

## The crystal structure of dachiardite

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With 6 figures

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### Riassunto

Le ricerche strutturali sulla mordenite hanno suggerito una struttura per la dachiardite, una rara zeolite trovata all'isola d'Elba, Italia. La struttura proposta è stata confermata e parzialmente affinata mediante sintesi bidimensionali di Fourier.

I cristalli sono monoclino, con gruppi spaziale  $B2/m$ ,  $Bm$  o  $B2$ . L'impalcatura di tetraedri della dachiardite ha strette relazioni con quella della mordenite. Vi sono canali relativamente larghi parallelamente agli assi  $b$  e  $c$ . Le geminazioni osservate nella dachiardite possono essere facilmente spiegate sulla base dell'impalcatura dei tetraedri alluminio-silicio-ossigeno.

### Auszug

Durch andere Verknüpfung der Alumosilikatketten der Mordenitstruktur ergab sich eine mögliche Struktur für Dachiardit, einen seltenen Zeolith von Elba, Italien. Diese Struktur wurde bestätigt und unter Verwendung von zwei-dimensionalen Fouriersynthesen teilweise verfeinert.

Dachiardit ist monoklin mit der Raumgruppe  $B2/m$ ,  $Bm$  oder  $B2$ . Die Gerüststruktur von Dachiardit ist eng verwandt mit der von Mordenit. Verhältnismässig weite Kanäle durchsetzen die Struktur in den Richtungen der  $b$ - und der  $c$ -Achse. Die charakteristische Zwillingsbildung des Dachiardits läßt sich auf Grund der Gerüststruktur leicht erklären.

### Abstract

Structural work on mordenite suggested a possible structure for dachiardite a rare zeolite occurring on Elba, Italy. This trial structure has been confirmed and partially refined by two-dimensional Fourier syntheses.

The crystals are monoclinic with space group  $B2/m$ ,  $Bm$  or  $B2$ . The framework structure of dachiardite is closely related to the mordenite structure. There are comparatively wide channels along both the  $b$  and  $c$  axes. The observed twinning of dachiardite can be readily explained on the basis of the aluminosilicate framework.

### Introduction

Dachiardite is a rare zeolite which occurs in association with mordenite in the western part of Elba, Italy (D'ACHIARDI, 1906). Its composition,



is nearly that of mordenite. The latter has a somewhat higher Si/Al ratio of 5, however. The crystal data of the two zeolites are as follows<sup>1</sup>:

<i>Dachiardite</i> (D)	<i>Mordenite</i> (M)
monoclinic	orthorhombic
$a = 18.73 \text{ \AA}$	$a = 18.13 \text{ \AA}$
$b = 10.30 \text{ \AA}$	$b = 20.49 \text{ \AA}$
$c = 7.54 \text{ \AA}$ $\gamma = 107^\circ 54'$	$c = 7.52 \text{ \AA}$
Space group: $B2/m$ , $Bm$ or $B2$	$Cmcm$ or $Cmc2_1$ .

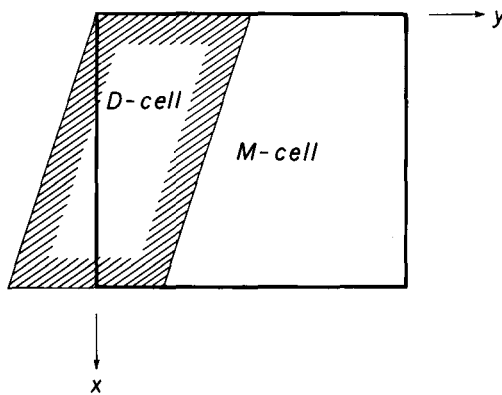


Fig. 1. Unit cells of D and M

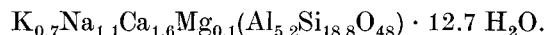
The cell dimensions of D were first reported by BONATTI (1942). The crystal data of D quoted above are those determined by BONATTI and GOTTARDI (1960). The unit cells of D and M contain 48 and 96 (Si+Al) atoms respectively. The relationship between the unit cells of the two zeolites, as shown in Fig. 1, was first noted by GOTTARDI (1960).

