

## The crystal structure of $\text{CoGeO}_3$ \*

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(Received February 27, 1967)

### Auszug

Die Struktur von  $\text{CoGeO}_3$  wurde nach dem Ausgleichsverfahren verfeinert. Die Verbindung ist isotyp mit den zur Raumgruppe  $C2/c$  gehörenden diopsidischen Pyroxenen. Die Sauerstoffatome sind sehr angenähert kubisch-dichtest gepackt und allen Co-Atomen oktaedrisch koordiniert. Die Ketten der Ge-Tetraeder unterscheiden sich wesentlich von den analogen Ketten der isotypen Pyroxene. Die Polytypie beim  $\text{CoGeO}_3$  wird durch die fast ideale dichteste Packung der Sauerstoffatome erklärt.

### Abstract

A least-squares refinement of the structure of  $\text{CoGeO}_3$ , which is isotypic with the diopsidic pyroxenes (space group  $C2/c$ ), has been carried out. The arrangement of oxygen atoms very closely approximated cubic closest packing, with both Co(1) and Co(2) being octahedrally coordinated, and with the chain of Ge tetrahedra having a significantly different geometry than equivalent chains in the isotypic pyroxenes. The polytypism shown by this compound is explained by the approach of the structure to geometrically ideal closest packing.

### Introduction

The structures of several naturally occurring pyroxenes have been examined in detail (e.g. johannsenite,  $\text{CaMnSi}_2\text{O}_6$ , FREED and PEACOR, 1967) and their general crystal chemical features were reviewed by PREWITT and PEACOR (1964). They are based on an approximation to closest packing of oxygen atoms, with planes of tetrahedrally coordinated Si atoms alternating with planes of octahedrally coordinated cat ions, with the Si tetrahedra sharing vertices to form chains which parallel bands of edge-sharing octahedra. The pyroxenes with space group  $P2_1/c$  (e.g.  $\text{MgSiO}_3$  —  $\text{FeSiO}_3$ ) exhibit polytypism, while those with space group  $C2/c$  (e.g.  $\text{CaMgSi}_2\text{O}_6$ ) do not. Refined struc-

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tures show that this is due to a closer approximation to closest packing in the pyroxenes having relatively small octahedrally coordinated cations (space group  $P2_1/c$ ). The diopsidic pyroxenes ( $C2/c$ ) contain large cations such as Ca or Na which cause considerable distortion in the closest-packing arrangement; this at least partially explains the lack of polytypism shown by them.

TAUBER and KOHN (1965) reported, however, that synthetic  $\text{CoGeO}_3$  is isotypic with those monoclinic pyroxenes having symmetry  $C2/c$ , but inverts to an orthorhombic phase which is isotypic with rhombic enstatite, a high-temperature polytype of clinoenstatite, space group  $P2_1/c$ . We have carried out a refinement of the monoclinic form of  $\text{CoGeO}_3$  in order to determine those structural features controlling polytypism. In addition, detailed data on a germanate isotypic with well refined silicate structures should provide data on the general relationships between germanates and silicates.

#### Preliminary data

Crystals of  $\text{CoGeO}_3$  were kindly provided by Dr. J. A. KOHN. As reported by TAUBER and KOHN (1965), all crystals were twinned. However, since the width of twin domains was about 0.05 mm, it was possible to separate a small untwinned crystal after extensive sampling. Weissenberg and precession photographs confirmed that the space group is  $C2/c$ . Several photographs were given long exposures in order to detect the presence of weak, extra reflections inconsistent with this space group, but none were observed. Unit-cell parameters, as obtained through least-squares refinement of  $\text{FeK}$  zero-level Weissenberg data, are  $a = 9.692 \pm .004 \text{ \AA}$ ,  $b = 9.018 \pm .003 \text{ \AA}$ ,  $c = 5.181 \pm .002 \text{ \AA}$ , and  $\beta = 101.2 \pm 0.1^\circ$ . The  $c$  translation is parallel to the chain of Si tetrahedra in the pyroxenes, and generally has a value of 5.2 to 5.25  $\text{\AA}$  in these compounds. Since Ge has a greater radius than Si, and since the magnitude of  $c$  is less for  $\text{CoGeO}_3$  than for pyroxenes in general, a significant distortion in the chain of tetrahedra in  $\text{CoGeO}_3$ , relative to that in pyroxenes, is indicated.

