THE STRUCTURE OF EUDIDYMITE ($HNaBeSi_3O_8$)

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An intimate relationship has been supposed to exist between epididymite and eudidymite ever since these rare dimorphous minerals of the composition $HNaBeSi_3O_8$ were described by Brögger[1] and by Flink.[2] In 1929 Gossner[3] (with Kraus) and Zachariasen[4] determined the unit cell and space group of these minerals. More recently Palache,[5] basing his results on the work of Zachariasen, proposed a new set of axes for eudidymite.

The present writer examined epididymite by means of x-ray methods and obtained a structure which explains to a certain extent the experimental data, although minor adjustments of the positions of atoms were considered necessary to secure a better agreement between the theoretical and experimental F-values.[6,7]

The writer further, in discussing the structural relationship between them, pointed out that epididymite may be regarded as an *internal twin* of eudidymite, "twinning" being effected between groups of atoms within the unit cell.[8]

The purpose of the following investigation is two-fold. We intend to decide experimentally if the structural scheme proposed for epididymite will also apply to eudidymite, and to establish the phenomenon of internal twinning on a firmer basis, if such exists in minerals.

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[1] Brögger, W. C., *Zeits. Krist.* **16,** 586 (1890).

[2] Flink, G., *Zeits. Krist.* **23,** 353 (1894).

[3] Gossner, B., and Kraus, W. O., *Centralbl. Miner.*, **A,** 257 (1927).

[4] Zachariasen, W. H., *Norsk. geol. Tidsskr.*, **10,** 449 (1929).

[5] Palache, C., *Zeits. Krist.* **85,** 425 (1933).

[6] Ito, T., *Zeits. Krist.*, **88,** 142 (1934).

[7] Wyckoff, R. W. G., *The Structure of Crystals*, Supplement 1930–1934 to the 2nd Ed., 108 (**1935**).

Wyckoff considered that the structure should be revised since some of its interatomic distances are impossible. He seems to stress minor points while the present writer's efforts were directed only to work out the structure in its main features but not all the details. It may be pointed out here, however, that there is actually a misprint concerning the coordinates of Be in Table 1 of the original paper, *viz.*

	x_a	y_b	y_c
Be	.035	.250	*.250* (instead of .052)

This correction, it is hoped, will clear up Wyckoff's remark.

[8] Ito, T., *Proc. Impl. Acad.*, **9,** 528 (1933).

MATERIAL

The crystal specimens used in the investigation came from Langesundfjord, Norway, and were purchased from Dr. F. Kranz, Bonn am Rhein. They are colorless, transparent crystals, tabular after (001), up to several mm. in thickness and up to 2 cm. in length; (331) and (111) together with (001) are well developed (Palache's notation). The platy crystals are often warped and overlap irregularly. Cleavage after (001) is very perfect, almost to the same extent as in mica. From these crystals cleavage pieces were obtained and ground for the spectrometer measurements, as oriented pieces were almost impossible to obtain owing to the high perfection of the cleavage.

UNIT CELL

The unit cell was found to be $a=12.62$ Å, $b=7.37$ Å, $c=13.99$ Å, $\beta=103°43'$. (Direct spectrometer measurement.) This gives for the axial ratio, $a{:}b{:}c{:}=1.712{:}1{:}1.898$, which agrees well with that obtained by Palache from the measurements published by Brögger in 1890.

There are eight molecules of $HNaBeSi_3O_8$ in the cell, giving for the theoretical density 2.561, compared with 2.553 as measured by Brögger.

SPACE GROUP

The results of our experimental work in which several Weissenberg-Buerger photographs ($CoK\alpha$ 1.788 Å) were taken show the following:

Reflections (hkl) are absent when $h+k$ is odd.
Reflections ($h0l$) are absent when h is odd, l is odd.
Reflections ($0k0$) are absent when k is odd.

From these data the space group for eudidymite is determined as C_{2h}^6—$C2/c$.

This is in accord with that given by Zachariasen and by Gossner and Kraus. Formerly the present writer considered C_{2h}^5 rather than C_{2h}^6 as the space group for eudidymite, for the reason that C_{2h}^5 is a subgroup of V_h^{16} which is the space group of epididymite. He considered that if epididymite were an internal twin of eudidymite, the space group of the latter would be reasonably a subgroup of the space group of the former. The experimental data, however, did not substantiate his opinion, but confirmed the work of Zachariasen and others.

