1. The Structure of Enstatite $MgSiO_3$.

By

B. E. Warren and D. I. Modell.

(With 5 Figures.)

Abstract:

From rotation photographs made by rotating a Hypersthene crystal about the three principal axes, the axial lengths were calculated as $a = 18.20$ Å $b = 8.86$ Å $c = 5.20$ Å. Comparison with the crystallographic axial ratio shows that the previously accepted "a" axis must be doubled. From a series of 15° oscillation photographs about the three principal axes indices were assigned to about 300 reflections. Assuming holohedral orthorhombic symmetry the space group is found to be V_h^{15}. There are 16 molecules $(Mg, Fe) SiO_3$ in the unit cell.

There is a close connection between the diopside structure and the space group V_h^{15}, such that with slight alterations the whole diopside unit cell can be inserted in the half unit cell of the enstatite space group. Ca in diopside is replaced by Mg and approximate coordinates obtained for all the atoms in the enstatite structure. Calculated amplitude contributions for about fifty planes compare favorably with the visually estimated intensities of the corresponding spots. The unit cell of the orthorhombic pyroxene is very nearly two unit cells of the monoclinic pyroxene joined together on the "a" face through a glide plane of reflection. The characteristic and distinguishing features of the pyroxenes and amphiboles lie in the possession of the single and double type of silicon-oxygen chains. Enstatite has the single type of chain and the orthorhombic pyroxene are therefore to be classed as true members of the pyroxene group.

I. Introduction.

The pyroxenes are a well defined group of metasilicates, closely related in composition, optical properties, axial ratio, and cleavage, and with members in both the monoclinic and orthorhombic systems. They are characterized by a good prismatic cleavage, with cleavage angle of about 93°. The structure of Diopside[1] $CaMg(SiO_3)_2$ which has recently been completely determined can be considered as typical of the whole group of monoclinic pyroxenes. As yet there has been no structure determination of a member of the orthorhombic group.

Enstatite $(Mg, Fe) SiO_3$ is the simplest member of the orthorhombic group of pyroxenes. The present investigation has shown that there

---

[1] The Structure of Diopside $CaMg(SiO_3)_2$ B. Warren and W. L. Bragg, Z. Krist. **69**, 118. 1928.

is a very close relationship to the structure of the monoclinic pyroxene diopside, and by means of this close relationship it has been possible to determine the positions of all the atoms in the orthorhombic structure.

The enstatite structure is built up out of silicon-oxygen chains, lying parallel to the "c" axis and similar to the silicon-oxygen chains which were found to exist in the monoclinic pyroxene diopside. Each silicon atom is surrounded by four oxygen atoms as in other silicates, but two oxygen atoms of each tetrahedral group are held in common with neighboring groups in accord with the three to one ratio of oxygen to silicon atoms. The tetrahedra thus linked together by shared oxygen atoms form endless chains parallel to the "c" axis of the crystal; they lie side by side and are held together by the (Mg, Fe) atoms.

Doubt has sometimes been expressed as to whether the orthorhombic pyroxenes should be classed as true pyroxenes. It will be shown in the latter part of the paper that the logical criterion for a pyroxene is the possession of the single type of silicon-oxygen chain, that this is the type of chain out of which both diopside and enstatite are built, and that both structures can therefore be classed as true pyroxenes and as distinct from the amphiboles which are built up out of double silicon-oxygen chains[1]).

II. Description of Hypersthene crystal used in investigation.

Crystals of enstatite which were suitable for the X-ray investigation were not available, and it was necessary to use a specimen of Hypersthene $(Fe, Mg) SiO_3$. The material used was from Mt. Dore, Auvergne, France and was in the form of small single crystals about $0.4 \times 0.4 \times 1.0$ mm. with the prismatic tabular habit shown in Fig. 1. The forms $a(100)$, $b(010)$, $m(110)$, and $p(211)$ were present, and from goniometric measurements gave an axial ratio

$$a : b : c = 1.0265 : 1 : 0.5854$$

in satisfactory agreement with the axial ratio for the orthorhombic pyroxene group given by Goldschmidt $a : b : c = 1.0308 : 1 : 0.5885$. It is to be noted that this set up of
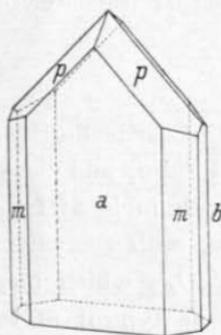

Fig. 1. Crystal habit of the Hypersthene crystal used in present investigation. The indices correspond to the Goldschmidt axes, not to the axes of the true unit cell.

