Crystal Structures of Three Polymorphs of Co₂SiO₄

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Abstract

The crystal structures of three polymorphs of Co_2SiO_4 have been studied in detail. Relevant data are:

Phase	Structure type	Cell dimensions (Å)			Z	Space group	Mean distances (Å)	
		a	*b*	*c*			Si–O	Co–O
α	olivine	4.782	10.302	6.003	4	*Pbnm*	1.627	2.134
β	modified spinel							
	or β-Mn₂GeO₄	5.753	11.524	8.340	8	*Imma*	1.642	2.114
γ	normal spinel	8.138			8	*Fd3m*	1.646	2.104

The site occupancy refinement of the γ-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 Co octahedra and Si tetrahedra. The change of polyhedra around Co and Si 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 (α-phases) were transformed to their spinel polymorphs (γ-phases). The structures of α-phases belonging to the Mg_2SiO_4-Fe_2SiO_4 system have been studied in detail by Birle *et al* (1968). Ma (1972) studied a polycrystalline Ni_2SiO_4 spinel and indicated that 8 ± 6 percent of the total silicon ions are octahedrally coordinated. However, the structure of a silicate γ-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 (β-phase) was found at high pressures in Co_2SiO_4, Mg_2SiO_4, Mn_2GeO_4, and Zn_2SiO_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 β-phase, the stability of this phase has been seriously questioned. However, recent calculations on the electrostatic energy of the three polymorphs of Co_2SiO_4, based on their preliminary structures, reveal that the modified spinel (β) structure is not necessarily unstable relative to the spinel (γ) 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 β-phase could be more stable than that of the γ-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 α-, β-, and γ-Co_2SiO_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 Co_2SiO_4 (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-Co_2SiO_4

Data collection. A mixture of Co_3O_4 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-Co_2SiO_4 were found in the product. Cell dimensions are compared with those of α-phases of Mg_2SiO_4 and Mn_2GeO_4 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 $MoK\alpha$ radiation ($\lambda = 0.71069$ Å), intensities of 501 symmetrically independent reflections were measured out to a maximum diffraction range of $\sin \theta/\lambda = 0.72$ by the $\omega - 2\theta$ scan method. The scanning width $\Delta\omega$ was given by the relation: $\Delta\omega = 0.60 + 0.30 \tan \theta$ (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 $\Sigma 1/\sigma^2_{hkl} \ |s(F_o - F_c)|$, where σ_{hkl} is the value given by the counting statistics when $|F_o| \neq 0$, and is 10.0 when $|F_o| = 0$; 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 Co^{2+} and those for Si^{4+} were taken from *International Tables for X-ray Crystallography* (1962), while scattering factors for O^{2-} were taken from the values reported by Tokonami (1965). Anomalous dispersion corrections for O^{2-} 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. F_o and F_c values are listed in Table 3.

(b) β-Co_2SiO_4

Data Collection. The single crystals used for the structure study were synthesized at 1420°C and 81 kbar from α-Co_2SiO_4. The cell dimensions and

TABLE 1. A Comparison of Crystallographic Data for α-, β-, γ-Co_2SiO_4 with Mg-, Co-, and Fe-Olivine

Polymorph	a (Å)	b (Å)	c (Å)	Space group	Density (g·cm^{-3})
α-Co_2SiO_4	4.782(4)	10.302(4)	6.003(4)	Pbnm	4.73
β-Co_2SiO_4	5.753(4)	11.524(4)	8.340(2)	Imma	5.05
γ-Co_2SiO_4	8.138(3)	–	–	Fd3m	5.17

