreover, means that the ions can only move by 0·75 Å from the mirror plane position of *Pnam* if the space group were in fact $Pna2_1$. From the intensity data a far smaller distortion from these planes could only be tolerated for the metal ions. Even slight distortion of the oxygen ions is then unlikely from packing considerations. The strongest argument for thinking that no departure from *Pnam* exists is based on the residual disagreement factor (see below) for *hk*1 reflexions (19%) being actually better than that for the *hk*0 reflexions (26%). It is the larger pseudo-symmetry of the [001] projection that causes a great increase in the number of absent and very weak reflexions and a corresponding increase in the disagreement factor for the *hk*0 reflexions. For the same reason the structure cannot be easily refined by reference to *hk*0 reflexions alone and two-dimensional methods of structure determination tend to be at a disadvantage compared with methods using all or at any rate *hkl* (l odd) data.

Any further refinement of the structure must depend on better and more complete observed intensity data, although it is quite clear that some improvement could be achieved simply by calculation of metal co-ordinates to fractions of a degree. Optical-analogue work showed that agreement may be further improved by the application of an anisotropic temperature factor.

As the type of major distortions from pseudo-symmetry is no longer in doubt this will not be attempted by the present authors, who have confined themselves to obtaining a three-dimensional Fourier section of the structure at height $z = \frac{1}{4}$ (Fig. 3(*b*)). This is unusual for a relatively complex structure because it shows the centres of all the structural sites. It was computed from *hk*0 and *hk*1 reflexions only. The error so introduced is not large owing to the exceptionally short c dimension, as a result of which the semi-cone angle for equi-inclination photographs of *hk*2 reflexions is, even for Cu $K\alpha$ radiation, smaller than can be accommodated on most commercial Weissenberg cameras. The co-ordinates obtained are in good agreement with those shown in the Fourier projection (Fig. 3(*a*)). The final co-ordinates are:

Fe_I (28°, 38°, 270°),
Fe_{II} (155°, 40°, 90°),
Ca (93°, 124°, 90°),
O_I (139°, 167°, 270°),
O_{II} (8°, 78°, 90°),

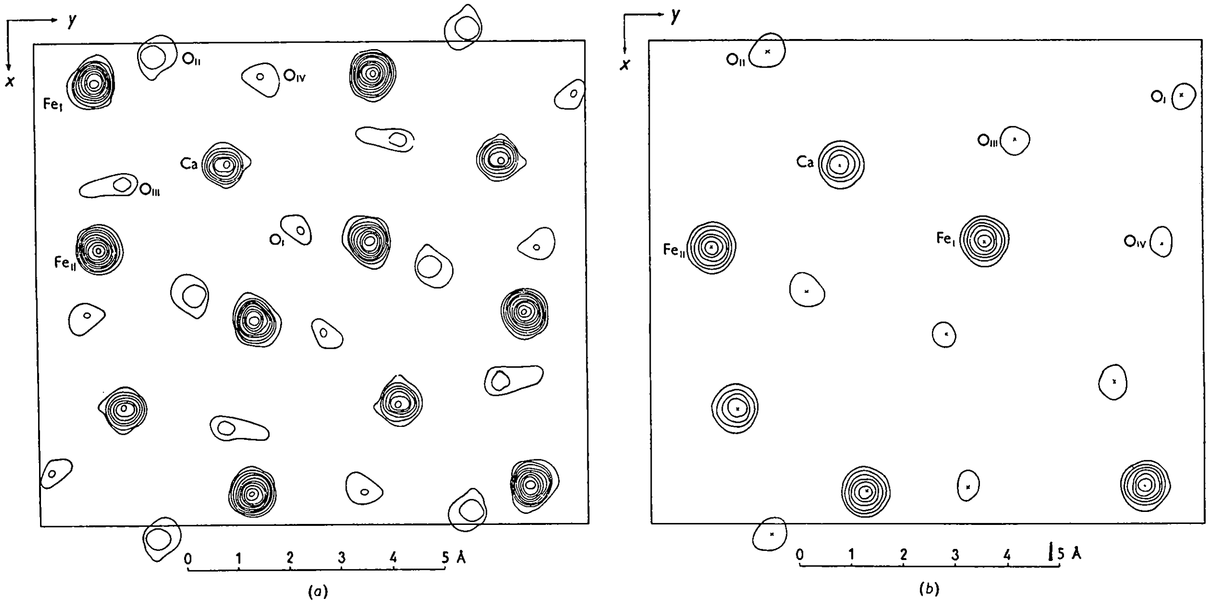
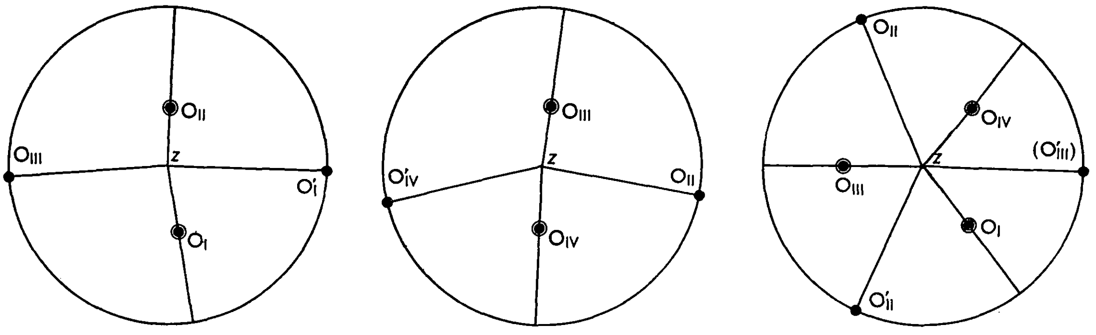