Figure 1 shows the space group as found in eudidymite. There are two different sets of glide planes of two each, one set of four digonal rotation axes, one set of four digonal screw axes and two different sets of eight symmetry centers.

An atom in the general position has eight equivalent positions. These reduce to four if the atom is either on the reflection planes or on the centers of symmetry.

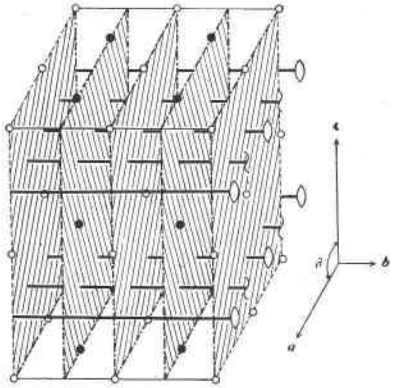


FIG. 1. Symmetry elements of the space group $C_{2h}^6 - C2/c$. Small white and black circles represent centers of symmetry. Shaded planes represent glide planes.

We have to determine altogether the positions of seven oxygen atoms, three silicon atoms, one sodium atom, one beryllium atom and one (OH) group; the number of parameters to be determined amounting to thirty-nine as a maximum.

The intensity of reflection for the plane (*hkl*) is proportional to the square of

$$F = \Sigma 8f \cos^2 2\pi \frac{h+k}{4} \cos 2\pi\left(hx + lz + \frac{l}{4}\right) \cos 2\pi\left(ky - \frac{l}{4}\right),$$

where f is the atomic scattering factor appropriate to each atom and the summation is to be taken over all atoms in the cell.

ANALYSIS

We began the analysis by comparing x-ray and other data on eudidymite and epididymite (Tables 1 and 2).

TABLE 1. COMPARISON OF THE LATTICE CONSTANTS AND OTHER PHYSICAL CONSTANTS OF EUDIDYMITE AND EPIDIDYMITE

		Eudidymite	Epididymite
a		12.62 Å	12.63 Å
b		7.37 Å	7.32 Å
c		13.99 Å	13.58 Å
β		103°43′	
Specific gravity		2.553	2.548
Refractive indices	n_α	1.545	1.565
	n_β	1.546	1.569
	n_γ	1.551	1.569
2V		29°55′(+)	31°4′(−)
Hardness		6	6

We see that the two crystals have almost identical cell dimensions. The *a*- and *b*-lengths of both crystals are nearly equal, while $c \sin \beta$ of eudidymite is equal to the *c*-length of epididymite, with the result that the volume of the unit cell is, respectively, 1264.1 Å^3 (eudidymite) and 1255.5 Å^3 (epididymite), each containing eight molecules of $HNaBeSi_3O_8$.

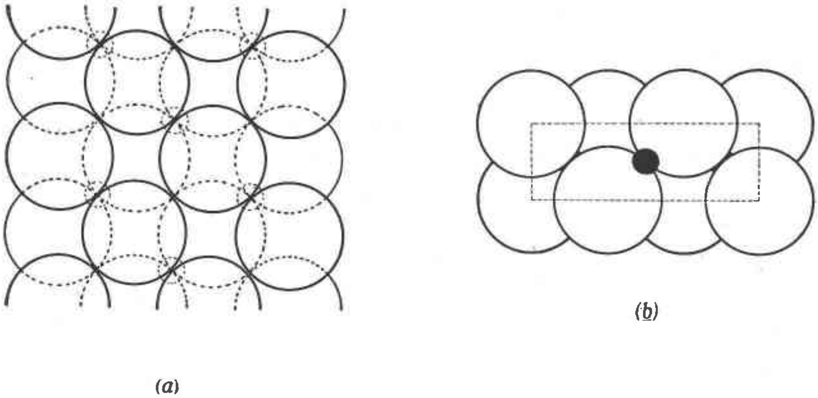
The intensity of the reflections, on the other hand, shows a marked difference as well as certain similarities. We note that, whereas the (*h*00) and (00*l*) spectra indicate generally analogous trends, the (0*k*0) spectra are decidedly different in the two crystals.