Composition				References	
Mg_2SiO_4	4.7553(6)	10.1977(14)	5.9820(7)	Matsui and Syono (1968)	
Co_2SiO_4	4.782(4)	10.302(4)	6.003(4)	This study (1972)	
Fe_2SiO_4	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$_4$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{31}	β_{23}	B equiv.
				α-Co$_2$SiO$_4$						
Co(1)	0	0	0	.0038(4)	.0015(1)	.0034(3)	.0001(2)	-.0002(4)	-.0002(1)	.49
Co(2)	.9917(3)	.2765(1)	1/4	.0047(5)	.0013(1)	.0039(3)	.0001(2)	0	0	.51
Si	.4292(5)	.0951(3)	1/4	.0025(10)	.0013(2)	.0033(6)	.0001(3)	0	0	.42
O(1)	.7662(13)	.0924(6)	1/4	.0087(29)	.0017(6)	.0041(18)	.0010(12)	0	0	.70
O(2)	.2121(13)	.4504(6)	1/4	.0085(28)	.0020(6)	.0032(15)	-.0006(11)	0	0	.69
O(3)	.2835(8)	.1639(4)	.0349(7)	.0068(16)	.0017(4)	.0042(12)	-.0001(7)	.0007(13)	-.0002(6)	.66
				β-Co$_2$SiO$_4$						
Co(1)	0	0	0	.0030(7)	.0005(2)	.0019(2)	0	0	-.0001(1)	.40
Co(2)	0	1/4	-.0286(2)	.0050(8)	.0008(2)	.0014(2)	0	0	0	.49
Co(3)	1/4	.1241(1)	1/4	.0037(3)	.0008(1)	.0019(3)	0	-.0002(2)	0	.48
Si	0	.1211(3)	.6169(3)	.0029(5)	.0008(1)	.0009(3)	0	0	-.0001(2)	.35
O(1)	0	1/4	.2175(11)	.0016(30)	.0014(7)	.0025(13)	0	0	0	.55
O(2)	0	1/4	.7154(11)	.0017(31)	.0018(7)	.0012(12)	0	0	0	.51
O(3)	0	-.0141(5)	.2567(8)	.0054(27)	.0017(5)	.0013(9)	0	0	.0002(6)	.66
O(4)	.2663(6)	.1227(7)	-.0083(5)	.0073(11)	.0002(3)	.0021(5)	.0002(13)	-.0005(8)	-.0002(3)	.55

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 × 0.06 × 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 the atomic coordinates and isotropic temperature factors of β-Mn$_2$GeO$_4$ described by Morimoto *et al* (1972). After several cycles of refinement in which atomic coordinates, isotropic temperature factors, and one scale factor were varied, the R value for 485 reflections reached 0.109. Temperature factors were then converted to anisotropic form, and four cycles of refinement—varying the scale factor, atomic coordinates, and anisotropic temperature factors, and one secondary extinction factor—further reduced the R value to 0.053 for all reflections. The weighted R value is 0.032. The final parameters, the individual anisotropic temperature factors, and the equivalent isotropic temperature factors are listed in Table 2. F_o and F_c values are listed in Table 3.

(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$_4$. An approximately spherical crystal (diameter $\sim$0.03 mm) was used for collecting the three-dimensional intensity data. 670 reflections with $\sin \theta / \lambda < 1.0$ were measured using the procedures described above. Taking the average of the observed structure factors of symmetrically equivalent reflections, 136 independent F_o's were obtained. We assigned to σ_{hkl}, the larger of the two values of σ_{equi} or σ_{st}, where σ_{equi} is the standard deviation of F_o values of equivalent reflections and σ_{st} is the largest estimated standard deviation given by counting statistics.

Structure Refinement. For the determination of the spinel structure, only one geometrical parameter of oxygen atoms—the u-parameter—is necessary. Structure refinement began with $u = 0.365$, a value proposed by Kamb (1968) for Fe$_2$SiO$_4$ spinel, and with the isotropic temperature factors obtained for the final structure of β-Co$_2$SiO$_4$.

Four cycles of refinement of one scale factor and the u-parameter were made with isotropic temperature factors, and four more cycles were made with anisotropic temperature factors. The final R value is 0.079 and the weighted residual is 0.037. The final positional parameter, anisotropic temperature factors, and

TABLE 3. Observed and Calculated Structure Factors (×10) for
α-, β-, and γ-Co₂SiO₄

TABLE 3a. α-Co₂SiO₄

(Table 3a: multi-column listing of H, K, L, FO, FC values for α-Co₂SiO₄)

(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

TABLE 3b. β-Co₂SiO₄

(Table 3b: multi-column listing of H, K, L, FO, FC values for β-Co₂SiO₄)

equivalent isotropic temperature factors are given with their standard deviations in Table 4(a). F_o and F_c values are listed in Table 3.

