

724. *Crystal Structures with a Chabazite Framework. Part IV.*
Reconnaissance of the Chlorine Complex.*

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Ca-chabazite was vacuum-dehydrated near 350° and exposed to chlorine at room temperature. X-Ray diffraction intensities were collected at room temperature for two crystals and at -150° for one. Electron density maps yielded six chlorine peaks lying at the corners of a distorted octahedron centred in the large cavity of the aluminosilicate framework. Peaks for the two calcium atoms occurred near the six-membered aluminosilicate rings. The peaks for the chlorine were non-circular, but not sufficiently elongated for oriented chlorine molecules. Four possible explanations are: the chlorine molecules have dissociated into chlorine atoms; hydrolysis of chlorine to hydrogen chloride has occurred; chlorine molecules occur, but rotate or oscillate; the structure has lower symmetry than rhombohedral, resulting in averaging of several molecular configurations. The latter is the preferred explanation because (a) vacuum dehydration near 350° removes almost all the water, (b) the dissociation energy of chlorine molecules is very high, (c) the electron density maps for room and low temperatures are closely similar, (d) hydrated Ca-chabazite gives biaxial optical properties and electron-density maps that are explained best by sextuple twinning of a triclinic, pseudo-rhombohedral structure with an ordered Al₂Si configuration, (e) the best packing of dumb-bell shaped molecules may require symmetry lower than rhombohedral. The calcium atoms are near to the chlorine molecules suggesting the occurrence of bonding.

ONE aim of this Series¹⁻³ is the determination of the co-ordinates of the exchangeable cations and adsorbed molecules in zeolites to elucidate the nature of the bonding forces. Following the study of the hydrated and dehydrated zeolites we wished to study the sorption of a larger, less polar molecule. Although reactive chlorine is hard to handle, its dumb-bell shape with two atoms separated by 2 Å, and its moderately high X-ray scattering factor, made it suitable for studying the orientation and environment of adsorbed molecules. We now describe the structure determination of the chlorine complex of chabazite, and interpret the observations. In Part V the crystallographic data of Parts I—IV will be used to extend the detailed physico-chemical interpretations of sorption and ion-exchange put forward by Professor R. M. Barrer and his school. Suggestions will be made for further X-ray and physicochemical studies.

Detailed analysis of Fang's original electron-density maps suggested that chlorination of his chabazite crystal had been incomplete, so a new crystal was prepared and studied. To evaluate the effect of temperature on molecular orientation, measurements were made on it at both room temperature and -150°.

EXPERIMENTAL

The first crystal of chabazite was placed in a thin silica capillary attached to a vacuum system and heated to 300—350° for 17 hr. at 0.5 microns Hg. After cooling to room temperature the crystal, still under vacuum, was equilibrated for ½ hr. with chlorine at *ca.* 0.6 atm. (Ohio Chemical and Surgical Equipment Co., 99.8% chlorine). The second crystal was similarly treated but under the following conditions: 16 hr. at 350 ± 12° at 8 microns Hg, and equilibration for 1½ hr. at 1 atm. of Matheson Co. chlorine (greater than 99.5% chlorine). Both crystals are yellow-green and optically birefringent.

• Part III, *Acta Cryst.*, 1964, **17**, 374; Part V, following Paper.

¹ Smith, *Acta Cryst.*, 1962, **15**, 835.

² Smith, Rinaldi, and Dent Glasser, *Acta Cryst.*, 1963, **16**, 45.

³ Smith, Knowles, and Rinaldi, *Acta Cryst.*, 1964, **17**, 374.

The first crystal was mounted on a precession camera and a series of photographs obtained for the rhombohedral $hk0$ reflections using filtered Mo- K_α radiation. Intensities were estimated by eye. The reflections, being broad and irregular, were hard to measure and the observed structure amplitudes are probably not accurate to better than 10%. Much, if not all, of the irregularity arises during dehydration because all six crystals so far dehydrated gave broad and irregular diffraction peaks. No absorption correction was necessary because the crystal was equant and about 0.3 mm. in diameter. Because of the scattering from the silica capillary, the observed range of intensities of 1200 is smaller than customary.

