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THE POLYMORPHISM OF CORDIERITE
I: THE CRYSTAL STRUCTURE OF LOW CORDIERITE

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ABSTRACT

Low cordierite [$(Mg, Fe, Mn)_2Al_4Si_5O_{18}nH_2O$ plus minor amounts of alkaline earth and alkali metal atoms; *Cccm*; *a* 17.083, $\hat{\sigma}(a)$ 0.004; *b* 9.738, $\hat{\sigma}(b)$ 0.003; *c* 9.335, $\hat{\sigma}(c)$ 0.002A; Δ (distortion index) $= 0.24°$], refined by 3D least-squares and Fourier methods, has an ordered framework structure in which Al- and Si-rich tetrahedra are in perfect alternation in all directions except for two Si-rich tetrahedra that share a common oxygen atom in the six-membered ring. The Si- and Al-rich tetrahedra have mean T-O bond lengths of 1.614 and 1.748A, respectively. The ordered nature of the tetrahedral atoms in low cordeirite shows that any consideration of the disorder-order transformation must take into account the framework with its four Al- and five Si-atoms. Cordierite should be classified with the framework rather than with the ring silicates. Weak, broad peaks of electron density centered at $(00\frac{1}{4})$ suggest that the channel atoms (molecular water, alkaline earth and alkali metal atoms) are randomly distributed at the periphery of the large cavity rather than fixed at its center.

INTRODUCTION

The polymorphic transformation of cordierite, $Al_3(Me)_2\ (AlSi_5)O_{18}nH_2O$ where $Me = (Mg,Fe,Mn)$, has been assumed by previous investigators to be related to disorder-order of one Al- and five Si-cations in a six-membered ring of tetrahedra (Miyashiro *et al.*, 1955). The nature of this transformation has been examined by several workers (Miyashiro, 1957; Iiyama, 1960; Schreyer and Schairer, 1962; Schreyer and Yoder, 1964) whose researches indicate that the mineral can exist in all structurally intermediate states ranging from high cordierite (a modification with hexagonal geometry and a distortion index of 0°) to low cordierite (an orthorhombic modification with a distortion index greater than 0.20°). It has been generally accepted, but not proven, that the one Al- and five Si-cations in the ring are ordered in low cordierite, disordered in high cordierite and of intermediate order in the intermediate states.

Figure 1 shows the crystal structure of cordierite viewed along the *z*-axis (Bystrom, 1942). The emphasis that this drawing places on the six-membered rings has misled workers in the past: the Al-containing tetrahedra that join these rings into a three-dimensional framework have been neglected and the mineral has been classified with the ring silicates. On the other hand, Zoltai (1960) has argued that cordierite is more logically classified with the framework silicates along with feldspar, zeolite, scapolite, etc. If this is correct, then the prevailing interpretation of the

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polymorphic transformation is unsatisfactory as it fails to embrace the Al-cations outside the rings in the order-disorder transformation. A more reasonable interpretation and the one borne out by the present investigation is to take these Al-cations into account and to consider the order-disorder transformation as involving four Al- and five Si-cations in a tetrahedral framework of $Al_4Si_5O_{18}$ composition.

The intention of the present series of papers is to provide data on the atomic parameters of the different structural states (low, intermediate state and high cordierite) in order to clarify the nature of the proposed disorder-order transformation and to provide answers to such pertinent questions as:

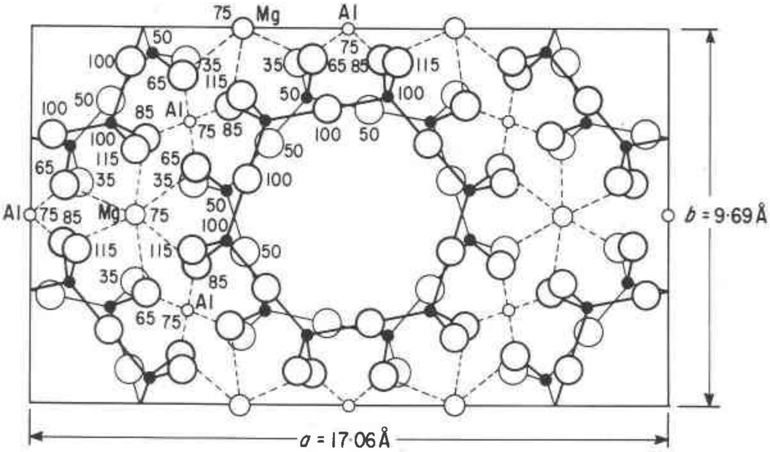


FIG. 1. Structure of cordierite with its six-member ring of tetrahedra viewed down the z-axis, after Bystrom, 1942.

(1) Is the distortion index Δ a reliable parameter for characterizing the polymorphs or the polymorphic transformation, or is it related to some other property of the mineral such as the chemistry? (2) Does the polymorphic transformation involve cations other than aluminum and silicon? (3) Is high cordierite truly hexagonal or is it dimensionally hexagonal but with a lower crystallographic symmetry? (4) Is the space group symmetry of intermediate state and low cordierite *Cccm* or are there cordierites with lower symmetry? and (5) How is the structural state related to such physical properties as the optic angle, birefringence, cell parameters, etc.?

The present paper in the series describes an analysis of the crystal structure of low cordierite $\Delta = 0.24$ (cf. Gibbs *et al.*, 1963); the second paper will describe similar analyses of "intermediate state" ($\Delta = 0.12$) and "high cordierite" (*cf.* Meagher and Gibbs, 1965) and the third and final paper in the series will examine the polymorphism and the polymorphic transformation of cordierite in light of results provided by papers I and II.

