

Crystal Structures with a Chabazite Framework. I. Dehydrated Ca-Chabazite*

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The crystal structure of dehydrated Ca-chabazite (composition $\text{Ca}_{1.95}\text{Al}_{3.9}\text{Si}_{8.1}\text{O}_{24}$) was determined from the [001] projection of the rhombohedral cell ($R\bar{3}m$; $a = 9.37 \text{ \AA}$, $\alpha = 92^\circ 01'$). Each corner of the rhombohedral cell is occupied by a ditrigonal prism of twelve linked tetrahedra with an Si, Al–O tetrahedron lying at each vertex of the prism. The resulting three-dimensional network contains large ellipsoidal cavities linked together by apertures to form a honeycombed structure. The apertures are bounded by 8-membered rings of tetrahedra and have an approximately rectangular free area of 3.1 by 4.4 Å. Three peaks for Ca atoms were located, the electron density corresponding to 0.6 (1-fold) and 0.35 (2-fold) atoms. The total (1.3) is less than the 1.95 found by chemical analysis but slight evidence for a possible 12-fold position occupied on the average by one/sixteenth of a Ca atom was found. The charge distribution in the structure is poor, as would be expected for such an unstable structure as this. Dehydration causes a major change in the Si, Al–O framework.

General introduction

For both academic and practical reasons the zeolite family of minerals has become the object of increasing research activity in the last decade. When dehydrated, the sponge-like structure of a zeolite offers a large, electrically active, internal surface, to which access is controlled by limiting apertures. As a result, zeolites can be used in the separation of molecules by selective adsorption, and as catalysts in chemical reactions, to mention just two of the many possibilities. In addition, it seems possible that zeolites may become important in solid-state electronic and optical technology. Turning to petrology, zeolites have been found to occur over a wide range of rocks: for example, from deep-sea ocean sediments, low-grade metamorphic rocks and the cavities of volcanic rocks—and are becoming of especial significance in diagenetic and metamorphic rocks.

The object of the present series of papers is to produce data on the atomic coordinates of different states of a zeolite in order to provide a basis for interpretation of the chemical and physical properties. Chabazite was chosen for this work because it shows adsorption characteristics similar to the commercial molecular sieves, and unlike them occurs in crystals large enough for single-crystal work. Although good results have been obtained by powder X-ray studies on the Linde *A* synthetic zeolite (Reed & Breck, 1956; Howell, 1960) and on both *A* and *X* zeolites (Brousard & Shoemaker, 1960), these studies fall short of revealing the positions of H_2O molecules in the hydrated zeolites and leave some doubt about the exact cation positions. Indeed it will appear that

difficulties of interpretation arise even with single-crystal data.

In 1956, Dr D. W. Breck (private communication) pointed out that the observed sorptive properties of chabazite were not consistent with the crystal structure proposed by Wyart (1933). Subsequently a new Si, Al–O framework was determined by Dent & Smith (1958), which did explain these properties. The new structure also permitted an explanation of the occurrence of intergrowths of chabazite and gmelinite, and allowed a prediction of the structure of gmelinite. Working independently Nowacki, Koyama & Mladek (1958) confirmed the correctness of the new structure, while Fischer (1960) has described the structure of gmelinite. The new Si, Al–O framework had been determined for the hydrated Ca-exchanged chabazite, but the early attempts to determine the positions of the Ca ions and the H_2O molecules proved abortive. Consequently, a chabazite crystal was dehydrated and the crystal structure determined. Considerably different coordinates were obtained for the framework indicating a marked distortion upon dehydration. This time it was possible to locate the Ca ions. Further studies permitted a solution of the structure of the hydrated Ca chabazite, which will be described by Glasser (née Dent) and Smith in a subsequent paper. Following this work, Fang & Smith determined the structure of a Ca– Cl_2 -chabazite, in which the H_2O molecules were replaced by Cl_2 .

Chabazite is a rare mineral of variable composition occurring mainly in cavities of basaltic rocks, with habits varying from the simple rhombohedral to the complex interpenetrating hexagonal (phacolite) arrangement. Walker (1951) in a detailed study of the occurrence of chabazite and other zeolites in the basalts of N. Ireland has shown that the habit of chabazite is a function of geographic position and presumably of the nature of the solution from which

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the chabazite was formed. Considerable variation of the optics of chabazite has been found, indicating a range from uniaxial to quite markedly biaxial material (Winchell & Winchell, 1951). Majer (1953) has found that well-developed pseudo-rhombohedral chabazite crystals from veins in a Yugoslavian andesite rock consist of twins of six triclinic individuals with

$$\alpha = 1.4848, \beta = 1.4852, \gamma = 1.4858$$

and

$$2V = +55 \text{ to } +82^\circ.$$

Hewett, Shannon & Gonyer (1928) record that chabazite from Grant County, Oregon is biaxial positive with $2V$ about 30° . Ventriglia (1953) reports that chabazite is slightly piezoelectric. In spite of these observations all X-ray measurements on chabazite recorded to date (Wyart, 1933; Strunz, 1956; Nowacki, Koyama & Mladeck, 1958; Dent & Smith, 1958) are consistent with rhombohedral symmetry. Because of the lack of any X-ray evidence that requires a space group of lower symmetry, the space group $R\bar{3}m$ has been assigned by these investigators. The chabazite crystals used in the present series of studies are from Benton County, Oregon and show the biaxial optical properties characteristic of chabazite. In spite of this, the X-ray measurements of the hydrated zeolite are consistent with rhombohedral symmetry. In the determination of the crystal structure of the dehydrated Ca-chabazite, there has been no need to postulate twinning of a structure with symmetry lower than rhombohedral, but in hydrated Ca-chabazite it is possible to interpret the arrangement of some of the water molecules as the consequence of such twinning.

Experimental data

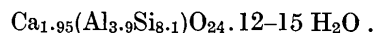
The chabazite crystals were kindly supplied and chemically analyzed by courtesy of Drs D. W. Breck and P. A. Howell of the Linde Company with the following results:

	Wt. %
SiO ₂	48.5 ± 0.2
Al ₂ O ₃	19.6 ± 0.3
CaO	9.82 ± 0.05
Na ₂ O	0.62 ± 0.05
K ₂ O	0.55 ± 0.05
Ignition loss	18.1 ± 0.3
	97.2

The calculated contents of the rhombohedral chabazite cell, based on 24 oxygen atoms, are: Ca_{1.8}(Na + K)_{0.3}(Al_{3.9}Si_{8.1})O₂₄· x H₂O, where x is uncertain. The ignition loss was determined after heating overnight at 450 °C. and is probably smaller than the initial water content. Vacuum activation on the McBain system gave a weight loss of 26.7% in close agreement with the saturation water capacity (26.2%) found for the same material. The water content in chemical analyses of natural chabazites is typically

about 22% but this value may be too low because of difficulty in removing the last traces of water. Twelve molecules of water in the unit cell correspond to 22 wt.% of water, whereas fifteen water molecules would give 27 wt.%. Consequently the value of x for the Benton County chabazite can be expected to lie between 12 and 15.

The natural chabazite was ion-exchanged by Dr P. A. Howell to give a product that contains more than 99% Ca atoms in the exchangeable positions. The composition of this Ca-chabazite is



Another portion was ion-exchanged to give a product more than 99% in the sodium variety.