Fig. 3. (*a*) Calcium ferrite [001] Fourier projection. Contours drawn at equal arbitrary intervals. (*b*) Calcium ferrite three-dimensional Fourier section at $z = \frac{1}{4}$. Contours drawn at equal arbitrary intervals. Centres of atoms (final co-ordinates) indicated by crosses.



(a) (b) (c)

Fig. 4. Co-ordination of (a) Fe_{I} atom, (b) Fe_{II} atom, (c) Ca atom in stereographic projection.

O_{III} (106°, 59°, 270°),
O_{IV} (28°, 154°, 270°).

The combined residual disagreement factor $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ for the $hk0$ and $hk1$ reflexions is 22%. In calculating the R values, randomly absent reflexions were given the value of half the minimum observable intensity (to which figure the stated corrections were applied).

Description of structure

In the structure of calcium ferrite there are two non-equivalent Fe ions, each octahedrally surrounded by oxygens as shown stereographically in Fig. 4(a), (b). The calcium can be described as eightfold co-ordinated (a ninth neighbouring O ion O'_{III} is too far at 3·47 Å to be counted as a 'nearest neighbour') (Fig. 4(c)). Six oxygens form a trigonal prism with axis parallel to c; the remaining two oxygens are on the same level as the calcium in staggered bond position (cf. Bunn, 1945). The bonds terminating on the O ions obey Pauling's rule perfectly.

The interatomic distances (see Table 3) are in good agreement with those of similarly co-ordinated atoms reported in the literature. In ludwigite (Takéuchi, Watanabé & Ito, 1950) Fe^{3+}–O distances in the $Fe^{3+}O_6$ octahedra showed greater variations: from 1·98 to 2·45 Å. Low values have also been reported elsewhere, e.g. 1·94 Å in pharmacosiderite (Zemann, 1947). In dicalcium phosphate (MacLennan & Beevers, 1955), where one Ca ion is sevenfold and another is eightfold co-ordinated, the Ca–O distance varied from 2·29 to 2·69 Å.

Table 3. *Interatomic distances*

(Estimated probable error ±0·04 Å)

Fe_{I}–O'_{I}	1·89 Å	Fe_{II}–O'_{IV}	1·95 Å
2 × Fe_{I}–O_{II}	1·98	2 × Fe_{II}–O_{III}	2·03
Fe_{I}–O_{III}	2·08	Fe_{II}–O_{II}	2·01
2 × Fe_{I}–O_{I}	2·15	2 × Fe_{II}–O_{IV}	2·06
2 × Ca–O_{III}	2·46	(Ca–O'_{III}	3·47)
Ca–O_{II}	2·55	2 × Ca–O_{I}	2·29
2 × Ca–O_{IV}	2·40	Ca–O'_{II}	2·50

There is no observed cleavage plane and the structure cannot be broken along any plane without rupturing Fe–O bonds. The hardness (~ 6 on Mohs scale) is probably also explained by the framework of the structure being held by Fe^{3+}–O bonds.

The pseudo-hexagonal symmetry (cell geometry, intensities of $hk0$ reflexions, Fig. 1, and projection of atomic arrangement, Fig. 3(a)) are fortuitous in the sense that owing to differences in levels no small distortion of the three-dimensional structure will render it truly hexagonal. Strontium ferrite, therefore, cannot be both isostructural with calcium ferrite and hexagonal.

No small distortion of the structure will, furthermore, halve the b axis (except in the projection perpendicular to [001]). Only the two types of Fe ions could by small shifts be placed into positions related by a c glide (corresponding to $Pcam$ with a halved b dimension). Consequently the Fe ions contribute little to k-odd reflexions. This results in a relative weakening of these reflexions that is less pronounced at high angles (because the Fe ions are not accurately related by a c glide) and for $l = 1$ (because the Ca ions by themselves show very marked pseudo-A-face centring, thus enhancing only k-odd reflexions).

