

Fig. 2. Relative orientations of the twin components at the twin boundary. The twin boundary is shown by the broken line. The fractional a coordinates are shown as percentages of the a length.

sites in the above compounds are all more distorted than those at the Li(1) sites.

Fig. 2 shows a probable model for twinning. The twin symmetry relating the two twin components is 2_1 parallel to a , by which the arrangements of the O, Si and Li(2) atoms remain almost unchanged since originally they have pseudo 2_1 symmetry. The positions

of the Zn and Li(1) atoms are also approximately related to each other by 2_1 symmetry, and further Zn²⁺ and Li⁺ ions in fourfold coordination have nearly equal effective ionic radii (Whittaker & Muntus, 1970). Therefore the ZnO₄ and Li(1)O₄ tetrahedra at the twin boundary do not suffer significant distortions.

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Structure of Cobalt Dilithium Silicate β_{II} -Li₂CoSiO₄

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Abstract. Li₂CoSiO₄, orthorhombic, $Pbn2_1$, $a = 6.253$ (5), $b = 10.685$ (9), $c = 4.929$ (9) Å, $Z = 4$, $D_x = 3.33$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 5.50$ mm⁻¹. The structure of the β_{II} modification has been solved by the heavy-atom method and refined by the least-squares method to $R = 0.044$ for 789 observed reflections. The Co²⁺ ion is coordinated tetrahedrally by O atoms. The

Co–O distances range from 1.966 (5) to 1.983 (6) Å with a mean of 1.975 Å.

Introduction. Crystals of β_{II} -Li₂CoSiO₄ were grown from a LiCl flux (Setoguchi, 1979). They were granular in shape with diameters ranging from 0.3 to 2 mm. Weissenberg photographs of all 17 crystals examined

showed that the reflections with k odd were significantly broadened along b^* , and that the degree of diffuseness varied from crystal to crystal. A crystal showing minimum (very small) elongation of diffuse reflections was selected for the data collection and ground to a sphere of diameter 0.2 mm. Systematic absences of the type $h0l$ for $h + l$ odd and $0kl$ for k odd indicated that the space group is $Pbnm$ or $Pbn2_1$. Cell dimensions and intensity data were measured on a Rigaku four-circle diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation. The cell dimensions were determined by a least-squares fit to the setting angles of 24 reflections. A total of 2798 reflections ($2\theta < 70^\circ$) were measured with the ω - 2θ scan technique, a scan range of $(1.2 + 0.5 \tan \theta)^\circ$ and a receiving slit with an aperture of 3.5×3.5 mm. The intensities were averaged to yield a set of 789 independent values after L_p corrections. No correction for absorption was made.

The space group $Pbn2_1$ was chosen for solving the structure. A three-dimensional Patterson map revealed positions of the Co atoms, and Si and O atoms were located from subsequent Fourier maps. The atomic parameters were refined to $R = 0.09$ by the block-diagonal least-squares method (HBL5 V; Ashida, 1973) with isotropic temperature factors and unit weights. A subsequent difference map revealed the positions of the remaining Li atoms. Further refinements were continued for all atoms to $R = 0.06$. Atomic scattering factors for Co^{2+} , Si, Li^+ and O^- were taken from *International Tables for X-ray Crystallography* (1974).

At this stage it was found that Li(1) has a very small temperature factor ($B = 0.2 \text{ \AA}^2$) compared with that of Li(2) ($B = 1.4 \text{ \AA}^2$). Therefore we recalculated a difference Fourier synthesis and found a remarkably large peak density at the Li(1) position. As shown in a separate paper (Takaki & Yamaguchi, 1979), this large peak height was attributed to the superposition of a ghost due to truncation errors in the integrated intensity measurements of the diffuse reflections. Corrections of observed structure factors for reflections with k odd were made by multiplying by $1/\epsilon$, where ϵ^2 is the ratio of an observed intensity recorded through the receiving slit to the total intensity of the diffuse reflection.