---

1) The crystal structure and chemical composition of the monoclinic amphiboles. B. E. Warren. Z. Krist. **72**, 493. 1930.

the crystal differs from that adopted by Dana and Hintze in that the "a" and "b" directions are interchanged.

The optical properties of the crystal were determined as follows:

$$\alpha = 1.696 \qquad 2V = 62° \pm 5°$$
$$\beta = 1.709$$
$$\gamma = 1.712 \qquad Y = a; \text{ optic plane } (100).$$

Chemical analyses of the material used were not available, so that the approximate composition was determined from the optical properties. From Winchell's [1] chart for variations in composition and optical properties in the enstatite series, it was found that the optical properties of the material corresponded to a molecular composition 30 % $FeSiO_3$, 70 % $MgSiO_3$ and specific gravity 3.43. A direct determination of the specific gravity gave $\sigma = 3.39$.

III. Unit Cell and Space Group of Enstatite.

The three primitive translations of the unit cell were determined in the usual way from rotation photographs, made by rotating the crystal in turn about the three principal axes. The crystal was about $0.4 \times 0.4 \times 1.0$ mm. and was completely bathed in the radiation $(K_\alpha Mo)$. From the layer line distances the three primitive translations were calculated as follows [2]:

$$a = 18.20 \text{ Å}$$
$$b = 8.86 \text{ Å}$$
$$c = 5.20 \text{ Å}.$$

From these axial lengths the axial ratio is calculated as $a : b : c = 2.055 : 1 : 0.587$ as compared with the axial ratio in Goldschmidt $a : b : c = 1.0308 : 1 : 0.5885$. It is evident that in the true unit cell the "a" axis must be taken double the value which has previously been assumed. The general plane (hkl) in the old set up will have indices $(2h, k, l)$ in terms of the new axes. In this paper the new axes of the true unit cell will be used henceforth.

The number of molecules in the unit cell is given by:

$$n = \frac{V \sigma N}{M}$$

1) Winchell, Elements of Optical Mineralogy **II**, p. 177. 2) Gossner gives essentially the same axial lengths but with "a" and "b" interchanged. $a = 8.84$ $b = 18.23$ $c = 5.20$ Å. B. Gossner und F. Mussgnug "Über Enstatit und sein Verhältnis zur Pyroxen- und Amphibolgruppe." Z. Krist. **70**, 234. 1929.

$V =$ volume of unit cell,
$\sigma =$ density of crystal,
$N =$ Avogadro number
$M =$ molecular weight.

Using the approximate chemical composition deduced in II from the optical data the molecular weight is calculated as:

$$M = 0.3 \, Fe + 0.7 \, Mg + SiO_3 = 109.8$$

$$N = \frac{18.20 \times 8.86 \times 5.20 \times 10^{-24} \times 3.39 \times 6.06 \times 10^{23}}{109.8} = 15.8.$$

There are accordingly 16 molecules $(Mg, Fe) \, SiO_3$ in the unit cell.

Table I.

Tabulation of observed Reflections.

$h00$	$hk0$	$h0l$	$0kl$
400	230	102	021
600	250	202	023
1200	420	302	024
1400	430	502	042
1600	440	702	043
	460	902	044
$0k0$	610	104	061
040	620	304	
060	630	404	
080	650		
	820		
$00l$	840		
002	860		
004	1010		
	1030		
	1040		
	1050		
	1220		
	1240		
	1260		

A series of $15°$ oscillation photographs were made about each of the three principal axes, and indices assigned to about 300 reflexions. The following conditions were found to obtain:

General planes (hkl) $h + k + l =$ odd and even
Prism planes $(h0l)$ $h + l$ $=$ odd and even
               $(hk0)$ $h + k$ $=$ odd and even
               $(0kl)$ $k + l$ $=$ odd and even.

