Crystal Structures of Three Polymorphs of \( \text{Co}_2\text{SiO}_4 \)

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Abstract

The crystal structures of three polymorphs of \( \text{Co}_2\text{SiO}_4 \) have been studied in detail. Relevant data are:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure type</th>
<th>Cell dimensions (Å)</th>
<th>Space group</th>
<th>Mean distances (Å)</th>
<th>Si-O</th>
<th>Co-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>olivine</td>
<td>( a ) 4.782, ( b ) 10.302, ( c ) 6.003</td>
<td>Pbnm</td>
<td>1.627, 2.134</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta )</td>
<td>modified spinel</td>
<td>( a ) 5.753, ( b ) 11.524, ( c ) 8.340</td>
<td>Imma</td>
<td>1.642, 2.114</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>normal spinel</td>
<td>8.138</td>
<td>Fd3m</td>
<td>1.646, 2.104</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The site occupancy refinement of the \( \gamma \)-phase indicates that 3.4 ± 0.8 percent of the total silicon atoms are at the octahedral sites, and the \( u \)-parameter of the oxygen atoms is 0.3666(4).

The close-packed structures of the three polymorphs are explained as differences in stacking of bands composed of \( \alpha \) and \( \beta \) octahedra and \( \gamma \) tetrahedra. The change of polyhedra around \( \alpha \) and \( \gamma \) atoms in the transformations induced by pressure is also discussed.

Introduction

High pressure phase transformations of silicates and germanates have been extensively studied for clues to possible phase transformations in the Earth's mantle. Among the silicates and germanates subjected to pressures of more than 100 kbar, several olivine-type structures (\( \alpha \)-phases) were transformed to their spinel polymorphs (\( \gamma \)-phases). The structures of \( \alpha \)-phases belonging to the Mg₃SiO₄–Fe₂SiO₄ system have been studied in detail by Birle et al (1968). Ma (1972) studied a polycrystalline Ni₂SiO₄ spinel and indicated that 8 ± 6 percent of the total silicon ions are octahedrally coordinated. However, the structure of a silicate \( \gamma \)-phase has never been studied by single crystal methods.

Kamb (1968) first discussed the relative stability and structural relations between olivine and spinel. He gave an explanation for the stability of olivine structure compared with spinel structure at atmospheric pressure based on Pauling's rules for edge-sharing by coordination polyhedra.

A new modification of a spinel-type structure with orthorhombic symmetry (\( \beta \)-phase) was found at high pressures in \( \text{Co}_2\text{SiO}_4 \), \( \text{Mg}_3\text{SiO}_4 \), \( \text{Mn}_3\text{GeO}_4 \), and \( \text{Zn}_2\text{SiO}_4 \) (Akimoto and Sato, 1968; Ringwood and Major, 1970; Morimoto et al, 1969, 1970; Syono, Akimoto, and Matsui, 1971). Morimoto et al (1969, 1970), and Moore and Smith (1969, 1970) have shown that this modification has a modified spinel structure with a peculiar atomic arrangement. Because Pauling's electrostatic balance rule is not obeyed for some oxygen atoms in the \( \beta \)-phase, the stability of this phase has been seriously questioned. However, recent calculations on the electrostatic energy of the three polymorphs of \( \text{Co}_2\text{SiO}_4 \), based on their preliminary structures, reveal that the modified spinel (\( \beta \)) structure is not necessarily unstable relative to the spinel (\( \gamma \)) structure (Tokonami et al, 1972). Syono, Tokonami, and Matsui (1971) studied the crystal field effect on the olivine-spinel transformation, and suggested that the structure of the \( \beta \)-phase could be more stable than that of the \( \gamma \)-phase at high pressure without crystal field stabilization when the ionic radius ratio of divalent and tetravalent cations has a high value.

