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The Crystal Structure of Hydrogen Peroxide*

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Hydrogen peroxide forms tetragonal crystals, space group D_4^4–$P4_12_1$. There are four molecules in the unit cell of dimensions $a = 4{\cdot}06$, $c = 8{\cdot}00$ A. The crystal structure has been completely determined, using both double Fourier series and least-squares methods, based on visual intensity measurements of the reflections from three zones. The O–O bond distance is 1·49 A., the angle made by the hydrogen bond with the O–O bond is about 97°, and the azimuthal angle between planes containing the hydrogen bonds and the O–O bond is 94°. Each oxygen atom has two close approach distances of 2·78 A. and two longer ones of 2·90 A., resulting in a very compact crystal. Assuming hydrogen bonds in the 2·78 A. distances, no measurable retention of entropy is to be expected at absolute zero. A mechanism for the formation of hydrogen peroxide–water solid solutions is also suggested.

Introduction

The geometrical configuration of the hydrogen peroxide molecule became the subject of a large number of investigations following the valence-bond treatment of Penney & Sutherland (1934*a*, *b*). These authors concluded that the most likely structure was one in which the angle (θ) made by the O–H bond with the O–O bond was about 100°, and the azimuthal angle (ϕ) between the O–H bonds, as seen when projected on to a plane normal to the O–O bond, was between 90 and 100°. An X-ray study of the hydrogen peroxide–urea addition complex was made by Lu, Hughes & Giguère (1941), in which the O–O bond distance was reported to be 1·46 A., $\theta = 101{\cdot}5°$ and $\phi = 106°$; an infra-red study of hydrogen peroxide by Zumwalt & Giguère (1941) led to the assignment of 1·48 A. for the O–O distance, and an electron-diffraction study by Giguère & Schomaker (1943) gave this distance as 1·47 A. An electron-diffraction study of dimethyl peroxide has also been made by Shand (1946), in which the O–O distance is given as 1·47 A., θ as 105° and ϕ as 135°. The accuracy of these values, however, must be less than usual owing to the difficult problem of resolution between the O–O and C–O (1·43 A.) distances, and the dependence of ϕ upon relatively small terms. The present study of the crystal structure of hydrogen peroxide is thus a further contribution to the subject.

The nature of the hydrogen bonds formed in this crystal are also of interest, both in view of the unusually high density (1·70 g.cm.$^{-3}$), and in comparison with those formed in ice (Barnes, 1929), where the distance is given as 2·76 A. The location of the hydrogen bonds, and, by inference, of the hydrogen atoms provides information concerning the entropy retained at very low temperatures. This study further affords a good opportunity for extending the methods of single-crystal X-ray analysis to compounds melting below room temperature.

Crystal data

Hydrogen peroxide, H_2O_2. Mol.wt. 18·016. Melting-point – 0·89°C. (Giguère & Maass, 1940). $D_{\text{obs.}}$ 1·64 (*International Critical Tables* (1926), vol. 1, p. 106), $D_{\text{calc.}}$ 1·70. Tetragonal with $a = 4{\cdot}06 \pm 0{\cdot}02$, $c = 8{\cdot}00 \pm 0{\cdot}02$ A. (hkl) present in all orders, ($00l$) only when $l = 4$, and ($h00$) only when $h = 2$. Space group D_4^4–$P4_12_1$ (enantiomorphous with D_4^8–$P4_32_1$). Four molecules per unit cell. No molecular symmetry required. Volume of the unit cell, 131·9 A.^{3}. Total number of electrons per unit cell = $F(000) = 72$.

Earlier determinations of the crystal data were made by Fehér & Klötzer (1935, 1937) who found $a = 4{\cdot}02$ and $c = 8{\cdot}02$ A. in a tetragonal system. They were unable to identify the space group, but Natta & Rigamonti (1936) suggested the space group D_4^4 or D_4^8. These cell constants were measured both from powder data and single-crystal rotation photographs, and are in substantial agreement with our values taken from Buerger precession photographs.