<sup>1</sup> D stands for dachiardite and M for mordenite in this paper.

The first monoclinic setting has been adopted in this paper in order to ensure basically the same nomenclature for the related structures of D and M.

### Experimental data

Natural crystals of D were used in this study. Their composition is



according to a previous analysis (GOTTARDI, 1960). Weissenberg photographs around  $c$  and precession photographs around  $a$  and  $b$  were taken with  $\text{CuK}\alpha$  and  $\text{MoK}\alpha$  radiation, using small crystal fragments of about 0.4 mm thickness. Intensities for the zero layers were measured photometrically. Only 242 out of 413 permissible reflections with  $(\sin \theta)/\lambda \leq 680$  could be observed on these photographs. No absorption corrections were applied.

The observed reflections were in accordance with space group  $B2/m$ ,  $Bm$  or  $B2$ . Intensity statistics suggested a centric structure ( $B2/m$ ).

### Determination of the structure

The structure determination of M disclosed that the aluminosilicate framework of this zeolite is based on characteristic chains parallel to the fibre axis  $c$  (MEIER, 1961). Figure 2a shows how these chains are linked up with each other in M. It was soon realized that these same chains could also be interconnected in the way shown in Fig. 2b. The maximum symmetry of the resultant monoclinic framework would be  $B2/m$  and the cell dimensions of the undistorted structure were also found to be in good agreement with the observed data on D.

Assuming that the same chains occur in both M and D, one would expect the relative intensities of the  $00l$  reflections to resemble each other. This was in fact the case as the following comparison of the observed structure factors shows:

$l$	$F_o(\text{M})$	$F_o(\text{D})$
2	218	89
4	457	209
6	195	81
8	20	12

A less pronounced resemblance was also noticed when the intensities of the  $h0l$  reflections were compared. This reflects the close similarity

of the  $[010]$  projection of D and M, and thus supplied some further supporting evidence for the trial structure of D.

Structure factors for the trial structure comprising only the atoms of the framework were then calculated for the  $hk0$ ,  $h0l$ , and  $0kl$  reflections. The initial  $R$  values<sup>2</sup> for these projections were 0.37, 0.32, and