Intensity data were obtained using a crystal mounted for  $c$ -axis rotation on a Buerger single-crystal diffractometer. Pulse-height analysis was used with  $\text{MoK}\alpha$  radiation. Since the small crystal size resulted in relatively weak intensity values with a relatively high background, integrated intensities were obtained by graphically recording peaks and measuring their area with a planimeter. Only those data were measured which are included in the equivalent

Table 1. Observed and calculated structure factors at termination of refinement

h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>
4 0 0	28.95	28.62	3 3 1	5.10	4.58	-4 2 2	11.37	10.77	10 2 3	9.47	8.63
6	50.99	55.67	5	82.19	101.75	2	32.84	31.00	-11 3 3	42.93	43.13
8	16.01	12.33	7	5.13	5.11	4	7.65	1.43	-9	17.95	18.86
10	53.44	58.12	9	27.42	27.32	6	12.57	11.25	-7	21.77	20.25
12	15.07	8.37	11	22.21	22.59	8	11.18	10.85	-5	46.73	49.10
3 1 0	57.99	64.37	-12 4 1	18.63	17.56	10	8.03	4.98	-3	13.99	14.60
5	35.56	32.36	-10	20.59	20.80	-11 3 2	6.42	5.57	-1	81.66	94.95
7	32.72	37.56	-8	24.94	24.26	-9	5.76	2.32	1	26.52	24.33
9	7.55	6.41	-6	7.01	7.11	-7	0.00	0.33	3	0.00	1.26
11	0.00	0.87	-4	8.10	5.54	-5	10.21	9.51	5	52.58	53.74
2 2 0	40.02	37.09	-2	25.96	23.96	-3	7.48	5.48	7	5.39	3.56
4	6.68	0.19	0	33.40	30.37	-1	15.80	14.47	9	44.67	42.69
8	22.64	21.42	2	45.58	42.58	1	0.00	0.93	-10 4 3	8.39	7.63
10	5.51	2.03	4	15.19	14.60	3	4.58	3.11	-8	24.77	24.36
12	14.26	12.66	6	0.00	0.80	5	13.52	12.73	-6	25.22	24.73
1 3 0	8.06	5.52	8	25.47	23.46	7	5.55	3.70	-4	20.67	19.93
3	0.00	1.26	10	19.69	19.40	9	7.12	4.54	-2	17.46	17.48
5	16.41	14.28	-11 5 1	0.00	4.32	-12 4 2	10.06	9.30	0	23.94	25.27
7	6.24	5.53	-9	0.00	2.34	-10	18.39	17.96	2	35.13	32.83
9	4.82	4.25	-7	13.17	11.81	-8	29.67	28.17	4	16.70	15.34
11	7.74	5.25	-5	5.15	6.23	-6	17.02	16.24	6	10.65	9.68
0 4 0	35.76	32.99	-3	21.40	19.35	-4	9.29	9.29	8	8.48	9.06
2	35.32	36.20	-1	4.77	4.90	-2	19.66	18.97	-11 5 3	0.00	4.39
4	9.36	7.51	1	12.91	11.80	0	29.95	30.14	-9	8.84	11.42
6	10.01	8.37	3	15.45	14.34	2	40.53	38.15	-7	4.55	5.21
8	26.14	25.20	5	0.00	0.52	4	14.94	14.80	-5	0.00	0.51
