Chapter 5

The Enstatite-IV Homologous Series, $\text{Me}_{-x/3}\text{Mg}_{-2/3}\text{Si}_{(x-4)/3}\text{O}_x$ or $\text{Me}_{-x/3}\text{Li}_{-4/3}\text{Si}_{(x-4)/3}\text{O}_x$, with $\text{Me} = \text{Mg}, \text{Sc}$ and $x = 88, 100, 112$ or 124

INTRODUCTION

This is the case of a chemical series which is derivable from a C-centered clinopyroxene (CPX), accompanying the HVVC substitution characterized basically by the scheme:

$$3 \times \text{Mg}^{2+} \rightleftharpoons 2 \times \text{Sc}^{3+} + \square.$$

The crystals closely related to those of this series were discovered by Jun Ito (1926–1978) by serendipity:—One wintry day around the end of the year 1975, the main electricity supply of a laboratory building, where he was carrying out crystal synthesis, was accidentally cut off. He just about threw away the unexpected product in a crucible which had been unwillingly cooled off, by the accident, from a temperature above $1400^\circ\text{C}$. Some incomprehensible power, however, changed his mind and let him take a precession photograph of a crystal piece in the product. It turned out to exhibit a striking pattern, simulating that of a clinopyroxene but showing marked superstructure reflections along $c^\ast$. This finding was presented to the Annual Meeting of the Geological Society of America held in the next year (Ito and Steele, 1976).

Meanwhile, in March of 1976 I was at Swarthmore, Pa., to attend a business meeting of JCPDS—International Centre for Diffraction Data. On my way back, though my ordinary practice was to fly straight back to Tokyo, I somehow changed my schedule and decided to drop in Chicago to pay Ito a visit, still unaware of the Ito’s discovery. When I looked at the precession photograph, it was more than a surprise. A thought flashed on me that the new material might be a pyroxenoid-like phase having a long chain periodicity never been found before in the wollastonite-pyroxene series, which has been called the $w$-$p$ series (Takéuchi, 1976). That was the kind of material in which the writer had been interested for years.

A joint work by Ito and the writer was immediately started: the former continued the synthesis and the latter took part in the structural study. With the determination of the crystal structure before long, the complexity in chemistry of this interesting material was basically disclosed (Takéuchi et al., 1977). The structure first determined was in fact a member of the structural series occurring at high temperatures in the Mg-rich region of the $\text{MgSiO}_3$-($\text{Li,Sc}$)$\text{Si}_2\text{O}_6$ system. Noting that three structure types are known for enstatite MgSiO$_3$, we denoted the phases having this series of structures enstatite-IV (En-IV). Their chemistry may be characterized by the atomic substitution scheme which is closely expressible by $3\text{Mg} + \text{Si} \rightleftharpoons 3\text{Sc} + \text{Li}$ (Takéuchi et al., 1984a) but in fact falls in the category of the HVVC substitution.
At an early stage of the structural study of En-IV, there was a serious argument whether the Li atom really exists in the crystals. Although its existence was confirmed beyond doubt by the atomic-absorption method, the argument eventually led us to find, by synthesis, another new chemical series of magnesium scandium metasilicates which are isotypic with the corresponding structures of En-IV but free from Li. We called it the Sc series of enstatite-IV and denoted En-IV’ (Takéuchi et al., 1984b). This is the major subject to be discussed in the following article.

Our joint work extended to reveal that the structures of both En-IV and En-IV’ may further be modulated, by variation in composition, to yield a group of higher-order superstructures (Takéuchi et al., 1984c). Before looking at those series of papers published in 1984, however, Ito passed away by cancer with which he had been afflicted with for several years, leaving a pile of letters of about 2 cm thick on the writer’s desk. This article is dedicated to the memory of Jun Ito, who achieved outstanding contribution to mineralogy through his original philosophy for crystal synthesis (Sadanaga, 1979).

PYROXENOID HOMOLOGOUS SERIES

The structures of En-IV in a way share features with those of pyroxenoids, a group of triclinic metasilicates which form a a variable-fit homologous series (Table 1). General structural features of pyroxenoids will then be discussed first because they will facilitate understanding of the structure of En-IV. Among six pyroxenoids listed in Table 1, ferrosilite III has a stability field at high temperature and pressure (Lindsley, 1980) and does not exist in nature.

There are two structural series of pyroxenoids, one is the w-p series, as mentioned before, and the other p-p (pectolite-pyroxene) series (Takéuchi, 1976). We are here interested in the former case. In Fig. 1, we compare the structure of wollastonite CaSiO₃ (Prewitt and Buerger, 1963), a representative member of the w-p series, with that of protoenstatite at 1260°C (Murakami and Takéuchi, 1984), the high-temperature phase of enstatite MgSiO₃. As will be observed in this figure, in which both structures are projected along the metasilicate chains, they are built up of similar structure units, each consisting of a band of edge-sharing octahedra formed by oxygen atoms about cations and a pair of silicate chains flanked to the band in the manner as shown in Fig. 2. The end views of the structure units of two representative pyroxenoids, wollastonite and pectolite, are schematically compared in Fig. 3 with that of the structure unit of the pyroxene type.

The structures of pyroxenoids are, however, characteristic of having large cations compared to those of pyroxenes. This situation gives rise to a significant difference in the shape of silicate chains between the two mineral groups. As will be observed in Table 1, the periodicity of silicate chains in pyroxenoids increases with the decrease of the size of cations contained. In the case of wollastonite characterized by the largest cation Ca in the group, the silicate chain is three tetrahedra long while the band of octahedra is two octahedra long.

The structure unit of pyroxenoids in general consists of silicate chains of N tetrahedra long and octahedral bands of N – 1 octahedra long (Fig. 4). The excess
Table 1. Representative pyroxenoids. The periodicity along silicate chains are given in bold face. The cell dimensions and chemical composition of protoenstatite at 1360°C are listed in the last line for comparison.

<table>
<thead>
<tr>
<th>N</th>
<th>Pyroxenoids</th>
<th>Cell dimensions</th>
<th>Contents in octahedral bands (atom %)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a(Å)  b(Å)  c(Å)</td>
<td>Ca  Mn  Fe²⁺  Mg</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------------</td>
<td>-----------------</td>
<td>---------------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>3</td>
<td>Wollastonite</td>
<td>7.07  7.94  7.32</td>
<td>100</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>103.4  90.0  95.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Bustamite</td>
<td>2 x 6.908 7.718</td>
<td>50  37  12  1</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>103.8  90.5  94.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Rhodonite</td>
<td>6.707  7.682  <strong>12.234</strong></td>
<td>16  78  3  3</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111.54  85.25  93.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>111.15  84.56  94.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Pyroxmangite</td>
<td>6.67  7.56  17.45</td>
<td>4  41  55</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>113.7  84.0  94.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>114.27  82.68  94.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>115.29  80.65  95.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.628  7.467  22.607</td>
<td>100</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>115.32  80.56  95.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pyroxene*</td>
<td>9.349  8.929  <strong>5.361</strong></td>
<td>100</td>
<td>[9]</td>
</tr>
</tbody>
</table>


The sets of axes (a, b, c) originally described in [1] and [2] have been transformed to (b, c, a) in order to compare with those of other pyroxenoids. The unit cell of [4] is originally given by the reduced cell.


tetrahedron of a silicate chain takes an offset position as labeled Q in Figs. 2 and 3, thus giving rise to a specific configuration of the chain as represented by triplet of tetrahedra P, Q, and R. In contrast to this, in pyroxene the same number of tetrahedra and octahedra respectively define the periodicity of the structure along the chain extension.

According to Burnham (1966), the silicate chain of a pyroxenoid may be regarded as an analogue of pyroxene chain in which every Nth tetrahedron takes an offset position. As a result, in the repeat unit along chain extension, the number of tetrahedra is increased by one compared to that of octahedra; thus adjustment is achieved of misfit between tetrahedral chain and octahedral bands. The structural mechanism underlying the morphotropy of pyroxenoids is hence a vernier-like misfit between the silicate chains and the octahedral bands; the smaller the misfit, the
Fig. 1. A comparison between the crystal structures of protoenstatite at 1200°C (a) and wollastonite (b), both showing end views of the chain structures.

longer is the periodicity along the chain extension.

General discussions on the influence of cation size on the shape of silicate chains will be found in an elaborate work by Liebau (1985).

Configuration of octahedral bands

We study here the above feature of pyroxenoids a little further in terms of geometry of the octahedral bands. Let \( n \) and \( m \) be respectively finite linear arrays of linked \( n \) regular-octahedra and \( m \) regular-octahedra as displayed in Fig. 5. Then the array \( n \) can be so juxtaposed on \( m \) as shown in Fig. 5 based on either one of the stacking vectors \( t \) or \( \text{\textbar}t \). To distinguish, with respect to \( m \), the location of \( n \) in the latter case from the former, we put a bar on the symbol \( n \), like \( \text{\textbar}n \). The two sets of arrays (Fig. 5) may thus be symbolized by \( mn \) and \( m\text{\textbar}n \), respectively. If finite number of \( m \), for example, stack one after another based on one kind of the stacking vectors, say \( t \), an infinite band, \( m \) octahedra wide, is constructed. This band can be designated by \( m\text{\textbar}m\text{\textbar}m\text{\textbar}m \ldots \) or \( m \). The angle \( \varphi \) between the direction of the extension of \( m \) and the normal, \( z \), to this array is evidently \( 30° \) (Fig. 5).