Analysis of the structure

The space group D_4^4–P4_12_1 contains eight general positions (*Internationale Tabellen*..., 1935, vol. 1):

(1) x, y, z, (2) $\bar{x}, \bar{y}, \tfrac{1}{2}+z$, (3) $y, x, \bar{z}$,
(4) $\bar{y}, \bar{x}, \tfrac{1}{2}-z$, (5) $\tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{4}-z$,
(6) $\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{3}{4}-z$, (7) $\tfrac{1}{2}-y, \tfrac{1}{2}+x, \tfrac{1}{4}+z$,
(8) $\tfrac{1}{2}+y, \tfrac{1}{2}-x, \tfrac{3}{4}+z$,

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and since there are four molecules of hydrogen peroxide in the unit cell, there must be one oxygen and one hydrogen atom per general position. For the purpose of easier calculation, the hydrogen atom contribution was ignored in the earlier stages of this work, so that the problem became one involving only three parameters.

The ($hk0$) zone was initially examined, since it involved only two parameters, and since it possessed a center of symmetry. The area to be explored for a fit of calculated with observed intensities was very small, and good agreement was soon obtained. When this agreement became no better, on making further small adjustments in x and y, refinement was then carried out by the double Fourier-series method until there were no more changes in sign. The results of the final summation are given in Fig. 1 as an electron-density map. This shows a group of ten molecules, projected on to the (001) plane, and the explanation of this map is given in Fig. 2. On the basis of this projection alone there are two possible atomic arrangements consistent with the space group. Consideration of the $h0l$ data showed that our initial interpretation of molecules formed from each unresolved pair of atoms in Fig. 1 was incorrect, and that the interpretation shown in Fig. 2 was the correct one. Adjacent pairs of molecules in the projection have their centers half a c-translation apart in the crystal.

The value of $x+y$ may be very accurately determined by locating the center line of this electron mass, although the overlap does not permit precise values for x and y to be made separately. It is of interest to note the very high resolution in this zone, in which a separation of about 0·5 A. in projection is achieved, and also the surprisingly high electron density at the peaks. It appears to be a fairly general phenomenon that when a projection is made through a considerable distance, as in this case, the electron densities at the peaks are higher than usual.

Employing a distance of 1·48 A. for the O–O bond, and knowing the projected bond length in the ($00l$) plane, it is easy to calculate the z co-ordinate. The ($h0l$) structure factors, based on the eight general positions given in the *Internationale Tabellen...*, are not centrosymmetric, and so they were evaluated on the basis of the following co-ordinates:

(1) $-\frac{1}{4}+x,\ -\frac{1}{4}+y,\ \frac{5}{8}-z,$ (2) $-\frac{1}{4}-x,\ -\frac{1}{4}-y,\ \frac{1}{8}-z,$
(3) $-\frac{1}{4}+y,\ -\frac{1}{4}+x,\ \frac{5}{8}+z,$ (4) $-\frac{1}{4}-y,\ -\frac{1}{4}-x,\ \frac{1}{8}+z,$
(5) $\frac{1}{4}-x,\ \frac{1}{4}+y,\ \frac{3}{8}+z,$ (6) $\frac{1}{4}+x,\ \frac{1}{4}-y,\ -\frac{1}{8}+z,$
(7) $\frac{1}{4}-y,\ \frac{1}{4}+x,\ \frac{3}{8}-z,$ (8) $\frac{1}{4}+y,\ \frac{1}{4}-x,\ -\frac{1}{8}-z.$

Several Fourier syntheses were made on this zone until no further signs changed, and the final result, expressed as an electron-density map, is given in Fig. 3. The series used was incomplete, owing to experimental difficulties, so that the map in Fig. 3 lacks accuracy because of non-convergence. However, it does give a value for z which is good enough for use in the subsequent least-squares treatment. A line diagram of this projection is given in Fig. 4, where the atoms are numbered in accordance with the latter system.

In the ($h0l$) projection, the asymmetric unit consists of two oxygen atoms which is double the true asymmetric unit. This is required in order to express all three co-ordinates. In calculating the (hhl) structure factors, a new origin at a center of symmetry was again used.