Although the stability of the three polymorphs in the \( \alpha \rightarrow \beta \rightarrow \gamma \) transformation has been studied extensively, the precise crystal structures of the three polymorphs have not been previously described. In this paper, we report the crystal structures of \( \alpha \), \( \beta \), and \( \gamma \)-\( \text{Co}_2\text{SiO}_4 \) in detail and discuss their crystal-chemical relationships. Preliminary descriptions of the present work have already appeared (Morimoto et al, 1969, 1970; Tokonami et al, 1970, 1972).
Experimental

The cell dimensions, space groups, and densities at atmospheric pressure are given for the three polymorphs of Co₅SiO₄ (Table 1). The cell dimensions measured on the four-circle diffractometer are in good agreement with those measured by the powder method (Akimoto and Sato, 1968).

(a) α-Co₅SiO₄

**Data collection.** A mixture of Co₅O₄ and quartz in the proper stoichiometric ratio was used as starting material. The mixture was melted at 1500°C in air and cooled slowly to room temperature. Good single crystals of orthorhombic α-Co₅SiO₄ were found in the product. Cell dimensions are compared with those of α-phases of Mg₂SiO₄ and Mn₂GeO₄ in Table 1. The diffraction aspect is Pbn*, giving the space group Pbnm of olivines.

A nearly spherical crystal (diameter 0.03 mm), was used for collecting intensity data. Using a RIGAKU automatic four-circle diffractometer and Zr-filtered MoKα radiation (λ = 0.71069 Å), intensities of 501 symmetrically independent reflections were measured out to a maximum diffraction range of sin θ/λ = 0.72 by the ω-2θ scan method. The scanning width Δω was given by the relation: Δω = 0.60 + 0.30 tan θ (degrees). Of these reflections, 24 were the same as or less than the background value and were regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization effects. No absorption correction was made.

**Structure Refinement.** The initial atomic coordinates and isotropic temperature factors were taken from those of the fayalite structure described by Birle et al (1968). The refinement was carried out by a full-matrix least-squares method using a FACOM 230-60 version of the program ORFLS of Busing, Martin, and Levy (1962). The function minimized in this refinement was Σ1/σ² |s(Fo - Fs)|, where σ is the value given by the counting statistics when |Fs| ≠ 0, and is 10.0 when |Fs| = 0; s is the scale factor. Only the final refinement was carried out using equal weight for all reflections, as described later. Scattering factors and the real and imaginary anomalous dispersion corrections for Co²⁺ and those for Si⁴⁺ were taken from International Tables for X-ray Crystallography (1962), while scattering factors for O²⁻ were taken from the values reported by Tokonami (1965). Anomalous dispersion corrections for O²⁻ were assumed to be zero.

Three cycles of refinement of the atomic coordinates and one scale factor were made with individual isotropic temperature factors, and after three further cycles of refinement in which the scale factor, one secondary extinction factor, atomic coordinates, and the anisotropic temperature factors were varied, no further change of parameters took place. The final unweighted and weighted residuals are 0.046 and 0.035, respectively, for all 501 reflections.

The final parameters, the individual anisotropic temperature factors, and the equivalent isotropic temperature factors are listed with their estimated standard deviations in Table 2. Fσ and Fσ values are listed in Table 3.

(b) β-Co₅SiO₄

**Data Collection.** The single crystals used for the structure study were synthesized at 1420°C and 81 kbar from α-Co₅SiO₄. The cell dimensions and

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Space group</th>
<th>Density (g·cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Co₅SiO₄</td>
<td>4.782(4)</td>
<td>10.302(4)</td>
<td>6.003(4)</td>
<td>Pbnm</td>
<td>4.73</td>
</tr>
<tr>
<td>β-Co₅SiO₄</td>
<td>5.753(4)</td>
<td>11.524(4)</td>
<td>8.340(2)</td>
<td>Imma</td>
<td>5.05</td>
</tr>
<tr>
<td>γ-Co₅SiO₄</td>
<td>8.138(3)</td>
<td>-</td>
<td>-</td>
<td>Pd3m</td>
<td>5.17</td>
</tr>
</tbody>
</table>