10	21.32	18.43	7	18.50	17.63	6	6.74	4.80	-3	19.70	20.08
12	14.63	15.38	9	4.28	4.02	8	14.44	14.44	-1	3.25	3.25
1 5 0	24.17	22.08	-10 6 1	12.05	12.01	10	16.13	16.16	1	10.25	10.88
3	63.17	65.95	-8	8.67	8.25	-11 5 2	9.72	9.71	3	11.17	11.36
5	24.80	22.88	-6	17.86	15.93	-9	24.23	23.42	5	0.00	0.41
7	50.60	51.48	-4	8.09	5.60	-7	43.42	44.29	7	11.81	10.76
9	15.31	15.24	-2	9.08	9.60	-5	12.64	11.22	-10 6 3	8.53	12.16
11	6.59	5.39	0	27.92	26.55	-3	60.48	63.77	-8	8.55	9.60
0 6 0	81.16	96.82	2	6.76	6.95	-1	5.95	5.41	-6	14.34	14.83
2	5.43	3.50	4	11.99	9.54	1	41.09	38.17	-4	0.00	2.11
4	23.16	22.07	6	7.75	5.14	3	47.92	49.99	-2	0.00	0.28
6	36.04	35.70	8	0.00	2.02	5	13.91	14.45	0	15.17	14.01
8	5.95	5.50	10	13.88	13.57	7	48.04	46.95	2	8.04	7.97
10	43.31	43.32	-9 7 1	0.00	1.67	9	0.00	1.58	4	19.83	17.03
12	9.12	7.97	-7	14.61	14.85	-10 6 2	31.74	32.99	6	0.00	2.09
1 7 0	14.92	12.34	-5	33.05	33.13	-8	9.22	9.86	8	0.00	1.35
3	21.90	20.16	-3	30.59	30.84	-6	28.72	28.72	-9 7 3	7.35	7.80
5	23.70	22.27	-1	21.19	19.03	-4	22.97	22.31	-7	6.08	6.63
7	15.99	9.17	1	8.07	7.57	-2	7.82	7.37	-5	21.31	24.28
9	0.00	3.96	3	20.50	19.36	0	59.82	61.69	-3	24.30	25.24
11	0.00	3.89	5	30.85	30.05	2	7.80	6.06	-1	25.37	25.70
0 8 0	16.87	6.89	7	23.77	22.58	4	51.45	49.53	1	11.25	10.39
2	8.33	8.26	9	14.21	12.17	6	8.87	6.74	3	6.94	5.85
4	8.47	6.73	-8 8 1	41.09	40.61	8	0.00	2.21	5	26.04	23.82
6	0.00	2.46	-6	0.00	2.13	-9 7 2	0.00	4.06	7	22.04	21.19
8	7.09	5.28	-4	28.16	27.13	-7	14.30	9.05	-8 8 3	44.83	45.82
10	8.59	8.39	-2	30.47	34.26	-5	24.23	23.75	9	7.39	10.62
12	0.00	2.63	0	16.23	16.14	-3	19.54	17.44	-4	26.29	30.43
1 9 0	9.75	8.70	2	52.38	54.39	-1	12.91	12.36	-2	33.28	36.31
3	7.14	7.10	4	11.05	9.69	1	0.00	0.26	0	0.00	1.45
5	24.73	23.28	6	30.56	21.37	3	6.56	5.09	2	46.25	49.15
7	12.09	11.38	8	37.91	35.50	5	18.00	16.71	4	6.67	7.87
9	8.58	7.10	-7 9 1	8.88	8.50	7	16.62	15.18	6	27.77	27.96
11	12.11	9.92	-5	41.48	40.27	-8 8 2	9.55	8.66	-7 9 3	7.51	7.55
0 10 0	34.36	34.11	-3	0.00	2.01	-6	6.98	7.30	-5	21.79	24.69
2	17.48	16.67	-1	33.45	32.13	-4	0.00	2.80	-3	12.03	11.15
4	17.98	14.87	1	9.34	9.02	-2	6.71	5.93	-1	43.93	44.19
6	13.52	13.06	3	0.00	3.19	0	8.52	7.97	1	8.68	8.07