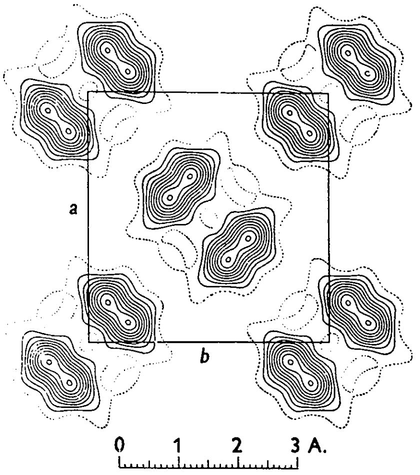

Fig. 1. A group of ten molecules in the c-axis projection. Each contour line represents a density increment of 2 e.A.$^{-2}$, the two-electron line being dotted.

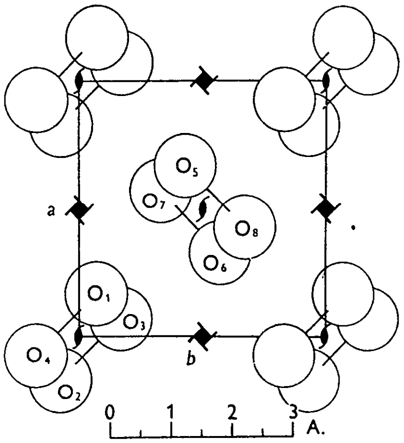

Fig. 2. Arrangement of the molecules in the c-axis projection.

The x, y and z co-ordinates thus obtained were sufficiently close to the true values to give the structure factors their correct signs. Since further refinement by the Fourier-series method was not possible, owing to non-convergence in the ($h0l$) and (hhl) data (Robertson & White, 1946), the least-squares method was applied to these two zones. The treatment was the same as described by Hughes (1941), in which the weighting factors were given the value unity.

In this way, a final set of co-ordinates was obtained and, using an empirical atomic scattering curve (Table 3), and expressing the discrepancies between the observed and calculated structure factors in the usual way, the results for the three zones considered become: $(hk0) = 13{\cdot}8$, $(h0l) = 14{\cdot}5$ and $(hhl) = 11{\cdot}6\,\%$, with an average of 13·5 % for all these structure factors taken together.

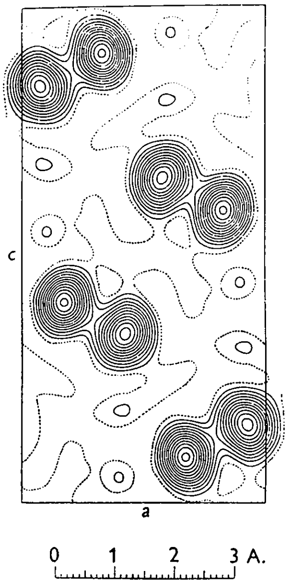

Fig. 3.

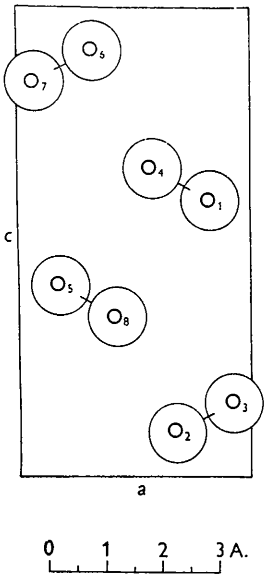

Fig. 4.

Fig. 3. Projection of the unit cell along the *b*-crystal axis. Each contour line represents a density increment of 1 e.A.$^{-2}$, the one-electron line being dotted.

Fig. 4. Arrangement of the molecules in the *b*-axis projection.

Co-ordinates and dimensions

The various co-ordinates obtained by the methods already described, with reference to the *Internationale Tabellen...* origin, are collected in Table 1.