HISTORICAL BACKGROUND

Since Rankin and Merwin (1918) first recognized cordierite in the ternary system $MgO\text{-}Al_2O_3\text{-}SiO_2$ and discovered its unusually low thermal expansion, considerable research has been devoted to characterizing the phase relationships and the polymorphism of the mineral. Gossner and Mussgnug (1928) in the first *x*-ray crystallographic study of the mineral concluded that it is homotypic with beryl $Be_3{}^{IV}Al_2{}^{VI}Si_6{}^{IV}O_{18}$, with the structural formula $(Me_2Al)^{IV}Al_2{}^{VI}(AlSi_5)^{IV}O_{18}$. After a consideration of the ionic radii, however, Bragg (1930) suggested it was more plausible to assign the Al- and the Me-cations to the four- and the six-fold sites, respectively; he accordingly wrote the structural formula as $Al_3{}^{IV}Me_2{}^{VI}(Si_5Al)^{IV}O_{18}$. Nevertheless, this is an ideal formula and Folinsbee (1941) has since found that the majority of chemical analyses recorded for cordierite reveal the presence of significant but variable amounts of alkali metal (Li, Na, K, Rb, Cs) ions. Since at least three of these ions (K, Rb, Cs) are too large to be accommodated in the four- and six-coordinated sites, it was suggested that they are located within the large channels that parallel the *z* axis.

The first qualitative structural analyses of cordierite were carried out independently by Takane and Takeuchi (1936) and by Byström (1941). They confirmed the homotypic relationship with beryl, assigned a random distribution of one Al- and five Si-atoms to the six-membered ring and determined the space group symmetry Cccm. However, in some of the rotation photographs exposed by Takane and Takeuchi, weak reflections of the type h0l with *h* even and *l* odd were detected in violation of the diffraction conditions of space group Cccm. This evidence led Miyashiro *et al.* (1955) to consider the space group as uncertain.

Later, in an investigation of the system $MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$, Yoder (1952) discovered that cordierite synthesized above 830° C. has significantly lower refractive indices than that synthesized below 830° C. This evidence led Karkhanavala and Hummel (1953) to propose that the two forms synthesized by Yoder were polymorphs related by a high-low inversion similar to that encountered in high and low sanidine. A year later Miyashiro *et al.* (1955), published results of an extensive powder *x*-ray diffraction and petrographic study of both natural and synthetic specimens in an attempt to relate the physical properties and the paragenesis of the mineral. Miyashiro (1957) concluded from this investigation that cordierite could exist in all structurally intermediate states ranging between disordered and ordered end-members. He assumed, on the basis of the earlier structural analyses, that the tetrahedral atoms in the six-membered rings were ordered and disordered, respectively, in the two end-members and that they were partly ordered in intermediate members. The structural states were characterized and named by Miyashiro on the basis of the distortion index

$$\Delta = 2\theta_{131} - (2\theta_{511} + 2\theta_{421})/2$$

and the optical properties (Table 1). The distortion index relates the separation of three peaks in the powder diffraction pattern recorded with CuKα radiation to the deviation from the hexagonal geometry of the disordered end-member (Iiyama, 1956). The distinction made between the high and the low forms (Table 1) is based on optical data with the low forms possessing, in general, higher refractive indices and being stable with respect to the high form at temperatures somewhat below 830° C. (Iiyama, 1958). Deer *et al.* (1962) have recently suggested that this high-low transition may be related to ordering of the Al_3Me_2 ions.

TABLE 1. NOMENCLATURE OF THE STRUCTURAL STATES OF CORDIERITE
[Modified after Miyashiro *et al.* (1955) and Miyashiro (1957)]

Mineral Name	Distortion Index	Structural State	Refractive Indices	Occurrence
High Indialite	$\Delta=0$	Disordered	$\epsilon 1.524$ $\omega 1.528$	In fused sediments; products synthesized above 830° C.
Low Indialite			$\epsilon 1.537$ $\omega 1.541$	Products synthesized below 830° C.
High Subdistortional Cordierite	$0.29>\Delta>0$	Intermediate Order	$\alpha 1.53$–1.54 $\gamma 1.54$–1.55	Volcanic rocks, fused sediments and synthetic cordierite bodies
Low Subdistortional Cordierite			$\alpha 1.52$–1.56 $\gamma 1.53$–1.57	Metamorphic rocks, pegmatites and quartz veins
High Perdistortional Cordierite	$\Delta=0.29$–0.31	Ordered	$\alpha 1.53$–1.54 $\gamma 1.54$–1.55	Blast furnace linings; xenoliths in volcanic rocks
Low Perdistortional Cordierite			$\alpha 1.52$–1.56 $\gamma 1.53$–1.57	Not yet found in nature

In detailed studies of the phase relations and the thermal behavior of dry and water-bearing varieties of synthetic cordierite, Schreyer and Schairer (1961) and Schreyer and Yoder (1964) have concluded that the alleged high-low transition proposed by Karkhanavala and Hummel (1953) and adopted by Miyashiro (1957) is nonpolymorphic and due to variable amounts of water incorporated in the structure. Utilizing a plot of the mean refractive index versus the water content of cordierites of identical Δ-values, Schreyer and Yoder were able to show that the differences in refractive indices used to characterize the high and the low forms (Table 1) were due to compositional rather than polymorphic variations.

Because the mean refractive index reflects both the compositional and the structural variations, Schreyer and Schairer have found it convenient to subdivide the structural states of cordierite on the basis of the distortion index alone (Fig. 2).