In Fig. 2, which shows the octahedral bands of wollastonite and pyroxene, we observe that the former can be looked upon as consisting of triplets of octahedra; they stack one after another based on \( t \). This band is then expressed by \( 3_k \) for a stack of
K triplets, or \(3_\infty\) for infinite case. In the latter case, pairs of octahedra are stacked based on \(t\) and \(\bar{t}\) alternately. The band of pyroxene is hence symbolized by \(\bar{2} 2 2 2 \bar{2} 2 \ldots\), or \((\bar{2} 2)_K\) for the repetition of K pairs, and \((\bar{2} 2)_{\infty}\) for that of infinite pairs. The latter symbol may be simplified to \((\bar{2} 2)\) and it can be used to denote the octahedral band of pyroxenes.

In terms of the above symbolism applied to the repeat unit of octahedral bands, those of pyroxenoids in the \(w\)-\(p\) series may be represented as follows:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>wollastonite</td>
<td>3(_2)</td>
</tr>
<tr>
<td>rhodonite</td>
<td>3(_2(\bar{2} 2))</td>
</tr>
<tr>
<td>pyroxmangite</td>
<td>3(_2(\bar{2} 2)_2)</td>
</tr>
<tr>
<td>ferrosilite III</td>
<td>3(_2(\bar{2} 2)_3)</td>
</tr>
<tr>
<td>? (hypothetical)</td>
<td>3(_2(\bar{2} 2)_4)</td>
</tr>
<tr>
<td>pyroxene</td>
<td>3(<em>2(\bar{2} 2)</em>{\infty}) (\rightarrow) ((\bar{2} 2))</td>
</tr>
</tbody>
</table>

The number of symbols denoting the array of octahedra for each band plus 1 corresponds to the number of tetrahedra, \(N\), in the repeat length of the silicate chains associated with the band, e.g. in the case of pyroxmangite \([3\(_2(\bar{2} 2)_2 = 3 3 2 2 2\)\], \(N = 6 + 1 = 7\) (Siebenerketten (Liebau, 1962)). The symbolism for octahedral bands discussed here is a revised version of the one previously proposed by Takéuchi and Koto (1977).
Fig. 2. Schematic illustration of octahedral bands and silicate chains of wollastonite (i) and pectolite (ii), the label Q indicating offset tetrahedra characteristic of pyroxenoids. They are compared with the octahedral band coupled with a silicate chain of the pyroxene type (iii). The component octahedra in the three cases are drawn with the same orientation which is referred to the axes, y and z.

Fig. 3. Structure units of two basic pyroxenoids and pyroxene, each viewed along an axis of the silicate chain.
The symbols for the above series of pyroxenoids may be given in a general form

$$3_2(\overline{2} 2)_K,$$

where the cases $K = 0, 1, 2$ and $3$ correspond to the octahedral bands of the members of the $w$-$p$ series having Dreierketten, Fünferketten, Siebenerketten and Neuenerketten.
(Liebau, 1962), respectively. In the symbols we can readily observe that the increase of the repeat length of the octahedral bands is incorporated with the addition of the component of pyroxene band $\overline{2} 2$. The octahedral band of pyroxene may then be regarded as an extreme case of that of pyroxenoid in which $K \to \infty$. The following relation holds between $\varphi$ and $N$:

$$\varphi = \tan^{-1}\left[2 / \sqrt{3}(N - 1)\right].$$

The octahedral bands in the $p-p$ series are, in contrast to those of the $w-p$ series, solely two-octahedra wide and can be characterized by $2_{2}(\overline{2} 2)_{K}$.

The cases $K = 0$ and 1 are known, e.g. pectolite $\text{Ca}_2\text{NaHSi}_3\text{O}_9$ (Prewitt, 1967) (Fig. 2b) and babingtonite $\text{Ca}_2\text{Me}^{2+}\text{Fe}^{3+}\text{HSi}_3\text{O}_{15}$ (Araki and Zoltai, 1971), respectively, where $\text{Me}^{2+} = \text{Fe}, \text{Mn}, \text{Mg}$. The case of babingtonite is shown in Fig. 6 together with a hypothetical case, $K = 2$.

Through an inspection of the foregoing list of symbols denoting the octahedral bands for pyroxenoids, one might raise a question if the existence of a pyroxenoid having such an octahedral band as indicated by question mark ($K = 4$) is likely the case. We come to this point later.

Effect of cation size on the configuration of silicate chains

Of the two independent cations commonly denoted $M1$ and $M2$ in pyroxene, the size of $M1$ is primarily responsible for the configuration of the silicate chains. This

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Fig. 6. Showing octahedral bands coupled with silicate chains (schematic) of babingtonite (i), $k = 1$, and a hypothetical homologue (ii), $k = 2$, of the pectolite-pyroxene homologous series.
is because the octahedron about M1 has a pair of edges, each being formed by the apical oxygen atoms of an adjacent pair of tetrahedra of the silicate chain. Such an edge has been designated as a 'type A' edge (Takéuchi, 1979). This edge corresponds to O1A1–O1A2 designated by Burnham et al. (1967) for the C2/c structure type of pyroxenes.

By analogy with the pyroxene case, the cation sites in the structures of pyroxenoids may well be classified into two groups, M1i and M2j; where \( i = 0, 1, 2 \) \( \ldots \) and \( j = 1, 2, \ldots \). In the case of pyroxmangite (\( N = 7 \)) (Fig. 7), for example, \( i = 0, 1 \) and 2, while \( j = 1 \sim 4 \), the maximum values of \( i \) and \( j \) thus designated for a pyroxenoid structure of \( N \) tetrahedra long being given by \( i_{\text{max}} = (N - 3)/2 \) and \( j_{\text{max}} = (N + 1)/2 \). If labeling of M1i is made starting from the cross striped octahedra as shown in Fig. 7, we find that the octahedra M11, M12 \ldots M1n, i.e. other than M10, closely share features in common with M1 octahedra in pyroxene. Note that the octahedra, M10, thus labeled are characteristic of pyroxenoids (Takéuchi, 1977); the octahedra topologically similar to M10 do not occur in pyroxenes. The octahedra about M1i have edges of type A while this type of edges are missing in M2j. The configuration of the silicate chains of pyroxenoids are likewise basically controlled by the size of the M1i cations.

When the M2j octahedra are so designated as shown above, the existence of the array of three successive octahedra, M21, M22, and M23, is common to all structures of the \( w \)-\( p \) series (note in the particular case of the wollastonite type, M23 is equivalent to M21). Of these, M22 and M23 are different from M21 because they share an edge with a silicate tetrahedron. The remaining M2j octahedra, if any in a structure, are topologically much similar to the M2 octahedra in pyroxenes.

To study the relationship between the size of M1i and the shape of silicate chain, we here define the lengths \( l_j \) (\( j = 1 \sim N \)), and \( l_0 \) as shown in Fig. 8. The length \( l_j \) is a

![Fig. 7. Designation of cation sites in the structures of wollastonite-pyroxene homologous series, showing the case of pyroxmangite \((N = 7)\). Stars indicate centers of symmetry locating in the edges shared by octahedra.](image-url)
distance between apical oxygen atoms of an adjacent pair of tetrahedra of the silicate chain of N tetrahedra long, while $l_0$ that of a specific pair of tetrahedra which are denoted P and R in Figs. 2 and 4. Then we introduced a quantity,

$$L = \left( \frac{\sum_{j=1}^{N} l_j + l_0}{(N+1)} \right),$$

and made an L versus $\overline{Mli}$ plot for each structure of pyroxenoids and various pyroxenes (Murakami and Takéuchi, 1979), where $\overline{Mli}$ denote an average of the M1i-O bond lengths. For pyroxenes, L corresponds to the distance between the pair of apical oxygen atoms O1 of adjacent tetrahedra, i.e. O1A1–O1A2.

The result given in Fig. 9(a) clearly shows that each structure type of pyroxenoids is characterized by a specific range of L, the correlation lines for different types having almost the same slope. The manner of variation in L according to the change in $\overline{Mli}$ for pyroxenoids as a whole in fact can be very closely correlated by a straight line (Fig. 9b). From the diagram in Fig. 9(a) we may draw the following inference: the silicate chain in a structure type would be distorted, with the decrease of $\overline{Mli}$, so as to decrease its L value along the slope, specific to the structure type, and when it exceeds a limit characteristic of the structure type, a per saltum change occurs in the repeat length of the chain, giving rise to the change in structure type.

In Fig. 9(a), the entries of high-temperature phases of pyroxenes, such as high

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**Fig. 8.** Notations of distances between apical oxygen atoms of adjacent tetrahedra of silicate chains in pyroxenoids, showing $l_0$ and $l_j$, where $j = 1$–$N$. The case of pyroxene is compared in the left.
Fig. 9. (a) Variations of $L$ versus $\overline{M_{II}}$ for various pyroxenoid solid solutions and pyroxenes (read $\overline{M_{II}}$ as $\overline{M_{I}}$ for pyroxenes). Notations of pyroxenoid solid solutions are: Wo = wollastonite, Bus = bustamite, Rh = rhodonite, Pym = pyroxmangite. Entries of ferrosilite III (FsIII) and protoenstatite (PEn) are indicated. (b) A comparison of the correlation line for pyroxenoids as a whole, with that for pyroxenes. (c) Enlarged diagram of the shaded area indicated in (a). Ruled area covers high-temperature phases of pyroxenes; 1: high clinoferrilite (Sueno et al., 1984), 2: orthoferrolite (Sueno et al., 1976), 3: high clinohypersthene (Smyth, 1974), 4: high pigeonite (Brown et al., 1972). The open square indicates the entry for an average of six EnIV-N structures. The heavy line passing through the square shows that individual distances, corresponding to $l$ of pyroxene, in EnIV-N structures extend over the whole range of $L$ shown in this diagram.
clinohypersthene ($M_1 = 0.50 \text{ Mg}, 0.50 \text{ Fe}$) at 825°C, high clinoferrasilite ($M_1 = \text{ Fe}$) at 1050°C and protoenstatite ($M_1 = \text{ Mg}$) at 1360°C, are located in the ruled area, an enlarged diagram of which is given in Fig. 9(c).