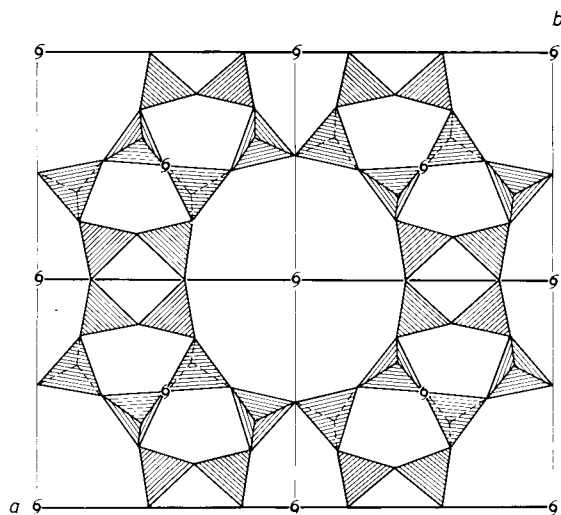


Fig. 2a. Framework structure of M

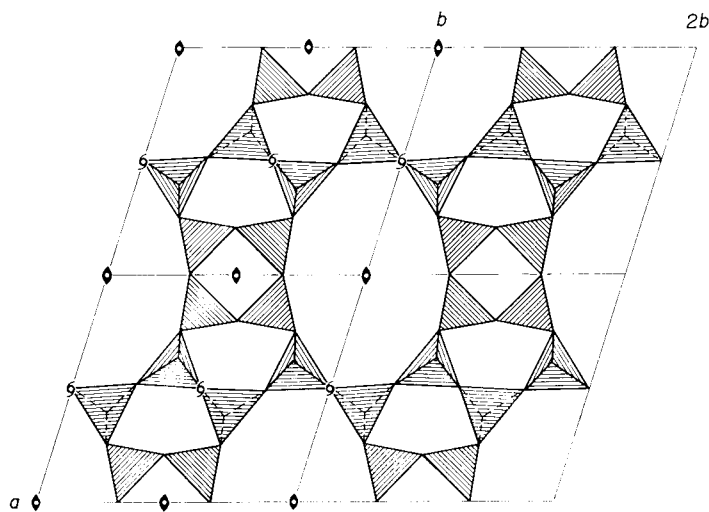


Fig. 2b. Framework structure of D

<sup>2</sup> Defined as  $\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ .

Table 1. Observed and calculated structure factors for dachiardite.

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>				
2	0	0	0	-133	$\bar{4}$	10	0	< 23	-40	$\bar{10}$	1	0	105	-105	14	8	0	< 15	-6				
4			53	26				11	< 23	2			2	77	-89	$\bar{16}$	1	0	60	-50			
6			54	-74				12	< 21	0			3	< 14	-1			2	59	-39			
8			31	21				13	< 17	7			4	80	-90			3	89	88			
10			177	164	4	1	0	100	102				5	41	13			4	< 21	34			
12			< 15	13				2	144	-157				6	38	35			5	< 22	-10		
14			48	36				3	120	-103				7	38	36			6	33	42		
16			< 19	-2				4	86	85				8	28	-58			7	68	-69		
18			33	-33				5	< 15	-1				9	67	-62			8	< 23	2		
20			< 21	11				6	< 18	7				10	< 23	-8			9	32	50		
22			26	11				7	41	31				11	< 23	27			10	< 21	-18		
24			< 11	12				8	30	-40				12	< 21	-3			11	25	23		
0	1	0	0	-52				9	26	-14				13	26	21			12	< 16	31		
	2		141	-169				10	< 23	-4			10	1	0	56	26	16	1	0	< 22	-1	
	3		88	82				11	< 20	0				2	67	-68			2	58	49		
	4		33	-23				12	< 14	42				3	77	96			3	< 23	12		
	5		27	21			$\bar{6}$	1	0	< 8	6			4	95	-77			4	< 23	-16		
	6		137	127				2	207	-217				5	68	-76			5	< 22	8		
	7		< 9	-31				3	67	-35				6	74	76			6	26	-13		
	8		15	18				4	54	-62				7	< 23	2			7	< 14	-22		
	9		28	0				5	58	58				8	< 23	6			$\bar{18}$	1	0	79	67
	10		22	-31				6	74	63				9	< 20	20			2	< 22	-14		
	11		< 13	3				7	72	-62				10	33	-35			3	29	-33		
	12		23	-5				8	62	-93			$\bar{12}$	1	0	53	-29			4	31	15	
	13		31	25				9	28	30				2	23	38			5	58	-57		
0	0	2	89	-87				10	< 23	-7				3	106	113			6	< 23	-30		
	4		209	225				11	32	34				4	40	35			7	70	77		
	6		81	86				12	40	38				5	101	-101			8	< 23	-4		
	8		< 12	3				13	46	-54				6	< 19	5			9	< 22	-1		