Dr P. A. Howell kindly activated four crystals of Ca-chabazite by heating to 350–370 °C. for 4½ hr. in a near vacuum of 0.02 microns. The crystals were sealed in thin-walled silica glass capillaries and cooled to room temperature. One of the crystals yielded fairly satisfactory reflections on a Buerger precession camera and a series of photographs was obtained for the [001] axis using Mo $K\alpha$ radiation. The reflections, even for this crystal, were somewhat irregular suggesting the presence of disorientation. During the last long-exposure photograph, the crystal broke into two pieces with an angular separation of about a degree. As a result of the halo from the glass capillary, the irregular intensity distribution of the reflections and the non-observance of the weak intensities, the accuracy of the structure amplitudes was not as good as can be obtained normally by eye-estimation. Because the process of dehydration causes cracks in the chabazite with resulting irregular spot profiles, there is little hope of obtaining accurate intensities by eye estimation. Further intensity measurements on zeolites are being made by a single-crystal counter Weissenberg and monochromatized Mo K radiation. By this method, irregular intensity profiles can be accurately integrated while the use of monochromatized radiation reduces the haloing from the glass capillary.

The dimensions of the rhombohedral cell of the dehydrated-Ca-chabazite are compared with those for the other variants in the following list:

	(Å)	α
Dehydrated-Ca	9.37	92° 01'
Hydrated-Ca	9.45	94° 28'
Hydrated-Na	9.40	94° 06'
Cl ₂ -Ca	9.41	95° 21'
	± 0.5%	± 7'

Whereas the cell edge changes very little between the different chabazite specimens, the angle α varies considerably. The small decrease in α during dehydration is remarkable in view of the loss of 12 to 15 water molecules, and shows that the Si-O framework in chabazite has a strong inherent rigidity.

The crystal used in the present study was a nearly

regular rhombohedron, about 0.3 mm. on edge. No absorption corrections were applied because they are insignificant compared to the other errors. Each reflection occurs four times on the precession photograph. The corresponding intensities were averaged and corrected for the Lorentz-polarization factors.

The structure was refined by successive ($F_o - F_c$) syntheses using signs determined by Dent & Smith (1958) for the framework of hydrated-chabazite as the starting point. Large shifts in the atomic coordinates of the Si, Al and oxygen atoms were found in the initial syntheses. Positions for calcium atoms were revealed by the occurrence of peaks that could not be explained by Si, Al and oxygen atoms. It was found that the peaks were not high enough for calcium atoms and it was necessary to assign fractional atoms on the basis of a statistical distribution. Structure factor calculations were made on the Pennstac digital computer using the empirical scattering factor curves of Bragg & West (1929). Because the intensity data are not very accurate and because there is uncertainty about the state of ionization in silicate structures, the calculations were not repeated for the more significant theoretical scattering factors given recently by Berghuis *et al.* (1955) and others. Comparison of the Bragg & West curves with the latter data shows that the effective temperature factors are: Al, Si; $B=0.3 \text{ \AA}^{-2}$, and Ca; $B=0.4 \text{ \AA}^{-2}$. It was found from the difference syntheses that the ratio of the Bragg & West scattering factors for oxygen to silicon

was about 10% too high, so a simple factor was used to take this into account. The actual scattering factors used in the final calculations are shown in Fig. 1. Examination of the difference syntheses revealed no systematic pattern of density that would require modification of the scattering factors.

The difference syntheses were summed either on XRAC (by kind permission of Prof. R. Pepinsky) or by Beevers-Lipson strips when XRAC was occupied with other work. Examination of the distribution of equivalent positions and symmetry elements of $R\bar{3}m$ shows that each set of general positions produces more than one peak in the [001] rhombohedral projection. Thus the equivalent position (x, y, z) leads to three independently-determined peaks whose coordinates in projection are (x, y) , (y, z) and (z, x) . Consequently all three coordinates (x, y, z) can be determined from this one projection, and moreover each coordinate is determined twice. Similar considerations apply to the variable parameters of those special positions which do not lie on the three-fold axes. The latter group give one independently-determined peak for each equivalent position.

Table 1. *Final atomic coordinates*

Atom	Multiplicity	x	y	z
Si	12	0.095	0.328	0.864
O ₁	6	0.284	-0.284	0.000
O ₂	6	0.124	-0.124	0.500
O ₃	6	0.238	0.238	0.878
O ₄	6	0.000	0.000	0.255
0.6 Ca ₁	1	0.000	0.000	0.000
0.35 Ca ₂	2	0.169	0.169	0.169
1/16 Ca ₃ ?	12	0.09 ₃	0.18 ₃	0.47 ₀

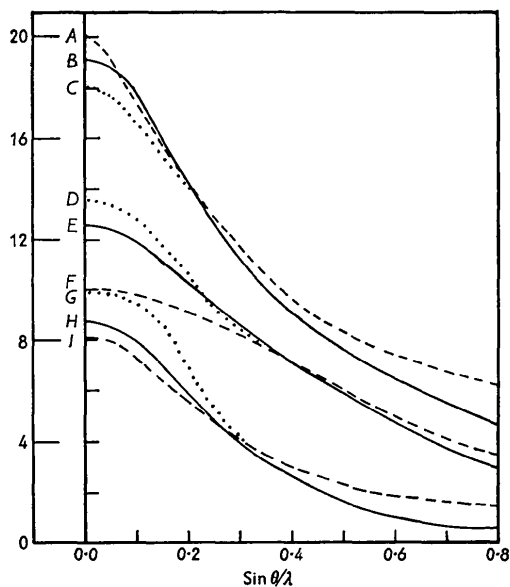


Fig. 1. Atomic-scattering factor curves. Curves B, E and H, respectively are the scattering curves used for the Ca, $(2/3 \text{ Si} + 1/3 \text{ Al})$ and O atoms in the calculations on dehydrated Ca-Chabazite. Curves A, F and I were listed by Berghuis *et al.* (1955) for Ca atoms, $(2/3 \text{ Si}^{+4} + 1/3 \text{ Al}^{+3})$ ions and O atoms, respectively. Curves C, D and G, respectively, are suggested modifications to curves A, F and I to give the scattering for Ca^{+2} ions, $(2/3 \text{ Si} + 1/3 \text{ Al})$ atoms and O^{-2} ions.