TABLE 2. INTENSITY OF REFLECTIONS. MEASUREMENTS WITH THE IONIZATION SPECTROMETER

Indices	Eudidymite (Mo K_α radiation 0.71 Å)			Epididymite (Rh K_α radiation 0.61 Å)		
	$\sin\theta$	$\rho\times10^6$	F obs.	$\sin\theta$	$\rho\times10^6$	F obs.
200	.0582	32.4	68.8	.0487	90.0	92
400	.1165	152.0	246.0	.0973	120.0	154
600	.1746	3.7	43.0	.1459	5.5	41
800	.2327	3.9	50.7	.1946	12.0	69
10.0.0	.2910	1.6	37.2	.2433	23.6	111
12.0.0	.3495	—	—	.2919	27.3	135
14.0.0				.3405	—	—
020	.0972	72.7	139.0	.0839	30.3	68
040	.1945	—	—	.1678	242.0	289
060	.2918	—	—	.2518	20.2	109
080	.3891	—	—	.3357	2.7	46
0.10.0	.4864	—	—	.4197	5.6	79
004	.1043	50.3	104.5	.0905	198.0	191
006	.1565	7.2	47.5	.1359	64.0	136
008	.2087	12.6	74.1	.1807	56.0	143
0.0.10	.2610	14.6	90.5	.2262	58.0	168
0.0.12	.3132	2.0	37.0	.2714	6.1	62
0.0.14	.3653	3.2	53.5	.3167	23.0	128
0.0.16				.3618	21.8	135

Further, epididymite has feldspathoid cleavages, namely two nearly equal perfect cleavage faces (001) and (100) which are at right angles. The cleavages of eudidymite are rather mica-like, one after (001) being highly perfect, the other after (110) (Palache's notation) not so perfect.

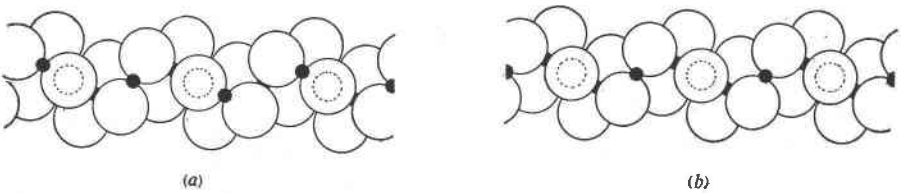
These suggest at once that, though they are built up on the same general plan, the two structures may reveal certain differences especially with regard to the *b*-parameters of the atoms.


(a)

(b)

FIG. 2. Si_3O_8-chain. Large circles represent oxygen atoms and small circles silicon atoms (*a*) plan; (*b*) elevation (as viewed from the chain-direction).

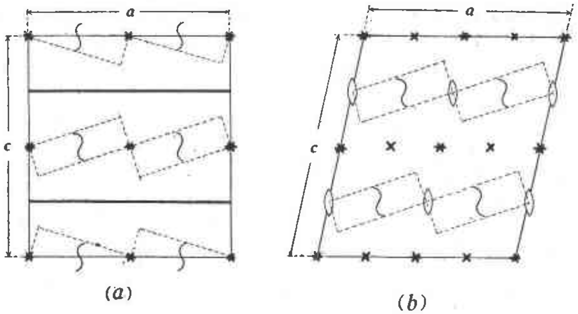
We assume now that the same Si_3O_8 groups (Fig. 2) as found in epididymite play a main rôle in the structure of eudidymite. In epididymite the Si_3O_8 groups are joined to form a sheet of the composition $NaSi_3O_7$ by Na atoms lying on the centers of symmetry. In eudidymite this must be done by Na atoms lying on the two-fold rotation axes. The ways in which two different sheets of the same composition $NaSi_3O_7$ are built from the Si_3O_8 groups and Na atoms are illustrated in Fig. 3. The one fits well into the space group $C_{2h}{}^6$ and the other into the space group $V_h{}^{16}$ as shown in Fig. 4.


(a)

(b)

FIG. 3. Two different modes of forming a $NaSi_3O_7$ sheet. Large circles represent oxygen atoms, medium sized circles represent sodium atoms, and small circles represent silicon atoms. (*a*) epididymite; (*b*) eudidymite.

The fundamental framework thus obtained, it is now comparatively easy to adjust the positions of atoms within the groups and to place the remaining Be atoms and (OH) groups in appropriate positions until the experimental *F*-values are satisfactorily accounted for.



(a) (b)

FIG. 4. The $\mathrm{Si_3O_8}$ groups arranged in the space group V_h^{16} (epididymite) and in the space group C_{2h}^6 (eudidymite). Dotted rectangles represent the $\mathrm{Si_3O_8}$ groups. Crosses and asterisks represent centers of symmetry. Heavy full lines represent the traces of reflection planes. Other symbols as in common use. Projections on (010). (*a*) epididymite; (*b*) eudidymite.