Among the values of L for high temperature phases of pyroxene, that of high clinohypersthene ($M_1 = 0.49 \text{ Mg}, 0.51 \text{ Fe}$) at 900°C, reported by Smyth and Burnham (1972) has an exceptionally large value 3.20 Å (Table 2) and does not fall in the ruled area; the value is practically the same with $L = 3.198 \text{ Å}$ for ferrosilite III. Since Smyth (1974) later reported a new set of high temperature structural data for clinohypersthene (Table 2), the above data by Smyth and Burnham (1972) have not been used to prepare the diagram. Then, the range of L values for pyroxenes, now concerned, extend from around 3.11 Å up to around 3.16 Å, leaving a little gap up to 3.198 Å for ferrosilite III (Fig. 9c). It is interesting to observe that the correlation line for pyroxenoids, if extended, will pass through the entry of protoenstatite indicated by a triangle in Fig. 9(b).

The structures of pyroxenoids having the values of L which fall in the gap, if existent, could have silicate chains whose repeat lengths are more than 9 tetrahedra long, i.e. N > 9 (or K > 3). Such a pyroxenoid having a large component of the pyroxene structure type may alternatively be regarded as a derivative of the pyroxene structure type. It is, in general, conceivable that pyroxene structures, at high temperatures, might be liable to form certain derivative structures of pyroxene, not necessarily of the pyroxenoid type, depending, to some extent, upon the size (or effective size) of $M_1$ cations. The discovery of enstatite-IV would endorse such a view.

<table>
<thead>
<tr>
<th>Material</th>
<th>$L^a$ (Å)</th>
<th>$M_1^b$ (Å)</th>
<th>$T^\circ \text{C}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinoferrasilite</td>
<td>3.142</td>
<td>2.176</td>
<td>1050</td>
<td>1</td>
</tr>
<tr>
<td>Orthoferrasilite</td>
<td>3.131</td>
<td>2.170</td>
<td>980</td>
<td>2</td>
</tr>
<tr>
<td>Clinohypersthene</td>
<td>3.120</td>
<td>2.149</td>
<td>825</td>
<td>3</td>
</tr>
<tr>
<td>Pigeonite</td>
<td>3.113</td>
<td>2.123</td>
<td>960</td>
<td>4</td>
</tr>
<tr>
<td>Clinohypersthene</td>
<td>3.20</td>
<td>2.17</td>
<td>900</td>
<td>5</td>
</tr>
<tr>
<td>Protoenstatite</td>
<td>3.156</td>
<td>2.128</td>
<td>1360</td>
<td>6</td>
</tr>
<tr>
<td>Ferrosilite III</td>
<td>3.198</td>
<td>2.16</td>
<td>1050/25GPa</td>
<td>7</td>
</tr>
<tr>
<td>EnIV-N</td>
<td>3.146*</td>
<td>2.130</td>
<td>-</td>
<td>8</td>
</tr>
</tbody>
</table>

*a: Read O1A1-O1A2 for CPX (C2/c) or corresponding distances for OPX. b: Read $M_1$ for pyroxenes.

PHASE RELATIONS IN THE SYSTEMS, MgSiO$_3$-LiScSi$_2$O$_6$ AND MgSiO$_3$-Sc$_2$O$_3$

In the MgSiO$_3$-LiScSi$_2$O$_6$ system, pyroxenes having four different structure types occur at 1250° (Ito and Steele, 1976); protoenstatite (PEn), orthopyroxene (OPX), clinopyroxene (CPX) with space group $C_2_1/c$ and CPX with $C2/c$ (Fig. 10). Among them PEn solid solution exists in the range 100–65 mol % MgSiO$_3$. It is non-quenchable if the LiScSi$_2$O$_6$ component is less than 10 mol %. The phases of En-IV were discovered at temperatures above those of the PEn field; the liquidus of En-IV

![Diagram 1](image1)

![Diagram 2](image2)

Fig. 10. (Top) The phase relation in the MgSiO$_3$-LiScSi$_2$O$_6$ system above 1000°C, the ruled area showing the En-IV field. The nonquenchable composition region is stippled. (Bottom) Details of the En-IV field proposed by Ito in 1976.

*MgSiO$_3$ is not pure but contains about 0.8 mol% Li$_2$O.
exists between 1550°C–1385°C (Ito and Steele, 1976). Below about 1400°C, these new phases are decomposed into the PEn type which is quenchable in contrast to PEn with En component greater than 90 mol %. When the PEn crystals are, in turn, heated at around 1400°C, they undergo incongruent melting to yield crystals of En-IV and melts (Fig. 11).

The series of En-IV phases form a homologous series based structurally on a C-centered CPX structure. A diagram showing phase relations proposed by Ito is given in Fig. 10. Three phases which have so far been discovered by Ito have been denoted En-IV-10, En-IV-9 and En-IV-8 in decreasing order of the MgSiO₃ component. Ito was successful in synthesizing crystals of each phase without contamination of others. The structures of these phases are, as will be shown later, built up of CPX slabs with the same principle but each differs from the others basically in the width of the CPX slabs, accompanying a change in chemical composition. They thus form a beautiful example of TCT series, with gliding as cell-twin operation. The phases, or homologues, have been designated by a general form En-IV-N, N denoting the number of tetrahedra in the span of the finite metasilicate chain across the unit CPX slab.

Using MgO, Sc₂O₃, and H₂SiO₃ as starting materials, Ito studied the En-rich region of the MgSiO₃-Sc₂O₃ system, showing that another series En-IV', free from Li, has stability field lying in a way closely similar to the case of En-IV. He likewise found three phases, EnIV'-10, EnIV'-9, and EnIV'-8. In both cases of En-IV and EnIV', he showed that the divalent cations such as Co, Mn, or Zn, doped in the

![Image of tabular crystals](image-url)

**Fig. 11.** Tabular crystals of En-IV produced through incongruent melting of a single crystal of Co-doped protoenstatite, (Mg, Li, Sc)SiO₃ at around 1000°C. The shape of a prismatic habit of the original crystal roughly remains preserved; the prismatic axis c is indicated. A sketch of an EN-IV crystal made by Jun Ito is given below the photograph.
crystals (ca. 5–10 wt. %) gave no influence upon the structure type, the contents of Sc being the major factor that differentiate the structure types of the homologues. The synthetic study of EnIV' carried out by Fukuda et al. (1984) revealed a fourth phase EnIV'-7 coexisting with EnIV'8. They eventually proposed the phase relations for EnIV' as shown in Fig. 12.

Both the homologous series En-IV-N and EnIV'-N as a whole will hereafter be represented by EnIV-N.

STRUCTURAL SCHEME OF THE EnIV-N SERIES

Supercell-subcell relation

The relationships between the unit cells (Table 3) of the two chemical series, now considered, and their CPX subcells are illustrated in Fig. 13. As will be observed in it, there are basically two ways, A and B, to choose the set of axes for the series of crystals. In the former case (Table 3), in which the c axis of EnIV is parallel to c of the CPX subcell, the unit cell of EnIV may simply be expressed as a stack, in parallel position, of N CPX cells along their common c axes; N being 10, 9, 8 and 7 for the unit cells of EnIV-10, EnIV-9, EnIV-8 and ENIV-7, respectively. The meaning of Arabic figure, which follows EnIV in the notation of each structure type is thus twofold: (1) it corresponds to the number of CPX cells that constitute the unit cell of the structure type. And (2) it denotes the number of tetrahedra in the span of the silicate chains that define the width of the CPX slab. In the A choice of axes, there is a simple rule between the space group and N: if N is even, the space group is
Table 3. Chemical compositions and cell dimensions of the En-IV and EnIV' series

<table>
<thead>
<tr>
<th>Chemical composition (wt%)</th>
<th>En-IV series</th>
<th>EnIV' series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>En-IV-10</td>
<td>En-IV-9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>58.07</td>
<td>55.69</td>
</tr>
<tr>
<td>MgO</td>
<td>37.53</td>
<td>28.92</td>
</tr>
<tr>
<td>CoO</td>
<td>-</td>
<td>8.30</td>
</tr>
<tr>
<td>Sc₂O₃</td>
<td>5.12</td>
<td>6.68</td>
</tr>
<tr>
<td>Li₂O</td>
<td>0.41</td>
<td>0.53</td>
</tr>
<tr>
<td>Total</td>
<td>101.13</td>
<td>100.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell dimensions (Å)</th>
<th>En-IV series</th>
<th>EnIV' series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axes set A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>8.748</td>
<td>8.756</td>
</tr>
<tr>
<td>c</td>
<td>55.416</td>
<td>50.058</td>
</tr>
<tr>
<td>β(°)</td>
<td>103.03</td>
<td>103.10</td>
</tr>
<tr>
<td>Axes set B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>8.748</td>
<td>8.756</td>
</tr>
<tr>
<td>c</td>
<td>27.038</td>
<td>48.792</td>
</tr>
<tr>
<td>β(°)</td>
<td>93.25</td>
<td>92.25</td>
</tr>
<tr>
<td>S.G</td>
<td>P2/a</td>
<td>I2/a</td>
</tr>
<tr>
<td>CPX subcell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>8.748</td>
<td>8.756</td>
</tr>
<tr>
<td>c</td>
<td>5.542</td>
<td>5.562</td>
</tr>
<tr>
<td>β(°)</td>
<td>110.40</td>
<td>110.44</td>
</tr>
</tbody>
</table>

B2/a, and if odd A2/a. The crystals of EnIV'-7 identified in the precession photographs gave cell dimensions: \(a = 9.43 \text{ Å}, b = 8.74 \text{ Å}, c = 39.03 \text{ Å}, \beta = 103.5^\circ\) (Fukuda et al., 1984).