	10		78	55			6	1	0	< 9	-21			7	< 21	9			10	< 20	-3		
$\bar{1}$	1	0	0	-15				2	< 12	-9				8	< 22	-8			11	22	-36		
	2		120	-129				3	< 14	25				9	< 22	26			12	< 13	-2		
	3		162	204				4	82	-70				10	< 23	51			18	1	0	< 23	-6
	4		162	162				5	58	-53				11	< 22	-24			2	< 25	-13		
	5		133	-167				6	66	-66				12	29	-17			3	< 38	-36		
	6		< 15	2				7	< 21	1				13	< 16	4			4	< 21	9		
	7		< 17	16				8	62	65			12	1	0	48	-42			5	< 17	10	
	8		38	-66				9	24	14				2	68	73			6	< 13	6		
	9		49	36				10	23	-29				3	56	25			$\bar{20}$	1	0	49	-40
	10		33	42				11	19	-6				4	32	27			2	< 25	-3		
	11		< 23	-14				12	< 10	-8				5	31	41			3	< 23	-5		
	12		< 20	-5				2	< 11	-15				6	69	-53			4	< 23	5		
	13		< 17	4			$\bar{8}$	1	0	< 11	3			7	< 22	-9			5	< 23	22		
2	1	0	< 4	-20				3	27	1				8	38	26			6	< 23	15		
	2		54	189				4	89	85				9	38	-31			7	< 22	9		
	3		< 9	-1				5	115	-111			$\bar{14}$	1	0	19	16			8	37	-28	
	4		86	-86				6	146	-140				2	39	30			9	31	-31		
	5		< 14	-12				7	109	104				3	78	-66			10	20	20		
	6		180	-170				8	< 20	45				4	83	-99			11	< 13	30		
	7		53	63				9	< 22	15				5	84	71			20	1	0	27	17
	8		32	12				10	< 23	32				6	52	47			2	< 20	-3		
	9		28	-44				11	51	-56				7	< 21	-19			3	34	36		
	10		35	50				12	26	-17				8	42	36			4	< 15	-4		
	11		< 22	7				13	< 17	18				9	< 23	-31			5	56	-45		
	12		40	-48			8	1	0	37	37			10	26	-34			$\bar{22}$	1	0	< 20	2
	13		< 10	4				2	75	-71				11	< 22	6			2	< 21	1		
$\bar{4}$	1	0	61	60				3	35	-44				12	< 20	-14			3	< 21	16		
	2		163	182				4	119	129				13	< 13	24			4	< 21	-5		
	3		81	-66				5	< 19	-7			14	1	0	94	68			5	33	-27	
	4		77	-58				6	46	42				2	75	-75			6	< 20	-15		
	5		25	-19				7	< 22	-10				3	67	-54			7	< 19	6		
	6		40	39				8	46	-61				4	< 23	34			8	< 17	-11		
	7		55	45				9	25	19				5	< 23	-2			9	< 15	33		
	8		112	125				10	24	39				6	< 22	-27			10	< 12	12		
	9		< 21	-29				11	< 11	-13				7	38	39			22	1	0	< 17	-16