In Table 3 we give the coordinates of atoms in the structure. In Table 4 are given the *F*-values obtained with the ionization spectrometer compared with those calculated for the structure. In Table 5 are given the intensity of reflections observed on Weissenberg photographs compared with the calculated *F*-values. The agreement between the theoretical and experimental values is very satisfactory, in view of the number of parameters involved.

TABLE 3. COORDINATES OF ATOMS IN DECIMAL FRACTIONS OF THE AXIAL LENGTHS. THE ORIGIN IS PLACED AT A CENTER OF SYMMETRY

Kind of Atom	Number in the Cell	x/a	y/b	z/c
$\mathrm{O_{I}}$	8	.052	.030	.396
$\mathrm{O_{II}}$	8	.552	.030	.396
$\mathrm{O_{III}}$	4	.000	.275	.250
$\mathrm{O_{IV}}$	4	.500	.275	.250
$\mathrm{O_{V}}$	8	.161	.030	.190
$\mathrm{O_{VI}}$	8	.661	.030	.190
$\mathrm{O_{VII}}$	8	.208	.315	.372
$\mathrm{O_{VIII}}$	8	.708	.315	.372
$\mathrm{Si_{I}}$	8	.063	.415	.312
$\mathrm{Si_{II}}$	8	.563	.415	.312
$\mathrm{Si_{III}}$	8	.241	.122	.243
$\mathrm{Na_{I}}$	4	.000	.030	.250
$\mathrm{Na_{II}}$	4	.500	.030	.250
Be	8	.427	.130	.320
(OH)	8	.303	.190	.494

TABLE 4. INTENSITY OF REFLECTIONS. MEASUREMENTS WITH THE IONIZATION SPECTROMETER (Mo Kα RADIATION 0.71 Å)

Indices	Sin θ	$\rho \times 10^6$	F obs.	F calc.
200	.0582	32.4	68.8	+ 99.6
400	.1165	152.0	246.0	+278.8
600	.1746	3.7	43.0	− 35.6
800	.2327	3.9	50.7	−117.7
10.0.0	.2910	1.6	37.2	− 84.0
12.0.0	.3495	—	—	+ 47.6
020	.0972	72.7	139.0	+197.2
040	.1945	—	—	+ 14.5
060	.2918	—	—	+ 2.9
080	.3891	—	—	− 16.8
0.10.0	.4864	—	—	+ 28.4
002	.0521	390.0	199.8	−391.0
004	.1043	50.3	104.5	+ 90.1
006	.1565	7.2	47.5	− 66.6
008	.2087	12.6	74.1	+ 78.0
0.0.10	.2610	14.6	90.5	+ 83.2
0.0.12	.3132	2.0	37.0	+ 32.3
0.0.14	.3653	3.2	53.5	+ 98.8

TABLE 5. INTENSITY OF REFLECTIONS. INTENSITY ESTIMATED ON THE WEISSENBERG PHOTOGRAPHS. (Co $K\alpha$ RADIATION 1.788 Å)

Indices	*I* obs.	*F* calc.	Indices	*I* obs.	*F* calc.
110	—	+ 6.0	113	m	+ 45.5
130	w	+ 5.1	11$\bar{3}$	m	+ 52.0
220	s	+150.0	114	m	− 10.4
310	—	+ 11.2	11$\bar{4}$	w	− 2.0
330	—	− 16.3			
440	m	+ 59.0	131	—	− 1.8
510	—	− 7.4	13$\bar{1}$	w	− 34.3
710	w	+ 17.1	132	w	+ 6.6
			13$\bar{2}$	w	+ 8.2
204	w	+ 14.6	133	w	− 31.9
20$\bar{4}$	w	+ 14.0	13$\bar{3}$	w	− 23.0
404	w	− 48.0			
40$\bar{4}$	s	+236.0	221	m	+ 88.0
402	m	+ 65.5	22$\bar{1}$	s	−216.8
40$\bar{2}$	s	−267.9	222	m	+ 77.5
			22$\bar{2}$	s	+105.5
021	w	+ 35.0	223	w	− 15.3
022	s	−172.0	22$\bar{3}$	m	+ 70.5
023	w	+ 43.5	224	—	− 25.0
041	m	−120.0	22$\bar{4}$	m	−158.6
042	w	+ 40.0			
311	w	+ 26.5			
31$\bar{1}$	m	− 31.5			
312	w	+ 35.5			
31$\bar{2}$	—	+ 8.0			
331	w	+ 19.0			
33$\bar{1}$	w	+ 16.5			
332	w	− 25.9			
33$\bar{2}$	m	+ 30.3			