Sugiura (1959) and Iiyama (1960) have examined the origin and the nature of water in the mineral and believe that it exists both as molecular H_2O in the channels and as tetrahedral $(OH)_4$ groups replacing some of the tetrahedral $(Si,Al)O_4$ groups in the structure. Smith and Schreyer (1962) have confirmed the existence of water in the channels and Eberhard (1962) has found evidence for the incorporation of $(OH)_4$ groups in Mn-cordierite synthesized at low temperatures. Smith and Schreyer were unable to infer from their data whether tetrahedral $(OH)_4$ groups occur in Mg-cordierite, however, they point out tnat it is possible that even the most refined single crystal *x*-ray techniques would not permit a detection of a small number of hydroxyl groups in the framework. More recently, however, infrared tracing of natural and synthetic hydrous specimens have led Schreyer and Yoder (1964) to conclude that essentially all the water in Mg-cordierite is of a molecular nature. They designated the water-bearing varieties as hydrous cordierites to distinguish them from the dry or anhydrous cordierites. In general, on the basis of their indices of refraction, Schreyer and Yoder's group of "hydrous cordierites" corresponds to Miyashiro's group of "low cordierites."

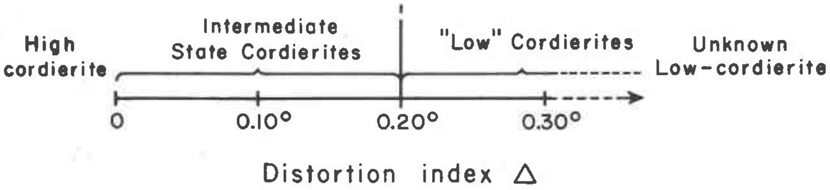


FIG. 2. Relations between the structural states of cordierite as a function of the distortion index Δ (after Schreyer and Schairer, 1961).

Finally, with the discovery that many pegmatitic cordierites are enriched in BeO, Newton (unpublished) has indicated that the small distortion indices ($\Delta \sim 0.1°$) characteristically recorded for such specimens may result from their BeO content (~0.5 weight per cent). Other data suggest that the observed variation of the distortion index is not dependent entirely on order-disorder of (Al, Si) but depends on (Me, Al) order-disorder as well.

EXPERIMENTAL DETAILS

The cordierite specimen selected for the structural analysis was kindly supplied by Dr. W. Schreyer who collected it from a pegmatitic quartz-plagioclase vein near Guilford, Connecticut (Schreyer, 1959). The material, distinctly pleochroic from clear to violet in hand specimen and of gem quality, gave a distortion index of 0.24° indicating an ordered structural state (Schreyer and Schairer, 1962). Table 2 gives the physical and optical properties and the chemical analysis of the specimen.

A fragment measuring 0.16×0.18×0.20 mm was selected from a crushed portion of the specimen. Particular care was devoted to the examination of the diffraction symmetry of the crystal since Takane and Takeuchi (1936) had observed weak reflections which violated the diffraction conditions of *Cccm*. Figure 3 is an *hk*0 precession photograph of the Guilford cordierite. It is evident from the quasihexagonal distribution of spots that it would be easy to misorient the crystal about the [130] (pseudo-*a*) or the [110] (pseudo-*b*) axes if care were not taken. When the crystal was deliberately oriented for rotation about the pseudo-*b* axis the Weissenberg photographs, in addition to being very similar to those obtained about the true *b*-axis, showed weak reflections of the type (*h0l*, *h* even, *l* odd) described by Takane and Takeuchi. However, when the crystal was reoriented about the true axes no reflections were observed which violate the diffraction conditions of the space group. An examination of two other cordierites, one from Kragerö, Norway and one from Orijärvi, Finland, gave similar results. It was concluded, therefore, that the probable space group symmetry of low cordierite is *Cccm* and that the alleged space group violations result from a registry of diffraction data about a pseudo-axis.

TABLE 2. PHYSICAL AND OPTICAL PROPERTIES AND CHEMICAL ANALYSIS OF THE GUILFORD CORDIERITE

Specific gravity		2.632	SiO_2	48.1 wt. %
			Al_2O_3	33.5
	α	1.539	FeO	5.3
Refractive indices	β	1.546	MgO	10.0
	γ	1.549	MnO	0.2
			Li_2O	0.3
Birefringence	$(\gamma\text{-}\alpha)$	0.010	Na_2O	0.5
			CaO	0.3
			K_2O	0.1
			Loss	1.4
			Total	99.7 wt. %

Unit cell content: $4[(Li_{0.12}Na_{0.10}Ca_{0.03}K_{0.02})\ (Mg_{1.53}Fe_{0.45}Mn_{0.02})\ (Si_{4.93}Al_{4.04})O_{18.07}\ (H_2O)_{0.48}]$.

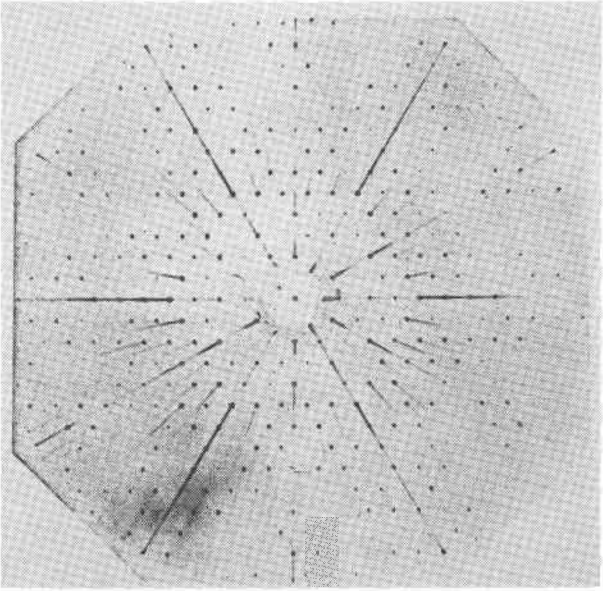


FIG. 3. An hk0 precession photograph of low cordierite, Mo*Ka* radiation. [130] (pseudo-*a*) is at six o'clock in the photograph; [110] (pseudo-*b*) at three o'clock; [100] (true *a*) at five o'clock and [010] (true *b*) at two o'clock.