8	15.03	14.48	5	47.56	48.05	2	5.89	5.45	3	0.00	1.69
10	26.61	25.13	7	7.85	5.89	4	7.33	7.24	5	30.24	28.29
12	7.50	9.68	-6 10 1	8.12	7.11	6	6.82	5.81	-4 10 3	0.00	2.26
1 11 0	16.95	16.18	-4	7.78	6.08	-7 9 2	0.60	2.51	-2	0.00	1.09
3	37.15	37.90	-2	0.00	1.13	-5	16.33	16.69	0	16.17	16.18
5	9.93	11.33	0	15.72	15.15	-3	11.44	12.26	2	8.57	5.72
7	35.26	37.48	2	8.48	7.70	-1	21.54	20.78	-10 0 4	38.41	39.16
9	15.35	14.25	4	11.94	12.21	1	0.00	0.14	-8	14.46	15.42
11	8.31	5.42	6	8.54	6.86	3	7.26	6.64	-6	57.89	64.92
-11 1 1	0.00	3.67	-5 11 1	10.24	10.84	5	21.81	21.65	-4	22.56	22.50
-9	4.52	2.78	-3	0.00	1.51	-6 10 2	23.07	22.03	2	13.22	13.63
-7	22.70	22.03	1	0.00	3.81	-4	0.00	0.52	4	64.91	74.26
-5	16.93	15.85	3	0.00	1.58	-2	7.27	6.03	6	11.86	10.99
-3	42.40	43.42	-12 0 2	9.62	8.21	0	33.53	32.68	8	8.45	7.82
3	29.48	29.22	-10	45.25	45.34	2	23.32	21.71	-11 1 4	16.65	15.15
5	19.93	18.31	-8	10.47	10.73	4	21.11	20.97	-9	17.18	16.87
7	31.44	31.08	-6	75.25	89.01	-3 11 2	40.99	40.01	-7	12.26	12.49
9	0.00	3.15	-4	38.91	40.37	-1	0.00	2.79	-5	0.00	2.49
11	0.00	0.54	2	26.55	24.70	1	27.12	26.12	1	32.87	32.24
-12 2 1	32.23	32.21	4	67.37	74.87	-11 1 3	10.71	8.03	3	15.15	15.74
-10	17.40	16.69	6	10.99	10.54	-9	15.48	15.08	5	11.19	11.00
-8	44.07	45.57	8	6.12	5.68	-7	12.00	10.81	7	31.56	31.27
-6	0.00	0.80	10	55.33	58.07	-5	15.44	15.88	-10 2 4	0.00	2.50
-4	30.72	30.88	-11 1 2	17.42	16.09	3	15.69	13.46	-8	16.85	15.96
-2	64.36	73.25	-9	20.07	17.60	5	14.03	13.67	-6	4.20	3.33
4	3.99	1.65	-7	34.42	35.05	7	26.35	23.58	-4	18.85	19.63
6	21.50	18.87	-5	28.29	27.40	9	8.37	5.66	0	0.00	1.82
8	40.29	41.49	3	42.06	34.77	-12 2 3	17.70	16.81	2	21.97	22.43
10	19.65	19.18	5	21.83	20.80	-10	0.00	2.45	4	7.02	5.75
-11 3 1	43.33	44.40	7	39.50	40.05	-8	46.53	48.29	6	15.02	14.20
-9	25.36	26.90	9	10.01	10.18	-6	22.92	22.23	8	8.53	8.03
-7	11.64	10.57	11	10.64	10.48	-4	38.11	38.05	-11 3 4	7.30	6.55
-5	71.51	82.51	-12 2 2	7.41	7.11	-2	54.53	59.30	-9	0.00	2.09
-3	27.04	25.55	-10	7.31	6.23	4	15.52	13.48	-7	0.00	2.90
-1	67.31	79.77	-8	27.35	26.82	6	26.33	26.45	-5	8.40	7.81
1	13.85	15.65	-6	0.00	0.51	8	24.36	24.23	-3	6.93	6.15