Table 1 (Continued)

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>	
22	2	0	<14	-24	6	0	6	<19	-3	15	0	1	33	-22	0	3	4	30	27	
	3		<10	1		8		<21	-31		5		<20	3		6		49	38	
24	1	0	40	-32		10		<10	-5		5		48	-31		8		20	14	
	2		<15	20	7	0	1	<10	-10		7		<19	11		10		21	14	
	3		<16	-14		3		141	-167	16	0	2	44	-32	0	4	2	49	29	
	4		<16	-23		5		63	57		4		<21	-17		4		39	-23	
	5		37	35		7		89	-73		6		<21	-9		6		21	-32	
	6		<15	12		9		<19	2		8		17	-15		8		17	17	
	7		<14	-4	8	0	2	38	-43	17	0	1	26	-28		10		21	-30	
	8		<11	11		4		<15	-13		3		61	-54	0	5	2	37	-31	
	9		<8	-26		6		<19	-9		5		<21	-1		4		<12	-3	
24	1	0	53	35		8		<21	10		7		36	-29		6		<12	-7	
	1	0	1	0	87	9	0	1	57	37	18	0	2	<21	-6		8		19	-7
	3		31	47		3		54	53		4		<21	-18		0	6	2	76	-71
	5		32	39		5		<18	-3		6		<18	-11		4		49	46	
	7		55	54		7		47	42	19	0	1	<21	-12		6		34	17	
	9		<21	11		9		<17	-3		3		<21	8		8		17	-16	
2	0	2	215	266	10	0	2	<14	22		5		<19	-15	0	7	2	19	32	
	4		32	-39		4		88	71	20	0	2	<21	-6		4		23	-2	
	6		22	30		6		43	50		4		<20	9		6		<13	-4	
	8		46	36		8		<21	-4	21	0	1	<21	13		8		18	6	
	10		34	-14	11	0	1	31	30		3		<20	13		0	8	2	32	-27
3	0	1	26	43		3		69	60		5		<13	9		4		32	19	
	3		<10	-9		5		21	23	22	0	2	<19	23		6		18	-13	
	5		75	72		7		28	24		4		<14	12		8		<6	0	
	7		52	-39		9		21	22	23	0	1	<17	15	0	9	2	23	-39	
	9		47	29	12	0	2	128	136		3		<13	8		4		23	-17	
4	0	2	130	-118		4		46	49	24	0	2	<10	6		6		19	-5	
	4		61	65		6		<21	10		0	1	2	82	-71	0	10	2	51	57
	6		74	-66		8		60	49		4		30	-47		4		<11	4	
	8		<21	6	13	0	1	37	36		6		46	-57		6		18	5	
	10		<14	-4		3		<18	16		8		<12	-20		0	11	2	<13	11
5	0	1	207	-205		5		45	40		10		19	-14		4		<10	7	
	3		38	34		7		<21	5	0	2	2	35	31		0	12	2	37	-41
	5		173	-182		9		17	17		4		54	-55		4		23	-11	
	7		31	25	14	0	2	34	-14		6		54	-56	0	13	2	<5	13	
	9		68	-42		4		<20	9		8		<12	10						
6	0	2	26	-7		6		<21	5		10		42	-22						
	4		33	-32		8		<14	-10	0	3	2	92	98						

Table 2. Parameters of the framework atoms

Atom	Position (based on B2/m)	x	y	z	B
Si <sub>1</sub>	8j	0.213	0.844	0.295	1.8 Å <sup>2</sup>
Si <sub>2</sub>	8j	0.193	0.351	0.296	1.8
Si <sub>3</sub>	4i	0.096	0.698	0	1.6
Si <sub>4</sub>	4i	0.0825	0.378	0	1.6
O <sub>1</sub>	8j	0.135	0.781	0.179	2.9
O <sub>2</sub>	8j	0.1165	0.326	0.180	3.0
O <sub>3</sub>	8j	0.226	0.226	0.272	3.4
O <sub>4</sub>	4i	0.087	0.538	0	2.5
O <sub>5</sub>	4i	0.169	0.371	1/2	3.2
O <sub>6</sub>	4i	0.1865	0.808	1/2	3.2
O <sub>7</sub>	4e	1/4	0	1/4	3.7
O <sub>8</sub>	4f	1/4	1/2	1/4	3.6
O <sub>9</sub>	4i	0.008	0.690	0	2.5

0.39 respectively. Two-dimensional Fourier and difference maps confirmed the general features of the framework. The principal projections of the framework structure were then simultaneously refined by means of Fourier and difference syntheses. Additional peaks whose heights were around  $15 e/\text{\AA}^2$  appeared more or less consistently at

$$\begin{aligned} &(0.01, 0.88, 0.26), \\ &(0.08, 0.05, 0.42), \\ &(0.08, 0.02, 0.07), \\ &\text{and } (0.01, 0.73, 0.47). \end{aligned}$$

The last mentioned was attributed to cations and the others to water on the basis of stereochemical considerations. These probable positions of the cations and water molecules were eventually included in the structure-factor calculations. The observed peak heights indicated about 50% occupancy for the water positions and about 30% occupancy for the cationic position. A total of eight refinement cycles reduced the  $R$  factor for the observed reflections  $hk0$ ,  $h0l$ , and  $0kl$  to 0.17. The observed and calculated structure factors are given in Table 1.