Most known ferrites of formula MFe_2O_4 have the spinel structure. Calcium ferrite is an exception because of the large size of the Ca ion, which tends to be 8- or 9-fold co-ordinated.

Mr H. G. Midgley of the Building Research Station, Watford, very kindly provided single crystals of calcium ferrite. Dr L. G. Finch of the Hadfields Laboratories took the X-ray photographs of β calcium chromite and derived a rough [001] Patterson synthesis.

The authors are indebted to Prof. H. Lipson, Manchester College of Science and Technology, and Dr H. J. Grenville-Wells, University College, London, who permitted the use of optical-analogue machines in their laboratories. The results of these trials, while not actu-

ally influencing the structure determination as described in the paper, confirmed in principle that these machines may be capable of aiding the evaluation of structures with marked pseudo-symmetry (actual or in projection).

Finally, the authors wish to thank Mr E. W. Colbeck, Metallurgical Director of Messrs Hadfields Limited, for his continued interest and encouragement, and for permission to publish this communication.

References

A. S. T. M. *Index of X-ray Diffraction Data* (1950*a*). Card 3-0825.

A. S. T. M. *Index of X-ray Diffraction Data* (1950*b*). Card 1-1027.

BUNN, C. W. (1945). *Chemical Crystallography*, p. 277. Oxford: Clarendon Press.

FORD, W. F. & REES, W. J. (1949). *Trans. Brit. Ceram. Soc.* **48**, 291.

HARGREAVES, A. (1955). *Acta Cryst.* **8**, 12.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

MACLENNAN, G. & BEEVERS, C. A. (1955). *Acta Cryst.* **8**, 579.

MALQUORI, G. L. & CIRILLI, V. (1952). *Third International Symposium on the Chemistry of Cement.* London: Cement and Concrete Association.

TAKÉUCHI, Y., WATANABÉ, T. & ITO, T. (1950). *Acta Cryst.* **3**, 98.

ZEMANN, J. (1947). *Experientia*, **3**, 452.

Acta Cryst. (1956). **9**, 986

The Crystal Structure of an Unstable Form of Chloroacetamide

BY MIKIO KATAYAMA

Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo, Japan

(*Received* 23 *April* 1956)

Chloroacetamide, $CH_2Cl.CONH_2$, was found to have two modifications, both of which belong to the same space group ($P2_1/a$, 4 molecules per unit cell) and have almost the same cell dimensions. The difference is only in the value of the angle β: 102·5° in the unstable, and 98° 49′ in the stable form. The crystal and molecular structure of the unstable form have been determined from a study of the two-dimensional projections of ϱ and $(\varrho_o-\varrho_c)$ along the a and b axes. Bond lengths are almost the same as those in the related molecules: C–Cl = 1·76 Å, C–C = 1·51 Å, C–O = 1·25 Å and C–N = 1·40 Å (the estimated standard deviation of oach atom is about 0·03 Å). The C–Cl bond takes approximately the *cis* position to the C–N bond. An interesting rule is found in the bond lengths and bond angles of the terminal amide group. N–H · · · O hydrogen bonds are relatively weak in this crystal, the shortest N–H · · · O distance being 3·05 Å and others about 3·37 Å and 3·39 Å.

Introduction

For some years past the protein structure has been approached by means of detailed X-ray analysis of some amino acids and related compounds which constitute the polypeptide chain of proteins. Much information has already been obtained concerning not only the dimensions and configurations of these molecules but also the nature and strength of the forces which bind them together. The structure of the terminal amide group has been studied for oxamide (Romers, 1953; Ayerst & Duke, 1954), succinamide (Pasternak, 1953), nicotin amide (Wright & King, 1954), glycyl-L-asparagine (Pasternak, Katz & Corey, 1954), L-glutamine (Cochran & Penfold, 1952), acetamide (Senti & Harker, 1940), 6-amido-3-pyridazone (Cucka & Small, 1954), and tetradecanamide (Turner & Lingafelter, 1955), but the dimensions reported for the group are appreciably different from each other. For this reason an accurate analysis of the crystal structure of simple amides and the comparison of the results with those already reported would be of interest.

Recently Dejace (1955) reported an X-ray analysis of the crystal structure of chloroacetamide. He prepared the crystals from alcoholic or benzene solution. The present author obtained another form of the crystal by slow evaporation of its aqueous solution; for convenience, this will be termed the unstable form in this article. An accurate analysis of the structure of this crystal and the comparison of the results with the structure of the stable form are reported here.

Crystal data and experimental measurements

Chloroacetamide, $Cl–CH_2CO.NH_2$, was prepared by Dr I. Nakagawa, and its purity was examined by use of the Raman and infra-red spectra. Single crystals were obtained from aqueous solution in plate form or