The second crystal was measured on a scintillation-counter Weissenberg camera using monochromatized Mo- K_α radiation. Integrated peaks were obtained with the stationary-counter and moving-crystal technique. Peaks were irregular in width and shape, and it was not possible to align the crystal to obtain equal intensities for $hk0$, $k\bar{h}0$, $h\bar{k}0$, and $k\bar{h}0$ reflections. By comparison of intensities for groups of neighbouring reflections it appeared that there was a reasonable approximation to the intensity requirements for $R\bar{3}m$, and that the deviation was

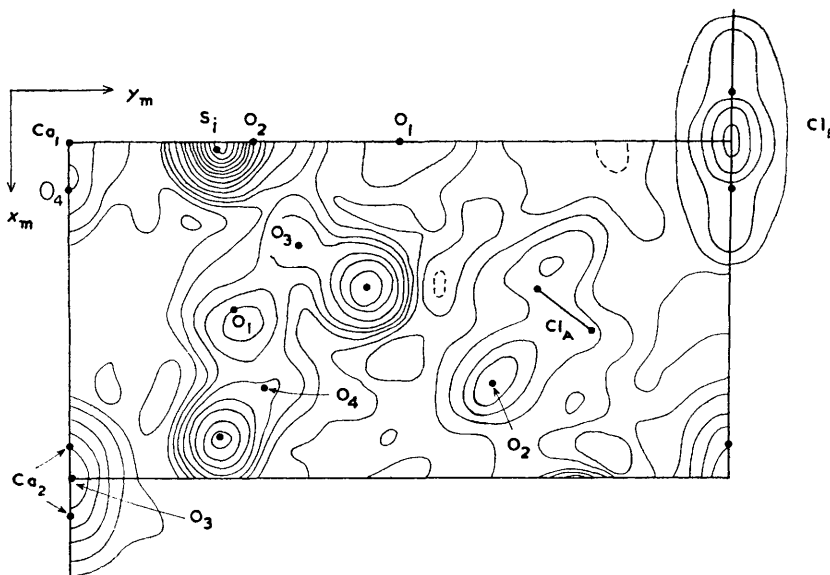


FIG. 1. Final F_0 projection of crystal I referred to axes x_m and y_m which are parallel to the short and long diagonals of the c -axis projection of the rhombohedral cell. There are planes of symmetry along the top edge and both sides of the diagram, and an inversion half-way along the lower edge. The calcium atom is represented by two half-atoms. The chlorine peak labelled A is represented by a dumb-bell. When the contribution of the oxygen atom is subtracted, the dumb-bell gives a better fit to the electron density than appears in this F_0 projection. The chlorine peak labelled B is formed by superposition of two dumb-bells.

caused by an angular spread too large for simultaneous satisfaction of Bragg's law. It was not possible to determine whether the angular spread was due to twinning of a low-symmetry structure or to a random mosaic assemblage or both. By averaging all four equivalent reflections, a reasonably accurate set of intensities was obtained. Measurements were made both at room temperature and near -150° using a cryostat similar to that of Attard and Azaroff.⁴ The cell dimension a of the different varieties of Ca-chabazite hardly changes, but the angle α changes from $92^\circ 01'$ for the dehydrated variety, to $94^\circ 28'$ for the hydrated form and $95^\circ 21'$ and $95^\circ 11'$ for crystals 1 and 2, respectively, of the chlorine complex. No change of dimension was found for the chlorine complex between room temperature and -150° .

The data for crystal I were refined by successive structure factor calculations and Fourier syntheses of the $\{hk0\}$ reflections using the Pennstac and XRAC computers. Initially only

⁴ Attard and Azaroff, *J. Sci. Instr.*, 1960, **37**, 238.

the strong terms were included in the Fourier syntheses and the first set of signs was based on those previously determined for hydrated and dehydrated chabazite. After the silicon, aluminium, and oxygen atoms had been accurately located, additional irregular peaks were found near $(\frac{1}{2} \frac{1}{2} -)$, $(\frac{1}{4} \frac{1}{2} -)$, $(\frac{1}{2} \frac{1}{4} -)$ and $(\frac{1}{4} \frac{1}{4} -)$. The first three were ascribed to chlorine molecules near $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and the fourth one to calcium atoms near $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$. Further calculations using these positions proved reasonably satisfactory when pairs of half-atoms were used to approximate the elliptical shapes of the peaks, and when the atomic scattering factors were reduced for partial occupancy of the sites. Because of overlap of atoms the interpretation is less certain than desirable. On the $(F_o - F_c)$ map there was excess of electron density at the origin after subtraction of the O_4 atoms, and $\frac{1}{3}Ca$ was placed there. Three-fifths of a calcium atom was placed on either side of the O_3 atom to explain the large elongated peak. The chlorine peaks are elongated and the peak labelled *A* on Fig. 1, which corresponds to the rhombohedral co-ordinates $(\frac{1}{2} \frac{1}{2} -)$, was approximated by two partial atoms about 0.6 Å apart in projection. The chlorine peaks labelled *B* was also approximated by two superimposed pairs of partial atoms even though the peak contained a strong central maximum flanked by two other peaks.