The cell edges of the crystal a 17.083, $\hat{\sigma}(a)$ 0.004; b 9.738, $\hat{\sigma}(b)$ 0.003 and c 9.335, $\hat{\sigma}(c)$ 0.002 Å were obtained from a least-square analysis of data recorded with a precision, back-reflection, Weissenberg camera using a multiple radiation *x*-ray tube. The chemical formula, normalized on the

TABLE 3a. STARTING POSITIONAL PARAMETERS AFTER BYSTROM (1942) AS MODIFIED BY SMITH AND SCHREYER (1962)

Atom	x	y	z	B
T_1	1/4	1/4	0.250	0.4
T_2	0	1/2	1/4	0.4
T_3	0.190	0.063	0	0.4
T_4	0.126	−0.255	0	0.4
T_5	0.062	0.316	0	0.4
Me	0.333	0	1/4	0.4
O1	0.240	−0.090	0.350	0.6
O2	0.070	−0.405	0.350	0.6
O3	−0.167	−0.315	0.350	0.6
O4	0.032	−0.284	0	0.6
O5	0.126	0.189	0	0.6
O6	0.158	−0.095	0	0.6
Channel atoms	0	0	1/4	2.0

basis of the measured cell volume and the specific gravity, is given in Table 2 and each unit cell contains on the average four such units. The specific gravity was measured using the sink-float method described by Midgley (1951).

The intensity measurement was made with an equi-inclination, Weissenberg, scintillation counter diffractometer using monochromatized Mo$K\alpha$ radiation. The peaks of about 690 non-equivalent reflections, traced out on a strip chart and integrated with a planimeter, were corrected on the IBM 1620 computer for absorption (assuming a spherical crystal) and for the Lorentz-polarization factor and converted to unscaled $|F_{obs}|$. No correction was made for the polarizing effect (about 1% in intensities) of the bent quartz crystal monochromator. The resulting unscaled structural amplitudes were then submitted to a least-squares refinement (Busing and Levy, 1959) on the IBM 704 computer at the Argonne National Laboratories, using unitary weights and the atomic coordinates published by Bystrom (1941) and modified by Smith and Schreyer (1961) (Table 3a). A scattering curve of $4/9f_{Al}+5/9f_{Si}$ was initially used for all tetrahedral atoms assuming a random distribution of Al,Si. The scattering factor functions used in this and later calculations were those of Berghius *et al.* (1955) for Al^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Si^{4+} and those of Suzuki (1960) for O^{-2}, each adjusted in an arbitrary way for half-ionization.

TABLE 3b. INITIAL REFINEMENT USING UNITARY WEIGHTING SCHEME

Atom	x	y	z	B
T_1	1/4	1/4	0.249(5)[1]	0.13(8)
T_2	0	1/2	1/4	0.01(11)
T_3	0.1922(2)	0.0780(6)	0	−0.02(6)
T_4	0.1352(2)	−0.2367(6)	0	0.43(10)
T_5	0.0504(2)	0.3085(6)	0	0.88(11)
Me	0.3370(2)	0	1/4	0.28(8)
O1	0.2465(4)	−0.1011(10)	0.3584(8)	1.05(18)
O2	0.0610(3)	−0.4166(9)	0.3497(7)	0.10(14)
O3	−0.1730(3)	−0.3065(9)	0.3588(7)	0.23(14)
O4	0.0433(5)	−0.2446(13)	0	−0.23(19)
O5	0.1226(5)	0.1886(13)	0	−0.42(17)
O6	0.1628(7)	−0.0798(15)	0	1.39(25)
Channel atoms		Not included in refinement		

[1] Estimated standard deviations are given in parentheses.

Following four iterations of refinement in which the scale factor and the individual positional and thermal parameters were varied, a set of atomic parameters (Table 3b) was obtained from which the dimensions of individual tetrahedra were calculated. Using the mean T-O bond length for each tetrahedraon and a curve prepared by Smith and Bailey (1963), the Al,Si occupancy of each site was estimated. These results indicate that tetrahedra T_2, T_3 and T_4 are Si-rich and T_1 and T_5 are Al-rich (Gibbs *et al.*, 1963). In addition, $\rho(xyz)$ and $\Delta\rho(xyz)$ maps were calculated at 0.1A intervals along *z* in an attempt to learn the spatial distribution of the molecular water, the alkaline earth and the alkali metal ions (Table 2) in the channels. These syntheses were summed on the IBM 1620 computer using the phases calculated in the fourth cycle of the least-squares refinement, 517 observed structural amplitudes and the van der Helm (1961) 3D Fourier summation program. The $\rho(xyz)$ maps gave two broad low peaks, one at the center of the ring (000) and one at the center of the cavity at $(00\frac{1}{4})$. The $\Delta\rho(xyz)$ maps corroborated the peak at the center of the cavity; however, the other was revealed to be a Fourier ripple.

TABLE 3c. FINAL REFINEMENT USING CRUICKSHANK'S WEIGHTING SCHEME (1965)

Atom	x	y	z	B
T_1	1/4	1/4	0.2500(3)[1]	0.22(5)
T_2	0	1/2	1/4	0.20(6)
T_3	0.1923(1)	0.0781(3)	0	0.26(5)
T_4	0.1351(1)	−0.2372(4)	0	0.23(5)
T_5	0.0506(1)	0.3084(4)	0	0.25(5)
Me	0.3374(1)	0	1/4	0.23(5)
O1	0.2466(2)	−0.1040(6)	0.3591(5)	0.27(8)
O2	0.0616(2)	−0.4167(6)	0.3494(5)	0.24(8)
O3	−0.1730(2)	−0.3091(6)	0.3583(5)	0.31(8)
O4	0.0434(3)	−0.2453(8)	0	0.25(11)
O5	0.1224(4)	0.1848(9)	0	0.65(12)
O6	0.1639(4)	−0.0788(9)	0	0.54(11)
Channel atoms	0	0	1/4	7.13(97)

[1] Estimated standard deviations are given in parentheses.