In the latter choice of axes (Fig. 13), the unit cell become primitive if N is even, while it becomes body-centered if N is odd (Table 3). Choice A is better for discussing the relationship between the superstructure of EnIV and the CPX structure, while B is geometrically simpler than A particularly if N is even; the following crystal-chemical discussion on EnIV will be referred to B unless otherwise specified. The A choice of axes, when we hereafter refer to it, will be denoted by \(a_A\), \(b_A\), \(c_A\) and \(\beta_A\).

**Derivation of structure series from a clinopyroxene**

Prior to discussing details of the EnIV structures, we make here a quick survey of the structural features. The structure of EnIV-N consists of a unit slab cut out of a CPX structure parallel to (10̅1̅). It is hence convenient to take, in the CPX lattice,
a cell in which one axis is parallel to $\mathbf{a}_o + \mathbf{c}_o$ of the CPX cell as illustrated in Fig. 14.

The new cell has dimensions:

\[
\begin{align*}
\mathbf{a}' &= 9.42 \, \text{Å}, \\
\mathbf{b}' &= 8.75 \, \text{Å}, \\
\mathbf{c}' &= 5.54 \, \text{Å}, \\
\beta' &= 103^\circ.
\end{align*}
\]

This set of axes is related to those of the parent CPX cell, $\mathbf{a}_o$, $\mathbf{b}_o$, $\mathbf{c}_o$ and $\beta_o$, and the EnIV-N cell, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\beta$, as follows:

\[
\begin{align*}
\mathbf{a}' &= \mathbf{a} = -\mathbf{a}_o - \mathbf{c}_o, \\
\mathbf{b}' &= \mathbf{b} = \mathbf{b}_o, \\
\mathbf{c}' &= \mathbf{c}_o, \\
\mathbf{c} &= (-\mathbf{a}' + n\mathbf{c}')/2 \text{ if } N \text{ is even and} \\
&= (-\mathbf{a}' + n\mathbf{c}') \text{ if } N \text{ odd,}
\end{align*}
\]

where $n$ is the number of the CPX cells that defines the width of a cut (Fig. 14) and related to $N$ as $2n = N$. 

---

Fig. 13. The monoclinic cells of En-IV-10 and En-IV-9, showing their relationships to the unit cell of a $C$-centered clinopyroxene. The light lines trace the lattice of the clinopyroxene; the rotation axes and centers of symmetry viewed down $b$ are indicated in a unit cell at the upper right corner. Heavy lines and broken lines show the B and A set of axes, respectively. The centers of symmetry and twofold axes newly generated in the supercells are distinguished from those retained by the size of the corresponding symbols.
Fig. 14. The relationships between the CPX slabs of enstatite-IV (the case of $n = 5$ is shown) and the unit cell of clinopyroxene.

Fig. 15. Comparison of the En-IV-11 (hypothetical), En-IV-10, En-IV-9, and En-IV-8 structures, each being expressed by a regular repetition of slip of a block of CPX slabs.
When those \((10\overline{1})\) cuts of CPX, with \(n\) cells wide (\(N\) even), are juxtaposed with a glide \(a'\overline{2}\), a structure of EnIV-N results in which \(N\) is even. On the other hand, when we start with \((10\overline{1})\) CPX cuts with \(n\) cells wide (\(N\) odd), we obtain an EnIV-N structure through a juxtaposition of the cuts with a glide, \(b'\overline{2}\). These procedures are schematically shown in Fig. 15.

As an example of the structures thus derived, the \(b\) axis projection of the structure of En-IV-10, which represents well the En-IV homologous series, is illustrated in Fig. 16. In this figure, we observe that the structure consists of \((10\overline{1})\) CPX slabs, each being 10 tetrahedra wide. Along the interface, the plane of gliding between adjacent pair of CPX slabs, a layer structure is formed which is not found in the CPX structure. In Fig. 17, we present a HREM image showing 27.0 Å (=27.04 Å \(\times \sin\beta\)) fringes of an En-IV-10 crystal piece, which happened to be twinned on (100). The projection of the structure of En-IV-10 along the CPX chain (down \(c\) of the \(A\) choice of axes) is given in Fig. 18, which should be compared with

---

**Fig. 16.** (a) The \(b\)-axis projection of an En-IV-10 structure bounded by \(y = -0.12\) and \(y = 0.62\). Solid lines trace the unit cell. (b) HREM direct image of the EN-IV-10 crystal, showing well ordered sequence of slabs of 27 Å thick (taken by E. Watanabe with JEOL 100C-X at 100 Kv).
Fig. 17. Electron micrograph showing a crystal fragment of En-IV-10 twinned on (100) (taken by T. Ozawa); the axes are referred to the A choice (Fig. 13).

Fig. 18. The c-axis projection of the crystal structure of En-IV-10 bounded by $z = 0.29$ and $z = 0.71$, showing end view of the silicate chains. To avoid confusion, the tetrahedra, T's, are not shown except for one portion at the left corner of the bottom. We have taken off a tetrahedron in that portion, which is equivalent to the tetrahedron IV by $b$ translation, thus disclosing T which is otherwise hiding under the tetrahedron.
the c-axis projection of PEn (Fig. 1a).

The boundary layer is made up of three types of polyhedra; octahedron, trigonal prism and tetrahedron (see Fig. 27 beyond). Among them the tetrahedron formed about the site, which we denote T*, is so distorted that it may alternatively be interpreted as an octahedron. This "tetrahedron" plays, as will be found later, an essential role in adjusting the chemistry of the homologous series; the tetrahedron tends to accommodate a majority of vacancies left over in the structure after its formation through cell-twinning. The structure of EnIV-N is indeed greatly characterized by having this tetrahedron in the boundary of its constituent CPX slabs.

Details of the structural features, including, for example, the mode of variation in Si-O distances from one end to the other in the span of a chain and the construction of the interfacial layer, are shared by EnIV-N homologues in common regardless of N. One differs from another basically only in the width of the CPX slabs, accompanying the change in chemical composition (Table 3); the higher the Sc/Mg ratio, the smaller is the slab width (i.e. the smaller is the value of N).

Contents of the unit cell

From the chemical composition of En-IV-10 (Table 3), we may derive a formula

$$(\text{Mg}_{0.932}\text{Sc}_{0.074})_{\Sigma=1.006}(\text{Si}_{0.969}\text{Li}_{0.028}\text{Mg}_{0.003})_{\Sigma=1.000}\text{O}_{3}.$$  

The chemical formula thus expressed is almost exactly that of a metasilicate type. Since the structure analysis brought out that the unit cell contains 124 oxygen atoms, the above formula can be rewritten in the following style:

$$(\text{Mg}_{38.63}\text{Sc}_{3.10})_{\Sigma=41.73}[(\text{Li}_{1.16}\text{Si}_{0.07})\text{Si}_{40}]_{\Sigma=41.23}\text{O}_{124}.$$  

The primitive unit cell of this material contains one formula unit.

The atoms, 1.16 Li and 0.07 Si, in the right parentheses of the above formula are located at the twofold site T*, while the atoms, Mg and Sc, in the left parentheses are distributed over a total of 42 (=36 + 2 + 4) positions in the unit cell (Table 4). Accordingly, the above formula may further be modified to

$$(\text{Me}_{41.73}\square_{0.27})(\text{T}_{1.23}\square_{0.77})\text{Si}_{40}\text{O}_{124},$$  

where Me represents Mg and Sc, while T the cations at the T* site. The formula thus written is closely similar to the following formula of the metasilicate type:

$$\text{Me}_{41.33}\square_{0.66}\text{T}_{1.33}\square_{0.66}\text{Si}_{40}\text{O}_{124},$$  

in which the ratio, Me:(T+Si):O = 1:1:3. Making allowance for minor variation in chemical composition in the solid solution range, we may decide that the metasilicate formula will represent an ideal chemical composition for En-IV-10.

Noting that T represents cations at T*, we may regard that the metasilicate type
of the formula is accomplished by incorporating cations at the T* site in the boundary layer formed by cell-twinning.

An extensive survey of crystals by chemical analyses and X-ray studies, including structure determination of six homologues, suggests that the chemical formula for En-IV-N in general may be approximated by a compact form;

\[ \text{Me}_{x/3}\text{Li}_{4/3}\text{Si}_{(x-4)/3}\text{O}_x, \]

and for EnIV'-N by

\[ \text{Me}_{x/3}\text{Mg}_{2/3}\text{Si}_{(x-4)/3}\text{O}_x. \]

Putting \( x = 124, 112, 100 \) or 88, we obtain, in both cases, the formulae with \( N = 10, 9, 8, \) and 7, respectively.