TABLE 1.

Atomic co-ordinates using space group $R\bar{3}m$.

Atom	Room temp. (1)			Room temp. (2)			Low temp. (2)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Si, Al	0.107	0.3325	0.883	0.1045	0.3335	0.8825	0.1050	0.3335	0.8815
O ₁	0.250	0.750	0.000	0.254	0.746	0.000	0.250	0.750	0.000
O ₂	0.140	0.860	0.500	0.140	0.860	0.500	0.141	0.859	0.500
O ₃	0.251	0.251	0.906	0.264	0.264	0.895	0.262	0.262	0.900
O ₄	0.035	0.035	0.330	0.040	0.040	0.332	0.033	0.033	0.326
Ca	0.250	0.250	0.250	0.2525	0.2525	0.2525	0.2535	0.2535	0.2535
Ca	0.000	0.000	0.000	—	—	—	—	—	—
Cl	0.500	0.500	0.250	0.534	0.534	0.243	0.540	0.540	0.259

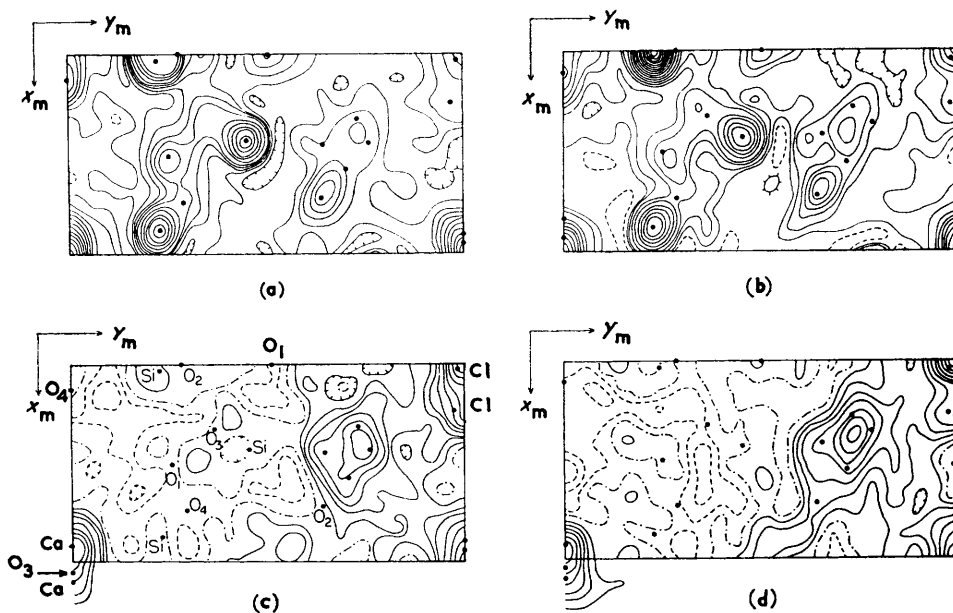


FIG. 2. (a) and (b). F_o projections for crystal 2 at room and low temperature, respectively. (c) and (d). Projections obtained by subtracting the contributions of the silicon, aluminium, and oxygen atoms from the F_o values of the room and low temperature structure, respectively. There is no extra density at the origin, thus indicating absence of calcium from the Ca_1 position shown in Fig. 1. As in Fig. 1, the calcium atom at the lower left is represented by two positions. The chlorine peaks at low are slightly more elongated than those at room temperature, and are each represented by four positions.

TABLE 2.