Table 1. (Continued)

h k l	F <sub>a</sub>	F <sub>b</sub>	h k l	F <sub>a</sub>	F <sub>b</sub>	h k l	F <sub>a</sub>	F <sub>b</sub>	h k l	F <sub>a</sub>	F <sub>b</sub>
-1 3 4	10.69	10.58	-5 7 4	10.32	8.23	-5 3 5	36.22	39.50	0 8 5	9.68	9.23
1	0.00	0.33	-3	12.51	11.61	-3	13.92	14.80	-8 0 6	0.00	0.94
3	0.00	1.07	-1	20.47	20.51	-1	50.68	53.56	-6	38.54	43.23
7	0.00	2.50	1	11.63	11.11	1	12.38	11.27	2	9.53	9.77
-19 4 4	9.89	8.82	3	0.00	0.77	3	29.68	29.46	4	37.79	40.67
-8	22.08	22.04	5	15.39	13.67	5	24.56	23.47	-7 1 6	8.82	7.87
-6	21.37	21.92	-6 8 4	7.56	8.05	-8 4 5	24.52	25.21	-5	0.00	3.21
-4	19.16	18.89	-4	8.26	7.09	-6	21.42	20.47	1	23.02	23.08
-2	6.20	6.66	0	7.31	4.64	-4	13.96	14.23	3	0.00	1.05
0	15.11	15.48	2	6.63	5.41	-2	0.00	2.75	-6 2 6	8.21	7.77
2	25.29	25.43	4	6.19	4.38	0	0.00	3.51	-4	16.25	15.87
4	20.47	19.19	-5	15.23	13.50	2	20.47	19.72	0	2.36	3.20
6	13.41	14.71	-3	12.57	12.86	4	20.90	18.69	2	12.28	13.55
-9 5 4	24.99	25.57	-1	19.13	18.81	-7 5 5	8.31	8.25	-7 3 6	0.00	3.26
-7	17.42	18.22	1	0.00	1.75	-5	0.00	1.72	-5	0.00	3.40
-5	7.56	5.27	-9 1 5	16.76	16.06	-3	9.41	9.68	-3	0.00	2.03
-3	52.76	56.11	-7	0.00	4.15	-1	0.00	2.14	-1	0.00	6.99
-1	20.28	18.93	-5	0.00	2.40	1	11.42	11.01	1	0.00	2.63
1	37.40	37.25	1	20.49	19.46	3	6.76	5.19	3	6.44	4.33
3	25.39	25.18	3	4.26	4.48	5	0.00	3.73	-6 4 6	17.28	17.95
5	0.00	1.18	5	0.00	2.62	-6 6 5	13.42	13.27	-4	17.44	16.56
7	41.25	38.55	-10 2 5	0.00	1.39	-4	6.06	5.24	-2	4.45	4.62
-8 6 4	14.54	13.73	-8	39.42	42.55	-2	8.50	6.94	0	3.75	0.82
-6	43.99	44.97	-6	15.85	16.53	0	9.79	8.60	2	15.51	16.36
-4	13.52	13.05	-4	29.35	30.98	2	8.26	8.12	-5 6	9.41	8.14
-2	22.50	22.35	0	0.00	5.37	4	13.28	14.08	-3	37.89	40.25
0	30.27	30.79	2	38.16	40.99	-5 7 5	7.88	8.35	-1	10.26	10.43
2	11.53	12.07	4	17.85	17.49	-3	17.17	18.76	1	34.23	31.61
4	53.16	53.39	6	28.18	27.72	-1	26.11	27.49			
6	7.00	6.81	-9 3 5	0.00	1.33	1	15.24	14.68			
-7 7 4	0.00	1.63	-7	31.72	33.21	-2 8 5	12.56	11.20			

sphere of reflection for  $\text{CuK}\alpha$  radiation. All data were corrected for both Lorentz-polarization factors and absorption. The latter correction was necessary since the linear absorption coefficient of this compound for  $\text{MoK}\alpha$  radiation is of the same order of magnitude as those of silicates when using  $\text{CuK}\alpha$ .

Refinement was carried out using the least-squares program SFLSQ2, which utilizes the full matrix, written and kindly made available by Dr. C. T. PREWITT. Conditions of refinement included: (1) use of scattering curves for half-ionized atoms, (2) use of the weighting scheme recommended by CRUICKSHANK (1965), (3) use of correction for anomalous scattering, and (4) initial coordinates those of the isotypic compound jadeite,  $\text{NaAlSi}_2\text{O}_6$  (PREWITT and BURNHAM, 1966). The refinement rapidly converged during least-square cycles in which atom coordinates and the scale factor were varied. Final convergence was achieved by cycles of isotropic temperature-factor refinement alternating with cycles of scale-factor and coordinate refinement. Although isotropic temperature-factor values were in the

Table 2. Coordinates and isotropic temperature factors  
Standard errors in parentheses

Atom	$x$	$y$	$z$	$B$
Co(1)	0	.0923 (3)	3/4	.38 (4) $\text{\AA}^2$
Co(2)	0	.2694 (3)	1/4	.40 (4)
Ge	.0301 (1)	.0939 (1)	.2153 (3)	.28 (2)
O(1)	.1187 (10)	.0926 (10)	.1351 (21)	.20 (13)
O(2)	.3831 (10)	.2421 (11)	.3888 (21)	.49 (14)
O(3)	.3588 (11)	.0665 (12)	.9099 (23)	.55 (15)

expected range, refinement of anisotropic factors resulted in two non-positive definite matrices, and the refinement was terminated. The final structure factors are listed in Table 1 and the final atom parameters in Table 2. The conventional  $R$  value for all reflection is 9.2%, while excluding reflections with  $F_0 = 0$ , it is 7.3%.