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

TABLE 3c. γ-Co₂SiO₄

```
M K L                    2 6 12  124  116    8 10 10   42  122   3 3 11  477  481
0 0 4  2001 1995           6 14  354  304    1  1  1  572  576     3 13  272  287
  0 6  1456 1462           8  8   57   46     1  3 1156 1098       3 15  238  202
  0 12  591  579           8 10  139  129     1  5  785  786     5 5    591  611
  0 16  601  567           8 12   46   48     1  7  369  388       5 7  287  284
2 2    413  393            8 14   12   69     1  9  166  165       5 9  126  158
  2 6  263  268           10 10  346  329     1 11  466  464       5 11 418  392
  2 10 183  202           10 12   31   77     1 13  301  275       5 13 236  264
  2 14 190   96          4 4 4  1173 1181     3 3   198  187       5 15 209  165
4 4   2045 2092            4 6   52   17      3 3   593  595     7 7    553  562
  4 8  838  852            4 8 1110 1150      3 5   354  388       7 9  426  386
  4 12 842  818            4 10 124   10      3 7   711  732       7 11 183  238
6 6    249  269            4 12 532  512      3 9   451  471       7 13 133  128
  6 10  61  111            4 14   2    5      3 11  257  242     9 9    274  296
  6 14 152  137          6 6   141  172       3 13  139  129       9 11 158  162
8 8    937  953            6 8  105   22      3 15  318  317       9 13  71   92
  8 12 489  460            6 10  71  178    5 5 5   255  231    11 11   344  326
10 10  225  166            6 12  42   22       5 7  567  579   5 5 5    496  479
2 2 2  787  747            6 14 120   56       5 9  369  387       5 7  215  226
  2 4  320  291          8 8   618  584        5 11 221  212      5 9   50   99
  2 6  686  712            8 10  54   14       5 13 168   83      5 11 352  350
  2 8  215  214            8 12 654  641       5 15 297  285      5 13 240  212
  2 10 439  480           10 10  50   55     7 7   278  294    7 7    481  467
  2 12 114  126           10 12   2   15       7 9  177  187      7 9  346  341
  2 14 339  337          6 6 6  487  475       7 11 424  400      7 11 204  184
  2 16  40   80            6 8  158  164       7 13 266  260      7 13  48  120
4 4     73   29           6 10  401  363     9 9   156   99    9 9    135  243
  4 6  225  249           6 12  101   81       9 11 350  306      9 11 187  152
  4 8   46   30         8 8    2   36          9 13 225  200   7 7 7   206  269
  4 10 187  141           8 10 103   76      11 11 109  186       7 9  171  172
  4 12  31   28           8 12 171   39   3 3 3  1032 1035        7 11 348  368
  4 14 145  108        3 10 10 298   39       3 5  745  752     9 9    101  127
6 6    555  580        8  8 8  711  720        3 7  375  385       9 11 342  264
  6 8  164  160           8 10  29   24        3 9  223  217   9 9 9    80   59
  6 10 390  414
```

0.037 and the weighted *R*-value is 0.027. About 3.4 ± 0.8 percent of the Si atoms were octahedrally coordinated, which means that 1.7 ± 0.4 percent of Co atoms were tetrahedrally coordinated.

The positional parameters, site occupancies, anisoropic 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).

TABLE 4. Final Atomic Coordinates plus Anisotropic and Equivalent Temperature Factors for γ-Co₂SiO₄

Atom	site occupancy		x (=y,z)	β_{11} (=β_{22}=β_{33})	β_{12} (=β_{31}=β_{23})	B (equiv.)
(a) Refinement without site occupancy change						
Co	5/8			.0013(1)	0	0.38
Si	0			.0009(2)	0	0.25
O	.3668(3)			.0019(2)	.0006(4)	0.50
(b) Refinement with site occupancy change						
M	Co	.984(4)	5/8	.0013(1)	0	0.34
	Si	.016(4)				
T	Co	.032(8)	0	.0014(2)	0	0.37
	Si	.968(8)				
O		.3666(3)		.0019(2)	.0005(4)	0.50

M and T represent octahedral and tetrahedral sites, respectively. The standard deviation, σ, in parentheses are expressed in units of the last digit.