Observed and calculated structure amplitudes.

h	k	Room temp. (1)		Room temp. (2)		Low temp. (2)		h	k	Room temp. (1)		Room temp. (2)		Low temp. (2)	
		F _o	F _c	F _o	F _c	F _o	F _c			F _o	F _c	F _o	F _c	F _o	F _c
1	0	79	+79	42	+64	44	+64	10	8	0	-6	0	-2	4	-4
2		20	-21	20	-19	23	-24								
3		10	-6	11	-10	13	-7	9	9	nm		23	+28	28	+30
4		0	-3	5	-9	0	-11								
5		87	-85	92	-91	91	-88	1	1	31	-18	37	-37	35	-32
6		0	-6	3	-5	0	-6	2		71	-70	76	-71	71	-72
7		7	+5	5	+6	7	+9	3		8	+13	9	+12	0	-8
8		35	+45	41	+42	44	+42	4		17	-8	13	-2	15	+4
9		52	+53	50	+50	55	+57	5		10	+10	5	0	5	+3
10		7	+2	8	+11	9	+12	6		47	+49	49	+48	51	+47
11		5	-5	5	-5	9	-9	7		0	+10	0	+6	0	+5
12		0	+2	6	+4	9	+4	8		11	+7	8	+10	12	+12
13		16	-13	34	-25	26	-26	9		11	+16	16	+17	17	+16
14		nm		14	-15	nm		10		7	-8	10	-16	13	-16
1	1	9	+15	16	+22	13	+23	11		11	-11	13	-14	14	-13
2		26	+22	22	+16	26	+14	12		5	+5	0	+6	9	+9
3		76	+81	84	+84	83	+84	13		5	-5	0	-5	6	-6
4		16	-8	12	-17	14	-15	2	2	73	-65	70	-66	73	-67
5		45	-43	51	-41	46	-39	3		18	-17	21	-27	22	-25
6		12	-3	12	-11	12	-9	4		23	-19	22	-25	24	-23
7		24	-30	25	-27	30	-26	5		11	+7	6	+6	7	+6
8		7	-8	0	-7	4	-7	6		44	+46	53	+51	50	+50
9		14	+19	22	+19	22	+21	7		20	+23	23	+21	21	+24
10		0	+5	0	0	0	+2	8		8	+2	7	-6	6	-6
11		0	-1	0	+2	0	+4	9		6	-6	7	-5	9	-2
12		9	+9	11	+15	15	+16	10		8	-15	13	-12	12	-9
13		4	-6	0	-6	nm		11		10	-14	14	-15	16	-17
2	2	40	+43	45	+32	45	+36	12		6	-5	10	-11	12	-15
3		44	+47	40	+42	45	+47	13		4	-3	8	-6	0	-4
4		27	+3	0	0	0	0	3	3	47	+41	53	+48	52	+40
5		4	+7	0	+8	6	+6	4		0	+7	0	-5	0	-6
6		4	-6	0	-5	0	+1	5		0	+11	2	-5	5	+6
7		26	-23	33	-27	33	-30	6		10	-1	12	-10	14	-9
8		17	-17	20	-20	20	-23	7		32	+37	46	+38	48	+42
9		9	-1	10	-6	10	-4	8		10	+7	11	+7	12	+12
10		0	-3	0	-3	0	-1	9		8	-4	0	-1	0	-1
11		0	+3	0	+4	0	+2	10		0	+1	0	+1	0	+2
12		10	+9	10	+12	13	+16	11		0	-2	0	-2	0	-4
13		nm		10	+5	5	+9	12		14	-11	19	-15	24	-19
3	3	13	+19	0	+7	0	+2	13		0	-3	0	-3	0	-4
4		16	+2	15	+8	19	+15	4	4	100	+111	93	+95	90	+102
5		5	+4	0	+1	0	+3	5		44	+45	55	+47	56	+49
6		39	-33	42	-43	43	-43	6		5	-5	0	-2	5	-5
7		15	-18	16	-19	19	-17	7		21	+22	28	+25	31	+25
8		3	+3	0	+4	0	+5	8		0	+7	0	+4	0	+2
9		9	+4	0	+4	7	+6	9		30	-30	41	-39	44	-42
10		8	+12	10	+10	0	-3	10		10	-12	12	-15	15	-14
11		11	+10	14	+19	15	+20	11		0	+3	0	0	0	0
12		10	-1	10	-5	5	-6	12		0	0	0	0	0	-0
13		nm		nm		0	-3	13		nm		22	+19	28	+24
4	4	55	+56	58	+53	59	+50	5	5	43	+45	53	+45	46	+47
5		48	+46	46	+39	45	+43	6		13	-17	14	-16	16	-17
6		26	-27	27	-27	26	-26	7		7	0	0	-4	5	-3
7		5	-4	0	-5	4	-5	8		10	-17	13	-17	16	-15
8		8	-8	0	-5	0	-6	9		17	-19	24	-23	28	-24
9		23	-20	27	-29	29	-30	10		0	+4	0	+1	0	0
10		4	-7	0	-2	5	-3	11		0	+5	3	0	0	+2
11		7	+8	0	+6	8	+5	12		0	-1	0	-3	0	-1
12		nm		0	-3	0	-3	13		nm		16	+18	nm	
13		nm		11	+11	nm		6	6	13	-9	16	-15	16	-12
5	5	53	+53	67	+59	61	+60	7		4	-5	7	-11	7	-10
6		7	+8	0	0	5	+1	8		4	-1	0	-6	0	-7
7		0	-5	0	0	5	+2	9		0	-1	0	-3	0	-2
8		9	-8	11	-13	13	-13	10		12	+14	18	+20	20	+22
9		26	-29	32	-33	31	-37	11		7	+5	9	+10	10	+10
10		5	-9	11	-16	12	-15	12		0	-1	0	-3	0	-5
11		0	0	0	+1	0	+2	7	7	12	-10	19	-12	19	-17
12		nm		nm		0	-3	8		11	-12	15	-15	17	-15
6	6	12	+6	6	+6	14	+11	9		3	-1	0	-8	6	-8
7		13	+16	12	+14	15	+13	10		4	+4	3	+3	5	+3
8		16	+12	18	+21	17	+22	11		10	+7	14	+14	18	+17
9		7	-3	7	-6	7	-5	12		4	+10	12	+14	nm	
10		0	-2	0	-1	0	-1	8	8	11	+9	13	+16	19	+15
11		4	-5	0	-6	4	-7	9		10	+12	15	+15	20	+20
12		nm		10	-9	nm		10		3	+2	0	-2	0	-1
7	7	13	+7	13	+14	15	+16	11		0	+2	0	+4	0	+7
8		0	+6	0	+3	0	+2	12		nm		11	+14	nm	
9		6	-2	0	-2	0	-2	9	9	29	+25	38	+38	24	+44
10		5	-4	0	-6	4	-7	10		6	+4	8	+8	11	+8
11		nm		nm		5	-10	10	10	0	-3	0	-6	nm	
8	8	4	+1	0	0	5	-2								
9		7	+6	0	+5	6	+7								