Therefore the lattice cannot be body centered, side centered, or all face centered. It follows therefore, that the lattice must be the simple orthorhombic lattice Γ_0.

Assuming holohedral orthorhombic symmetry, and with lattice Γ_0 only the space groups $V_h^1 - V_h^{16}$ are possible. Referring to Table I it is seen that the prism reflections obey the following laws:

$(h\,0\,l)$ $h + l =$ odd and even l occurs only even
$(h\,k\,0)$ $h + k =$ odd and even h occurs only even
$(0\,k\,l)$ $h + l =$ odd and even k occurs only even.

Of the 16 possible space groups all but V_h^1, V_h^5, V_h^{11} and V_h^{15} are immediately excluded by reflections actually appearing. The observed halvings are exactly those demanded by V_h^{15}, and as it would be very difficult to explain this regular absence of large groups of reflexions for the space groups V_h^1, V_h^5 and V_h^{11} it appears justifiable to conclude that the space group of Hypersthene (Enstatite) is V_h^{15}.

IV. Relation of Enstatite to Diopside.

The structure of the monoclinic pyroxene diopside $CaMg\,(SiO_3)_2$ has recently been completely determined[1] Comparison of the axial lengths in enstatite with those which were found for diopside discloses a very close connection between the unit cells of the two substances.
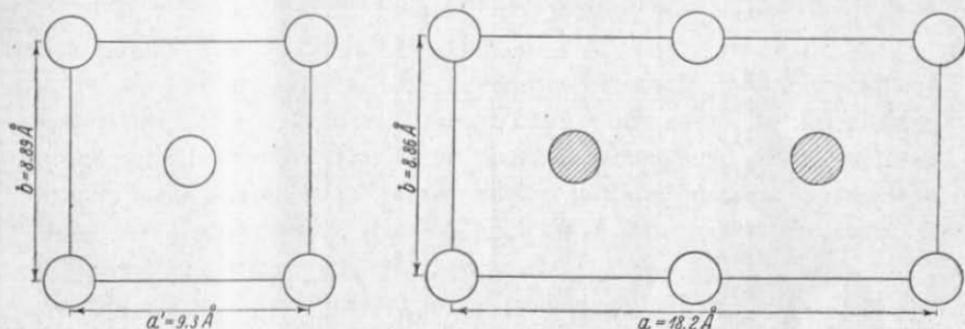

Fig. 2. Schematic representation of side centering of the diopside and enstatite projections on (001). In diopside (001) is truly side centered, while in enstatite the projection upon $a/2 \times b$ is approximately side centered. The cross hatched circles represent units which are slightly different from those represented by the open circles.

Diopside (monoclinic)
$a = 9.71$ Å $a' = 9.34$ Å
$b = 8.89$ Å
$c = 5.24$ Å
$\beta = 74^\circ 10'$

Enstatite (orthorhombic)
$a = 18.20$ Å
$b = 8.87$ Å
$c = 5.20$ Å

a' in diopside is the projection of "a" perpendicular to "b" and "c", so that $a' = a \sin 74°10'$. It is seen that the axes "b" and "c" in the two structures are practically identical and that "a" in enstatite is just about double the value of a' in diopside. This fact suggests immediately that the structures themselves must be closely related and the Xray investigation has shown that this is actually the case. Projected upon the "c" face, the two structures have practically the same atomic arrangement, and this is borne out in a very striking way by the whole set of $(hk0)$ reflexions. The projection of the two structures perpendicular to "c" is represented schematically in Fig. 2.

Table II. Comparison of $(hk0)$ reflexions from Enstatite and Diopside.