Discussion of the Structures

(a) α-Co₂SiO₄

This structure consists of hexagonal closest-packed oxygen atoms with half of the otcahedral 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 Mg₂SiO₄-Fe₂SiO₄ system (Birle *et al*, 1968). The

TABLE 5. Interatomic Distances and Angles in α-Co₂SiO₄

SiO₄ tetrahedron

Si-O(3)	1.629(4) Å		O(1)-O(2)	2.715(9) Å		O(1)-Si-O(2)	113.4(3)°	
Si-O(1)	1.612(6)		O(1)-O(3)	2.745(7)	[×2]	O(1)-Si-O(3)	115.8(2)	[×2]
Si-O(2)	1.638(7)		O(2)-O(3)	2.551(6)	[×2]	O(2)-Si-O(3)	102.7(2)	[×2]
Si-O(3)	1.629(4)		O(3)-O(3)	2.582(6)		O(3)-Si-O(3)	104.9(2)	
mean	1.627 Å		mean	2.648 Å		mean	109.2°	

CoO₆ octahedron

Co(1)-O(1)	2.100(4) Å	[×2]	O(1)-O(2)	2.893(9) Å	[×2]	O(1)-Co(1)-O(2)	87.1(2)°	[×2]
Co(1)-O(2)	2.100(4)	[×2]	O(1)-O(2)	3.045(2)	[×2]	O(1)-Co(1)-O(2)	92.9(2)	[×2]
Co(1)-O(3)	2.175(4)	[×2]	O(1)-O(3)	2.886(7)	[×2]	O(1)-Co(1)-O(3)	84.9(2)	[×2]
			O(1)-O(3)	3.154(6)	[×2]	O(1)-Co(1)-O(3)	95.1(2)	[×2]
			O(2)-O(3)	3.431(7)	[×2]	O(2)-Co(1)-O(3)	73.3(2)	[×2]
			O(2)-O(3)	2.551(6)	[×2]	O(2)-Co(1)-O(3)	106.7(2)	[×2]
mean	2.125 Å		mean	2.993 Å		mean	90.0°	
Co(2)-O(1)	2.182(5) Å		O(1)-O(3)	2.886(7) Å	[×2]	O(1)-Co(2)-O(3)	91.2(1)°	[×2]
Co(2)-O(2)	2.078(6)		O(1)-O(3)	3.040(6)	[×2]	O(1)-Co(2)-O(3)	81.7(2)	[×2]
Co(2)-O(3)	2.073(4)	[×2]	O(2)-O(3)	3.240(7)	[×2]	O(2)-Co(2)-O(3)	89.3(1)	[×2]
Co(2)-O(3)	2.227(4)	[×2]	O(2)-O(3)	2.917(6)	[×2]	O(2)-Co(2)-O(3)	97.6(2)	[×2]
			O(3)-O(3)	3.008(5)	[×2]	O(3)-Co(2)-O(3)	88.7(2)	[×2]
			O(3)-O(3)	3.421(6)		O(3)-Co(2)-O(3)	111.2(3)	
			O(3)-O(3)	2.582(6)		O(3)-Co(2)-O(3)	70.9(2)	
mean	2.143 Å		mean	3.015 Å		mean	89.9°	

TABLE 6. Interatomic Distances and Angles in β-Co_2SiO_4

	Si_2O_7 group					
Si–O(2)	1.697(5) Å		O(2)–O(3)	2.734(6) Å	O(2)–Si–O(3)	110.7(4)°
Si–O(3)	1.626(7)		O(2)–O(4)	2.633(8) [×2]	O(2)–Si–O(4)	104.9(3) [×2]
Si–O(4)	1.623(4) [×2]		O(3)–O(4)	2.693 [×2]	O(3)–Si–O(4)	111.9(3) [×2]
			O(4)–O(4)	2.692(5)	O(4)–Si–O(4)	112.1(2)
mean	1.642 Å		mean	2.688 Å	mean	109.4°