The final atomic coordinates are given in Table 1, and calculated and observed structure amplitudes in Table 2. From the difference maps, peaks equivalent in electron density to 0.6 of a calcium atom at the origin of the unit cell and 0.35 at each of two positions on the three-fold axis at $\pm(0.169, 0.169, 0.169)$ were found. The atomic scattering factors for these positions were adjusted until the peaks disappeared (apart from the random fluctuations of electron density). The total of the Ca atoms comes to 1.3, significantly less than the 1.95 in the chemical analysis. A careful search was made of the difference maps and three small peaks, only slightly greater than the average random fluctuations, were found in positions that cross-checked well according to the relation described earlier for general equivalent positions. Accordingly, 1/16 of a Ca atom was placed in this general 12-fold position—thus providing another 0.75 atom, which together with the 1.3 atoms found earlier gives a total of 2.05 in good accord with the chemical analysis. Unfortunately the contribution from this last postulated position is so small, and the intensity data are sufficiently inaccurate, that it has not been possible to come to any conclusion as to the validity or not of this position. The problem is similar to that of finding

Table 2. *Calculated and observed structure amplitudes*

<i>h</i>	<i>k</i>	<i>F_o</i>	<i>F_c</i>	<i>F_{Ca3}</i>	<i>h</i>	<i>k</i>	<i>F_o</i>	<i>F_c</i>	<i>F_{Ca3}</i>	<i>h</i>	<i>k</i>	<i>F_o</i>	<i>F_c</i>	<i>F_{Ca3}</i>
1	0	118	+119.7	+1.0	4	4	31	+31.2	0.0	10	$\bar{2}$	0	-9.6	-0.7
2		21	-17.8	+2.6	5		38	+38.4	+0.4	11		6	-7.6	+2.0
3		12	-2.1	-7.6	6		24	-21.2	-2.1	12		9	-9.2	-0.1
4		14	-16.5	+0.2	7		28	+26.6	-1.5	13		13	-9.6	0.0
5		66	-68.2	-1.8	8		44	+49.5	-2.1	3	$\bar{3}$	30	+30.3	+3.4
6		30	+29.6	+0.5	9		11	+13.3	-0.8	4		46	+47.8	-2.1
7		33	+34.6	-2.9	10		0	+6.4	0.0	5		15	+16.0	+1.8
8		36	+40.1	-2.1	11		21	+15.9	0.5	6		8	-5.2	+1.1
9		44	+48.4	+0.5	5	5	48	+52.2	-1.5	7		53	+53.6	+4.0
10		14	+15.1	+2.4	6		?	-7.8	-2.3	8		25	+25.8	+0.2
11		5	-3.5	+3.5	7		0	-0.1	0.0	9		17	-14.1	-1.6
12		20	+18.9	+0.1	8		0	+8.0	+1.8	10		9	0.0	-3.1
13		5	+5.3	+0.1	9		28	-24.7	+1.8	11		15	+10.2	-1.3
1	1	30	+38.3	-7.5	10		14	-15.0	0.0	12		8	-5.5	+0.2
2		13	+8.0	0.0	11		24	+19.7	-0.7	13		3	+1.6	+0.5
3		51	+49.3	-4.5	6	6	?	+2.8	-0.3	4	$\bar{4}$	95	+99.9	-2.8
4		38	+40.9	+3.8	7		13	+13.8	+0.2	5		59	+63.2	-1.1
5		45	-41.8	-2.0	8		14	+12.0	+0.5	6		0	+2.3	-0.1
6		11	-6.9	-2.8	9		0	-2.8	-0.7	7		34	+31.1	+0.9
7		10	-6.9	-1.2	10		7	+4.4	0.0	8		17	-14.7	+1.8
8		15	+16.8	+3.1	11		15	+16.5	+0.4	9		39	-38.0	+1.4
9		32	+34.7	0.0	7	7	14	+17.8	+2.0	10		0	+5.6	+1.4
10		17	+20.5	+1.2	8		9	+7.3	+2.1	11		16	+16.7	0.0
11		0	-1.1	-1.4	9		12	+11.4	+0.7	12		0	+1.2	0.0
12		12	+5.3	-0.7	10		17	+18.5	0.0	5	$\bar{5}$	41	+38.9	-2.5
13		5	-11.4	-0.7	8	8	15	-18.9	-1.3	6		19	-16.5	-0.8
2	2	39	+33.8	-2.5	9	9	10	-9.1	-1.1	7		7	+1.2	+0.9
3		53	+50.1	-3.5	1	$\bar{1}$	37	-41.0	-0.4	8		18	-18.9	+1.2
4		34	+36.8	+1.6	2		59	-55.9	+4.3	9		18	-17.5	-0.6
5		12	+8.7	0.0	3		20	+12.1	+1.5	10		18	+18.2	-1.1
6		6	-5.3	+2.1	4		16	+16.4	+0.5	11		13	+13.0	-0.4
7		25	-29.2	-2.7	5		11	+11.8	+1.3	12		7	-6.5	+0.9
8		29	-28.4	+0.6	6		57	+63.0	-0.2	6	$\bar{6}$	29	-28.5	-2.9
9		11	-10.5	-1.2	7		23	+20.3	+1.5	7		0	-4.0	-1.0
10		0	+3.8	+2.9	8		0	-5.9	-2.6	8		0	-0.5	+0.2
11		0	+2.3	-0.2	9		0	-1.2	-0.2	9		0	+2.5	+1.9
12		9	+7.0	+0.4	10		18	-20.6	-3.1	10		18	+18.6	+0.7
3	3	41	+45.0	+3.8	11		10	-10.4	+1.1	11		19	+15.2	+0.2
4		25	+23.1	+3.2	12		21	+21.8	-0.5	12		4	+6.0	-0.4
5		20	+21.9	+1.8	13		16	+17.8	+1.8	7	$\bar{7}$	14	-13.4	-0.3
6		19	-14.3	0.0	2	$\bar{2}$	46	-55.9	-2.1	8		7	-5.2	-1.0
7		12	+8.7	-0.1	3		19	-21.5	0.0	9		0	-2.3	-1.2
8		18	+18.2	+1.9	4		17	-14.3	-2.9	10		9	+3.7	-1.0
9		0	+6.5	+0.2	5		12	-0.6	+3.3	11		15	+16.2	-0.8
10		9	+10.7	-0.2	6		28	+21.5	-0.7	8	$\bar{8}$	31	+37.4	+1.4
11		15	+8.7	-2.7	7		35	+38.1	+1.4	9		30	+36.0	+0.6
12		10	-10.0	-0.8	8		26	+24.9	-3.6	10		7	+7.7	+1.1
					9		11	+7.8	+0.4	9	$\bar{9}$	30	+29.9	-1.1

hydrogen atoms. The calculated structure amplitudes are given in Table 2 where F_c includes the contributions of all three calcium atoms and F_{Ca_3} is the contribution for the uncertain 12-fold position. Corresponding R -factors are 12.3% including Ca_3 , and 12.7% excluding Ca_3 , both calculated by ignoring unobserved reflections; 14.8% including Ca_3 and 15.0% excluding Ca_3 , both calculated for all reflections. It is clear that further data, using a counter method and three-dimensional collection, are needed to resolve this problem. In the discussion, the consequences of the presence or otherwise of the third type of calcium atom are considered, but it must be emphasized that this is purely speculative.