Table 1. *Co-ordinates expressed as fractions of the cell edges*

	$(h0l)$ Fourier	$(h0l)$ least squares	(hhl) least squares	$(hk0)$ Fourier	Weighted average
x	0·075	0·072	0·070	—	0·071
y	0·176	0·171	0·172	—	0·172
z	0·218	0·216	0·217	—	0·217
$x+y$	0·251	0·243	0·242	0·243	0·243

Assuming the hydrogen atoms to lie along the closest O...O approaches between adjacent molecules, the molecular dimensions are found to be:

$$\text{O–O} = 1{\cdot}49 \text{ A.},$$

$$\angle \text{H}_2\text{–O}_1\text{–O}_4 = \theta = 96^\circ\ 52',$$

$$\angle \text{H}_1\text{–O}_4\text{–O}_1 = 112^\circ\ 15',$$

and the azimuthal angle ϕ between the two planes containing H_2, O_1, O_4 and H_1, O_4, O_1 is 93° 51′. This distance is probably correct to within 0·02 A. and the angles to within 1·5°. A perspective view of the molecule is given in Fig. 5.

Intermolecular distances

The closest approach distances between neighboring molecules in this crystal are collected in Table 2, using the same numbering system as before, and naming the four adjoining unit cells seen looking along the *c* axis thus:

A	*D*
B	*C*

Table 2. *Intermolecular distances*

$4_A \ldots 5_B = 2{\cdot}78$ A.
$4_A \ldots 6_A = 2{\cdot}78$ A.
$4_A \ldots 7_B = 2{\cdot}90$ A.
$4_A \ldots 7_C = 2{\cdot}90$ A.
$4_A \ldots 8_A = 3{\cdot}31$ A.
$4_A \ldots 6_B = 3{\cdot}31$ A.
$4_A \ldots 2_A = 3{\cdot}52$ A.
$4_A \ldots 7_D = 3{\cdot}62$ A.

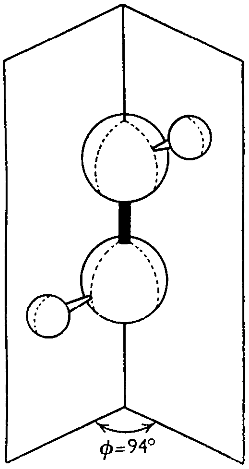

Fig. 5. A perspective view of the hydrogen peroxide molecule. The hydrogen atoms are represented by the smaller spheres, being assumed to lie along the hydrogen bonds.

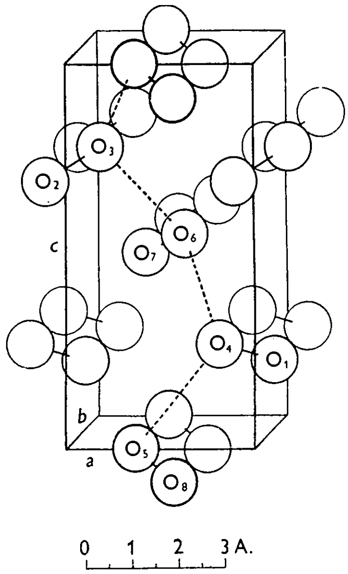

Fig. 6. An isometric view of the structure, with the *Internationale Tabellen...* origin.

The shortest approaches are 2·78 A., and it is most likely that these distances indicate the presence of hydrogen bonds. An isometric view of the structure is given in Fig. 6, in which the disposition of these hydrogen bonds is indicated. They form infinite helices around the four-fold screw axes.

Discussion

The O–O bond distance of 1·49 A. found in this investigation is slightly larger than the distances previously reported, which range from 1·46 to 1·48 A., but, nevertheless, lies within the limits of error placed on these values. The small number of parameters in the present study, and the consistency among the co-ordinates obtained from the three zones (see Table 1), makes it likely that this slight increase in the bond distance is real. A parallel investigation of hydrazine (Collin & Lipscomb, 1951) finds the N–N distance in that molecule to be 1·46 A., which is slightly less than the value of 1·47 A. given by Giguère & Schomaker (1943). These small revisions in the covalent radii of oxygen and nitrogen are of interest in view of the deviations from the additivity rule (Pauling & Huggins, 1934) and the subsequent discussion by Schomaker & Stevenson (1941), but leave their conclusions substantially unaltered.