The peak at the cavity center may be ascribed to both the molecular water and the alkaline earth and alkali metal atoms. The broad nature of the peak suggests that the channel atoms are randomly distributed at the periphery of the large cavity rather than fixed at its center. A similar conclusion was reached on the position of the water in hydrous cordierite by Smith and Schreyer (1962). No evidence was found to support the conclusion that some of the water occurs in the form of hydroxyl groups replacing oxygen anions in the framework.

The least-squares refinement was completed on the IBM 7074 computer at The Pennsylvania State University using a modified version of

TABLE 4. T-O AND Me-O BOND LENGTHS AND BOND ANGLES FOR LOW CORDIERITE

T-O bonds (A)			Bond angles (degrees)		
		tetrahedron about T_1			
T_1-O1(1)	[2][1]	1.749(5)[2]	O1(1)-T_1-O1(3)	[1]	108.8(3)
T_1-O3(1)	[2]	1.756(5)	O1(3)-T_1-O3(4)	[2]	95.4(2)
			O1(1)-T_1-O3(4)	[2]	125.2(2)
			O3(3)-T_1-O3(4)	[1]	109.8(2)
average		1.753(4)	average		110.0(1)
		tetrahedron about T_2			
T_2-O2(1)	[4]	1.621(5)	O2(3)-T_2-O2(2)	[2]	99.0(9)
			O2(3)-T_2-O2(6)	[2]	119.9(7)
			O2(3)-T_2-O2(7)	[2]	110.2(8)
average		1.621(5)	average		109.7(5)
		tetrahedron about T_3			
T_3-O1(1)	[2]	1.630(4)	O1(1)-T_3-O1(2)	[1]	107.4(5)
T_3-O5(1)	[1]	1.582(8)	O1(1)-T_3-O5(1)	[2]	109.1(3)
T_3-O6(1)	[1]	1.603(9)	O5(1)-T_3-O6(1)	[1]	113.5(4)
			O1(1)-T_3-O6(1)	[2]	108.6(3)
average		1.611(4)	average		109.4(2)
		tetrahedron about T_4			
T_4-O3(1)	[2]	1.630(5)	O3(1)-T_4-O3(2)	[1]	108.5(6)
T_4-O4(1)	[1]	1.568(6)	O3(1)-T_4-O4(1)	[2]	112.0(3)
T_4-O6(1)	[1]	1.620(9)	O4(1)-T_4-O6(1)	[1]	110.6(4)
			O3(1)-T_4-O6(1)	[2]	106.8(3)
average		1.612(4)	average		109.4(2)
		tetrahedron about T_5			
T_5-O2(1)	[2]	1.768(5)	O2(1)-T_5-O2(2)	[1]	105.6(5)
T_5-O4(1)	[1]	1.719(7)	O2(1)-T_5-O4(2)	[1]	108.2(3)
T_5-O5(1)	[1]	1.720(8)	O2(1)-T_5-O5(1)	[2]	109.9(3)
			O2(1)-T_5-O4(2)	[2]	114.6(3)
average		1.744(4)	average		110.5(2)
		octahedron about Me			
Me-O2(1)	[2]	2.120(5)	O2(1)-Me-O1(3)	[2]	101.7(2)
Me-O1(3)	[2]	2.113(5)	O2(1)-Me-O3(1)	[2]	101.2(2)
Me-O3(2)	[2]	2.124(5)	O1(3)-Me-O3(1)	[2]	97.4(2)
			O2(3)-Me-O2(2)	[1]	71.0(9)
			O3(4)-Me-O2(2)	[2]	86.6(2)
			O3(4)-Me-O1(4)	[2]	75.4(2)
			O1(5)-Me-O1(4)	[1]	85.6(7)
average		2.119(3)	average		90.1(2)

[1] Frequency of occurrence denoted in brackets.

[2] Estimated standard error in parentheses.

TABLE 5. OXYGEN-OXYGEN DISTANCES IN LOW CORDIERITE

Polyhedron	O-O (A)					
tetrahedron about T_1	O1(3)-O3(3)	[2][1]	3.112(7)[2]	O1(3)-O3(4)	[2]	2.592(6)[3]
	O1(1)-O1(3)	[1]	2.873(12)	O1(2)-O1(4)	[1]	2.845(15)
			average 2.854(5)			
tetrahedron about T_2	O2(1)-O2(8)	[2]	2.807(12)	O2(1)-O2(4)	[2]	2.464(14)
	O2(1)-O2(5)	[2]	2.659(13)			
			average 2.643(8)			
tetrahedron about T_3	O1(1)-O5(1)	[2]	2.617(7)	O1(1)-O6(1)	[2]	2.626(8)
	O1(1)-O1(2)	[1]	2.631(14)	O5(1)-O6(1)	[1]	2.662(12)
			average 2.630(5)			
tetrahedron about T_4	O3(1)-O6(1)	[2]	2.608(9)	O3(1)-O3(2)	[1]	2.646(13)
	O3(1)-O4(1)	[2]	2.651(7)	O6(1)-O4(1)	[1]	2.620(10)
			average 2.631(5)			
tetrahedron about T_5	O2(1)-O5(1)	[2]	2.856(9)	O2(1)-O4(2)	[2]	2.826(8)
	O2(1)-O2(2)	[1]	2.812(15)	O5(1)-O4(2)	[1]	2.895(9)
			average 2.845(5)			
	O2(1)-O2(4)	[1]	2.464(14)[3]	O1(3)-O3(4)	[2]	2.592(6)[3]
octahedron about Me	O2(1)-O3(4)	[2]	2.910(6)	O1(3)-O1(5)	[1]	2.873(14)
	O1(3)-O2(1)	[2]	3.282(6)	O1(5)-O3(4)	[2]	3.184(8)
	O2(3)-O3(4)	[2]	3.279(7)			
			average 2.989(4)			

[1] Frequency of occurrence.