Description of the structure

The Si, Al-O framework of chabazite is formed by joining together four, six and eight-membered rings of tetrahedra. It is very easy to demonstrate the spatial relationships of the framework from a three-dimensional model formed by packing spheres which represent the oxygen atoms: on the contrary, it is difficult to show the properties on two-dimensional figures. To visualize the structure it is best at first to consider only the Si, Al atoms (Fig. 2). The most important sub-unit of the chabazite framework is formed by linking together two six-membered rings, each of di-trigonal symmetry, to form an arrangement in which the Si, Al atoms lie at the corners of a deformed hexagonal prism. The sides of the hexagonal prisms are formed of four-membered rings. Other four-

membered rings are used to join together the deformed hexagonal prisms to form a framework in which there are large ellipsoidal cavities linked by apertures. Each deformed hexagonal prism lies at the corner of a rhombohedral cell, and each face of the cell contains an aperture formed from an eight-membered ring. There is one cavity to each unit cell. Oxygen atoms lie between each pair of Si, Al atoms and in a packing model completely hide the Si, Al atoms so that the chabazite framework appears to consist solely of oxygen atoms. Fig. 3 is a projection parallel to the z -axis of the rhombohedral unit cell. The body diagonal of the cell is the inverse three-fold axis, and it is rather difficult to locate in Fig. 3 the triplest of atoms related by the symmetry axis. The six-fold rings look very distorted in this projection because of the oblique angle. Fig. 4 which is a projection down the three-fold axis gives a true perspective of the deviation from six-fold symmetry. Each corner of the unit cell in Fig. 3 is surrounded by two of the di-trigonal rings, and each face contains one of the eight-membered rings which form the connecting apertures. To avoid

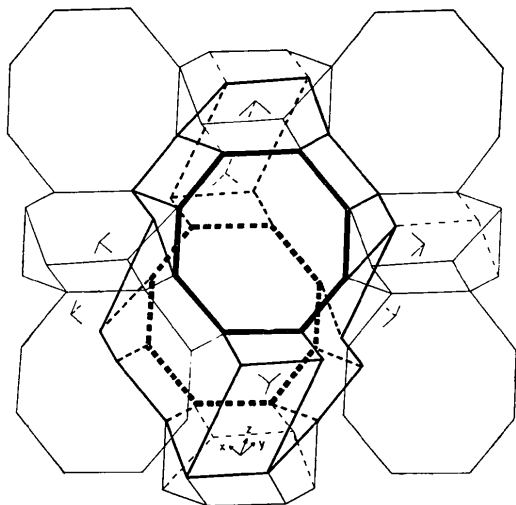


Fig. 2. Three-dimensional pattern of the chabazite framework, depicted in a simplified way by giving only the positions of the Si, Al atoms. The Si, Al atoms lie at the corners of very distorted pseudo-hexagonal prisms, which are linked by 4-membered rings to give a honeycombed structure. The center of each prism is at the corner of the rhombohedral unit cell. The oxygen atoms lie approximately halfway along the lines which join each pair of Si, Al atoms, but displaced away from the lines to give the tetrahedral angles between the Si, Al-O bonds. Each cavity is outlined by two 6-membered, six 8-membered and twelve 4-membered rings. Each 6-membered ring joins the base of a pseudo-hexagonal prism to the cavity, and six of the 4-membered rings join the side faces of pseudo-hexagonal prisms to the cavity. The other six 4-membered rings are each common to two cavities. Each 8-membered ring contains an aperture through which molecules may pass. The shape of the aperture is given in Figs. 8 and 9. An idealized version of this diagram was published by Dent & Smith (1958) in which the prisms were given a regular hexagonal shape. If the present diagram is hard to visualize, the earlier simplified diagram should be consulted.

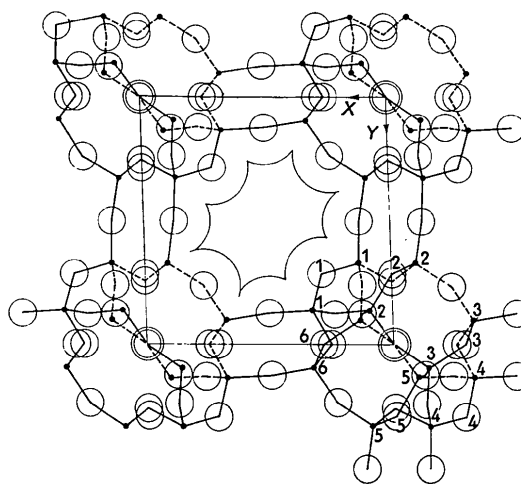


Fig. 3. Projection down the rhombohedral [001] axis of the Si, Al-O framework of dehydrated-Ca-chabazite. The Si, Al atoms are shown by solid circles and the oxygen atoms by small open circles of size about one-third the ionic radius. In the centre of the eight-membered ring is a representation of the aperture, using 1.35 Å as the effective radius of the oxygen atom. The Si, Al atoms that form one of the double six-membered rings are numbered 1-6, as also are the O_1 oxygen atoms that link together the Si, Al atoms of the framework.

confusion in Fig. 3, the oxygen atoms are shown by circles only one-half the true radius, but the true extent of the oxygen atoms that form the aperture in the middle of the diagram is shown. The aperture is slightly tilted out of the plane of projection but the rectangular shape shown in Fig. 3 is almost a true representation of the free area available to molecules. Fig. 4 shows that the six-membered rings lie in layers which repeat every six units along the three-fold axis. If the levels are denoted 0, 1, 2, 3, 4, 5, 6 etc., the rings occur in pairs at 1, 2 and 3, 4 and 5, 6 etc. to form the pseudo-hexagonal prisms described earlier. The centers of these prisms lie in an $ABCABC$ -sequence such as occurs in the cubic close-packing of spheres.

The basic unit in chabazite is the pseudo-hexagonal prism containing two di-trigonal rings of Si, Al-O tetrahedra. Fig. 5 is a perspective view of this unit, showing the way in which the oxygen atoms are packed together, and their relation to the calcium atoms. The six oxygen atoms that join with the Si, Al atoms to form six-membered rings are alternatively of types O_3 and O_4 . Around the calcium atom, Ca_1 , which lies at the origin of the unit cell, the three O_4 atoms from one ring of the pseudo-hexagonal prism join with the three O_4 atoms from the other ring to form a polyhedron which is almost an octahedron. The other oxygen atoms, O_3 , lie further away from the three-fold axis, forming together with the O_4 atoms a deformed hexagonal ring which only has trigonal symmetry. The two rings are joined by six O_1 atoms which lie on a ring of true hexagonal symmetry.

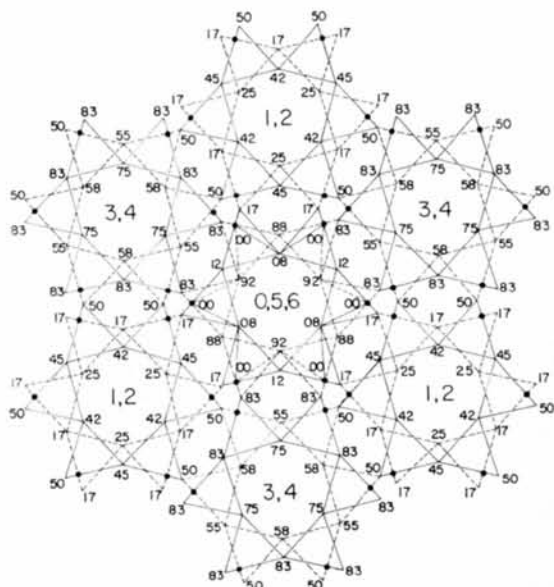


Fig. 4. Projection down the hexagonal [0001] axis of the oxygen framework of dehydrated Ca-chabazite. The oxygen atoms lie at the corners of the tetrahedra. In the centre of the diagram only four lines are used to represent a tetrahedron because the O_1 atoms (shown by a solid circle at height 00) lie in projection on the line joining the O_3 atoms (height 12 or 88) and the O_2 atoms (height 17 or 83). In the outer parts of the diagram only three lines are used to outline a tetrahedron. The small numbers give the heights of the atoms, expressed as percentages of the hexagonal c -axis spacing. Dent & Smith (1958) found, that to a first approximation, the hexagonal rings in chabazite lay in layers displaced $c/6$ apart, that the rings occurred in pairs to form hexagonal prisms, and that the centers of the hexagonal prisms fell in an $ABCA$ sequence such as in cubic close-packing. The large numbers in the present diagram show the heights of the six-membered rings and the pseudo-hexagonal prism 12 corresponds to A , 34 to B and 56 to C . This diagram gives a true perspective of the deviation from hexagonal symmetry of the six-membered rings.