nm = not measured.

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Study of the difference map after placing a total of one-quarter of a chlorine atom in each of the twelve sites showed only small residual peaks not much larger than the peaks remaining near the silicon, aluminium, and oxygen atoms. Fig. 1 shows the final F_o projection referred to axes x_m and y_m , the short and long diagonals, respectively, in the xy plane of the rhombohedral cell. The final atomic co-ordinates are in Table 1 and the observed and calculated structure amplitudes in Table 2. For all reflections the discrepancy index is 0.22, but for observed reflections only it is 0.17.

Although the interpretation was somewhat unsatisfactory the following conclusions were drawn: (a) the chlorine occupies six pairs of sites in the unit cell at the corners of a distorted octahedron, (b) most of the calcium atoms lie on the body diagonal displaced away from the six-membered rings of the aluminosilicate framework, (c) only partial chlorination had been achieved. The evidence for (c) was based on the low electron density of the chlorine peaks, which corresponds to a total of 3 chlorine atoms (*i.e.*, $1\frac{1}{2}$ molecules) for six sites, and on the placing of $\frac{1}{3}$ Ca atom at the origin of the cell which is the preferred position for dehydrated chabazite.¹ This is why it was decided to chlorinate another crystal more rigorously. There was little difference between the intensities collected for the new crystal at room temperature and at -150° ; both sets of intensities deviated about 50% more from the intensities of the dehydrated structure than those for the first crystal, indicating a greater loading of chlorine. In addition it was not necessary to postulate that calcium atoms occurred at the origin, thus suggesting that all of this crystal had been chlorinated. (Table 3 shows that the temperature factor for the O_4 atom near the origin is less than that for the O_4 atom away from the origin. This might indicate a small amount of extra density at the origin to be ascribed to calcium atoms, but the effect is probably within experimental error.)

TABLE 3.

Atomic co-ordinates for crystal 2 using the monoclinic unit cell.