We give in Tables 4 and 5 the number of distinct atomic sites, types of polyhedra about the sites, and total atomic positions in the unit cell of each structure type.

**Nomenclature**

The following symbols will be used in subsequent paragraphs; \( \text{M1} \): a family of the cation sites which correspond to the M1 site of a C-centered CPX. \( \text{M2} \): a family of the cation sites which correspond to the M2 site of a C-centered CPX. In addition, \( \text{O1, O2, and O3} \) have been defined similarly. The site M(o) in Tables 4 and 5 is an octahedral site and represents the originally denoted M(12), M(10) and M(10) sites (Takéuchi et al., 1984a) in the structures of EnIV-10, EnIV-9, and EnIV-8, respectively. The site denoted M(p) has a coordination in the form of a trigonal prism.

**Table 4. Number of atomic positions and types of polyhedra about the atomic sites in the unit cell of the EnIV-N structure type (for \( N \) even).** \( \text{M} \) represents the two families of cation sites \( \text{M1} \) and \( \text{M2} \)

<table>
<thead>
<tr>
<th>Atomic site</th>
<th>CPX slab</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{M} ) (Mg, Sc)</td>
<td>( \text{Si} )</td>
</tr>
<tr>
<td></td>
<td>( \text{M(o)} ) (Mg, Sc)</td>
<td>( \text{M(p)} ) (Mg, Sc)</td>
</tr>
<tr>
<td>Equipoint</td>
<td>4(g) 2(e) 4(g)</td>
<td>2(b) 4(g) 2(f)</td>
</tr>
<tr>
<td>Site symmetry</td>
<td>1 2 1</td>
<td>1 1 2</td>
</tr>
<tr>
<td>Cation polyhedron</td>
<td>Octahedron Tetrahedron</td>
<td>Octahedron Trigonal-prism Tetrahedron (Octahedron)</td>
</tr>
<tr>
<td>No. of distinct sites</td>
<td>( N = 10 ) 8 2 10</td>
<td>1 1 1</td>
</tr>
<tr>
<td>8</td>
<td>6 2 8</td>
<td>1 1 1</td>
</tr>
<tr>
<td>No. of total positions</td>
<td>( N = 10 ) 36 40 2 4 2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>28 32 2 4 2</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Number of atomic positions and types of polyhedra about the atomic sites in the unit cell of the EnIV-N structure type (for N odd). M represents the two families of cation sites M1 and M2.

<table>
<thead>
<tr>
<th>Atomic site</th>
<th>CPX slab</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M (Mg, Sc)</td>
<td>Si</td>
</tr>
<tr>
<td>Equipoint</td>
<td>8(f)</td>
<td>8(f)</td>
</tr>
<tr>
<td>Site symmetry</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cation polyhedron</td>
<td>Octahedron</td>
<td>Tetrahedron</td>
</tr>
<tr>
<td>N = 9</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>N = 7</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

and likewise represents M(6), M(5) and M(5) in EnIV-10, EnIV-9, and EnIV-8, respectively.

**CHARACTERISTICS OF THE CPX SLABS**

*Silicate chains*

The structure of the CPX slab (Fig. 19) is closely similar to the structure of a C-centered CPX such as high clinohypersthene (Smyth, 1974) or LiScSi2O6 (Hawthorne and Grundy, 1977); the silicate chain elements are in an O-rotated configuration (Thompson, 1970). The mode of scattering of Si-O bond lengths in each tetrahedron of every structure determined shares a feature with those of tetrahedra of CPX structures (Clark et al., 1969). Namely, the bond corresponding to Si-O2 is shortest and that corresponding to Si-O1 is second shortest: the former bonds in the six structures of EnIV-N are in the range from 1.583 Å to 1.604 Å, giving a mean value 1.591 Å, while the latter bonds from 1.600 Å to 1.633 Å, giving a mean value 1.617 Å.

There is, however, a marked difference in Si-O-Si bond angle between the chain units of the EnIV-N slab and the silicate chains in CPX. While the bond angle at the bridge O atom is constant for a given tetrahedral chain in a CPX structure, those in the chain unit of each EnIV-N show a spectrum of values. Thus, in the structure of En-IV-10 (Fig. 19), for example, the variation is such that the angle at the bridge O atom, O(1), in the central region of the chain unit has a maximum value of 142.0° but the angles gradually decrease as the location of the bridge O atoms approach both ends of the chain unit, e.g. at O(13) the angle has a value as small as 128.4°. The ways
of variation in Si-O-Si angle in the structures of both the En-IV-N and EnIV'-N series are illustrated in Fig. 20, showing that they are much alike. The two series of structures in general share such a close structural similarity as mentioned earlier. The notation of bridge oxygen atoms for En-IV-9 is given in Fig. 21.

The chain unit is in fact highly stretched in the region of its central portion, the angle O3-O3-O3 showing a value of 175.5° at O(1) of the En-IV-10 structure (Fig. 19). The corresponding angle for EnIV'-8 shows a highest value of 177.9° among the six structures. Those values compare with the high value of 179.3° which has been observed for the A chain in orthoferricosilite, FeSiO₃ (space group Pbca), at 980°C (Sueno et al., 1976). The mode of variation of the O3-O3-O3 angles for EnIV'-N is shown in Fig. 22. The way the Si-O3-Si bridge bonds in the chain unit of En-IV-10 vary is shown in Fig. 23 together with that of Si-O3-Si angles.

The mean Si-O bond length of each structure (Table 6) is closely similar to that of PEn at 1260°C (Murakami and Takéuchi, 1984), while it is significantly smaller than those of low-temperature polymorphs of En. The decrease which amounts to 0.01 Å is fairly large compared with the cases of high-temperature structures of pyroxenes such as, for example, orthoferricosilite (Sueno et al., 1976).
Fig. 20. The mode of variation in the Si-O-Si angle of the finite silicate chains in the EnIV'-10 (filled circles), EnIV'-9 (plain circles), and EnIV'-8 (filled triangles) structures. The bridge oxygen atoms in each chain are indicated along the horizontal axis successively from that at one end of the chain through to that at the other.

Fig. 21. The b-axis projection of the structure of En-IV-9, showing approximately lower half of the cell (cf. Fig. 16). The notations of octahedral cations and Si atoms are given by Roman figures, while those of the bridge oxygen atoms by Arabic figures.
**Octahedral bands**

The mean cation-oxygen distances, M1-O and M2-O, of each EnIV structure are likewise closely similar to the respective distances of PEn 1260°C (Table 6). Contrary to the case of Si-O, however, they are significantly longer than the corresponding distances of the low-temperature forms of En.

The Sc atoms are mainly distributed over the cation sites which belong to M1; the values are in the range from around 9 atom% to 25 atom% regardless of slab width. The Sc contents of the cation sites which belong to M2 are extremely low (1–3%) except those at the sites closest to the CPX boundaries (5–10%). Such a way of allocation of Sc to M1 and M2 in the CPX slabs is basically parallel to those of Mg-Sc-Li pyroxenes (Hawthorne and Grundy, 1977; Smyth and Ito, 1977). The octahedron M(o) in the boundary layer shows the highest Sc content in every...
Table 6. Mean cation-oxygen distances (Å) in the members of the two enstatite-IV series (EnIV-N) compared with those in the polymorphs of enstatite (En)

<table>
<thead>
<tr>
<th></th>
<th>M1 - O</th>
<th>M2 - O</th>
<th>Si - O</th>
</tr>
</thead>
<tbody>
<tr>
<td>EnIV-10</td>
<td>2.121</td>
<td>2.183</td>
<td>1.623</td>
</tr>
<tr>
<td>EnIV-9</td>
<td>2.124</td>
<td>2.184</td>
<td>1.623</td>
</tr>
<tr>
<td>EnIV-8</td>
<td>2.124</td>
<td>2.174</td>
<td>1.628</td>
</tr>
<tr>
<td>EnIV'-10</td>
<td>2.119</td>
<td>2.177</td>
<td>1.623</td>
</tr>
<tr>
<td>EnIV'-9</td>
<td>2.120</td>
<td>2.174</td>
<td>1.623</td>
</tr>
<tr>
<td>EnIV'-8</td>
<td>2.128</td>
<td>2.178</td>
<td>1.623</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>M1 - O</th>
<th>M2 - O</th>
<th>Si - O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protoenstatite at 1360°C [1]</td>
<td>2.121</td>
<td>2.198</td>
<td>1.625</td>
</tr>
<tr>
<td>Orthoenstatite [2]</td>
<td>2.0780</td>
<td>2.1509</td>
<td>1.6339</td>
</tr>
<tr>
<td>Clinoenstatite [3]</td>
<td>2.078</td>
<td>2.142</td>
<td>1.634</td>
</tr>
</tbody>
</table>


Fig. 24. A plot of the Sc contents (atom%) of the M1 octahedra in the CPX slab. The octahedral sites are indicated, along the horizontal axis, successively from that at one end of the array of the octahedra through that at the other end. The top of the three rows of symbols of the octahedral sites give sites for EnIV'-10, the middle for EnIV'-8, and the bottom for EnIV'-9. The solid, broken, and dotted lines show the modes of variation in Sc content for EnIV'-10, EnIV'-9, and EnIV'-8, respectively. The symbols with primes represent the octahedral sites which are symmetrically related to those having the corresponding symbols without primes.
structure; the occupancy is in the range from around 25% to 60%.