Oxygen atoms of type O_2 complete the tetrahedra around the Si, Al atoms. The six O_2 atoms of each ring occur in three pairs of two atoms, each pair being almost in contact and separated from the other pairs by about half an ionic radius. The O_2 atoms join up the pseudo-hexagonal prisms and can be loosely regarded as forming 'hinges' between the clusters of atoms that form the hexagonal prisms.

Fig. 6 is a diagram obtained by considering only the positions of the O_2 atoms. Polyhedra have been drawn whose corners are the twelve O_2 atoms projecting from each pseudo-hexagonal prism. The position of the six apertures that lie at the faces of each unit cell are shown by the shaded areas. It should be realized that the shaded areas do not correspond to the free area; in fact the approximately rectangular free area shown in Fig. 3 has its long axis parallel to the short axis of the shaded area in Fig. 6.

The Ca_2 atoms lie on the body diagonal of the cell near the center of the six-membered rings formed from the O_3 and O_4 atoms but displaced away from the

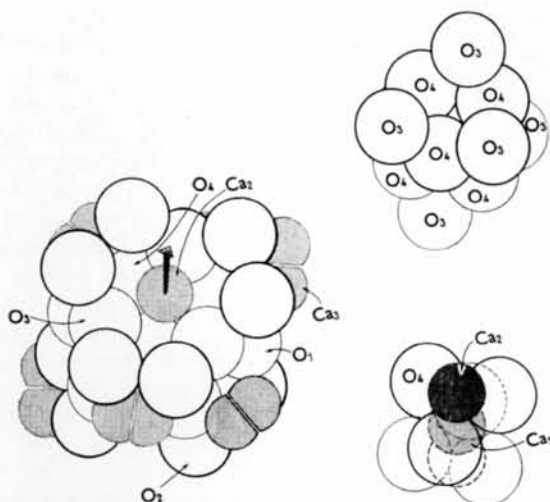


Fig. 5. Perspective drawing of one of the pseudo-hexagonal clusters of Si, Al and O atoms that lie at each corner of the rhombohedral unit cell. The diagram at the lower right shows how six O_4 atoms form an octahedron around a Ca_1 atom, and how three of them are in contact with a Ca_2 atom on one side of the octahedron, and three others in contact with another Ca_2 atom on the other side. The diagram at the upper right shows the relation between the O_3 and O_4 atoms that form the two 6-membered rings. At the upper left is the complete diagram showing all the atoms of the cluster, except those hidden by other atoms. Note how the O_2 atoms occur in six pairs almost in contact. The postulated Ca_2 atoms occur in six pairs of positions, each pair about 1 Å apart. In the centre of the diagram is shown the $\bar{3}$ axis.

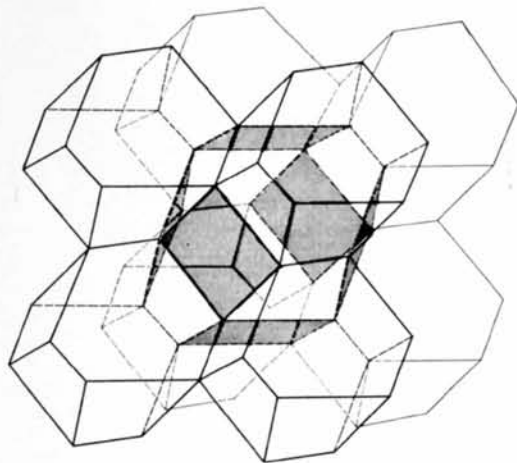


Fig. 6. Perspective drawing using polyhedra formed by joining the O_2 atoms. Each polyhedron consists of two hexagons of ditrigonal symmetry linked by six quadrilaterals. A polyhedron lies at each corner of the unit cell to form a framework with cavities. Each cavity has six windows, depicted by the shaded areas, that permit sorption in all three directions. When the oxygen atoms are shown by spheres the apertures have the shape given in Figs. 8 and 9. The perspective of this drawing is slightly different from that of Figs. 2 and 9.

center of the hexagonal prism. There are two of them, corresponding to the two six-membered rings that form each prism.

The Ca_3 atoms, if they exist at all, occur in pairs of positions, 0.8 Å apart, lining the inside of the cavities.

Discussion of the structure

(a) Arrangement of calcium atoms, order disorder of Al, Si atoms and charge distribution

The most striking thing about the structure is the arrangement of the calcium atoms. Given a framework of the chabazite type, one can soon discover that there is no way of placing two calcium atoms per unit cell in such a way that Pauling's rules are accurately satisfied. The best position one can discover is at the origin of the unit cell. This assumes that the Si, Al-O framework is sufficiently flexible for the calcium atom to pull in six oxygen atoms to form an octahedron around it. Unfortunately there is only one position of this type in each unit cell. The next best position is at the center of the six-membered ring, of which there are two in each unit cell. Here the coordination polyhedron is incomplete because all the oxygen atoms lie in a plane, and there is no possibility of a distortion large enough to give an octahedron of oxygen atoms around each calcium atom. Furthermore the average Ca-O distance to the six oxygen atoms is 2.7 Å, rather larger than the usual value of 2.4 Å. All other positions are much worse for they can only provide oxygen atoms on one side of the polyhedron. Such a position is that postulated for the Ca_3 atoms which lie on the surface of the cavity.

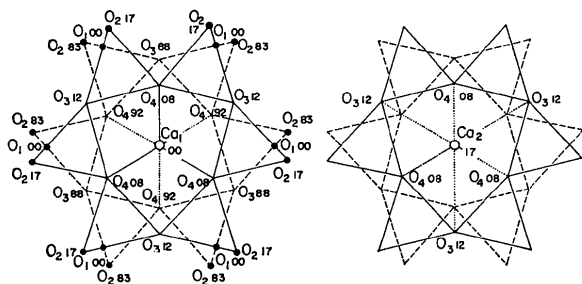


Fig. 7. Hexagonal [0001] projection of the cluster of atoms that form the double six-membered rings. The diagram on the left shows the coordination around the Ca_1 atom and that on the right the environment of one of the Ca_2 atoms. Note that the Ca_2 - O_3 distance is much greater than the Ca_2 - O_4 distance, and that the Ca_2 atom is displaced away from the centre of the six-membered ring formed from the O_3 and O_4 atoms. The heights of the atoms are expressed as percentages of the c -axis spacing.