The principal binding forces in the hydrogen peroxide crystal are the hydrogen bonds, of length 2·78 A., which extend in infinite helices around the four-fold screw axes. Each oxygen atom, of course, has the same environment as every other one, and there are two such close approaches to each atom. One of these will be caused by sharing its hydrogen with an oxygen atom of an adjacent molecule, and the angle made by this bond with the O–O bond is 96° 52′, which is close to earlier values found or predicted for this angle (θ). The other is presumably formed by the oxygen atom donating an electron pair to another molecule, and the angle made by this hydrogen bond with the O–O linkage is 112° 15′. The azimuthal angle (ϕ) between planes containing the hydrogen bonds and the O–O bond is found to be 93° 51′, about 12° less than in hyperol (Lu *et al.* 1941), apparently because of the different packing arrangements in the two crystals.

Each oxygen atom is also 2·90 A. removed from other adjacent atoms in the crystal, and it is probably to be expected that these approaches are caused by the strong hydrogen bonds already described. The result is the formation of a rather closely packed structure, as, indeed, might be expected by the unusually high density of the crystal.

It now seems feasible, from this examination of the crystal structure of hydrogen peroxide, to suggest a mechanism by which water may be taken into the structure to form the well-known solid solutions (Giguère & Maass, 1940). If the oxygen atom of the entrant water molecule occupies one of the general positions now ascribed to an oxygen atom of the hydrogen peroxide molecule, it will be able to form two hydrogen bonds of the same strength as those already present, 2·78 A. in length, and also use its other hydrogen atom in the formation of a third hydrogen bond, of length 2·90 A., with little or no strain in its configuration. Its other unshared electron pair will now lie nearly along the line normally occupied by the O–O bond of a peroxide molecule. This mechanism would thus replace four hydrogen bonds of about 2·78 A. by two others of the same distance and one of about 2·90 A., when one water molecule replaced one hydrogen peroxide molecule. In such a case it would seem likely that the water oxygen atom would shift slightly so as to make these three hydrogen bonds more nearly equal. (Pending further investigation we have assumed that the substitution of a water molecule at one of the oxygen positions is random, but some preliminary photographs of solid solutions of H_2O in H_2O_2 suggest that the C_{4l} symmetry shown by pure H_2O_2 appears to degenerate into C_{2l} symmetry as the water content increases. We are not yet certain of the reality of this small effect, however.)

The complete environment of the oxygen atoms in the hydrogen peroxide crystal may thus be described as lying very near a face of a tetrahedron, whose apices are either 2·78 or 2·90 A. removed from that atom. We have already referred to the existence of separate infinite helices of hydrogen bonds about the 4_1 (or 4_3) axes in this crystal (Fig. 6). Let us, for the sake of argument, disregard the configuration of the molecule as shown in Fig. 5. Then, assuming a double minimum in each hydrogen bond, there would be only two possible configurations of hydrogen atoms for each infinite chain, whereupon we would expect no measureable residual entropy. Alternatively, if the molecule does have the configuration shown in Fig. 5, the helices of hydrogen bonds, while separate, will be no longer independent. Thus we would again expect no measurable residual entropy. Moreover, in this case, we would not expect anomalous 'chain conductance' of H^+ in H_2O_2, in accordance with experiment (Shanley & Greenspan, 1947; cf. Bernal & Fowler, 1933). This agreement provides strong support for our interpretation of the 2·90 A. distances as contacts not involving hydrogen bonds, and for the assumed configuration of the molecule.