According to Takaki & Yamaguchi (1979), to a first approximation the value of ϵ can be taken as constant for reflections with given k (k odd), and it slightly increases with increasing k . In this study, however, we tentatively assumed the value of ϵ to be constant for all diffuse reflections. Least-squares calculations were then carried out for various values of ϵ , and a plausible value of 0.92 was chosen on the assumption that the temperature factor for the Li(1) atom is approximately equal to that for the Li(2) atom. A subsequent refinement with isotropic temperature factors for the Li atoms and anisotropic temperature factors for the Co, Si and O atoms gave the final R of 0.044. Final positional parameters are given in Table 1.* All computations were made on an ACOS System 800 computer of the Computation Center of Osaka University.

Discussion. Fig. 1 shows the structure viewed along c . It is based on a distorted hexagonal-close-packing arrangement of O atoms with layers stacked parallel to (001). The cations occupy half the available tetrahedral sites and are distributed over the sites on one side of the O layers; three of the four O atoms forming a cation-oxygen tetrahedron (MO_4) are in an O layer, and all pyramids of the MO_4 tetrahedra have the same orientations with respect to the layer. The SiO_4 and Li(2)O_4 tetrahedral pairs share corners to form a chain along a , and these chains are held together through other corners, thus forming puckered layers parallel to (010). In the same way, the CoO_4 and Li(1)O_4 tetrahedral pairs form a chain along a , and these chains also form puckered layers parallel to (010). These two kinds of layers are held together through common corners to

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34641 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates with their e.s.d.'s

	x	y	z
Co	0.4930 (1)	0.1648 (1)	0.2544 (5)
Si	0.2492 (2)	0.4136 (1)	0.2611 (6)
Li(1)	-0.0094 (25)	0.1602 (14)	0.2897 (43)
Li(2)	0.7394 (18)	0.4244 (11)	0.2553 (52)
O(1)	0.2489 (8)	0.4105 (4)	0.5896 (9)
O(2)	0.2533 (7)	0.5578 (4)	0.1525 (10)
O(3)	0.0309 (7)	0.3410 (4)	0.1521 (10)
O(4)	0.4644 (7)	0.3420 (4)	0.1481 (10)

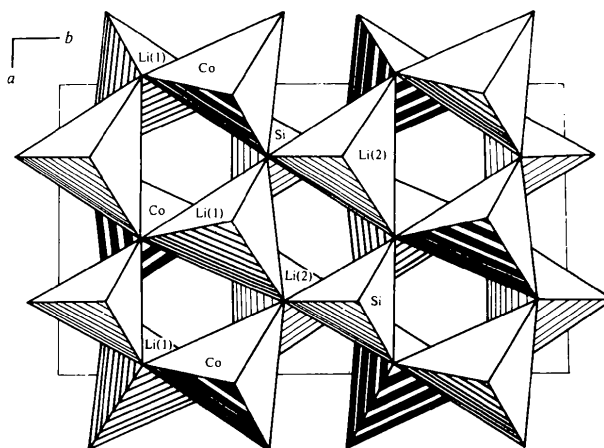


Fig. 1. The crystal structure viewed along c .

Table 2. Selected bond distances (Å) and angles (°)