#### Description of the $\text{CoGeO}_3$ structure

A polyhedral representation of the structure projected along  $a^*$  (which is normal to the planes of close-packing) is shown in Fig. 1. A portion of the lower plane of octahedra and the overlying plane of tetrahedra are included. Several similar diagrams of isotypic silicates are available in the literature (e.g. PREWITT and BURNHAM, 1966) and no further description is therefore given here. This diagram is included because the deviations of atom positions from those of pyroxenes is much greater than the corresponding deviations among pyroxenes alone.

The arrangement of oxygen atoms closely approximates ideal closest packing, as can be seen from the relative positions of polyhedron vertices in Fig. 1. Although only portions of three consecutive planes of oxygen atoms are shown in Fig. 1, a complete analysis shows that the stacking sequence is that of cubic closest-packing.

The isotypic pyroxenes show considerable distortions in the close-packed oxygen framework, and although it is possible to isolate close-packed oxygen planes, it is difficult, at best, to define a stacking sequence. This is partially due to the presence of the relatively large

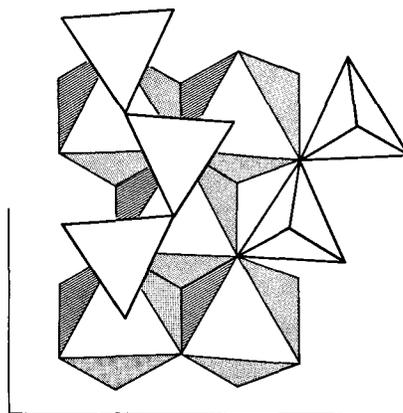


Fig. 1. Projection of a portion of the  $\text{CoGeO}_3$  structure parallel to  $a^*$ . Unit translations are shown in the lower left. Portions of three planes of oxygen atoms are included to show the oxygen closest-packing relations

cations Na or Ca in the  $M(2)$  sites of diopsidic pyroxenes (space group  $C2/c$ ), which have eight-fold coordination. The  $M(1)$  site generally contains a smaller cation (e.g. Fe or Mg) and has regular octahedral coordination. The relative degree of distortion is also partly a result of size differences in the octahedrally coordinated cations  $M(1)$  and  $M(2)$  and the tetrahedrally coordinated Si (or Al), relative to the close-packed oxygen framework. An equivalent situation in the phyllosilicates involves "misfit" of the octahedrally and tetrahedrally coordinated layers.

The occurrence of alternate stacking sequences for  $\text{CoGeO}_3$ , reported by TAUBER and KOHN, is readily explained in terms of the relatively ideal closest-packing arrangement. Anion layers with no distortion may be stacked, relative to an adjacent layer, in one of two ways which are symmetrically related. Alternatively, within equivalent closest-packed frameworks, cations may occupy alternate sets of sites. In general, distortion of the layers results in energetic non-equivalence of these related positions. The various structural modifications of  $(\text{Mg, Fe})\text{SiO}_3$  are, in part, related by stacking reversals of planes of oxygen atoms. The particular planes relative to which reversals occur are those between which octahedrally coordinated cations occur. The monoclinic and orthorhombic forms of  $\text{CoGeO}_3$  may, therefore, quite properly be called polytypes.

The idealization of closest-packing, arising in part from the relatively large size of the tetrahedrally coordinated Ge atom, results in a relatively large difference in the geometry of chains of tetrahedra relative to that in isotypic silicates. The single Ge—O—Ge angle is  $119.4^\circ$ . This is considerably different than the ideal value of  $109.5^\circ$  for closest-packing, but much nearer this value than the average for silicates in general, and pyroxenes in particular (about  $140^\circ$ ; LIEBAU, 1961). Since O(3) is the oxygen atom common to adjacent tetrahedra, the O(3)—O(3')—O(3'') angle is a parameter of chain geometry, in particular, the "straightness" of the chain. In jadeite ( $\text{NaAlSi}_2\text{O}_6$ ,  $C2/c$ , PREWITT and BURNHAM, 1966) it is  $174.7^\circ$ , and in johannsenite ( $\text{CaMnSi}_2\text{O}_6$ ,  $C2/c$ , FREED and PEACOR, 1967) it is  $163.8^\circ$ , for example. Smaller values correspond to relative rotation of tetrahedra. This angle is  $133.4^\circ$  in  $\text{CoGeO}_3$ , as reflected by the closest packing geometry, while it would be  $120^\circ$  for ideal closest packing. Since the Si—O bond is at least partly ionic, unless the Ge and Si bonds are quite different, the chain geometry thus appears to be controlled principally by space-filling requirements with special regard to closest packing, as in phyllosilicates.