The Sc contents in EnIV, particularly EnIV', however, show the salient feature that they systematically vary from one M1 octahedron to another as illustrated in Fig. 24. We observe in this diagram that the Sc contents show the smallest value in the
octahedra in the region of the middle of the CPX slab. The contents then gradually increase, particularly in the case of EnIV'-10, as the octahedra approach the slab boundaries; thus the way of the distribution of Sc along the octahedral bands simulates a triangular wave (Fig. 25). In accordance with such a way of variation in Sc content, the average bond lengths of individual M1 octahedra show an increasing trend as they approach towards the boundaries of the CPX slab (Fig. 26).

The octahedral bands in a CPX slab are joined together with those in adjoining CPX slabs through polyhedra, such as M(o) and M(p), in the boundaries of the CPX slabs. Then, by analogy with the case of the pyroxenoid-pyroxene series, the links of octahedral bands, along the band extension of EnIV-N structures, may be symbolized as shown below:

\[
\begin{array}{c|c}
N & \text{Octahedral band} \\
\hline
\text{odd} & 11 & I \quad (\tilde{2} \ 2)_5 \quad \tilde{I} \quad (\tilde{2} \ 2)_5 \quad I \\
9 & I \quad (\tilde{2} \ 2)_4 \quad \tilde{I} \quad (\tilde{2} \ 2)_4 \quad I \\
7 & I \quad (\tilde{2} \ 2)_3 \quad \tilde{I} \quad (\tilde{2} \ 2)_3 \quad I \\
\text{even} & 10 & I \quad (\tilde{2} \ 2)_4 \quad 2 \quad \tilde{I} \quad (\tilde{2} \ 2)_4 \quad 2 \quad I \\
8 & I \quad (\tilde{2} \ 2)_3 \quad 2 \quad \tilde{I} \quad (\tilde{2} \ 2)_3 \quad 2 \quad I \\
3 & 3 \quad (\tilde{2} \ 2)_3 \quad 3 \quad 3 \quad (\tilde{2} \ 2)_3 \quad 3 \quad 3 \quad \text{ferrosilite III}
\end{array}
\]

where the symbol, I, represents the links of polyhedra, M(o), M(p) and T, that form the boundary layer, I denoting inversion equivalent of I. The case for EnIV-8 shown in this diagram is compared with the octahedral band of ferrosilite III, showing that they have the same pyroxene component \((\tilde{2} \ 2)_3\) and that the length of the asymmetric unit of the former compares well with the repeat length of the latter.

While, in general, the octahedral bands of pyroxenoids can be expressed, as mentioned before, by alternate symbols of \((\tilde{2} \ 2)_k\) and of \(3_2\), those in EnIV by alternate symbols of \((\tilde{2} \ 2)_k\) and I. We thus observe that the boundary layer, I, in a way corresponds to one of the octahedral arrays, \(3_2\), in pyroxenoids, while the tetrahedron T corresponds to the offset tetrahedron of their silicate chain.

The M1-O distances of EnIV at temperatures above 1400°C would be longer than the values obtained for the quenched structures (Table 6). The O1-O1 distances (L values) are well longer than those found for the quenched structures; they are in the range from 3.0 to 3.2 Å. Then the octahedral band of En-IV-10, for example, whose M1 octahedra containing on the average 90% Mg and 10% Sc, would be of critical dimensions if the continuous extension of a pyroxene chain along it were to be allowed. The structure brought out for En-IV-10 shows that the
pyroxene chains in the structure are dimensionally adjusted to the octahedral bands by limiting their extension to 10 tetrahedra and adding extra tetrahedra T about T* to retain the continuity of the chain structure. Compared with the pyroxene structures in which the ratio of the number of octahedra to the number of tetrahedra, both defining their c periodicity, is 2:2, the corresponding ratio in EnIV-N is N:(N+1). We may consider that the addition of extra tetrahedra T provides pyroxene chains

Fig. 27. Polyhedral diagram showing the structure of the boundary of CPX slabs. (a) The octahedron M(o), trigonal prism M(p), and tetrahedron T are indicated, small plain circles showing cation positions (the cation site in M(o) is a split site). Twofold axes passing through tetrahedra are shown. (b) Additional neighbors, O14 and O14', of the tetrahedral cation are indicated (refer to Fig. 19). (c) Showing that T is modified to an octahedron by incorporation with O14 and O14'.
relaxed from the effects of misfitting between the octahedral bands and the chains which are otherwise hindered from extending continuously. The mode of variation in the Si-O-Si angle discussed before would be the result of such a relaxation taking place to form the structure.

BOUNDARY LAYERS

Each boundary layer is composed of a centrosymmetric pair of sheets, parallel to (001), consisting of O atoms which are arranged very closely in the fashion of a closest-packing. In the voids formed by the O sheets, cations are distributed so that their neighboring O atoms form octahedra, trigonal prisms or tetrahedra. The way in which these polyhedra are linked to form a layer of polyhedra is illustrated in Fig. 27.

In the octahedron about the twofold site M(o) (Tables 4 and 5), cations are statistically located at a centrosymmetric pair of split positions, the separation being around 0.44 Å regardless of structure type. The octahedron accommodates Mg and Sc; the contents of Sc in this octahedron shows a value which is greatest in each structure type, the occupancy being around 24% to 64%. The octahedron links together the chains of octahedra about M1 in adjoining slabs. The trigonal prism about the fourfold site M(p) contains mostly Mg and in general about 10% vacancy. This polyhedron links together a pair of M2 octahedra in adjoining slabs. These situations will be observed in Fig. 19. Two of distinct M2 cations in each structure share an additional oxygen neighbor at a distance of around 2.9 Å. In the case of the EnIV-10 type, the two cations are M9 and M10 and they share O(25) (Fig. 19). The M9-O(25) and M10-O(25) distances in the structure of En-IV-10, for example, are 2.922 and 2.912 Å respectively.

![Graphical representation of Si atoms in EnIV'-10, EnIV'-9, and EnIV'-8 structures.](image)

**Fig. 28.** The variation in isotropic temperature factor of the Si atoms of EnIV'-10 (filled circles), EnIV'-9 (plain circles), and EnIV'-8 structures (triangles).
Now, the tetrahedron $T$ on the twofold rotation axis has two further neighbor oxygen atoms at the same distance of around 2.7 Å. Their locations are such that they form together with the four corners of $T$ at the regular distances, the shape of a distorted octahedron (Fig. 27). Thus, we may regard $T$ as a specific tetrahedron formed inside a distorted octahedron as the result of a shifting of the central cation which would otherwise be octahedrally coordinated. According to the geometrical characterization of polyhedra (Appendix 2) based on the definition of coordination number proposed by O’Keeffe (1979), this polyhedron is of about 85% tetrahedral character.

![Diagram](image)

Fig. 29. Comparison of the structures of (a) En-IV-10, (b) En-IV-9, and (c) En-IV-8, each being projected on the (201) plane of the primitive cell. Note that each loop consisting of silicate tetrahedra and T’s in En-IV-9 is formed in a way which is different from those of En-IV-10 and En-IV-8 (cf. Fig. 30).
The temperature factors, which are relatively small for the atoms near the center of the slabs, increase as the locations of the atoms approach the boundaries (Fig. 28). This trend is probably due to the effect that the closer the atomic locations are to the boundaries, the more the static disorder of the atoms increases. According to such a situation and low atomic occupancy at T*, as discussed below, relatively large errors are associated with T*-O distances; the estimated error being ±0.01 ~ ±0.015 Å in contrast to ±0.003 ~ ±0.006 Å for both M-O and Si-O.

There are significant differences in the contents of the T* site between En-IV-N and EnIV'-N. While this site in the former case basically contains Li, that in the latter contains Mg. The occupancies in the former case are close to 0.67 and in the latter case close to 0.33. It then follows that the T* site in EnIV'-N is more vacant than that in En-IV-N. This site may also contain Si. Thus for example T* in the structure of EnIV'-10 contains 0.04 Mg and 0.22 Si. The structure analyses suggest that the occupancy of this site would not exceed the value of 2/3.

Detailed knowledge on cation distributions thus brought out now provides us
with idealized structural formulae for the two homologous series;

En-IV-N: \[ \text{[Mg}_{(x-12)/3}\text{Sc}_4][\text{Li}_{4/3}\text{Si}_{(x-4)/3}]O_x \]  \hfill (1)

EnIV'-N: \[ \text{[Mg}_{(x-7.5)/3}\text{Sc}_3][\text{Mg}_{2/3}\text{Si}_{(x-4)/3}]O_x \]  \hfill (2)

where \( x = 124, 112, 100, \) or 88.

STRUCTURAL RELATIONSHIP—DETAILS OF THE TCT MECHANISM

In Fig. 29, the structures of En-IV-10 and En-IV-8, each projected on (201), are compared with that of En-IV-9 projected on (101). In the former two cases (N even), we can trace in every slab the loops composed of 2\((N + 1)\) tetrahedra, including the two tetrahedra, \( T \), at the boundaries. Those loops of tetrahedra of En-IV-10 are separately shown in Fig. 30. In the latter case (N odd), however, longer loops are formed; each composed of 4\((N + 1)\) tetrahedra, including \( T \), and extending over two successive slabs (for further details of the loops, refer to Figs. 32 and 33). We observed that the space group is also different depending upon whether N is even or odd. Thus, in general, the structural series of EnIV-N can be classified into two families: N even and N odd. The former will be denoted \( N^e \) and the latter \( N^o \).