Enstatite		Diopside	
$(hk0)$	Obs. Int.	$(hk0)$	Meas. Int. ϱ
400	M.	200	—
600	V. W.		
800	Abs.	400	3.0
1200	V. S.	600	31.0
1400	V. W.		
1600	M. S.	800	21.0
040	W. M.	040	—
060	V. S.	060	28.0
080	W. M.	080	—
210	Abs.	110	—
230	W.	130	2.5
250	S.	150	27.6
420	V. S.	220	23.8
430	V. W.		
440	M.	240	2.7
460	V. W.	260	6.8
610	V. S.	310	32.8
620	V. W.		
630	M.	330	18.2
650	S.	350	16.2
820	W. M.	420	5.6
840	W. M.	440	14.8
1040	M.	540	21.8

Diopside is side centered on the "c" face and $(hk0)$ occurs only for $h + k =$ even. In Enstatite the "a" axis is twice as long and if the projection upon the "c" face is to be very similar to that of diopside, then $(hk0)$ can occur only for $\dfrac{h}{2} + k =$ even. Referring to Table II it is seen that in the $(hk0)$ reflections from enstatite, nearly the whole

group of reflections for $\frac{h}{2} + k =$ odd are missing and the few that occur are all very weak. For those reflections where $\frac{h}{2} + k =$ even, however, the observed intensities show a striking similarity to the intensities of the corresponding reflections from diopside. We are therefore, justified in concluding that projected perpendicular to "c", the enstatite structure is very similar to that of diopside.

V. Arrangement of the Atoms in Enstatite.

Our problem now becomes one of introducing sections of the diopside structure into the enstatite space group V_h^{15} and doing this in such a way as to alter as little as possible the projection of the diopside structure perpendicular to "c". In making this alteration the calcium in diopside will, of course, be replaced by one of the (Mg, Fe) in enstatite.

$$CaMg\ (SiO_3)_2 \longrightarrow 2\,(Mg,\ Fe)\ SiO_3$$
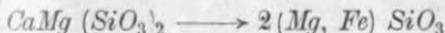
A very striking connection between the diopside structure and the enstatite space group V_h^{15} gives the clue to the way in which the diopside sections are to be introduced. In Fig. 3a is shown the unit cell of the diopside structure projected upon (010). In 3b is shown half of the unit cell of the enstatite space group V_h^{15} also projected upon (010). The half unit cell of enstatite $\frac{a}{2} \times b \times c$ has very nearly the same dimensions as $a' \times b \times c$ in diopside.