The actual distribution found from the crystal structure determination is a combination of the possible arrangements, and because of the low electron density at the sites for calcium atoms, these must be only partially occupied on either a time or space basis, or both. At the origin, 0.6 of a calcium atom lies in a near-octahedron of O_4 atoms at a distance of 2.38 Å (Figs. 7 and 8). At 3.3 Å lie the O_3 atoms, which together with the O_4 atoms form the six-membered

rings. It is reasonable to suppose that one of the major causes of the deviation of the rings from six-fold symmetry is the formation of this octahedron of O_4 atoms by the Ca_1 atom. Near the centres of the six-membered rings, but displaced away from the origin, are Ca_2 atoms occupying 30% of the sites. Each Ca_2 atom has three near oxygen neighbours, O_4 , at 2.37 Å and three distant ones, O_3 , at 2.84 Å. These O_4 atoms are the same ones that are bonded to the Ca_1 atom, and if only distances less than 2.5 Å are counted for the Ca-O valence, bonds, all the valence bonds from the calcium atoms go to the O_4 atoms. Consequently there should be strong local unbalances of charge in chabazite. If the Ca_3 atom really does exist, it occupies the next most suitable site, with distances ranging from the very short distance 2.15 Å up to the long distance 3.0 Å (Table 3 and Fig. 8).

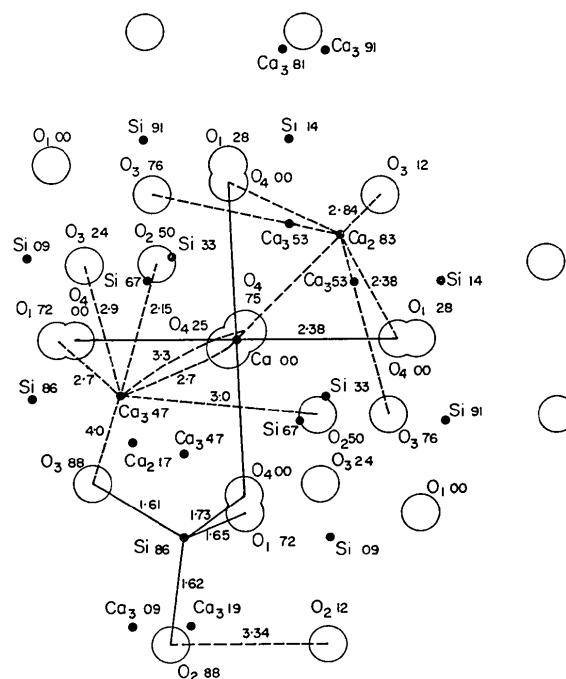


Fig. 8. Rhombohedral [001] projection of the cluster of atoms that form the double six-membered rings. The detailed coordination for a Ca_1 , Ca_2 and a postulated Ca_3 atom are shown, with the distances expressed in Å. The heights of the atoms are shown as percentages of c -axis spacing. The origin is at the centre of the diagram at the position of the Ca_{00} atom, and the x and y axes are parallel to the Ca- O_4 bonds. The two O_4 atoms which should project onto the origin have been slightly displaced to reduce confusion.

Because zeolites characteristically show ion-exchange properties, it is tempting to suggest that the calcium atoms in dehydrated Ca-chabazite are very mobile, and that part of the time they are not contributing to the coherent X-ray scattering. This would readily explain why the sum of the electron density for the Ca_1 and Ca_2 atoms is only 1.3 and not the 1.95 from the chemical analysis. Then there would be no need

to invoke the presence of the doubtful Ca_3 atoms. Unfortunately Ducros (1960) found from dielectric relaxation studies that during dehydration, after an initial increase in the critical frequency, there was a strong decrease such that the critical frequency came near zero for nearly complete dehydration. He interpreted this to mean that the relaxation time, which was about 10^{-2} sec. for the movement of Ca atoms in hydrated crystals at ordinary temperatures, decreased somewhat and then increased greatly, thus indicating that the calcium atoms were tightly held and relatively immobile in fully dehydrated crystals. It would seem likely from this that the statistical distribution of calcium atoms results from a spatial variation rather than a time variation. However, X-ray photographs are taken over periods of time that are very long compared with the dielectric relaxation times found by Ducros and it is not unlikely that slow movements of calcium atoms occur during the X-ray exposures.

Table 3. *Interatomic distances*

Si-O ₁	1.65(1) Å	Ca ₂ -O ₃	2.84(3) Å
Si-O ₂	1.62(1)	Ca ₂ -O ₄	2.37(3)
Si-O ₃	1.61(1)	Ca ₃ -O ₁	2.7 (1)
Si-O ₄	1.73(1)	Ca ₃ -O ₂	2.1 ₅ (1)
O ₁ -O ₂	2.67(1)	Ca ₃ -O ₂ '	3.0 (1)
O ₁ -O ₃	2.70(1)	Ca ₃ -O ₃	2.9 (1)
O ₁ -O ₄	2.68(1)	Ca ₃ -O ₄	2.7 (1)
O ₂ -O ₃	2.70(1)	Ca ₃ -O ₄ '	3.3 (1)
O ₂ -O ₄	2.83(1)	O ₂ -O ₂	3.34(1)
O ₃ -O ₄	2.55(1)	O ₄ -O ₄ '	3.44(1)
Ca ₁ -O ₄	2.38(6)	O ₁ -O ₁ '	5.82(1)
Ca ₁ -O ₃	3.3 (6)	O ₂ -O ₂ ''	7.50(1)
		O ₃ -O ₃ '	7.30(1)

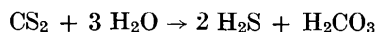
The number in brackets shows the number of bonds of this type attached to the first atom of the pair.

The distribution of the silicon and aluminum atoms in zeolites is very important in determining the charge distribution in a zeolite. Molecular sorption of polar molecules should depend strongly on the presence or absence of oxygen atoms linked to two aluminum atoms. The 8 Si and 4 Al atoms belonging to each unit cell of chabazite have been placed in a single general position of 12-fold multiplicity, which can only be strictly true if the atoms occupy the sites at random. It is probable from energy considerations that there is some local ordering of silicon and aluminum atoms such that no oxygen atom is linked to more than one aluminum atom. If the Si/Al ratio in chabazite were unity, this consideration would enforce long range order: however, the ratio is 8.1/3.9 and disorder can occur without juxtaposing two aluminum atoms. Complete long-distance order cannot occur because the Si/Al ratio is not a simple fraction, but if partial long-distance order occurs, the symmetry must fall lower than $R\bar{3}m$. It would not be possible to retain the three-fold axis but one of the mirror planes could remain. The resulting deviation from rhombohedral geometry should be very small, for the changes in rhombohedral cell dimensions caused by a much

greater change, dehydration, amount to 1% in length and 2° in angle. Thus it would be easy to overlook any lowering of symmetry in X-ray parameters, especially as twinning would probably occur. Optical properties tend to be more sensitive to Si, Al ordering than X-ray phenomena, and the biaxial optical properties of hydrated chabazite, described earlier, may be the consequence of Si, Al ordering. However, there are other possible sources of lowering of optical symmetry (such as in quartz, which is often biaxial) and the properties of chabazite may result from asymmetry in the position of the water molecules, or perhaps, merely from strain. Currently attempts are being made by other techniques, such as infra-red absorption, to obtain further evidence on this important problem.