**Composition**

| Mg₂SiO₄    | 4.7553(6)| 10.1977(14) | 5.9820(7) | Matsui and Syono (1968) |
| Co₅SiO₄    | 4.782(4)| 10.302(4) | 6.003(4) | This study (1972) |
| Fe₂SiO₄    | 4.821(1)| 10.477(1) | 6.086(1) | Akimoto and Fujisawa (1968) |

The standard deviations in parentheses are expressed in the unit of the last digit stated.
Table 2. Final Atomic Coordinates, Anisotropic Temperature Factors, and Equivalent Isotropic Temperature Factors for Atoms in α-Co$_2$SiO$_4$ and β-Co$_2$SiO$_4$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{31}$</th>
<th>$\beta_{23}$</th>
<th>B equiv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0038(4)</td>
<td>0.0015(1)</td>
<td>0.0034(3)</td>
<td>0.0001(2)</td>
<td>-0.0002(4)</td>
<td>-0.0002(1)</td>
<td>0.49</td>
</tr>
<tr>
<td>Co(2)</td>
<td>0.9917(3)</td>
<td>0.2765(1)</td>
<td>1/4</td>
<td>0.0047(5)</td>
<td>0.0013(1)</td>
<td>0.0039(3)</td>
<td>0.0001(2)</td>
<td>0</td>
<td>0</td>
<td>0.51</td>
</tr>
<tr>
<td>S1</td>
<td>0.4292(5)</td>
<td>0.0951(3)</td>
<td>1/4</td>
<td>0.0025(10)</td>
<td>0.0013(2)</td>
<td>0.0033(6)</td>
<td>0.0001(3)</td>
<td>0</td>
<td>0</td>
<td>0.42</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.7662(13)</td>
<td>0.0924(6)</td>
<td>1/4</td>
<td>0.0087(29)</td>
<td>0.0017(6)</td>
<td>0.0041(18)</td>
<td>0.0010(12)</td>
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<td>0.70</td>
</tr>
<tr>
<td>O(2)</td>
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<td>0.4504(6)</td>
<td>1/4</td>
<td>0.0085(28)</td>
<td>0.0020(6)</td>
<td>0.0032(15)</td>
<td>-0.0006(11)</td>
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<td>0</td>
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</tr>
<tr>
<td>O(3)</td>
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<td>0.1639(4)</td>
<td>0.0349(7)</td>
<td>0.0068(16)</td>
<td>0.0017(4)</td>
<td>0.0042(12)</td>
<td>-0.0001(7)</td>
<td>0.0007(13)</td>
<td>-0.0002(6)</td>
<td>0.66</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0030(7)</td>
<td>0.0005(2)</td>
<td>0.0019(2)</td>
<td>0</td>
<td>0</td>
<td>-0.0001(1)</td>
<td>0.40</td>
</tr>
<tr>
<td>Co(2)</td>
<td>0.1241(1)</td>
<td>0.6169(3)</td>
<td>0.029(5)</td>
<td>0.0037(3)</td>
<td>0.0008(1)</td>
<td>0.0019(3)</td>
<td>0</td>
<td>-0.0002(2)</td>
<td>0</td>
<td>0.48</td>
</tr>
<tr>
<td>S1</td>
<td>0.1211(3)</td>
<td>0.6169(3)</td>
<td>0.029(5)</td>
<td>0.0037(3)</td>
<td>0.0008(1)</td>
<td>0.0019(3)</td>
<td>0</td>
<td>-0.0002(2)</td>
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<td>0.48</td>
</tr>
<tr>
<td>O(1)</td>
<td>0</td>
<td>0.1275(11)</td>
<td>0.016(30)</td>
<td>0.0014(7)</td>
<td>0.0025(13)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.55</td>
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<tr>
<td>O(2)</td>
<td>0</td>
<td>0.1275(11)</td>
<td>0.016(30)</td>
<td>0.0014(7)</td>
<td>0.0025(13)</td>
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<td>0</td>
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<td>0.55</td>
</tr>
<tr>
<td>O(3)</td>
<td>0</td>
<td>0.1275(11)</td>
<td>0.016(30)</td>
<td>0.0014(7)</td>
<td>0.0025(13)</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0.55</td>
</tr>
<tr>
<td>O(4)</td>
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<td>0.016(30)</td>
<td>0.0014(7)</td>
<td>0.0025(13)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The estimated standard deviations, in parentheses, are expressed in units of the last digit.

space group are compared with the other polymorphs in Table 1. A single prism, 0.1 X 0.06 X 0.06 mm, was used for collecting intensity data. Three-dimensional intensities with $\sin \theta / \lambda < 0.71$ were obtained as already described for α-Co$_2$SiO$_4$. Of the observed 485 reflections, 36 were the same (or less) than the background values and were thus regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made.