SiO ₄ tetrahedron		O-M-O angles	
Si-O(1)	1.619 (6)	O(1)-O(2)	2.668 (7)
-O(2)	1.632 (6)	-O(3)	2.657 (7)
-O(3)	1.659 (6)	-O(4)	2.662 (7)
-O(4)	1.645 (6)	O(2)-O(3)	2.702 (7)
		-O(4)	2.656 (7)
		O(3)-O(4)	2.710 (7)
CoO ₄ tetrahedron			
Co-O(1)	1.966 (5)	O(1)-O(2)	3.173 (7)
-O(2)	1.983 (6)	-O(3)	3.178 (7)
-O(3)	1.976 (6)	-O(4)	3.245 (7)
-O(4)	1.973 (6)	O(2)-O(3)	3.224 (7)
		-O(4)	3.328 (7)
		O(3)-O(4)	3.189 (7)
Li(1)O ₄ tetrahedron			
Li(1)-O(1)	1.96 (4)	O(1)-O(2)	3.146 (7)
-O(2)	2.05 (4)	-O(3)	3.229 (7)
-O(3)	2.06 (4)	-O(4)	3.151 (7)
-O(4)	1.78 (4)	O(2)-O(3)	3.313 (7)
		-O(4)	3.198 (7)
		O(3)-O(4)	3.158 (7)
Li(2)O ₄ tetrahedron			
Li(2)-O(1)	2.01 (2)	O(1)-O(2)	3.319 (7)
-O(2)	1.97 (2)	-O(3)	3.212 (7)
-O(3)	2.09 (2)	-O(4)	3.224 (7)
-O(4)	2.00 (2)	O(2)-O(3)	3.227 (7)
		-O(4)	3.231 (7)
		O(3)-O(4)	3.542 (7)

form a three-dimensional framework. This structure is isotopic with that of the low-temperature form of Li₃PO₄ (Keffler, Mighell, Mauer, Swanson & Block, 1967) and essentially the same as that of γ_{11} -Li₂ZnSiO₄ (Yamaguchi, Akatsuka & Setoguchi, 1979) with the exception that the orientations of the SiO₄ and Li(2)O₄ tetrahedra in a chain are antiparallel to each other, giving shared edges between each of the Li(2)O₄-ZnO₄ and Li(2)O₄-Li(1)O₄ tetrahedral pairs.

Selected bond distances and angles are listed in Table 2. The SiO₄ tetrahedra are quite regular with a mean Si-O distance of 1.639 Å. The LiO₄ tetrahedra show marked departures from a regular tetrahedron. The Li-O distances range from 1.78 (4) to 2.06 (4) Å for Li(1) and from 1.97 (2) to 2.09 (2) Å for Li(2) with mean values of 1.96 and 2.02 Å respectively. These mean values may be compared with those of 1.96 and 2.01 Å in Li₃PO₄ and 1.97 and 2.01 Å in γ_{11} -

Li₂ZnSiO₄ for the corresponding Li(1) and Li(2) tetrahedral sites. Note that the coordination tetrahedra at the Li(2) sites in the above compounds are all more distorted than those at the Li(1) sites.

The Co²⁺ ions are coordinated tetrahedrally by O atoms. The Co-O distances range from 1.966 (5) to 1.983 (6) Å with a mean of 1.975 Å. The angles vary from 106.9 (2) to 114.6 (2)°. The O-O distances along tetrahedral edges range from 3.173 (7) to 3.328 (7) Å. It is of interest to compare the above tetrahedron with that in Co₂Mn₃O₈ (Riou & Lecerf, 1975) which is, with the exception of the spinel structure (Co₃O₄; Knop, Reid, Starno & Nakagawa, 1968), the only case where detailed dimensions for the coordination tetrahedron about Co²⁺ have been reported. The values for Co₂Mn₃O₈ are: Co-O distances ranging from 1.91 to 2.02 Å with a mean of 1.95 Å, angles from 106.6 to 112.5° and O-O distances from 3.15 to 3.27 Å. Comparison of the above two sets of values suggests that the coordination tetrahedra about Co²⁺ in the two compounds are very similar to each other. In addition the variances in tetrahedral angles [$\sigma_{\theta}^2 = \sum_i (\theta_i - 109.47)^2/5$ (Robinson, Gibbs & Ribbe, 1971)] are 8.52 and 6.13 for β_{11} -Li₂CoSiO₄ and Co₂Mn₃O₈ respectively, showing that the CoO₄ tetrahedra in both compounds are slightly distorted.

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