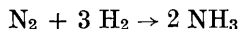
If we consider the bonding forces to be purely ionic, oxygen ions attached to aluminum ions will suffer a deficiency of electrostatic valence bonds and will attract the calcium ions more strongly than oxygen ions attached only to silicon ions. If there are different possible distributions of silicon and aluminum atoms in the unit cell it is possible that this would lead to different positions for the calcium atoms. Suppose that in each ring of six tetrahedra there are 2 Al and 4 Si atoms. The charge distribution is then equally balanced about the centre of the pseudo-hexagonal prisms formed from the two six-membered rings and a calcium atom might prefer to take a position at the centre i.e. at the Ca₁ site. For comparison, suppose that the Si, Al distribution is unbalanced so that 3 Al atoms go into one ring and only 1 Al atom into the other six-membered ring. Then the electric field would be unbalanced and the calcium atom should move nearer to the ring containing the 3 Al atoms, in a site such as the Ca₂ position found in this structure analysis. Thus different Si, Al distributions throughout the chabazite structure could lead to irregular arrangements of calcium atoms, but only if the Si, Al atoms were disordered. Twinning of ordered patterns could not lead to statistical occupancy of the Ca₁ site, for this position would be hardly affected by loss of 3-fold symmetry.

The poor local charge balance in dehydrated chabazite should result in an electrically active surface around each of the cavities. Such surfaces should have very interesting chemical properties and be able to catalyze some reactions between molecules that are small enough to pass through the apertures into the cavities. Weigel & Bezner (1927) found that CS₂ when sorbed in partially dehydrated chabazite reacted with the residual water. Upon heating, only H₂O and CO₂ were released, unless excess CS₂ were present, in which case CS₂ was also released. At the end of the heating, sulphur was formed. It seems likely that the zeolite catalyzed the reaction



followed by decomposition of the H₂CO₃ to H₂O + CO₂

and oxidation of the H_2S to $\text{H}_2\text{O} + \text{S}$. Rabinowitsch (1932), however, found that the reaction



was not catalyzed by chabazite and concluded, probably incorrectly, that gases do not take up fixed positions in zeolites. Detailed study of catalysis induced by zeolites should prove rewarding both from the theoretical and practical view points.

(b) *Molecular-sieve properties*

The process of molecular sorption depends on numerous factors but the simplest and most obvious is the size of the controlling apertures that link the cavities. Each cavity in chabazite is linked to six other cavities, through identical apertures, to give a system of inter-connected channels which cannot be blocked by impurities, such as might happen with unconnected channels. An elevation and plan of the aperture is shown in Fig. 9, where it may be seen that the oxygen atoms that form the aperture are nearly coplanar and that the free area is nearly rectangular (or elliptical). Fig. 10 shows the arrangement of apertures on one of the rhombohedral faces. If the oxygen atoms are assumed to be hard spheres with an effective radius of 1.35 Å, the long and short axes of the pseudo-rectangular free area become 4.4 Å and 3.1 Å in length, and the maximum width in the diagonal direction, 4.6 Å. Because of the importance of the data, the corresponding dimensions for the aperture in hydrated Ca-chabazite are given here for comparison, though details of the structure determination must await a later paper. The oxygen atoms that define the aperture (Fig. 9) are less coplanar than those in the dehydrated chabazite, and, what is more important, yield a free area much different in shape, and to a first approximation circular. The distances between the centres of the oxygen atoms vary from 6.36 to 6.90 Å, giving a variation in diameter from 3.7 to 4.2 Å. This large change in shape results from a whole reorganization of the framework, triggered by change in the position of the calcium atoms between the hydrated and dehydrated varieties, and in the interactions between the water molecules and the framework. Detailed discussion of the differences between the atomic positions will be given later, but at this time it should be mentioned that physico-chemical calculations on the sorption properties of molecules cannot be expected to be accurate unless they take account of the changes in the internal energy of the silicate framework caused by the sorption process.

During sorption, the shape of the aperture will change and because the minimum dimension is smaller in the dehydrated zeolite, it can be expected that the rate of sorption may be slow at first, gradually increasing as the presence of sorbed molecules leads to change in the framework, and probably slowing down again at high sorbate concentrations when the sorbed

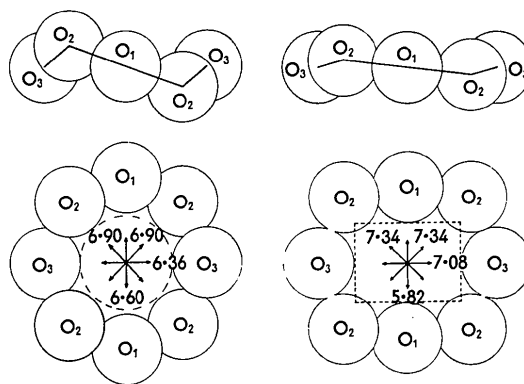


Fig. 9. Details of the apertures in chabazite. Lower left and right, respectively, are projections taken perpendicular to the apertures in hydrated and dehydrated-Ca-chabazite. The upper diagrams are corresponding projections taken parallel to the $\text{O}_1\text{-O}_1'$ vectors. The interatomic distances across the apertures are shown in Å. Note the almost circular but non-planar aperture in the hydrated form in comparison with the approximately rectangular planar window in the dehydrated form. There is a line of symmetry running between the O_3 atoms.

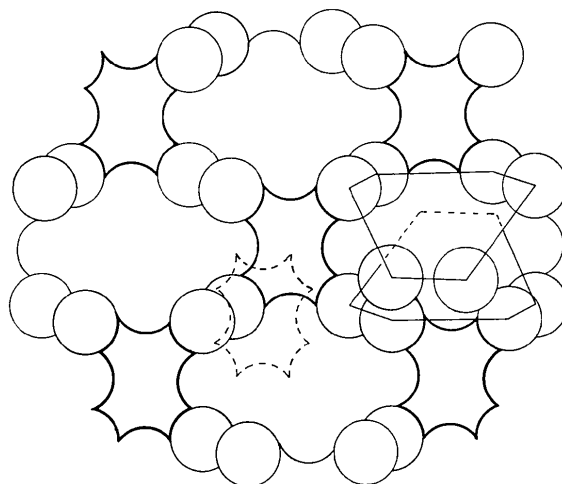


Fig. 10. View of several of the windows that lie parallel to the (001) rhombohedral face of dehydrated-Ca-chabazite, drawn from the same perspective as Fig. 2. Some of the O_2 atoms are shown as complete circles but the O_1 and O_3 atoms are only shown by the arcs which serve to define the boundaries of the apertures. The two six-membered rings of O_2 atoms that belong to one of the clusters are outlined by the di-trigonal polygons. One of the apertures in the next layer of unit cells is shown by the broken curves. In addition to the windows shown here, there are apertures on the other faces of the unit cell permitting sorption in the other two directions. Unfortunately, these are so distorted in projection, that it was less confusing to omit them from the figure.

molecules hinder the movement of incoming material. Measurements of the rate of sorption are very scanty because of the difficulty of measuring the high rates of sorption, but Garden, Kington & Laing (1955) found some weak evidence that the sorption of argon

in Ca-chabazite is slower at the low and high concentration ranges than in the middle region.

Differences in the atomic coordinates found by Howell (1960) for dehydrated synthetic sodium *A* zeolite and for the corresponding hydrated form by Broussard & Shoemaker (1960) almost certainly arise from movement of Ca ions and change in the shape of the silicate framework. It appears, however, that the changes in the framework of the *A* zeolite are rather less than in chabazite.