THE STRUCTURE DESCRIBED

The structure of eudidymite is shown in Fig. 5, which is a projection on (010). The structure, like that of epididymite, is built up of the complex chains Si_3O_8 stretched parallel to the *b*-axis. These Si_3O_8 groups are joined to each other holding in common oxygen atoms on the border and form with Na a sheet of the composition $NaSi_3O_7$ lying parallel to (001). In order to make the three-dimensional crystal the sheets are heaped one upon another in parallel position, beryllium atoms and the (OH) groups lying in between and linking them.

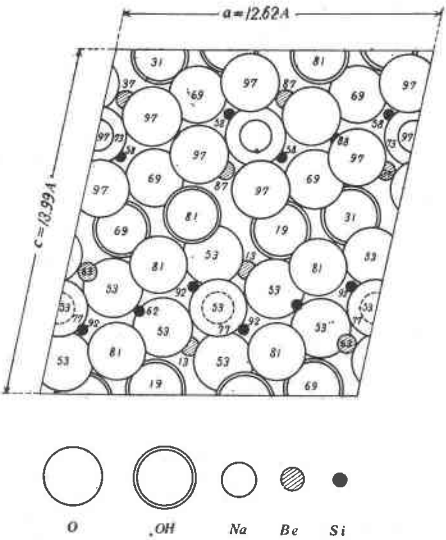


FIG. 5. The structure of eudidymite, projected on (010). Numbers given in decimal fractions of the *b*-length are the height of atoms.

In the structure thus built up Si atoms are surrounded by four oxygen atoms, Be atoms by three oxygen atoms and one (OH) group, both arranged nearly in tetrahedral fashion while Na atoms are at the center of more or less distorted octahedra formed of oxygen atoms. Each oxygen atom is shared either by two Si atoms or by one Si and two Na atoms, or by one Si, one Na and two Be atoms, while each (OH) group is linked to one Be atom. Ionic polyhedra, save Na octahedra which share faces with the adjoining Si tetrahedra, share only corners. Pauling's rule is obeyed completely. In Table 6 are given interatomic distances in the structure.

STRUCTURAL RELATION TO EPIDIDYMITE

In Fig. 6 the structure of epididymite is given contrasted to that of eudidymite. These are idealized projections on (001). We see here that the structural scheme is almost the same in both minerals. They have similar Si_3O_8 chains and $NaSi_3O_7$ sheets, the only apparent difference being that in epididymite one sheet lies on top of the other in a *symmetrical* position, while in eudidymite they lie in *parallel* position.[9]

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[9] In eudidymite the atoms in one sheet have not the same *b*-parameters with the corresponding atoms in the next sheet, while in epididymite they have exactly the same *b*-parameters owing to the reflection planes. This explains the difference in the *b*-spectra of the two crystals.

TABLE 6. INTERATOMIC DISTANCES IN EUDIDYMITE

Atom	Neighbor	Distance in Å	Atom	Neighbor	Distance in Å
Si_{I}	O_{I}	1.62	O_{VI}	O_{VII}	3.34
	O_{III}	1.45		O_{VIII}	3.24
	O_{V}	2.56			
	O_{VII}	1.89	O_{VII}	O_{VIII}	3.78
Si_{III}	O_{V}	1.44	(OH)	O_{II}	3.33
	O_{VI}	1.44		O_{III}	3.76
	O_{VII}	2.06		O_{VI}	3.06
	O_{VII}'	2.06		O_{VII}	3.32
O_{I}	O_{III}	2.71	(OH)′	O_{VII}'	2.12
	O_{V}	3.50		O_{II}'	2.66
	O_{VII}	2.65		O_{I}'	2.92
O_{II}	O_{II}'	3.48	Na_{I}	O_{I}	2.04
				O_{III}	1.84
O_{III}	O_{V}	3.03		O_{V}	2.36
	O_{VII}	2.80			
			Be	O_{I}	2.20
O_{IV}	O_{VII}	2.95		O_{III}	1.98
				O_{VI}	1.36
O_{V}	O_{VI}	2.48		(OH)	2.14
	O_{VII}	3.24			
	O_{VIII}	3.34			

Prime denotes atoms in the adjoining cell.