[2] Estimated standard error.

[3] Edges shared between TO_4 and MeO_6 groups.

TABLE 6. INTERATOMIC ANGLES AT OXYGEN ATOMS

Ring	T-O-T (Degrees)		
six-membered ring	T_3-O5(1)-T_5	[2][1]	176.5(3)[2]
	T_3-O6(1)-T_4	[2]	179.6(3)
	T_4-O4(1)-T_5	[2]	162.0(2)
			average 172.7(2)
four-membered rings	T_2-O2(2)-T_5	[2]	133.1(3)
	T_1-O1(2)-T_3	[2]	127.9(2)
	T_1-O3(2)-T_4	[2]	128.6(2)
			average 129.9(1)

[1] Frequency of occurrence.

[2] Estimated standard errors.

the Busing-Martin-Levy program and the weighting scheme proposed by Cruickshank (1965). In this calculation a specially prepared scattering curve, based on the water and the alkali earth and alkali metal content of the mineral, was used to approximate the atoms in the cavity, whereas curves for Si^{2+} and $Al^{3/2+}$ were employed for the Si- and Al-rich sites taking into account the real part of the anomalous dispersion correction (Dauben and Templeton, 1955; Templeton, 1955). The refinement converged in three cycles to the atomic parameters listed in Table 3c, reducing the weighted R from 13.6 to 9.7 per cent and giving a mean square deviation from regression of 0.68 which is close to unity, the value expected for properly weighted data and normally distributed observational errors (Brownlee, 1960; Cruickshank, 1965).

Upon completing the isotropic refinement, an attempt was made to extend the least-squares calculation to include a refinement of the anisotropic temperature factors. However, this was unsuccessful as the estimated standard deviations computed for some of the thermal parameters of the oxygen atoms were of the same order of magnitude as the thermal parameters themselves. In addition, there was a tendency for some of the parameters to be computed as negative. It was concluded, therefore, that the experimental data were not sufficiently accurate to determine meaningful anisotropic parameters and the results were disregarded.

TABLE 7. NEAREST NEIGHBOR CATION-CATION DISTANCES (A)

T_1–T_3	3.037(3)[1]	T_2–M	2.792(2)
T_1–T_4	3.037(3)	T_3–T_5	3.290(3)
T_1–Me	2.846(1)	T_3–T_4	3.211(3)
T_2–T_5	3.109(2)	T_4–T_5	3.255(3)
Me–Me	4.668(1)		

[1] Estimated standard error.

The geometrical details of the structure, listed in Tables 4 through 7, were computed on the IBM 1620 computer using the intra- and intermolecular distance program prepared by Chu and Shiono (1963) and the all-angles program prepared by Shiono (1963). The estimated standard errors, given in parentheses, were computed on the IBM 7074 computer using the estimated standard deviations obtained in the refinement and expressions derived from the propagation of variance formula (Beers, 1953).

DISCUSSION

The present study has confirmed, for the most part, the ideal structure published by Takane *et al.* (1936) and by Bystrom (1941) and has pro-

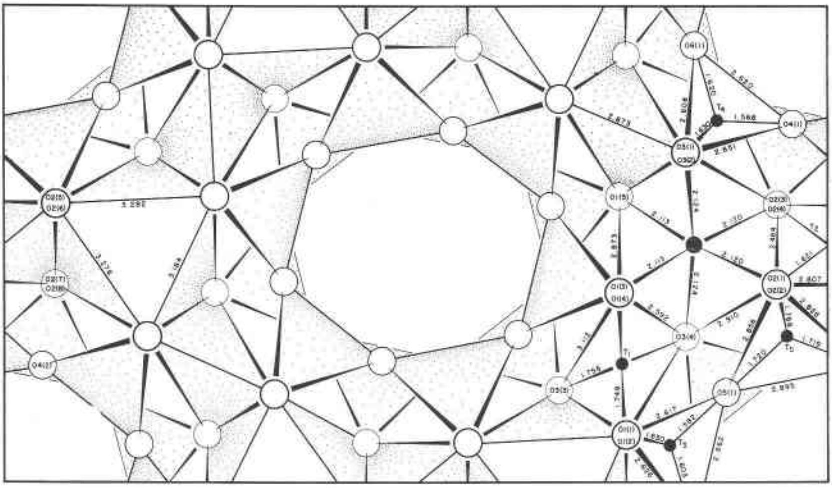


FIG. 4. The crystal structure of low cordierite viewed along the z-axis. The large open circles represent oxygen atoms, the large solid circle centering the octahedron represents the Me-atoms, the small circles centering T_1 and T_5 represent Al-rich sites and those centering T_2, T_3 and T_4 Si-rich sites. The nomenclature of the oxygen atoms is given in the large open circles and the values indicated between atoms refer to selected interatomic distances. Note that two of the tetrahedra in the central six-membered ring are significantly larger (Al-rich) than the remaining four (Si-rich); also note that the octahedron shares three of its edges, two with large tetrahedra and one with a small tetrahedron.

duced a more precise set of atomic parameters which clearly indicates an ordered Al and Si arrangement. Figure 4 is a drawing of the structure viewed down z. The TO_4 groups in the drawing can be divided into small and large tetrahedra on the basis of their T-O bond lengths (Table 4 and 5); following Smith and Bailey (1962) the large tetrahedra (T_1 and T_5) are presumed to be Al-rich and the small ones (T_2, T_3 and T_4) Si-rich

TABLE 8. AVERAGE Al-CONTENT PER UNIT CELL ESTIMATED FROM T-O BOND LENGTHS

Tetrahedron	Occurrence per unit cell	Mean T-O bond length	Al content per tetrahedron	Al content of tetrahedra per unit cell
T_1	8	1.753A	1.00	8.00
T_2	4	1.621	0.08	0.32
T_3	8	1.611	0.0	0.0
T_4	8	1.612	0.0	0.0
T_5	8	1.744	0.96	7.68
		Total Al per unit cell		16.00