It will be noted that the symmetry elements and their spacial arrangement in the section AA' are exactly the same in the diopside structure and in V_h^{15}. The whole central section AA' of the diopside structure can therefore be moved bodily into the enstatite space group. Along BB' the symmetry elements in 3a and 3b are not the same. In diopside there are centers and screw axes parallel to "b", while in V_h^{15} there is a screw axis parallel to "c" and a glide plane with glide $b/2$. A study of the coordinates of the atoms in the BB' section of diopside shows however, that with a very slight distortion of the atoms in the "c" direction only, the section BB' would be altered into one in which a glide plane with glide $b/2$ could be inserted along BB'. Making these slight distortions in the "c" coordinates of the atoms in the BB' section, the whole diopside unit 'cell of Fig. 3a can then be moved bodily into the space group V_h^{15}. By now replacing the Ca in diopside by an Mg atom, and allowing the symmetry elements along BB' in V_h^{15} to repeat the half cell, we have an atomic arrangement which must be very nearly the unit cell of the orthorhombic pyroxene enstatite. In replacing Ca
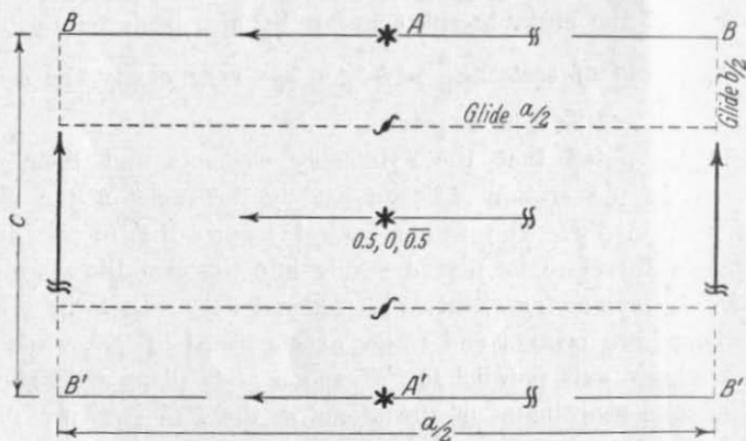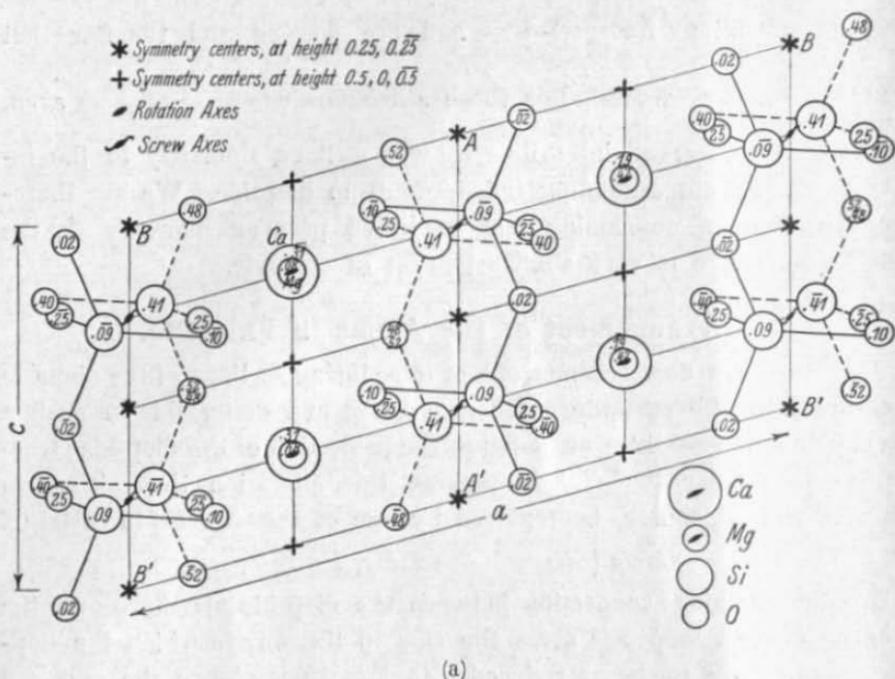
(a)

(b)

Fig. 3. Relation between diopside structure and the enstatite space group V_h^{15}. Only half of the V_h^{15} unit cell is shown, so as to correspond to the unit cell of diopside. It will be noted that the symmetry elements and their special arrangement are the same in the section AA' in both unit cells.

by (Mg, Fe) and distorting part of the atoms slightly in the "c" direction we have of course changed very little the projection of the diopside structure perpendicular to "c".

In arriving at the enstatite structure, we have taken the diopside unit cell practically unaltered, and then doubled it along a' by reflection across BB'. The relation between the original diopside cell and the enstatite cell finally produced is shown in Fig. 5. The enstatite structure projected on (010) is shown in Fig. 4. The origin of coordinates is a symmetry center and the figures within the circles represent the coordinates of the atoms in decimal parts of the length of the "b" axis. The symmetry center used as origin in enstatite is 0.25 b higher than the center used as origin in diopside so that the Y coordinates of the
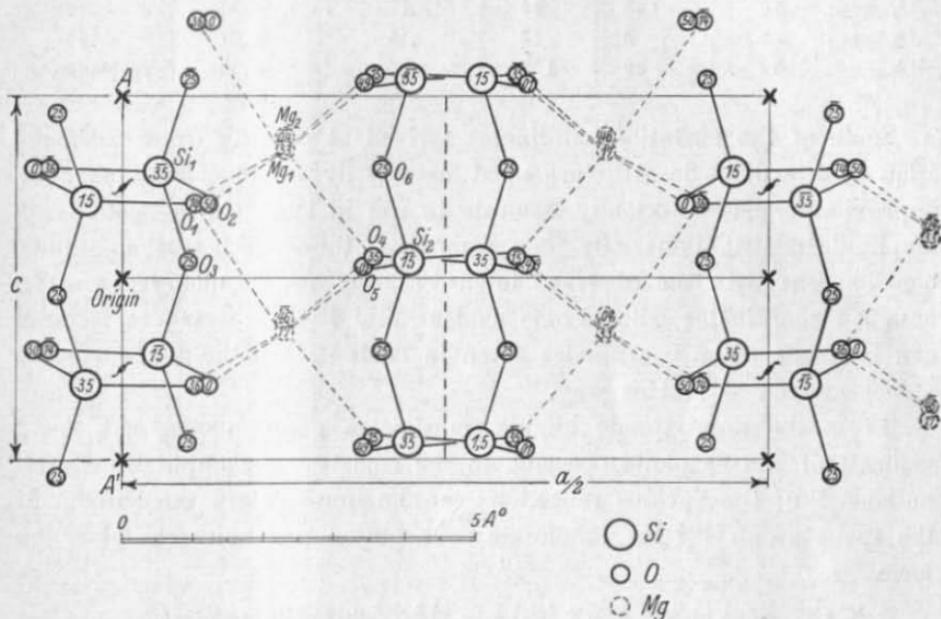