Experimental

The material used was very kindly supplied by the Buffalo Electro-Chemical Company in a state of high purity, and it was further purified to about 98·9 % by both fractional distillation and fractional crystallization. The very careful phase-rule diagram of the hydrogen peroxide–water system (Giguère & Maass, 1940) was used as a criterion for the purity of each sample. The method of introducing the samples into the Pyrex capillaries, about 1 cm. long and less than 1 mm. in cross-section, and the techniques for growing good single crystals have already been described elsewhere (Abrahams, Collin, Lipscomb & Reed, 1950). The crystals grow in prismatic needles along the *c* axis. They are considerably denser than the liquid, and so always tend to align themselves along the bottom of the capillary, with the result that the c axis invariably lay very near the capillary axis. While this is very useful for setting the crystal, the Buerger precession camera permits convenient photographs only of reciprocal lattices containing the l index, and the Weissenberg camera permits photography only of the zero and n-layer lines about the c axis.

Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ A.) radiation was used throughout. Unfortunately, the largest precession angle which could be obtained with the cooling system employed was 23°, corresponding to about $\sin\theta = 0{\cdot}4$. This was the limit at which the ($h0l$) and (hhl) data terminated. The ($hk0$) data, however, were quite complete. The multiple-film technique (Robertson, 1943) was used to obtain correlations between the strong and weak reflections, the films being interleaved with brass foil of 0·029 mm. thickness. The intensities were estimated visually, by two indpendent observers, and are probably correct to within 15 %. The ratio of the strongest intensity to the weakest in the various zones is 7000 to 1 in ($hk0$), 1000 to 1 in ($h0l$) and 300 to 1 in (hhl).

The values for the structure factor were derived from the intensities in the usual manner, and are collected in Table 4 under $F_{\text{obs.}}$. The calculated values are derived from the average co-ordinates in Table 1. An empirical atomic scattering curve was used, obtained by a correlation of the geometrical part of the calculated structure factor with the observed structure factor, and is given in Table 3.

Table 3. *f values for hydrogen peroxide at* −20° C., *including temperature factor*

($\lambda = 0{\cdot}7107$ A. Maximum = 100 at $\sin\theta = 0$)

$\sin\theta$	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
f	100	83	52	33	16	10	6	3	1	—	—

The numerical work of the Fourier synthesis was carried out by three-figure methods (Patterson & Tunell, 1942), sampling at 12° intervals along a, corresponding to every 0·135 A. and 6° intervals along c, every 0·133 A. The positions of the contour lines were obtained from the summation totals by graphical interpolation.

An attempt was made to improve the resolution in the two zones where the series had been artificially terminated by introducing a special temperature factor, $e^{-B(\sin\theta)/\lambda}$, with $B = 7{\cdot}0$, into the observed structure factors. The effect was to improve the appearance of the electron contour maps somewhat, but there was a correspondingly greater amount of difficulty in locating the centers of the atoms, so that this technique was abandoned in this study. Similarly, efforts were made to estimate the positions of the hydrogen atoms by carrying out a Fourier series summation on ($F_{\text{obs.}}-F_{\text{calc.}}$) terms. This series should represent the difference between the real scattering unit and a set of spherical atoms at the positions of the oxygen atoms. However, the results, though suggestive, were regarded as essentially inconclusive.

Table 4. *Observed and calculated values of the structure factor*

(Origins for the $hk0$ and $h0l$ are indicated in Figs. 1 and 3. Origin for hhl is at $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$ with respect to the origin in the *Internationale Tabellen*....)