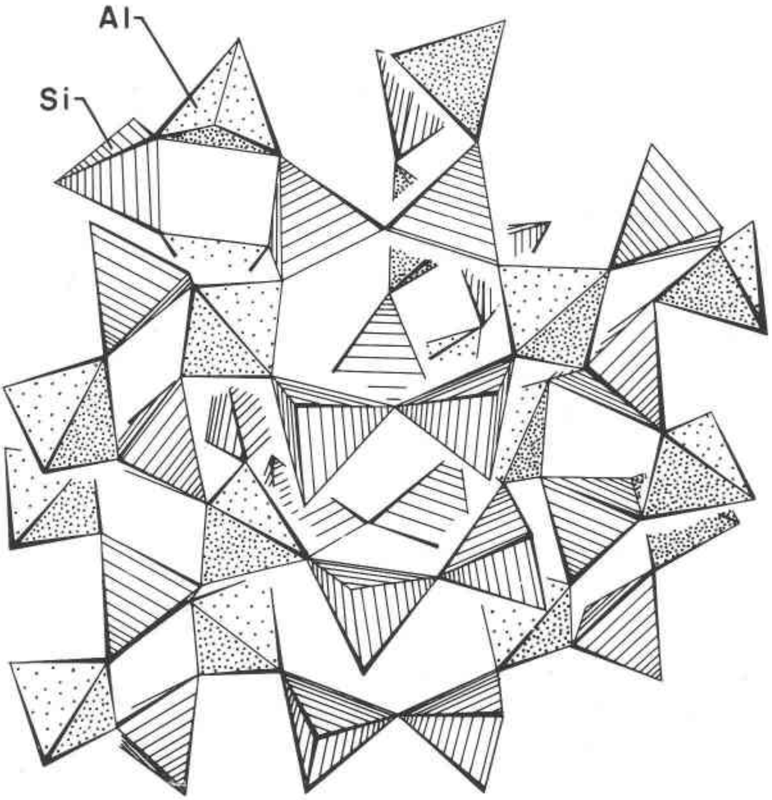


FIG. 5. An idealized drawing of the ($Al_4Si_5O_{18}$) framework in low cordierite. The Al-rich tetrahedra are stippled and the Si-rich ones are hatched. Note the stack of three six-membered rings at the center of the diagram and their linkage laterally and vertically by the tetrahedra outside the rings into a continuous framework. The cages between neighboring rings in the stack house the channel atoms (molecular water, alkaline earth and alkali metal atoms); these are not shown.

(Table 8). The overall mean T-O bond distances of the small and large tetrahedra, 1.614 and 1.748A, respectively, are in excellent agreement with the values 1.61 and 1.75A recorded for SiO_4 and AlO_4 tetrahedra in the framework silicates (Smith and Bailey, 1962). According to the equation of Bragg and Williams (1934), the degree of long-range order of the Guilford cordierite is 0.96. The small temperature-factors (Table 3c) of Al, Si, Me and O calculated in the final refinement are consistent with these results. It is apparent from Table 8 that the framework contains, on the average, 16 Al atoms per unit cell which is in harmony with the number found in the normalization of the unit cell contents (Table 2).

The nature of the tetrahedral linkage in the structure is depicted in

Figs. 5 and 6 where, for the sake of clarity, the octahedral atoms have been omitted and the Al- and Si-rich tetrahedra have been stippled and hatched, respectively. Each tetrahedron has a sharing coefficient of two (Zoltai, 1960) and, accordingly, shares four oxygen atoms in common with four nearest-neighbor tetrahedra to form a framework structure which consists of chains of four-membered rings linked laterally in six-membered rings. Figure 5 shows a stack of the six-membered rings and how it is produced by the lateral linkage of six chains. The nature of the linkage among the six-membered rings is revealed in Fig. 6 which shows three of the chains linking together to form a channel bounded by four- and nine-membered rings. These channels accommodate the Me-atoms which are situated in octahedra (Fig. 4). The disposition of the Al- and Si-rich tetrahedra is consistent with the aluminum avoidance rule which was proposed independently by Loewenstein (1954) and by Goldsmith

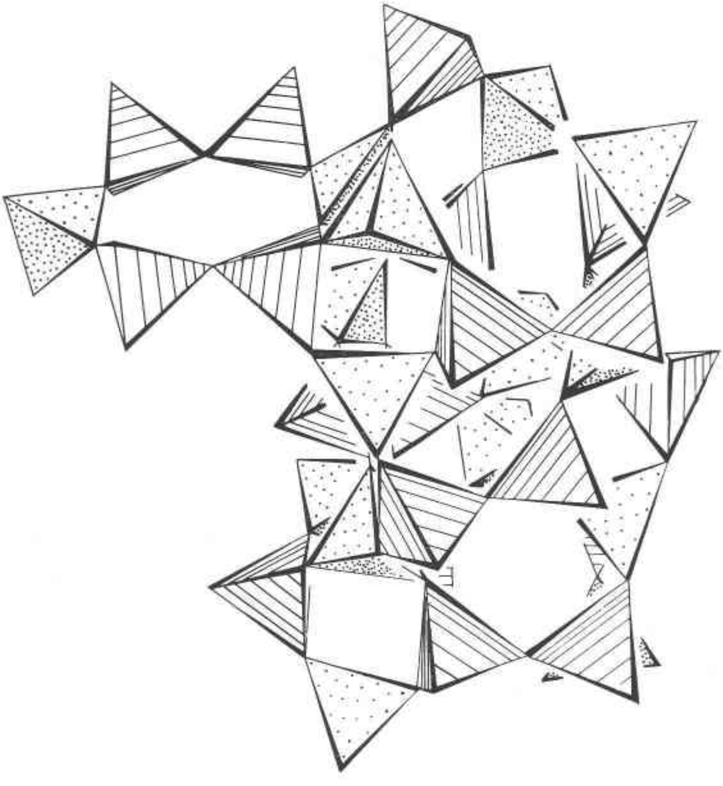


FIG. 6. An idealized drawing of the framework tetrahedra forming the channels that accommodate the Me-atoms in octahedral coordination. The Al-rich tetrahedra are stippled and the Si-rich ones are hatched.