Structure Refinement. A least-squares refinement, using the same procedures as for α-Co$_2$SiO$_4$, was initiated using a single prism, 0.1 X 0.06 X 0.06 mm, with the estimated standard deviations, in parentheses, expressed in units of the last digit. (c) γ-Co$_2$SiO$_4$

Data Collection. The single crystals of γ-Co$_2$SiO$_4$ were synthesized at 850°C and 68 kbar from α-Co$_2$SiO$_4$. A single prism, 0.1 X 0.06 X 0.06 mm, was used for collecting intensity data. Three-dimensional intensities with $\sin \theta / \lambda < 1.0$ were obtained as already described for α-Co$_2$SiO$_4$. Of the observed 670 reflections, 36 were the same (or less) than the background values and were thus regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made.

Structure Refinement. A least-squares refinement, using the same procedures as for α-Co$_2$SiO$_4$, was initiated using a single prism, 0.1 X 0.06 X 0.06 mm, with the estimated standard deviations, in parentheses, expressed in units of the last digit.
Table 3. Observed and Calculated Structure Factors (X10) for α-, β-, and γ-Co$_2$SiO$_4$

<table>
<thead>
<tr>
<th>α-Co$_2$SiO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 14 16 18 20</td>
</tr>
<tr>
<td>34 36 38 40 42</td>
</tr>
<tr>
<td>23 25 27 29 31</td>
</tr>
<tr>
<td>11 13 15 17 19</td>
</tr>
<tr>
<td>00 02 04 06 08</td>
</tr>
</tbody>
</table>

An attempted refinement of the site occupancies of Si and Co atoms in the octahedral and tetrahedral sites was carried out using Finger's RFINE program (1969) using the 88 most significant reflections. The refinements were initiated with the values obtained in the above refinement and without changing the site occupancy. The R-factor is 0.037 and the weighted R-factor is 0.029. The next four cycles were made by changing the site occupancy of Si atoms in the octahedral site under compositional constraint but by keeping the atomic coordinates constant at the values obtained in the last refinement. The final R-value is
0.037 and the weighted $R$-value is 0.027. About $3.4 \pm 0.8$ percent of the Si atoms were octahedrally coordinated, which means that $1.7 \pm 0.4$ percent of Co atoms were tetrahedrally coordinated.

The positional parameters, site occupancies, anisotropic temperature factors, and the equivalent isotropic temperature factors are given with the estimated standard deviations in Table 4(b).

The bond distances and angles for three polymorphs (Tables 5, 6, and 7) were calculated by using the FACOM 230-60 version of the program RDA4 of the UNICS system (Sakurai, 1967).

Discussion of the Structures

(a) $\alpha$-Co$_2$SiO$_4$

This structure consists of hexagonal closest-packed oxygen atoms with half of the octahedral sites occupied by Co atoms and one eighth of the tetrahedral sites occupied by Si atoms. The distortion of the Co octahedra in the structure resembles that found in the Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ system (Birle et al, 1968). The
Co-O distances of the two octahedra vary from 2.075 to 2.227 Å with a mean value of 2.134 Å. Thus the sizes of the Co octahedra are in good agreement with the sizes of the Mg/Fe-octahedra in hyalosiderite and hortonolite (Birle et al., 1968).