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$
110	19·3	+19·3	203	9·3	+9·9
120	18·4	−18·5	204	1·7	+0·6
130	10·0	−8·3	205	10·3	+11·4
140	2·3	−3·2	206	8·4	+10·4
150	1·4	+1·1	207	9·1	−8·2
160	0·5	−1·3	301	11·8	+11·0
170	0·9	−0·3	302	8·9	−8·4
200	1·6	+1·3	303	2·8	−2·6
220	11·2	−9·7	304	6·6	+8·5
230	7·9	−6·9	305	7·7	−6·9
240	0·4	−0·6	306	2·6	+1·7
250	1·1	−0·2	400	5·0	−4·4
260	0·8	+2·7	401	8·8	−9·6
330	2·7	−3·0	402	<0·6	+0·5
340	4·1	+4·2	403	8·5	−7·3
350	1·7	+2·5	404	0·6	+1·7
360	0·6	−0·3	004	21·5	+24·0
400	5·0	−4·4	008	2·0	−1·4
440	0·7	+0·6	110	19·3	+19·3
450	4·8	+4·5	111	16·0	−17·0
460	<0·6	+0·2	112	14·2	−14·1
550	1·2	−1·4	113	2·0	−2·0
560	0·6	+0·2	114	10·6	+8·8
600	<0·5	+0·2	115	13·3	−15·1
660	0·9	−1·0	116	3·6	−2·7
004	21·5	−24·0	117	5·6	−7·7
008	2·0	−1·4	118	1·0	−0·5
101	4·8	+2·9	220	11·2	−9·7
102	25·8	−28·5	221	12·3	−12·8
103	12·6	−15·6	222	14·8	−15·0
104	4·6	−5·2	223	8·0	+8·4
105	8·2	+9·2	224	3·7	−4·4
106	6·6	+5·3	225	5·2	−4·7
107	9·0	+8·8	226	5·7	−2·9
108	1·8	+2·7	330	2·7	−3·0
200	1·6	−1·3	331	4·3	−4·6
201	5·1	−4·8	332	2·6	+1·1
202	10·0	−8·0			

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The Structures of the Plagioclase Felspars. I

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X-ray diffraction patterns have been obtained for plagioclases of different compositions from nearly pure albite to nearly pure anorthite, and the positions of the subsidiary reflexions observed for materials with more than 30% anorthite have been determined.

Detailed analysis of the patterns of anorthite type, obtained from materials with more than 70% anorthite, reveals complexities not yet fully explained, while confirming the results previously obtained by Chao & Taylor.

The variation in the positions of the subsidiary reflexions given by intermediate plagioclases is discussed in detail, especially in relation to the chemical composition of the material. Preliminary experiments show that the subsidiary reflexions may be modified by heat treatment, and some consideration is given to the significance of Köhler's classification of plagioclases into high-temperature and low-temperature groups.

Possible structural schemes for the complete plagioclase series are considered, and a detailed discussion of a model for the intermediate plagioclases is to be given in Part II.

1. Introduction

The plagioclase felspars present a very complex series of structures for analysis by X-ray diffraction methods. The structure of albite ($NaAlSi_3O_8$) was determined with moderate accuracy by Taylor, Darbyshire & Strunz (1934), and shown to be essentially similar to that of orthoclase ($KAlSi_3O_8$), the differences corresponding to a slight collapse of the tetrahedron framework around the smaller cation in albite. The same authors pointed out that though anorthite ($CaAl_2Si_2O_8$), the other 'end-member' of the plagioclase series, also has a similar structure, the true periodicity in the direction of the *c* axis is 14 A., twice that of albite. Chao & Taylor (1940) showed that for some plagioclases with compositions around 60% anorthite, 40% albite, a characteristic feature was the appearance of pairs of weak subsidiary layer lines in oscillation photographs around the *c* axis, in place of the single subsidiary layer lines in the corresponding anorthite patterns. The general features of these patterns for intermediate plagioclases were interpreted by analogy with an optical model corresponding to an alternation, in the direction of the *c* axis, of slabs of albite-like and anorthite-like structure.

Many details of the experimental observations remained unexplained, the number of materials examined was insufficient to cover the whole range of composition of the plagioclases, and it has long been clear that there was need for a further development of the exploratory researches which terminated in 1940. In the meantime, in recent years a distinction has been established between high-temperature and low-temperature plagioclases (see, for example, Köhler, 1949), and 'subsidiary reflexions' of various kinds have been observed in the X-ray patterns of a large number of crystals. Thus, on the one hand, the scope of the problem is broadened by the necessity of considering the effects due to differences in the thermal history of the specimens, but, on the other, the successful treatment of a number of cases where a complex structure gives rise to subsidiary reflexions encourages the hope that a fairly detailed explanation may be found for the patterns given by plagioclases.

The present paper reports the results of a new examination of the plagioclases, which has enabled some progress to be made and at the same time has defined more clearly the questions still remaining unanswered.

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