	CoO_6 octahedron					
Co(1)–O(3)	2.144(7) Å [×2]		O(3)–O(4)	3.115(8) Å [×4]	O(3)–Co(1)–O(4)	85.2(1)° [×4]
Co(1)–O(4)	2.088 [×4]		O(3)–O(4)	2.865(8) [×4]	O(3)–Co(1)–O(4)	94.8(1) [×4]
			O(4)–O(4)	2.841(11) [×2]	O(4)–Co(1)–O(4)	85.7(3) [×2]
			O(4)–O(4)	3.061(5) [×2]	O(4)–Co(1)–O(4)	94.3(3) [×2]
mean	2.107		mean	2.977	mean	90.0
Co(2)–O(1)	2.053(9) Å		O(1)–O(4)	2.834(8) Å [×4]	O(1)–Co(2)–O(4)	85.4(1)° [×4]
Co(2)–O(2)	2.138(9)		O(2)–O(4)	3.133(8) [×4]	O(2)–Co(2)–O(4)	94.6(1) [×4]
Co(2)–O(4)	2.125(6) [×4]		O(4)–O(4)	3.061(5) [×2]	O(4)–Co(2)–O(4)	87.1(2) [×2]
			O(4)–O(4)	2.930(11) [×2]	O(4)–Co(2)–O(4)	92.1(2) [×2]
mean	2.115		mean	2.988	mean	89.9
Co(3)–O(1)	2.062(2) Å [×2]		O(1)–O(1)	2.927(3) Å	O(1)–Co(3)–O(1)	90.4(1)°
Co(3)–O(3)	2.146(4) [×2]		O(1)–O(3)	3.061(6) [×2]	O(1)–Co(3)–O(3)	92.3(1) [×2]
Co(3)–O(4)	2.155(3) [×2]		O(1)–O(4)	2.834(8) [×2]	O(1)–Co(3)–O(4)	86.7(2) [×2]
			O(1)–O(4)	3.136(9) [×2]	O(1)–Co(3)–O(4)	84.4(3) [×2]
			O(3)–O(3)	2.878(2)	O(1)–Co(3)–O(4)	96.0(3) [×2]
			O(3)–O(4)	2.952(8) [×2]	O(3)–Co(3)–O(3)	84.2(2)
			O(3)–O(4)	3.115(8) [×2]	O(3)–Co(3)–O(4)	92.8(2) [×2]
mean	2.121		mean	3.000	mean	89.9

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) β-Co_2SiO_4

This structure is isostructural with that of β-Mn_2GeO_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_2O_7 group. One oxygen atom in the structure is therefore not bonded to a Si atom. The structural relationship between the β- and γ-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_2O_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 β-Mn_2GeO_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 γ-Co_2SiO_4

	SiO_4 tetrahedron					
Si–O	1.646(3) Å [×2]		O–O	2.688(4) Å [×6]	O–Si–O	109.5(1)° [×6]

	CoO_6 octahedron					
Co–O	2.104(3) Å [×6]		O–O	3.066(4) Å [×6]	O–Co–O	93.6(1)° [×6]
			O–O	2.880(4) [×6]	O–Co–O	86.4(1)° [×6]
mean	2.104 Å		mean	2.973 Å	mean	90.0°

(c) γ-Co₂SiO₄

The *u*-parameter of the cubic closest-packed oxygen atoms in γ-Co₂SiO₄ 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 Mg₂SiO₄ 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 Co₂SiO₄. 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 γ-Co₂SiO₄ is a perfectly normal spinel. This result is not consistent with the prediction by Ma (1972) based on the structure of Ni₂O₄ spinel.

The Si-O distance in γ-Co₂SiO₄ 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 α-structure (Fig. 2a), chains of octahedra (Fig. 4a) are cross linked by SiO₄ 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.
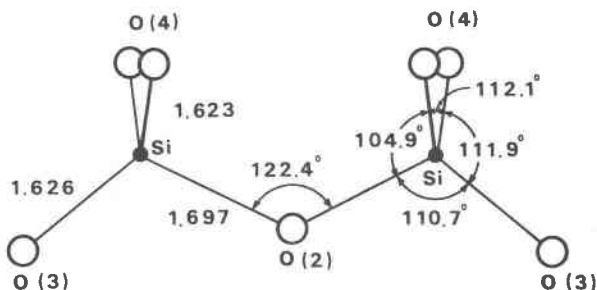
In the β-structure (Fig. 2b), two chains of octahedra

FIG. 1. The Si₂O₇ group in β-Co₂SiO₄.

(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 SiO₄ and CO₆ 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 γ-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 α-structure and becomes more regular in the γ-structure and the β-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 Co₂SiO₄