(b) $\beta$-Co$_2$SiO$_4$

This structure is isostructural with that of $\beta$-Mn$_2$GeO$_4$ (Morimoto et al., 1972) and is based on a cubic closest packed arrangement of oxygen atoms, with the Si atoms in tetrahedral and the Co atoms in octahedral sites. Two SiO$_4$ tetrahedra, which would be isolated in the spinel structure, now share an oxygen atom to produce an Si$_2$O$_7$ group. One oxygen atom in the structure is therefore not bonded to a Si atom. The structural relationship between the $\beta$- and $\gamma$-phases was first discussed by Morimoto et al (1970) and later by Moore and Smith (1970).

The Si-O distances range from 1.623 to 1.697 Å with a mean value of 1.642 Å. The Si$_2$O$_7$ group is schematically shown in Figure 1 with the bond distances and angles. The bridging Si-O bonds are much longer than the non-bridging bonds. The bond angle Si-O(2)-Si is 122°, in good agreement with that of Ge-O-Ge (121°) in $\beta$-Mn$_2$GeO$_4$. The Co-O distances vary from 2.053 to 2.155 Å with a mean value of 2.114 Å.

Table 7. Interatomic Distances and Angles in $\gamma$-Co$_2$SiO$_4$

<table>
<thead>
<tr>
<th>SiO$_4$ tetrahedron</th>
<th>CoO$_6$ octahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O 1.646 (3) Å [x2]</td>
<td>O-O 2.688 (4) Å [x6] O-Si-O 109.5 (1)° [x6]</td>
</tr>
<tr>
<td>Co-O 2.104 (3) Å [x6]</td>
<td>O-O 3.066 (4) Å [x6] O-Co-O 93.6 (1)° [x6]</td>
</tr>
<tr>
<td>mean 2.104 Å</td>
<td>mean 2.973 Å mean 90.0°</td>
</tr>
</tbody>
</table>
THREE POLYMORPHS OF Co$_2$SiO$_4$

The $u$-parameter of the cubic closest-packed oxygen atoms in $\gamma$-Co$_2$SiO$_4$ is 0.3668(3). This is the first $u$-parameter of a silicate spinel determined by single crystal methods and is in good agreement with the value (0.365) deduced by Kamb (1968) for Mg$_2$SiO$_4$ spinel based on its cell dimension.

The Si atom has a smaller isotropic temperature factor than the large, octahedrally coordinated cations in most silicates and in other polymorphs of Co$_2$SiO$_4$. With Si and Co atoms in tetrahedral and octahedral sites, respectively, we have normal isotropic temperature factors for all atoms. However, as a result of the site occupancy refinement, Si atoms in tetrahedral coordination showed higher equivalent isotropic temperature factors than those for Co atoms in octahedral coordination. Because of (1) the reverse change between the isotropic temperature factors for Si and Co atoms, and (2) the small percent of octahedral Si atoms obtained in the refinement, we consider that $\gamma$-Co$_2$SiO$_4$ is a perfectly normal spinel. This result is not consistent with the prediction by Ma (1972) based on the structure of Ni$_2$O$_4$ spinel.

The Si-O distance in $\gamma$-Co$_2$SiO$_4$ is 1.646 Å and the Co-O distance is 2.104 Å. The shared edges (3.066 Å) of the Co octahedra are much longer than the unshared ones (2.880 Å).

(d) Structural Relationships of the Three Polymorphs

The structures of the three polymorphs are compared schematically by the populations of octahedra and tetrahedra in the successive layers of close-packed oxygen atoms (Fig. 2, a, b, c). The stacking sequences of layers and the heights of metal atoms represented by numbers in these figures are shown in Figure 3.

Within the three structures, two different key structural units of octahedra and tetrahedra exist. In the first unit, the octahedra share edges with neighboring octahedra to make a serrated chain of octahedra (Fig. 4a; cf Birle et al, 1968). In the second unit, octahedra and tetrahedra share corners to make another serrated chain (Fig. 4b), here called a hybrid chain.

In the $\alpha$-structure (Fig. 2a), chains of octahedra (Fig. 4a) are cross linked by SiO$_4$ tetrahedra to form a two-dimensional layer. Each layer has the same patterns of combination of the two structural units. Two layers, superposed with the displacement of $a/2$, constitute the unit translation normal to the plane of the drawing.