The atomic scattering factors used in this work were those listed in "International tables for x-ray crystallography", Vol. III (1962) for the neutral atoms O, Si, Na, K, and Ca. Average values of  $f$  based on the chemical composition were used for the cations.

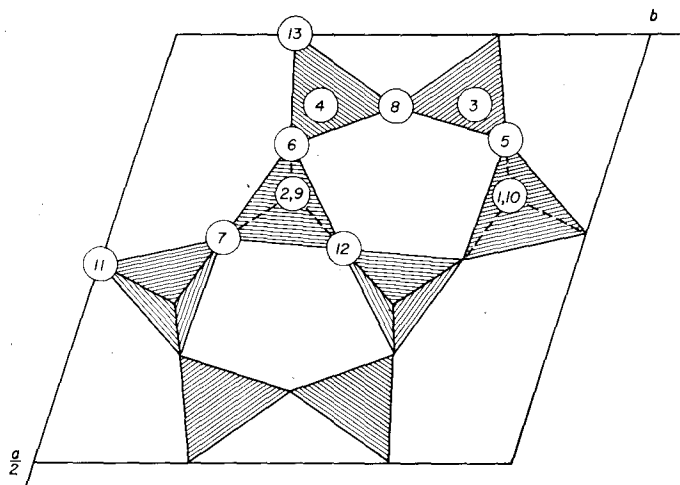


Fig. 3. Notation for the framework atoms.

1. Si <sub>1</sub>	4. Si <sub>4</sub>	7. O <sub>3</sub>	10. O <sub>6</sub>	13. O <sub>9</sub>
2. Si <sub>2</sub>	5. O <sub>1</sub>	8. O <sub>4</sub>	11. O <sub>7</sub>	
3. Si <sub>3</sub>	6. O <sub>2</sub>	9. O <sub>5</sub>	12. O <sub>8</sub>	

### Results

The final atomic coordinates and isotropic temperature factors for the atoms of the aluminosilicate framework are given in Table 2. The notation used for the atoms of the asymmetric unit cell is shown in