Fig. 4. Projection of Enstatite structure on (010). The figures within the circles are the Y coordinates in decimal parts of the length of the "b" axis. The section AA' corresponds to AA' in Fig. 3 a, and is a section of the diopside structure practically unaltered. Mg_1 corresponds to Mg in diopside and Mg_2 has approximately the position of calcium in the diopside structure.

atoms in enstatite recorded in Fig. 4 are obtained by subtracting 0.25 from the coordinates of the corresponding atoms in diopside (Fig. 3 a).

In the space group V_h^{15} an atom in the general position is multiplied by the symmetry elements into 8. In our enstatite structure all atoms are in the general position, and there are 16 (Mg, Fe), 16 Si, and 48 O in the unit cell. In assigning coordinates there will therefore be 2 sets of Mg, 2 sets of Si and 6 sets of O. The values of the coordinates finally arrived at are given in Table III, in degrees and also in decimal parts of the axial lengths. The origin of coordinates is a symmetry center in the V_h^{15} space group.

Table III. Coordinates of Atoms in Enstatite.

	θ_1	θ_2	θ_3	X	Y	Z
Mg_1	45	120	135	.13	.33	.37
Mg_2	45	— 13	135	.13	— .04	.37
Si_1	10	— 126	104	.03	— .35	.29
Si_2	80	— 55	16	.22	— .15	.04
O_1	20	+ 50	72	.06	+ .14	+ .20
O_2	22	180	72	.06	.50	+ .20
O_3	18	— 90	17	.05	— .25	.05
O_4	70	+ 125	20	.19	+ .35	.06
O_5	68	5	18	.19	+ .01	.05
O_6	72	— 90	108	.20	— .25	+ .30

Some of the enstatite coordinates arrived at directly from consideration of the diopside structure must necessarily be considered as only approximate, but sufficiently accurate to use in the first calculations of amplitude contributions. By then comparing these calculated amplitude contributions with the observed intensities, any appreciable errors in the assigned coordinates will become evident, and the necessary corrections can be made. The coordinates given in Table III are the final corrected values arrived at in this way.

From the approximate atomic coordinates given above, and the f values[1] of the elements occuring in the silicates the amplitude contributions F of the various reflections can be immediately calculated. In the space group V_h^{15} the amplitude contribution per unit cell takes the form:

$$F = \sum_n 2 f_n \begin{Bmatrix} \cos(h\theta_1 + k\theta_2 + l\theta_3) + (-1)^{h+k} \cos(h\theta_1 - k\theta_2 - l\theta_3) \\ + (-1)^{k+l} \cos(h\theta_1 - k\theta_2 + l\theta_3) + (-1)^{h+l} \cos(h\theta_1 + k\theta_2 - l\theta_3) \end{Bmatrix}$$

where the sum is taken over the various sets of crystallographically equivalent atoms. In the following table are given the calculated values of amplitude contribution F for about fifty planes. In making these calculations allowance was made for the relative amounts of Mg and Fe present by taking:

$$f(Mg, Fe) = 0.7 f(Mg) + 0.3 f(Fe).$$

In addition to the $hk0$ reflections given above, the whole set with $h/2 + k = $ odd give values of approximately zero, in good agreement with the observation that all $(hk0)$ for $h/2 + k = $ odd are for the most part absent and the few that are present are very weak.