In the $\beta$-structure (Fig. 2b), two chains of octahedra (as in Fig. 4a) are joined together with common salient octahedra, resulting in an extended double chain of octahedra. These chains combine with double hybrid chains consisting of corner-sharing SiO$_4$ and CO$_4$ polyhedra by again sharing salient octahedra. Each layer has the same combination of the two structural units. Stacking of six layers constitutes the unit translation (Fig. 4).

In the $\gamma$-structure (Fig. 2c) a whole layer is composed only of edge-sharing octahedra. This layer alternates with a layer composed only of corner-sharing tetrahedra and octahedra. Three pairs of these layers constitute the unit translation in this structure (Fig. 3).

The actual configuration of the octahedral chain is most distorted in the $\alpha$-structure and becomes more regular in the $\gamma$-structure and the $\beta$-structure, resulting in the different symmetries of the three polymorphs. The translation perpendicular to the stacking in the three polymorphs indicates a greater stacking density for the high-pressure polymorphs.

Pressure-Induced Phase Transition in Co$_2$SiO$_4$

Many phase transformations at high pressures involve an increase in the coordination number of the cations. Such phase transformations have been attributed to a change of the radius ratio between the cations and anions as a function of pressure. However, in the $\alpha \rightarrow \beta \rightarrow \gamma$ transitions of Co$_2$SiO$_4$, the coordination numbers of the cations remain unchanged, being based on the closest packing of oxygen atoms. Thus it has been necessary to introduce new concepts for an understanding of stability of the three polymorphs in the transition (Kamb, 1968; Tokonami et al, 1972; Syono et al, 1971). Because the differences between the preliminary atomic parameters and the final ones of the three polymorphs of Co$_2$SiO$_4$ are very slight, the conclusions of Tokonami et al (1972)
The crystal structures of the three polymorphs of \(\text{Co}_2\text{SiO}_4\), (a) \(\alpha\)-structure, (b) \(\beta\)-structure, and (c) \(\gamma\)-structure, schematically shown by the populations of octahedra and tetrahedra in the successive layers of close-packed oxygen atoms. The standard cell is outlined in each layer. The stacking sequence of layers and the heights of metal atoms represented by numbers are shown in Figure 3. Only one third of the unit translation is shown for the \(\beta\)- and \(\gamma\)-structures normal to the plane of the drawing.

Fig. 2. The crystal structures of the three polymorphs of \(\text{Co}_2\text{SiO}_4\), (a) \(\alpha\)-structure, (b) \(\beta\)-structure, and (c) \(\gamma\)-structure, schematically shown by the populations of octahedra and tetrahedra in the successive layers of close-packed oxygen atoms. The standard cell is outlined in each layer. The stacking sequence of layers and the heights of metal atoms represented by numbers are shown in Figure 3. Only one third of the unit translation is shown for the \(\beta\)- and \(\gamma\)-structures normal to the plane of the drawing.

Fig. 3. The stacking sequences of layers and the heights of metal atoms normal to the plane of drawing in Figure 2. Stacking of six layers constitute the unit translation in the \(\beta\)- and \(\gamma\)-structures.

on the stability of the three polymorphs remain unchanged.

However, it is of interest to compare the structures of the three polymorphs of \(\text{Co}_2\text{SiO}_4\), based on the data obtained in the present study, and to propose a general principle for the structural changes in the \(\alpha \rightarrow \beta \rightarrow \gamma\) transitions using a simple qualitative approach like that of Kamb (1968) for the olivine-spinel transition. The olivine structure \(\alpha\)-\(\text{Co}_2\text{SiO}_4\), because of the destabilizing effect of shared edges between the octahedra and tetrahedra (Table 8), appears unstable in respect to the normal spinel structure \(\gamma\)-\(\text{Co}_2\text{SiO}_4\).
Similarly, the sharing of a corner between tetrahedra to form an $\text{Si}_2\text{O}_4$ group in the modified spinel structure ($\beta$-$\text{Co}_2\text{SiO}_4$) seems distinctly unfavorable for its stability.