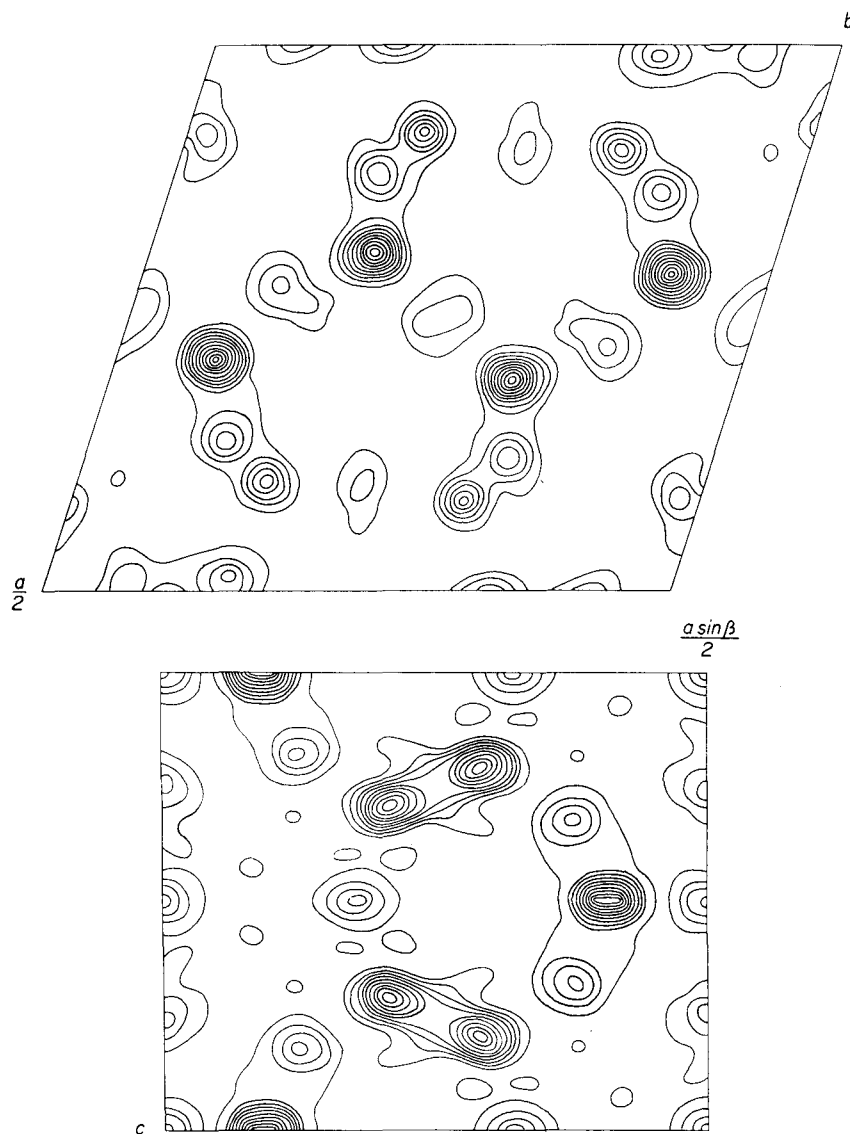


Fig. 4. Electron density projections along [001] and [010]. Contours are at intervals of  $5 e/\text{\AA}^2$



Fig.3. The atoms have been numbered in the same way as in M for easy comparison.

The standard deviations for the positional parameters listed in Table 2 are of the order of 0.02 Å except for the less accurate coordinates of O<sub>4</sub> and O<sub>9</sub>. The average Si—O distances based on the final atomic coordinates are:

$$\begin{aligned} 1.62 \pm 0.03 \text{ \AA} & \text{ for Si}_1 \text{ and Si}_2 \\ 1.63 \pm 0.03 \text{ \AA} & \text{ for Si}_3 \\ 1.64 \pm 0.03 \text{ \AA} & \text{ for Si}_4 \end{aligned}$$

The most likely positions for the cations and the water molecules have been mentioned in the previous section.

Fourier projections of the structure along [001] and [010] are shown in Fig. 4.

### Discussion

The foregoing results establish beyond doubt that D and M are based on the same type of aluminosilicate chains and can thus be grouped together in the structural classification of zeolites. The structure of D is in agreement with the rule that tectosilicates with a cell constant of 7.5 Å can be expected to contain 5-membered rings of tetrahedra (MEIER, 1961). In fact, 5-membered rings of (Si, Al)O<sub>4</sub> tetrahedra prevail in the D framework.

The structure of D is penetrated by a two-dimensional system of comparatively wide channels. The main channels run parallel to the *c* axis and are interconnected by channels parallel to the *b* axis. The free openings of both these channels are about 4 Å. The sorptive properties of dehydrated D have not been investigated so far, but its molecular sieve properties can be expected to resemble Linde Sieve 4A which sorbs small molecules such as C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> (cf. BARRER, 1959).

The Si and Al atoms cannot be distinguished on the basis of the results obtained so far. The observed average (Si, Al)—O distance of 1.63 Å is in good accord with the expected value of 1.64 Å based on the Si/Al ratio of 3.62 (SMITH, 1954). Complete long-range order of Si and Al cannot occur since the Si/Al ratio is not a simple fraction. Partial order is not unlikely, however, and this might reduce the symmetry. The somewhat elongated peaks of O<sub>7</sub> and O<sub>8</sub> might indicate some local departures from centrosymmetry rather than thermal anisotropy.

The characteristic twinning of D can be readily explained in structural terms. The cyclical twinning on (101) giving an octagonal group, shown in Fig. 5, is typical (BERMAN, 1925; DE-ANGELIS, 1925).