1) W. L. Bragg, and J. West "A technique for the x-ray examination of crystal structures with many parameters". Z. Krist. 69, 118. 1928.

Table IV. Comparison of Calculated Amplitude Contributions and observed Intensities of Spots.

hkl	$\sin\theta$	Calc. F	ξ	$\frac{F}{(\xi)^{\frac{1}{2}}}$	Obs. Int.
200	.039	nil	0.8	0	Abs.
400	.078	— 6.4	1.5	— 42	M.
600	.117	nil	2.3	0	V. W.
800	.156	— 1.5	3.0	— 7	Abs.
1000	.195	nil	3.8	0	Abs.
1200	.234	— 35.5	4.5	— 134	V. S.
1400	.273	nil	5.2	0	V. W.
1600	.312	+ 13.5	6.0	+ 44	M. S.
020	.080	— 1.1	1.60	— 8	Abs.
040	.160	— 5.1	3.20	— 24	W. M.
060	.241	+ 27.0	4.80	+ 99	V. S.
080	.321	+ 12.4	6.40	+ 38	W. M.
002	.136	— 1.0	2.7	— 5	W.
004	.272	— 5.8	5.4	— 20	M.
210	.055	+ 2.4	.75	+ 21	W.
230	.125	+ 1.3	.75	+ 10	W.
250	.205	— 24.9	4.0	— 100	S
420	.112	— 19.1	1.5	— 125	V. S.
440	.180	— 10.7	3.2	— 48	M.
460	.255	+ 0.9	4.8	+ 4	V. W.
610	.125	— 23.0	2.3	— 121	V. S.
630	.170	+ 14.3	2.3	+ 75	M.
650	.235	+ 21.5	2.3	+ 113	V. S.
820	.175	+ 7.7	3.0	+ 36	M.
840	.225	— 6.5	3.0	— 30	W.
860	.290	+ 9.3	4.8	+ 34	M.
1010	.200	— 9.6	3.9	+ 39	M.
102	.110	— 9.0	2.7	— 45	W. M.
202	.115	— 31.9	2.7	— 153	V. S.
302	.150	— 17.6	2.7	— 86	S.
402	.160	+ 0.4	2.7	+ 2	Abs.
502	.170	+ 23.4	2.7	+ 112	V. S.
602	.180	— 3.0	2.7	— 15	Abs.
702	.195	+ 18.2	2.7	+ 89	S.
802	.210	+ 1.4	2.7	+ 7	Abs.
902	.225	— 20.5	2.7	— 100	V. S.
104	.275	+ 15.6	5.4	+ 54	S.
204	.277	— 1.3	5.4	— 4	Abs.
304	.280	— 7.0	5.4	— 24	W. M.
404	.285	+ 20.5	5.4	+ 71	S.

Table IV.   Continued.

hkl	$\sin\theta$	Calc. F	ξ	$\dfrac{F}{(\xi)^{\frac{1}{2}}}$	Obs. Int.
021	.105	$+\ 0.8$	2.1	$+\ 4$	W.
022	.160	0.0	3.2	0	Abs.
023	.220	$-\ 26.7$	4.4	$-\ 102$	V. S.
024	.285	$-\ 8.2$	5.7	$-\ 28$	M.
041	.175	$-\ 3.9$	3.5	$-\ 16$	V. W.
042	.210	0.0	4.2	0	V. W.
043	.260	$+\ 14.0$	5.2	$+\ 50$	S.

The observed intensities are related to the calculated amplitude contributions by the following approximate relation.

$$I \; \alpha \left(\frac{F}{\xi^{\frac{1}{2}}}\right)^2$$

where in cylindrical coordinates ξ is the coordinate in the equatorial plane of the point (hkl) in the reciprocal lattice. The general agreement in Table IV between calculated values of $\dfrac{F}{\xi^{\frac{1}{2}}}$ and observed intensities is quite satisfactory, and allows one to accept immediately the proposed structure as correct. Although a few slight changes in the atomic coordinates would doubtless improve the general agreement, in view of the large number of parameters involved (30) it does not appear worth while to carry this work out.