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 α → β → γ transitions of Co₂SiO₄, 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 Co₂SiO₄ are very slight, the conclusions of Tokonami *et al* (1972)
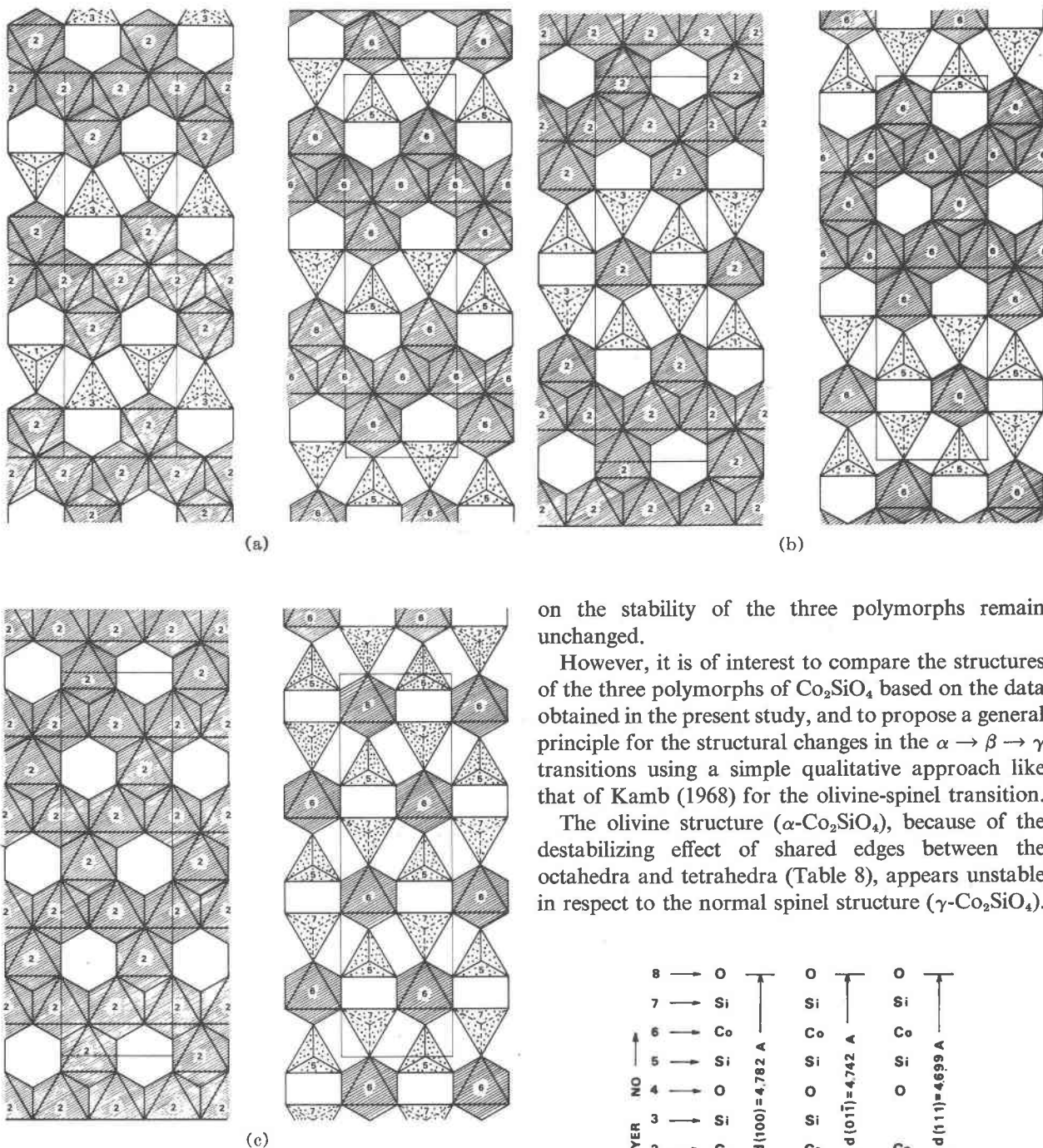
(a)

(b)

(c)

FIG. 2. The crystal structures of the three polymorphs of Co_2SiO_4, (a) α-structure, (b) β-structure, and (c) γ-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 β- and γ-structures normal to the plane of the drawing.

on the stability of the three polymorphs remain unchanged.

However, it is of interest to compare the structures of the three polymorphs of Co_2SiO_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 (α-Co_2SiO_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 (γ-Co_2SiO_4).
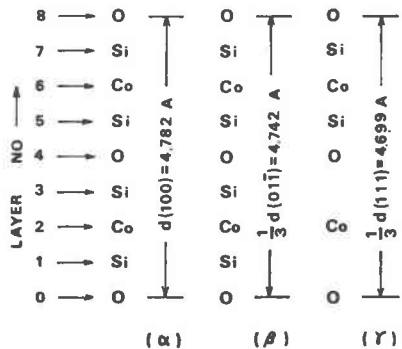