These differences between \( N^e \) and \( N^o \) simply originated from the following geometrical characteristics when limiting the pyroxene chains to the 'finite' extension of \( N \) tetrahedra long. Namely, if \( N \) is even, the direction of Si-O2 of the tetrahedron at one end of the chain is of opposite sense with respect to that of Si-O2 of the tetrahedron at the other end. While, if \( N \) is odd, they are of the same sense (this situation can be readily observed when we consider an ideally stretched pyroxene chain). Such a difference gives rise to a difference in relative level, along \( b \), of the tetrahedra \( T \) (Fig. 29) that connect chain units when constructing an EnIV structure from (10T) cuts of a CPX structure as described below.

Consider a \( C \)-centered CPX, its unit cell containing \( 4 \times \text{MSiO}_3 \). Suppose that the structure is cut, parallel to (10\( T \)) and passing through M, into slabs each containing silicate chains \( N \) tetrahedra long. Then, the slab will have a chemical composition

\[ 4\text{M}_N\text{Si}_N\text{O}_{3N+1} \text{ or } 4\text{M}_N\text{Si}_N\text{O}_{4(3N+1)}. \]

If these slabs are juxtaposed in parallel position so that each is related to its adjacent ones by a glide (or a slip) of \((a_o + c_o)/2\), the O atom of the terminal tetrahedra of the chain units form at each boundary a set of eight polyhedra including two tetrahedra as shown in Fig. 27. Since four cations are available at the boundary (they were located in the cut planes of a pair of the CPX cuts that form the boundary), we may add up to four cations including two tetrahedral cations; thus, the structure type of EnIV-N is constructed.

The above procedure for forming the structure is for the cases of \( N^e \). For \( N^o \), the CPX slabs must be so juxtaposed that each is related to its adjacent slab by a glide not of \((a_o + c_o)/2\) but of \( b_o/2 \). In both cases, the procedures for constructing EnIV-
N structures preserve the $n$-glide planes of the original CPX structure as $a$-glide planes in the resulting structure; some of the twofold axes in the original CPX structure are retained in the case of $N^c$, while some of the twofold screw axes are retained in the case of $N^o$ (Fig. 13).

The EnIV structural series thus characterized by cell-twinning has a marked feature that the extension of cell-twin individuals (CPX-slab width) varies depending upon the atomic ratio, Sc/Mg; the lower the ratio, the longer is the extension. This relation means that the larger the Sc content, the more frequently may take place the cell-twinning to effect the relaxation of the CPX chains as mentioned previously. The EnIV-N series may now be regarded as a typical example of tropochemical cell-twinning.
Compound superstructure

Crystals of EnIV, which were apparently, single, were sometimes found to be composites of crystals having different structure types. Thus, for example, the diffraction pattern of a crystal having the EnIV'-10 type was accompanied by that of an EnIV'-9 type in such a way that their reciprocal lattices are in parallel positions. Or, in another crystal, EnIV'-9 and EnIV'-8 coexisted. Crystals of EnIV, in particular EnIV', however, occasionally exhibit such a diffraction pattern that is not explainable in terms of a simple composite of structure types known to EnIV-N. In Fig. 31 is presented a portion of a precession photograph of a crystal which is composite of EnIV'-10 and EnIV'-9, showing extra reflections other than those of the two structure types.

An examination into the crystal with high resolution electron microscopy (HREM), revealed the coexistence of a structure whose repeat unit itself was a composite of two different kinds of slabs; one is a slab of the EnIV'-10 type and the

Fig. 31. Portion of the precession photograph (CuK) of a composite crystal consisting of an EnIV'-10 structure and an EnIV'-9 structure, showing extra reflections in the composite 201 reciprocal lattice row. The left of the pair of columns of figures gives the I indices of EnIV'-9 and the right those of EnIV'-10, those for EnIV'-9 being halved.
other of EnIV’-9 type (Ozawa et al., 1979). Further HREM observation has shown the existence of various examples of this kind of structures which may be called compound superstructure. The following article will show that the concept of TCT mechanism may be used to predict the chemical compositions of various compound superstructures observed.

As geometrical principles of combining different kinds of slabs are the basis for describing the compound superstructures, they are given first. The discussion will be referred to the A choice of axes in which the c axis is taken along the extension of the silicate chains of the CPX slabs.

Symbolism of the basic superstructures

We now adopt the symbol N of an EnIV-N structure type to denote the type of its CPX slab. The unit cell of the A type of an EnIV-N structure, regardless of its structure type, contains two slabs related to each other by a twofold rotation. The periodical repetition of the unit cell to yield the structure may then be expressed by a symbol (N,N). Thus, for example, the EnIV-10 and EnIV-9 structure type are expressed by (10,10) or (9,9), respectively.

Derivation and symbolism of the compound superstructures

The geometrical features of the CPX slab of an EnIV-N structure may well be represented by the portion of the slab bounded by $x = 0$ and $x = 1/2$ of the unit cell for the purpose of studying the combination of different types of slabs. That portion of slab 8 is illustrated in Fig. 32, as a representative of the family of even N ($=N^e$). The corresponding portion of slab 9 is given in Fig. 33 as a representative of odd N ($=N^o$). Although the silicate chains in each diagram are depicted as a stretched form, it does not spoil the essential geometrical features of the slab. Each pair of the boundaries of a slab so expressed is represented by an array of T’s, along b, on the same twofold rotation axis δ. When we combine two slabs, they must be juxtaposed in parallel position so that they share the T’s at the adjoining boundary of the slabs.

A comparison of these diagrams reveals the following important differences between 8 and 9:

(a) The tetrahedra T’s in one boundary of 8 are displaced, along b, by b/4 (or 3b/4) relative to those in the other boundary. In slab 9, however, T’s in one boundary are displaced, relative to those in the other, by b/2.

(b) T’s in one boundary of slab 8 are enantiomorphic to those in the other. This relation arises from the fact that the portion of the unit cell now considered has center of symmetry as indicated in Fig. 32. On the other hand, all T’s in 9 are congruent and in parallel orientation (Fig. 33). Accordingly, for the present purpose of deriving the repetition units which are composites of several 8’s and several 9’s, we consider the enantiomorphic analogue of 9’s. We hence introduce a symbol $\bar{9}$ to denote such a symmetrical counterpart of 9 (Fig. 33).

Now, consider the cases of composite superstructures in which a succession of $N^e$ and another succession of $N^o$ occur alternately. Then we find from the above relation the following rules for combining slabs:

(1) If the number of successive $N^e$’s is even in the sequence of slab symbols
that represents a repeat unit, the symbol that immediately precedes the succession of \(N^c\) should be the same as the one that immediately follows it. If odd, they may be preceded by \(N^0\) (\(N^0\)) and followed by \(N^0\) (or \(N^0\)). This rule is applicable regardless of the number of successions. An example of the former case is:

\[
\cdots 9 8 8 9 8 8 9 8 8 9 \cdots (9, 8, 8).
\]

That for the latter is:

\[
\cdots 9 8 8 9 8 8 8 9 8 8 9 \cdots (9, 8, 8, 9, 8, 8, 8).
\]

Let \(N*n\) be a symbol that represents the \(n\) succession of \(N\) where \(n\) is an integer larger than unity. Then, the above symbols for the compound superstructures are rewritten by new forms:

\[(9, 8\ast2)\]

and
Fig. 33. (a) The structure of slab $\bar{9}$, illustrating in a way which is similar to the case of $8$ (Fig. 32a). A pair of twofold axes $\delta$ passing through $T$ (ruled) and a twofold screw axis $\delta_i$ are shown. (b) The locations of $\delta$ and $\delta_i$, viewed down $b$. (c) Slab $9$ which is a mirror image of $9$ shown in (a).

$\bar{9}, 8 \ast 3, 9, 8 \ast 3$

respectively.

(2) A succession such as $\bar{N}^oN^o$ is not permissible.

(3) In a succession of symbols, both sides of $N^o$ (or $\bar{N}^o$) must be the same.

(4) The $a$ glides of the slabs are retained regardless of the types of combination.
Space group of the compound superstructures

As will be observed in Fig. 32, the symmetry characteristic of \( \text{N}^e \) is represented by an array, along \( c \), of the following symmetry elements

\[
\delta i \delta.
\]

(3)

While, that of \( \text{N}^o \) is represented by

\[
\delta \delta_t \delta.
\]

(4)

Then the array of symmetry elements corresponding to a succession \( \text{N}^e \text{N}^o \) is given by

\[
\delta i \delta \delta \delta_t \delta.
\]

Thus, for example, the corresponding array of symmetry elements for periodic structure \((8, 9, 8, 9)\) is

\[
\ldots \delta i \delta \delta_t \delta i \delta \delta_t \delta i \delta \delta_t \delta \ldots
\]

Since the twofold axes at the slab boundaries are obviously suppressed in this particular case, the symmetry elements retained in the above array are

\[
\ldots i \delta_t i \delta_t i \delta_t \ldots
\]

(5)

Noting that the compound superstructures now considered are monoclinic and have a glides, and that the twofold axes other than \( \delta \) in 8 and some inversion centers other than \( i \)'s are retained, we can readily find that the array of symmetry elements (5) which is parallel to \( c \) is that characteristic of \( I2/a \). The space group of the above periodic structure (superstructure) is thus determined. The cell dimensions of the structure are \( a = 9.4, b = 8.7, c = 94.8 \, \text{Å} \), and \( \beta = 103^\circ \). In any case, the essential key to derive the space group can be provided by studying, as demonstrated above, the combination of (3) and (4) corresponding to the slab sequence. As a result, the compound superstructures have been found to have one of the four space groups as listed in Table 7, depending upon whether the number of the succession of \( \text{N}^e \) (or \( \text{N}^o \)) is even or odd. The above consideration yields the space group \( A2/a \) for the compound superstructure \((9, 10*2)\).