Kington & Laing (1955), in an important paper, attempted to explain the molecular sieve effect of chabazite in terms of the six-membered ring aperture of the incorrect structure proposed by Wyart. After Dent & Smith had put forward the new structure, and pointed out that it gave a better explanation of the molecular sieve effect, Kington & MacLeod (1959) reinterpreted the molecular sorption in terms of the eight-membered ring aperture of the new structure.

The limiting aperture in a zeolite and the incoming molecules cannot be regarded as being built up from rigid spheres. It is a gross oversimplification, and probably a misleading statement, to talk about a free diameter or a limiting hole. Following other zeolite workers, the oxygen atoms have been assigned a radius of 1.35 Å, which is the value appropriate for ionic bonding according to Pauling. In reality the electron distribution of an atom does not fall abruptly at the ionic radius, it just happens that the balance between the attractive ionic and covalent forces and the repulsive forces is such that, to a first approximation, the ions act as solid spheres in contact. The approximation is quite good (to 0.3 Å) for strong bonds like Si-O but is often quite bad (to 0.3 Å) for weak bonds such as Na-O and K-O. In considering the interaction between a molecule such as ethane or nitrogen with the oxygen atoms of a limiting aperture, there is no attractive force between the atoms (except for weak dipole interaction) and the effective radius of the oxygen atoms can be regarded as greater than the 1.35 Å used for ionic structures in which there is strong Coulomb attraction. Counterbalancing this factor is the kinetic energy of the incoming molecule allowing it to surmount an energy barrier across the limiting aperture, if the barrier is not too large—actually because of the spread of kinetic energies there should always be some molecules with sufficient energy to surmount an energy barrier, though the percentage will decrease very greatly as the barrier energy passes a critical value. Another factor that must be considered in determining the effective size of a limiting aperture, is the thermal vibration of the oxygen atoms. At room temperature, the root-mean-square displacement of the atoms can amount to 0.1 to 0.2 Å, decreasing rapidly as the temperature is lowered. If a molecule approaches at a time when the oxygen atoms are vibrating away from the centre of the aperture, the energy barrier should be less. The atoms need not move outwards in phase but if more

than half of them are vibrating outwards the effective aperture will be increased. Consequently the effective aperture should increase with temperature thus reducing the apparent radius of the oxygen atoms. The effective shape and size of the incoming molecule is also imprecise. Kington *et al.* have proposed the use of the kinetic diameter (σ) rather than the equilibrium diameter (r_0) as a guide for molecular sorption. The two are related by $\sigma = r_0/2^{1/6}$, and the amount of energy required to compress a molecule from its equilibrium to its kinetic diameter is only about 200 cal./mole, showing how little energy barrier there is to a molecule only slightly larger than the 'free area' of a zeolite window.

Taking all these factors into account, the experimental data on the molecular-sieve effect in chabazite are well explained by the present structure. He, Ne, A, Kr, N₂, O₂, H₂ and CO are all readily sorbed by chabazite, whereas propane with a minimum kinetic diameter of 4.3 Å is sorbed slowly with a high activation energy of about 7 kg.cal./mole.

The change of shape of the aperture during molecular sorption suggests the possibility of using a small molecule to increase the minimum width (3.1 Å) of the aperture in activated Ca-chabazite, thus permitting the subsequent sorption of a larger molecule. Another interesting possibility, arising this time from the non-spherical aperture of the dehydrated Ca-chabazite, is that molecules with non-circular cross-sections will have to orient themselves at the correct angle in order to enter the aperture. This effect would reduce the rate of sorption.

Interatomic distances

It is difficult to estimate the precision of the interatomic distances but $\sigma(\text{Si-O})$ should be near 0.03 Å. The mean of the four Si, Al-O distances, 1.65 Å, fits well with the value 1.66 to be expected for a framework structure with this Si/Al ratio (Smith, 1954). As described earlier, all of the short bonds from the Ca₁ and Ca₂ atoms go to the O₄ atoms. This correlates well with the observation that the Si-O₄ distance (1.73 Å) is much larger than the other distances (1.61, 1.62 and 1.65). It seems highly probable that the strong deviation from local charge balance has caused a major variation in the lengths of the Si-O bonds.

The Ca₁-O₄ and Ca₂-O₄ bond distances (2.38 and 2.37 Å) agree well with the usual values found in silicates. The Ca₂-O₂ distance of 2.15 Å is very low, though a similar value of 2.14 Å was found by Howell (1960) in dehydrated Na-Type *A*-zeolite.

Thanks are expressed to Drs D. W. Breck and P. A. Howell for their assistance mentioned in detail in the next, and to the Linde Company for a grant-in-aid.

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Structure and Structure Imperfections of Solid β -Oxygen

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Electron diffraction studies were carried out on thin films of solid oxygen. The structure of β -oxygen was investigated and a rhombohedral structure of the space group $R\bar{3}m$ found. Its corresponding hexagonal cell has the dimensions $a = 3.307 \pm 0.008$, $c = 11.256 \pm 0.015$ Å and contains three O₂ molecules with their axis parallel to the hexagonal axis and their centers at the positions: $(\frac{1}{3}, \frac{1}{3}, 0)$, $(-\frac{1}{3}, 0, \frac{1}{3})$ and $(0, -\frac{1}{3}, \frac{2}{3})$. Faults in the stacking sequence of the (00*l*) layers were observed and the experimental results compared with the Paterson treatment of growth faults in f.c.c. crystals.

Introduction

Solid oxygen is known to have three modifications: an α -modification, stable up to 23.9 °K., a β -modification stable between 23.9 and 43.6 °K. and a γ -modification stable between 43.6 °K. and the melting point at 54.4 °K.

A series of attempts have been made to investigate the crystal structures and cell dimensions of these modifications using X-ray techniques. McLennan & Wilhelm (1927) were the first to carry out a structure investigation on a polycrystalline oxygen sample. At 20 °K. they found an orthorhombic cell ($a = 5.50$, $b = 3.82$, $c = 3.44$ Å) containing two molecules. Ruhemann (1932) observed powder patterns of the α -modification (at 16 °K.), of the β -modification (at 29 °K.) and also of the γ -modification. Ruhemann's patterns of the α - and β -modification were very similar. He therefore concluded, that the α - β transition changes the structure only very little, but still noticeably. Furthermore, his patterns of α - and β -oxygen showed lines which he could not explain by

the assumption of an orthorhombic cell. This led him to the conclusion, that McLennan's & Wilhelm's cell may come very close to reality, but still cannot be regarded as the real cell for the α - and β -structure. For the γ -modification he suggested the possibility of a hexagonal close packed structure. Mooy (1932) carried out investigations on α -oxygen at 20.5 °K. and found a hexagonal structure ($a = 5.75$, $c = 7.59$ Å) with 12 atoms per cell. Vegard (1935) reported investigations on the β - and γ -modification. He was led to the conclusion, that an orthorhombic cell cannot be the right one for the β -modification and interpreted his diffraction patterns on the basis of a rhombohedral cell ($a = 6.19$ Å and $\varphi = 99.1^\circ$) with 6 molecules in undetermined positions. For the γ -modification he found a face centered arrangement of O₂-O₂ complexes, with the symmetry of the $Pa\bar{3}$ space group. This result for γ -oxygen was also obtained by Keesom & Taconis (1936). Recently, Black *et al.* (1958) published X-ray diffractometer patterns of solid ozone and the three modifications of solid oxygen in connection with the description of a low temperature X-ray