In the relative stability of the three polymorphs, however, the shortening of shared polyhedral edges must play an important role (Kamb, 1968). This shortening can be seen for the three polymorphs in Table 9. Unshared octahedral edges are much longer than the edges shared between the octahedra in the $\alpha$-phase, whereas the unshared edges are shorter than the shared edges in the $\gamma$-phase. In the $\beta$-phase, the shared and unshared edges have almost the same lengths. The apparently destabilizing factor of the $\text{Si}_2\text{O}_4$ group in the $\beta$-phase, therefore, seems to be partly compensated by a significant shortening of the shared edges of the octahedra.

As indicated by average interatomic distances (Table 10), the $\text{Si}_4\text{O}_4$ tetrahedra clearly increase in size within the higher pressure polymorphs of $\text{Co}_2\text{SiO}_4$, whereas the $\text{Co}_6\text{O}_4$ octahedra display a remarkable decrease in size. Presumably, if the higher pressure structures had been studied at elevated pressures—instead of at one atmosphere—the size decrease in the $\text{Co}_6\text{O}_4$ octahedra would be even more striking. In response to pressure, the $\text{Si}_4\text{O}_4$ tetrahedra thus appear to be more rigid than the $\text{Co}_6\text{O}_4$ octahedra. Interestingly, in low- to high-pigeonite measured at room temperature and at 960°C, respectively, Brown et al (1972) observed negligible expansion of the $\text{Si}_4\text{O}_4$ tetrahedra but large expansion of the $\text{Fe}_2$, $\text{Mg}$, and $\text{Ca}$ octahedra. These results suggest that size of $\text{Si}_4\text{O}_4$ tetrahedra is relatively independent of pressure and temperature.

In the $\alpha \rightarrow \beta \rightarrow \gamma$ transitions of $\text{Co}_2\text{SiO}_4$, the polyhedra around metal ions generally become more regular in the polymorphs stable at higher pressures. Thus the ranges of bond lengths become smaller in the polymorphs stable at higher pressures (Table 10) even though one of the Si-O bonds in $\text{Co}_2\text{SiO}_4$ is exceptionally long because of corner-sharing between two $\text{Si}_4\text{O}_4$ tetrahedra. The change of the distortion of the polyhedra is quantitatively shown by the tetrahedral and octahedral angle variances. These variances are calculated by the following formulae (Robinson, Gibbs, and Ribbe, 1971):

\[
\sigma^2_{\text{tet}} = \frac{\sum (\theta_i - 109.47^\circ)^2}{5}
\]

\[
\sigma^2_{\text{oct}} = \frac{\sum (\theta_i - 90^\circ)^2}{11}
\]

where $\theta_i$ represents the angles between the metal-oxygen bonds in the tetrahedra or in the octahedra (Table 10). The decrease of the variances clearly indicates decrease in polyhedral distortion.

These changes of the polyhedra can be explained qualitatively by the repulsive forces in ionic crystals.
which increase very rapidly as interatomic distances approach some constant value. To form crystals of higher density under pressure, therefore, it seems most energetically efficient to bring atoms with longer bond lengths closer and to make all the coordination polyhedra of the cation more regular. In some cases, where the polyhedra behave rigidly with increasing pressure, the average bond lengths of the coordination polyhedra increase to give some space to the oxygen atoms approaching to the central metal atoms, resulting in smaller possible ranges for all bond lengths of the polyhedra (Table 10). This feature is observed for SiO₄ tetrahedra, not only in the high-pressure polymorphs of Co₂SiO₄ but also in other silicates which undergo polymorphic transformations at high pressures—for example, in Zn₂SiO₄ as observed by Marumo and Syono (1971).

More generally, an increase in the coordination number of the cations in the phase transitions at high pressures may be considered as an extension of this tendency, because some next-nearest neighbors become nearest neighbors during the transformations. This produces not only an increase of the coordination number but also of the average bond lengths.

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THREE POLYMORPHS OF Co$_3$SiO$_6$