Observed compound superstructures

The fragments from the \( \text{EnIV}^e \) crystal sample which was used to determine the structure of \( \text{EnIV}^e{-}9 \), in particular, exhibited several types of well defined compound superstructures, mainly consisting of slabs \( 9 \) and \( 8 \). The electron diffraction patterns did show that the crystal fragments were dominantly of the \( \text{EnIV}^e{-}9 \) type although they tend to be composite of the \( \text{EnIV}^e{-}8 \) type. As the chemical composition of the crystal piece used for structure determination is close to the ideal chemical formula
Table 7. Classification of the compound superstructures of the \((N^m \cdot n, N^O \cdot n)\) type, and unit slabs of the basic superstructures (En-IV-N). Examples of the compound superstructures given in the second and fourth rows are hypothetical

<table>
<thead>
<tr>
<th>Compound superstructures</th>
<th>Space group</th>
<th>Example</th>
<th>(d_{(001)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m) (n)</td>
<td>(C^6_{2n})</td>
<td>(I2/a)</td>
<td>((8 \ast 3, 9, 8 \ast 3, 9))</td>
</tr>
<tr>
<td>Odd Odd</td>
<td>(C^6_{2h})</td>
<td>(A2/a)</td>
<td>((8 \ast 2, 9 \ast 3))</td>
</tr>
<tr>
<td>Even Odd</td>
<td>(C^4_{2h})</td>
<td>(B2/a)</td>
<td>((8, 9 \ast 2, 8, 9 \ast 2))</td>
</tr>
<tr>
<td>Odd Even</td>
<td>(C^4_{2h})</td>
<td>(P2/a)</td>
<td>((10 \ast 4, 9 \ast 2))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Basic superstructures</th>
<th>Space group</th>
<th>(d_{(001)})</th>
<th>Unit slab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure type</td>
<td>(C^4_{2h})</td>
<td>(B2/a)</td>
<td>(10)</td>
</tr>
<tr>
<td>En-IV-10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>En-IV-9</td>
<td>(C^6_{2h})</td>
<td>(A2/a)</td>
<td>(9)</td>
</tr>
<tr>
<td>En-IV-8</td>
<td>(C^4_{2h})</td>
<td>(B2/a)</td>
<td>(8)</td>
</tr>
</tbody>
</table>

for EnIV'-9 as shown in (2), we may adopt the following ideal formula of slab 9 for subsequent discussion:

\[
[Mg_{34.83}Sc_3\square_{1/6}]_{\Sigma=38}[Mg_{2/3}\square_{4/3}Si_{36}]_{\Sigma=38}O_{112}.
\]  

(6)

Then, if we assume for slab 8 the following ideal chemical composition (see the chemical formula (2))

\[
[Mg_{30.83}Sc_3\square_{1/6}]_{\Sigma=34}[Mg_{2/3}\square_{4/3}Si_{32}]_{\Sigma=34}O_{100},
\]  

(7)

we can readily calculate, in terms of (6) and (7), the possible chemical compositions of the compound superstructures made up of 9 and 8. The following four types of compound superstructures have been found (Takéuchi et al., 1984c).

[1] In Fig. 34 is presented one of the simple examples which consists of an alternating sequence of 8 and 9. The periodic unit is then characterized by

\((8, 9, 8, 9)\).

A calculation of chemical composition based on (6) and (7) yields the following chemical formula for this compound superstructure:

\[
[Mg_{32.83}Sc_3][Mg_{2/3}Si_{34}]O_{106}.
\]
Fig. 34. Electron micrograph showing the compound superstructure (8, 9) occurring in a basic structure (9, 9), each triangle indicating the intergrowth of 8 in the structure.

Fig. 35. Electron micrograph showing the (8*3, 9) structure. The mode of variation in the Sc/(Mg + Sc) ratio along the direction perpendicular to the CPX slabs is schematically shown below the micrograph; it simulates the shape of a square wave. (b) The electron diffraction pattern corresponding to the lattice fringe image shown in (a).
Calculated crystallographic data are: \( M_r = 3599.9 \), \( d_{(001)} = 92.4 \ \text{Å} \), \( c = 94.8 \ \text{Å} \), \( V = 7556.4 \ \text{Å}^3 \), \( Z = 4 \), \( I2/a \).

[2] The lattice image shown in Fig. 35 consists of an alternating sequence of \( 8*3 \) and \( 9 \). As this is again the case in which both \( m \) and \( n \) are odd (Table 7), its periodic unit is expressed by

\[(8*3, 9, 8*3, \bar{9})\],

giving calculated chemical composition:

\[[\text{Mg}_{31.83}\text{Sc}_3][\text{Mg}_{2/3}\text{Si}_{33}]\text{O}_{103}].\]

The calculated spacing, \( d_{(001)} \), and space group of this structure are given in Table 7 (\( c = 184.3 \ \text{Å} \), \( V = 14685.8 \ \text{Å}^3 \), \( Z = 8 \)).

[3] The third example (Fig. 36) is characterized by a regular alternation of \( 9*2 \) and \( 8 \), providing an example of the \( m \) odd, \( n \) even case (Table 7). The periodic unit is then composed of six slabs:

\[(9*2, 8, \bar{9}*2, 8)\],

giving calculated chemical composition

\[[\text{Mg}_{33.50}\text{Sc}_3][\text{Mg}_{2/3}\text{Si}_{34.66}]\text{O}_{108}].\]

\( d_{(001)} \) and space group as listed in Table 7, \( c = 144.9 \ \text{Å} \), \( V = 11547.3 \ \text{Å}^3 \) and \( Z = 6 \).

[4] The fourth example shown in Fig. 37 (a) provides, contrary to the above simple cases, a striking feature of the higher-order modulations. A closer examina-
Fig. 36. (a) Electron micrograph showing the \((9\times2, 8, \overline{9}\times2, 8)\) structure. Two mistakes \(M\) and \(M'\) are indicated in the regular sequence of the repeat units, the former being characterized by the intergrowth of one excess 8, and the latter by that of three excess \(9's\).

(b) The electron diffraction pattern corresponding to the lattice fringe image (a).

tion of the lattice fringe image has revealed that the periodic unit consists of as many as 26 slabs with the sequence

\[(9\times11, 8\times2, 9\times4, 8, \overline{9}\times2, 8, 9\times2, 8, \overline{9}, 8).\]

Calculated structural data are:

\[[\text{Mg}_{33.9}\text{Sc}_3][\text{Mg}_{2.3}\text{Si}_{15.07}]\text{O}_{109.2},\]
Fig. 37. (a) Electron micrograph showing the compound superstructure \((9\times11, 8\times2, 9\times4, 8, 9\times2, 8, 9\times2, 8, 9, 8)\), having the periodicity \(u\). (b) Enlarged diagram showing details of the repeat unit \(u\). (c) The mode of variation in the Sc/(Mg + Sc) ratio along the direction perpendicular to the CPX slabs, showing that it assumes the shape of a saw-toothed wave.
$d = 618.8 \text{ Å}, c = 635.1 \text{ Å}, V = 50605.5 \text{ Å}^3, Z = 26$, and space group $Pa$.

In the above symbol characterizing this structure, the number of the succession of 9 with intervals of 8*2 or 8 shows a stepwise decrease from left to right. The sequence of the symbols may be divided into four parts to yield the expression (P Q R S) for the repeat unit, where $P = [9 \times 11, 8 \times 2]$, $Q = [9 \times 4, 8]$, $R = [9 \times 2, 8, 9 \times 2, 8]$ and $S = [9, 8]$. The Sc/(Mg + Sc) ratios calculated, based on (6) and (7), for $P$, $Q$, $R$, and $S$ are 0.0792, 0.0796, 0.0807, and 0.0823, respectively, showing a stepwise increase of the ratio in the repeat unit. The way of variation of the ratio may thus be expressed in the shape of a saw-toothed wave (Fig. 37b). It is remarkable that such a change in minor chemical composition taking place in a linear range of about 619
Å regularly repeats for a long range of ca. 0.6 μm. Similarly, the mode of variation in Sc/(Mg + Sc) ratio in the case of the second example, \((8\times3, 9, 8\times3, 9)\), may be expressed by the shape of a square wave (Fig. 35a).

The compound superstructures discussed above tend to occur, in a crystal fragment, between the regions having different basic-structure types (EnIV-N). Each compound superstructure was presumably generated under a specific condition of the melt which was compositionally fluctuating from the state yielding one structure type towards yielding another.

Besides the coherent composition modulations that generate regular compound superstructures, incoherent (or irregular) modulations are also frequently observed between two different structure types. An example of lattice images that shows incoherent modulations is given in Fig. 38.

![Image](image_url)

**Fig. 38.** Incoherent modulations taking place between the regions having different basic-structure types indicated. The area indicated by a rectangle is enlarged and given at the bottom, showing that the width of the succession \(9\times7, 10\times5\), terminating in a region of the \((8, 8)\) type, registers good matching with that of \(8\times14\). A calculation, using the slab widths of En-IV-N given in Table 7, yields 305.8 Å for the former and 305.2 Å for the latter, showing good agreement between the two.
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