Interatomic distances and angles, with standard errors, are listed in Table 3 and 4. Values were computed using the program ORFFE written by BUSING and LEVY, utilizing the final least-squares variance-covariance matrix and lattice-parameter standard errors. Values for  $M(1)$  and  $M(2)$ , and the coordination polyhedra diagrammed in Fig. 1,

Table 3. *Cation-anion interatomic distances*  
Standard errors in parentheses

Ge—O(1)	1.735 (10) Å	Co(1)—2 O(1)	2.101 (11) Å
O(2)	1.718 (11)	2 O(1')	2.173 (10)
O(3)	1.795 (12)	2 O(2)	2.085 (11)
O(3')	1.790 (11)	Average	2.120
Average	1.759	Co(2)—2 O(1)	2.117 (10) Å
		2 O(2)	1.993 (11)
		2 O(3)	2.279 (11)
		Average	2.130

Table 4. *Interatomic distances and interatomic angles*  
Standard errors in parentheses

Ge tetrahedron		
O(1)—O(2)	2.97 (1) Å	118.6 (4)°
O(1)—O(3)	2.81 (2)	105.4 (5)
O(1)—O(3')	2.87 (1)	108.8 (5)
O(2)—O(3)	2.91 (2)	112.1 (5)
O(2)—O(3')	2.80 (2)	105.7 (5)
O(3)—O(3')	2.85 (1)	105.5 (4)
Co(1) octahedron		
2 O(1)—O(1')	2.97 (2)	87.9 (4)
2 O(1)—O(1'')	3.08 (1)	92.3 (4)
2 O(1)—O(2)	2.82 (1)	84.6 (4)
2 O(1)—O(2')	3.09 (1)	95.3 (4)
O(1')—O(1'')	2.79 (2)	79.8 (5)
2 O(1')—O(2)	3.16 (1)	95.9 (4)
O(2)—O(2')	2.91 (2)	88.5 (6)
Co(2) octahedron		
O(1)—O(1')	2.79 (2)	82.3 (5)
2 O(1)—O(2)	2.82 (1)	86.4 (4)
2 O(1)—O(2')	2.88 (1)	89.1 (4)
2 O(1)—O(3)	3.09 (1)	89.4 (4)
2 O(2)—O(3)	2.97 (1)	88.0 (4)
2 O(2)—O(3')	3.18 (2)	95.9 (4)
O(3)—O(3')	3.46 (2)	98.9 (6)

show that the coordination polyhedra for both of these atoms are regular octahedra. Minor deviations from regularity are readily seen to be a result of edge sharing between octahedra. The Ge tetrahedron shows the usual distortions associated with electrostatic valency differences, the two Ge—O(3) distances (1.79 Å) being significantly larger than those for Ge—O(1) and Ge—O(2). In addition, all distances for Ge or Co to O(1) are smaller than those for these metals to O(2) and O(3), and all those for O(2) smaller than those for O(3). O(1) is coordinated to one Ge and two Co atoms, O(2) to one Ge and three Co atoms, and O(3) to two Ge and one Co atom. Thus the structure exhibits those general features which reflect ionic bonding. Despite the fact that the geometry of the chain of tetrahedra in  $\text{CoGeO}_3$  shows considerable differences from those in the isotypic pyroxenes, the geometries of the individual tetrahedra are quite similar. The relative magnitudes of the Si—O distances are similar to those listed above, and the interatomic angles show equivalent similarities. In jadeite, johannsenite and Al-augite (PEACOR, 1967) the O(3)—Si—O(3') angle is one of the smallest ( $104.7$  to  $106.3^\circ$ ,  $105.5^\circ$  in  $\text{CoGeO}_3$ ) and the O(1)—Si—O(2) angle the largest ( $116.8$  to  $118.5$ ;  $118.6^\circ$  in  $\text{CoGeO}_3$ ). Similar correlations occur for other angles and distances, reflecting the similarity in bonding mechanisms for Si and Ge.

Dr. J. A. KOHN of the U.S. Army Electronics Laboratories kindly made available the synthetic  $\text{CoGeO}_3$  used in this study. Support for this work was provided by the U.S. Army Electronics Command Contract No. DA-28-043-AMC-01338(E).

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