Epididymite, nevertheless, cannot be said in a strict sense to be an internal twin of eudidymite, since the $NaSi_3O_7$ group, which should be regarded as the constituent of "a twin," is different in the two structures.

It has been pointed out that in eudidymite the octahedral group of oxygen atoms around Na atom holds faces in common with adjoining tetrahedral groups around the Si atom. This is also the case with epididymite. The Na atom, however, in eudidymite, lies on the two-fold rotation axis and in epididymite on the center of symmetry. Faces commonly held by the octahedral and tetrahedral groups are *inclined* to each other in the former and *parallel* in the latter (Fig. 7). This point may be described thus: the arrangements of oxygen atoms are almost identical in both $NaSi_3O_7$ groups. There are, however, two different sets of positions for Si atoms, one being represented by Si atoms in eudidymite, the other by those in epididymite. Consequently epididymite should not be regarded as an internal twin of eudidymite, although very close to it.

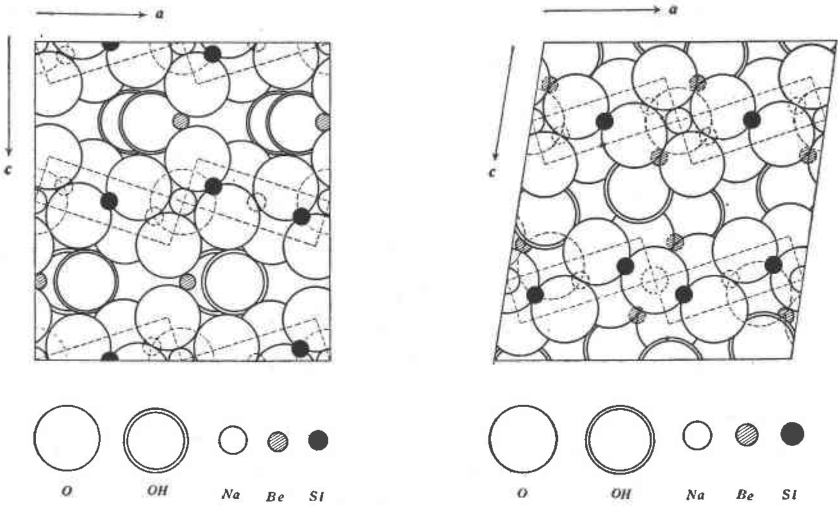
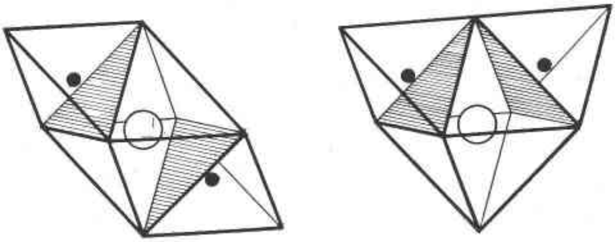


FIG. 6. The structure of epididymite (left) contrasted to that of eudidymite (right). The positions of atoms are displaced from their true positions to ideal positions to reveal the relationship of the two structures. Projections on (010).



(*a*) (*b*)

FIG. 7. Tetrahedral groups adjoining an octahedral group of oxygen atoms in epididymite (*a*) and in eudidymite (*b*). Common faces are shaded. Large open circles represent sodium atoms. Small black circles represent silicon atoms. Oxygen atoms, lying on the octahedral and tetrahedral corners are omitted.

A further difference between the two structures is the role of BeOH which binds the sheets to form the three-dimensional crystal. In epididymite Be is in the center of a tetrahedron formed of two oxygen atoms and two (OH) groups, one of the oxygen atoms belonging to a $NaSi_3O_7$ sheet and the other to the next one. The tetrahedron holds commonly the (OH) groups with the adjoining similar tetrahedrons, forming a chain of the composition BeO_2OH stretched parallel to the direction of the *b*-axis and also to the direction of the Si_3O_8 chains. The structure is ionic in bond in every respect. In eudidymite, on the contrary, the Be atom is in the center of a tetrahedron formed by three oxygen atoms of a $NaSi_3O_7$ sheet and one (OH) group, forming a giant sheet $BeOHNaSi_3O_7$ parallel to (001). Such sheets are held together by a van der Waal force between them. The structure is molecular. The extremely perfect, mica-like cleavage after (001) in eudidymite is thus explained.