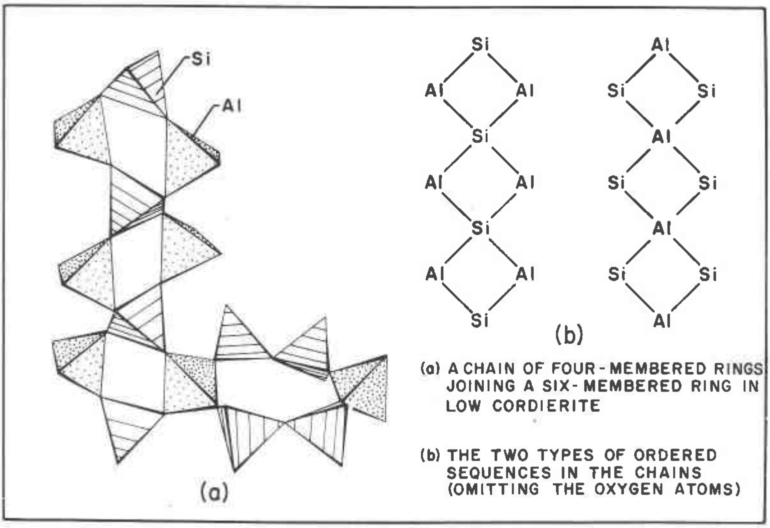
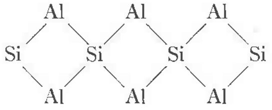
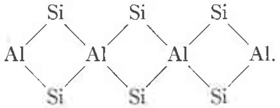


FIG. 7. A drawing of an isolated six-membered ring attached to a single chain of four-membered rings running parallel to *z*. The stippled Al-rich tetrahedra are in perfect alternation with the hatched Si-rich ones.

and Laves (1955), *i.e.*, the tetrahedra are in perfect alternation in all directions except for two Si-rich ones that share a common oxygen atom in the six-membered ring (Figs. 5 and 7). The nature of the ordering can be appreciated by examining the chains in Figs. 5 and 7. Those that are linked laterally by AlO_4 groups have (omitting the oxygen atoms) the ordered sequence



whereas those linked laterally by the SiO_4 groups have the sequence



The tetrahedral bond angles (O-T-O) of the Si- and Al-rich tetrahedra average 109.5 and 110.2°, respectively, closely approximating the ideal tetrahedral angle of 109.47°. The O-T-O angles within the tetrahedra comprising the six-membered ring have a spread of values (105.6–114.6°) similar to those recorded for other silicates with ordered framework structures (i.e., authigenic maximum microcline: (103.77–114.39°), Finney and Bailey, 1963; low albite: (102.67–116.07°), Ribbe, 1963;

igneous maximum microcline: (103.83–114.67°); Brown and Bailey, 1964, and reedmergnerite: (103.13–114.8°); Appleman and Clark, 1966). On the other hand, the O-T-O angles within the tetrahedra outside the ring show a somewhat larger spread, ranging from 95.4 to 125.2°. This larger range is not entirely unexpected because these tetrahedra, unlike those in the ring, share one-third of their edges with the MeO_6 coordination groups. As the shared edges of the tetrahedra are significantly shorter than the unshared ones (Pauling, 1928; see Table 5), the bond angles to the oxygen atoms comprising the shared edges must perforce be appreciably smaller than the ideal tetrahedral angle and those to the oxygen atoms comprising the unshared edges must be larger.

The interatomic angles (T-O-T) recorded between adjacent tetrahedra are of two kinds:

between tetrahedra in six-membered rings	T_3-O5(1)-T_5	176.5°
	T_3-O6(1)-T_4	179.6
	T_4-O4(1)-T_5	162.0
	mean	172.7
between tetrahedra in chains of four-membered rings	T_2-O2(2)-T_5	133.1
	T_1-O1(2)-T_3	127.9
	T_1-O3(2)-T_4	128.6
	mean	129.9

The T-O-T angles in the chains between adjacent Al- and Si-rich tetrahedra average 129.9° which is in reasonable agreement with corresponding angles tabulated for a number of silicate structures by Liebau (1961). However, the T-O-T angles in the ring are significantly wider and the one between the two Si-rich tetrahedra (T_3, T_4) is not significantly different from 180°, a value concluded by Liebau (1961) not to exist "under normal conditions."

The octahedron about Me, depicted in Fig. 4, shares two edges with Al-rich tetrahedra and one with an Si-rich tetrahedron. These edges, as described earlier, are shorter in conformity with Pauling's rules (1928). However, the individual Me-O distances show a very small spread of values (between 2.113 and 2.124A) and are not significantly different.

The oxygen atoms comprising the octahedron are three-coordinated by one Me- and two T-atoms. The remaining oxygen atoms in the structure are two coordinated by T-atoms. In a recent evaluation of the thermal parameters of ten well-refined ordered silicate structures, it was found that the rms amplitude of vibration of an oxygen atom is dependent upon its coordination number with three- and four-coordinated oxygens exhibiting lower amplitudes than two-coordinated ones (Burnham, 1964). With the exception of 04, the amplitudes obtained in this study agree with this observation:

Two-coordination oxygen		Three-coordinated oxygen	
Atoms	rms amplitude of vibration	Atoms	rms amplitude of vibration
O4	0.056A	O1	0.058A
O5	0.091	O2	0.055
O6	0.082	O3	0.062
mean	0.076	mean	0.058

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