FIG. 3. The stacking sequences of layers and the heights of metal atoms normal to the plane of drawing in Figure 2. Stacking of six layers constitute the unit translation in the β- and γ-structures.
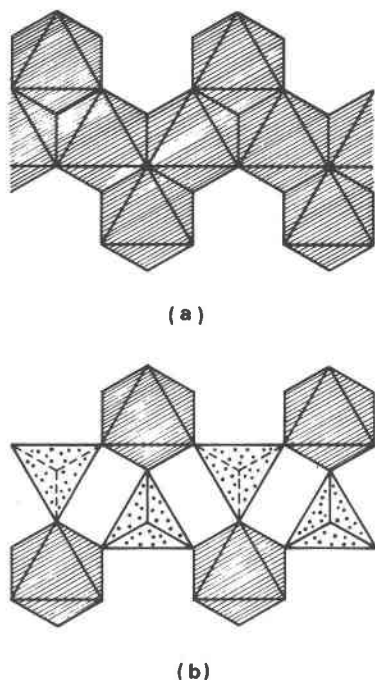
(a)

(b)

FIG. 4. Two different key structural units of octahedra and tetrahedra in the polymorphs of Co₂SiO₄: (a) a serrated chain of octahedra, and (b) a hybrid chain of octahedra and tetrahedra.

TABLE 8. Numbers of Shared Corners and Edges Between Metal Polyhedra in α-, β-, and γ-Co₂SiO₄

		α	β	γ
Shared corners	Co-Co	6(3.65)*	0	0
	Co-Si	6(3.32)	10	12(3.37)
	Si-Si	0	1(2.97)	0
Shared edges	Co-Co	3(3.22)	6(2.88)	6(2.87)
	Co-Si	3(2.76)	0	0
	Si-Si	0	0	0

* The numbers in parentheses represent average cation-cation distances in Angstroms.

to be more rigid than the CoO₆ 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 SiO₄ tetrahedra but large expansion of the Fe, Mg, and Ca octahedra. These results suggest that size of SiO₄ tetrahedra is relatively independent of pressure and temperature.

In the α → β → γ transitions of Co₂SiO₄, 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 Co₂SiO₄ is exceptionally long because of corner-sharing between two SiO₄ 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):

$$\sigma^2_{tet} = \sum_{i=1}^{6} (\theta_i - 109.47°)/5$$

$$\sigma^2_{oct} = \sum_{i=1}^{12} (\theta_i - 90°)/11$$

where θ_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

Similarly, the sharing of a corner between tetrahedra to form an Si₂O₇ group in the modified spinel structure (β-Co₂SiO₄) 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 α-phase, whereas the unshared edges are shorter than the shared edges in the γ-phase. In the β-phase, the shared and unshared edges have almost the same lengths. The apparently destabilizing factor of the Si₂O₇ group in the β-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 SiO₄ tetrahedra clearly increase in size within the higher pressure polymorphs of Co₂SiO₄ whereas the CoO₆ 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 CoO₆ octahedra would be even more striking. In response to pressure, the SiO₄ tetrahedra thus appear

TABLE 9. Mean Values for Shared and Unshared Edges (Å) of Metal Polyhedra in α-, β-, and γ-Co₂SiO₄

		α	β	γ
Co octahedron	shared	2.84	2.99	3.08
	unshared	3.14	3.00	2.88
Si tetrahedra	shared	2.56	-	-
	unshared	2.74	2.69	2.69

TABLE 10. The Longest and Shortest Interatomic Distances and the Angle Variances in the Metal Polyhedra of α-, β-, and γ-Co_2SiO_4*

| | SiO_4 tetrahedra | | | CoO_6 octahedra | | | | |
| | Si–O | O–O | σ^2_{tet} | Co–O | O–O | σ^2_{tet} | | |
						Co(1)	Co(2)	Co(3)
α	1.61–1.64(1.63)	2.55–2.75(2.65)	41.5	2.07–2.23(2.13)	2.55–3.43(3.01)	114.5	97.7	
β	1.62–1.70(1.64)	2.63–2.73(2.69)	12.2	2.05–2.16(2.11)	2.83–3.14(2.99)	23.5	17.7	26.2
γ	1.65–1.65(1.65)	2.69–2.69(2.69)	0	2.10–2.10(2.10)	2.88–3.07(2.97)	14.1		

* *Mean values in parentheses*

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 SiO_4 tetrahedra, not only in the high-pressure polymorphs of Co_2SiO_4 but also in other silicates which undergo polymorphic transformations at high pressures—for example, in Zn_2SiO_4 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.