VI. Discussion of the Enstatite Structure.

In the proposed structure each silicon is surrounded by four oxygens arranged approximately at the corners of a regular tetrahedron. In each tetrahedral group two oxygens are shared with neighboring groups, and the tetrahedra thus linked together by shared oxygen atoms form endless chains parallel to the "c" axis of the crystal; they lie side by side and are held together by the magnesium atoms. The crystal habit of enstatite with elongation along "c" and the cleavage and parting (210), (100) and (010) all in the zone [001] are reasonably explained in terms of the chain structure with chains parallel to "c".

Of the two magnesium atoms in enstatite, Mg_1 corresponds directly to the Mg in diopside, while Mg_2 has very nearly the position of calcium in diopside. There has been a slight shift in the coordinates of Mg_2 and of the surrounding oxygens in that Ca in diopside was surrounded by 8 oxygens, while Mg_2 in enstatite is surrounded by 6 oxygens.

From the coordinates in Table III the inter-atomic distances are calculated as follows:

$$Si_1 \begin{cases} O_1 & 1.54 \text{ Å} \\ O_2 & 1.54 \\ O_3 & 1.59 \\ O_3 & 1.59 \end{cases} \qquad Si_2 \begin{cases} O_4 & 1.53 \text{ Å} \\ O_5 & 1.60 \\ O_6 & 1.63 \\ O_6 & 1.59 \end{cases}$$

Average silicon-oxygen distance 1.58 Å.

$$Mg_1 \begin{cases} O_1 & 2.29 \text{ Å} \\ O_1 & 2.12 \\ O_2 & 2.10 \\ O_4 & 2.22 \\ O_4 & 2.10 \\ O_5 & 2.02 \end{cases} \qquad Mg_2 \begin{cases} O_1 & 2.18 \text{ Å} \\ O_2 & 2.08 \\ O_3 & 2.46 \\ O_4 & 2.28 \\ O_5 & 2.10 \\ O_6 & 2.34 \end{cases}$$

Average magnesium oxygen distance 2.19 Å.

The Pauling rule of electrostatic valence bonds is sufficiently well obeyed. The total valence bonding to the various oxygens lies between 1.7 and 2.3.
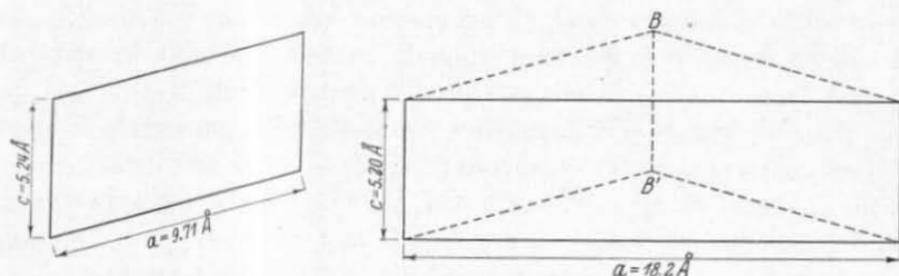

Fig. 5. Relation between the diopside and enstatite unit cells. The enstatite unit cell is practically two diopside cells connected along the section BB' through a glide plane of reflection. The section BB' corresponds to sections BB' in Figs. 3 a, 3 b.

In the papers on the structure of diopside and tremolite[1]) it was shown that the structure of the amphibole tremolite differed from that of the pyroxene diopside essentially in the fact that in the amphibole structure the silicon and oxygen atoms form a double chain, while in the pyroxenes a single chain is formed. The single and double chains appear to be the characteristic and distinguishing features of the pyroxene and amphibole groups. In the enstatite-hypersthene group we now find the single silicon-oxygen chain, and on this basis these orthorhombic minerals are definitely to be classed

1) loc. cit.

as true pyroxenes. The pyroxene group has both monoclinic and orthorhombic members, but both of these have the single silicon-oxygen chain as the distinguishing feature of the pyroxenes.

The relation between the monoclinic and orthorhombic members of the pyroxene group is shown schematically in Fig. 5. The orthorhombic unit cell is essentially two monoclinic cells joined on the "a" face through a glide plane of reflection.