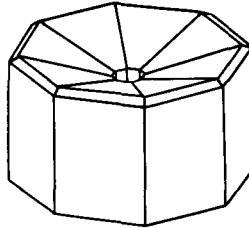


Fig. 5. Typical twinning of D

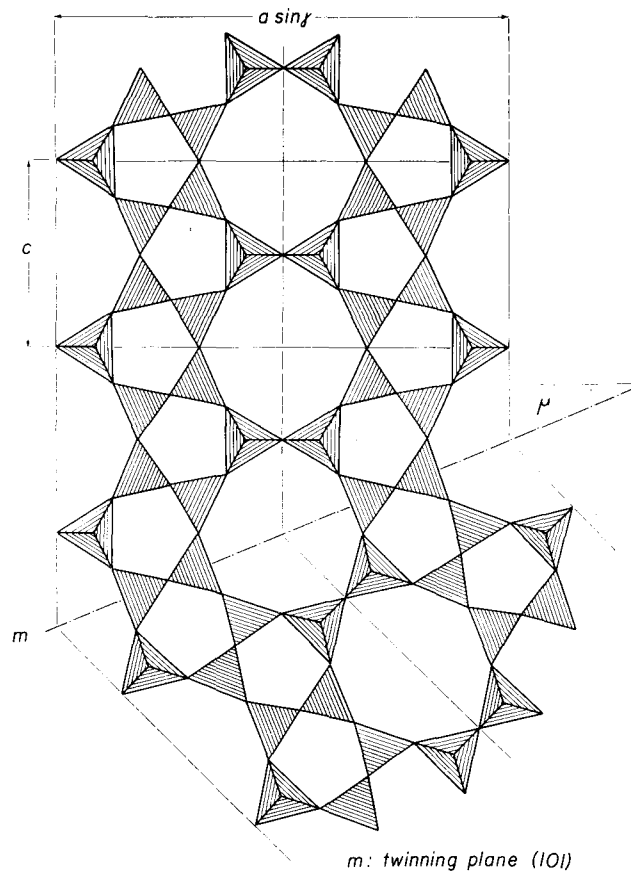


Fig. 6. Explanation of the observed twinning

An explanation for this type of twinning is offered in Fig. 6. The twinning plane (101) is parallel to recognizable "layers" of tetrahedra in the framework. The geometry of the structure is such that the twinning produces no appreciable local distortion of the framework. The occasional twinning on (010) can be similarly explained. The perfect cleavage along (100) and (010) is also well understandable on the basis of the structure.

The cations and water molecules could not be located with certainty. Natural zeolite crystals with their variable cationic composition are not suited for detailed structural analyses. A complete refinement of the hydrated Na-form of D using three dimensional low-temperature data has been taken up by one of us (G.G.).

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#### Appendix: Occurrence of dachiardite (by G. G.)

In the western part of Elba, Italy, is a small intrusive granodioritic cupola which has been protruded during the upper Miocene. The granodioritic mass contains, especially in its outer parts, many veins of aplites usually rich in tourmaline. Sometimes there are coarse-grained zones of pegmatitic type with fissures coated by well crystallized minerals in the inner parts of these veins. The variety and beauty of these minerals have made this locality wellknown among mineralogists. The fissures are normally coated by minerals typical of the pegmatitic and pneumatolitic phase. However, sometimes hydrothermal solutions rich in rare alkalies have deposited successively some characteristic minerals such as lepidolite rich in Rb, pollucite, and pink or colorless lithium tourmaline. In addition there are frequently some zeolites, such as stilbite, natrolite, heulandite, and mordenite. Dachiardite occurs only in the Speranza vein, about 200 meters south of the cemetery near the village of S. Piero di Campo. It appears in association with pink tourmaline, pollucite, "hydrocastorite" (a mixture of stilbite with minor quantities of petalite, quartz, and feldspar, as shown by COCCO and GARAVELLI, 1958), heulandite, and much mordenite. Crystallization of mordenite appears to have occurred after that of dachiardite, whereas the other minerals have been deposited before dachiardite.

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