Acknowledgments

References

AKIMOTO, S., AND H. FUJISAWA (1968) Olivine-spinel solid solution equilibria in the system Mg_2SiO_4-Fe_2SiO_4. *J. Geophys. Res.* **73**, 1467–1479.

———, AND Y. SATO (1968) High-pressure transformation in Co_2SiO_4 olivine and some geophysical implication. *Phys. Planet. Inter.* **1**, 498.

BROWN, G. E., C. T. PREWITT, J. J. PAPIKE, AND S. SUENO (1972) A comparison of the structures of low and high pigeonite. *J. Geophys. Res.* **77**, 5778–5789.

BIRLE, J. D., G. V. GIBBS, P. B. MOORE, AND J. V. SMITH (1968) Crystal structures of natural olivine. *Am. Mineral.* **53**, 807–824.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a fortran crystallographic least-squares program. *U. S. Atomic Energy Comm. Rep. No.* ORNL-TM-**305**.

FINGER, LARRY W. (1969) Determination of cation distributions by least-squares refinement of single-crystal X-ray data. *Carnegie Inst. Washington Year Book* **67**, 216–217.

KAMB, B. (1968) Structural basis of the olivine-spinel stability relations. *Am. Mineral.* **53**, 1439–1455.

MA, CHE-BAO (1972) *Phase Equilibria and Crystal Chemistry in the System SiO_2-NiO-$NiAl_2O_4$.* Ph.D. Thesis, Harvard University, Cambridge, Massachusetts.

MACGILLIAVRY, C. H., AND G. D. RIECK (1962) *International Tables for X-ray Crystallography*, Vol. **3**. Kynoch Press, Birmingham.

MARUMO, F., AND Y. SYONO (1971) The crystal structure of Zn_2SiO_4-II. A high-pressure phase of willemite. *Acta Crystallogr.* **B27**, 1868–1870.

MATSUI, Y., AND Y. SYONO (1968) Unit cell dimensions of some synthetic olivine group solid solutions. *Geochem. J.* **2**, 51–59.

MOORE, P. B., AND J. V. SMITH (1969) High pressure modification of Mg_2SiO_4: Crystal structure and crystallochemical and geophysical implications. *Nature*, **221**, 653–655.

———, AND ——— (1970) Crystal structure of β-Mg_2SiO_4: Crystal-chemical and geophysical implications. *Phys. Earth Planet. Inter.* **3**, 166–177.

MORIMOTO, N., S. AKIMOTO, K. KOTO, AND M. TOKONAMI (1969) Modified spinel, beta-manganous orthogermanate: Stability and crystal structure. *Science*, **165**, 586–588.

————, ————, ————, AND ———— (1970) Crystal structures of high pressure modifications of Mn_2GeO_4 and Co_2SiO_4. *Phys. Earth Planet. Inter.* **3,** 161–165.

————, M. Tokonami, K. Koto, AND S. Nakajima (1972) Crystal structures of the high pressure polymorphs of Mn_2GeO_4. *Am. Mineral.* **57,** 62–75.

Onken, H. (1965) Verfeinerung der Kristallstruktur von Monticellit. *Tschermak's Mineral. Petrogr. Mitt.* **10,** 34–44.

Ringwood, A. E., AND A. Major (1970) The system Mg_2SiO_4-Fe_2SiO_4 at high pressures and temperatures. *Phys. Earth Planet. Inter.* **3,** 87–108.

Robinson, Keith, G. V. Gibbs, AND P. H. Ribbe (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science,* **172,** 567–570.

Sakurai, T., Ed. (1967) *Universal Crystallographic Computation Program System.* Crystallogr. Soc., Japan.

Syono, Y., S. Akimoto, AND Y. Matsui (1971) High pressure transformations in zinc silicates. *J. Solid State Chem.* **3,** 369–380.

————, M. Tokonami, AND Y. Matsui (1971) Crystal field effect on the olivine-spinel transformation. *Phys. Earth Planet. Inter.* **4,** 347–352.

Tokonami, M. (1965) Atomic scattering factor for O^{2-}. *Acta Crystallogr.* **19,** 486.

————, AND N. Morimoto (1970) Structural relationship among three polymorphs of Co_2SiO_4. *Collected Abstr. IMA-IAGOD Meetings '70,* p. 167.

————, ————, S. Akimoto, Y. Syono, AND H. Takeda (1972) Stability relations between olivine, spinel and modified spinel. *Earth Planet. Sci. Lett.* **14,** 65–69.