Atom	Room temp.			Low temp.		
	x	y	B	x	y	B
Si, Al	0.220	0.114	0.7	0.220	0.113	0.4
	0.008	0.111	0.7	0.008	0.111	0.4
	0.1085	0.2245	0.9	0.108	0.226	0.6
O_1	0.127	0.127	3.5	0.125	0.125	4.0
	0.000	0.254	4.2	0.000	0.250	4.0
O_2	0.180	0.320	3.0	0.180	0.320	3.5
	0.000	0.140	3.0	0.000	0.142	3.5
O_3	0.082	0.182	3.4	0.081	0.181	3.5
	0.264	0.000	3.4	0.262	0.000	3.5
O_4	0.186	0.146	4.5	0.183	0.143	4.5
	0.032	0.000	3.5	0.026	0.000	3.0
Ca	0.230	0.000	0.7	0.232	0.000	0.7
	0.275	0.000	2.0	0.275	0.000	1.5
Cl	0.080	0.365	3.0	0.070	0.365	3.0
	0.110	0.380	3.0	0.090	0.390	3.0
	0.112	0.322	3.0	0.104	0.327	3.0
	0.144	0.352	3.0	0.138	0.358	3.0
	0.060	0.486	3.0	0.066	0.488	3.0
	0.007	0.491	3.0	0.011	0.489	3.0

Scattering factors were based on Vand's approximation using following constants.

Atom	A	a	B	b
Si, Al	7.955	3.09	5.721	67.450
O	3.093	2.51	4.907	29.545
Ca.....	1.449	1.98	1.162	32.900
Cl	1.000	2.01	0.880	55.428

Data were refined by successive structure factor calculations and ($F_o - F_c$) syntheses using programmes written for the IBM 1620 computer by Professor W. McIntyre of the University of Colorado, and Dr. R. Van der Helm of the Institute for Cancer Research, Philadelphia. Apart from the absence of electron density at the origin, there was no major difference between the electron-density maps of the two crystals. However, significant differences were found in the detailed shapes of the chlorine peaks. Figs. 2(a) and (b) show the F_o projections for crystal 2

at room and low temperature, while Fig. 2(c) and (d) are the projections obtained when the silicon, aluminium, and oxygen contributions are subtracted from F_o . The chlorine peaks spread considerably, and the simple 2-fold approximation used for crystal 1 is inadequate. A four-fold approximation led to reasonable backgrounds in the $(F_o - F_c)$ projections. The chlorine peaks do not show the simple dumb-bell pattern expected for an oriented chlorine molecule, nor the spherical peak for a rotating molecule. There is a small change between the peaks (including a greater elongation of the chlorine peaks) at room and at low temperature but it is of doubtful significance in view of the large errors. For crystal 1, the data show that a four-fold approximation would be better than the two-fold one used.

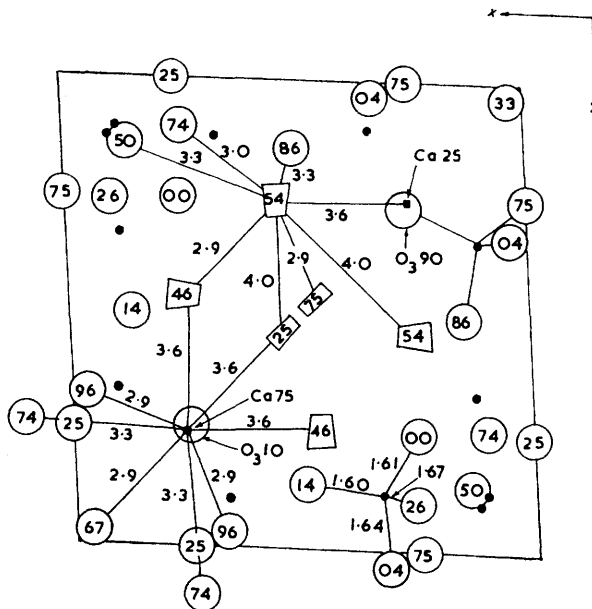


FIG. 3. Projection down the rhombohedral c -axis of crystal 2, using averaged co-ordinates for room and low temperature. The six chlorines are represented by the quadrilaterals whose corners correspond to the average of the positions in Fig. 2. The positions of the calcium atoms (squares) are the averages of the pair of co-ordinates in Fig. 2, and the line joining the two positions used to represent each calcium atom would be parallel to the short diagonal. The nearest neighbours of one of the atoms, one of the chlorine concentrations, and two of the silicon, aluminium atoms are shown. The heights of the atoms are shown by the two-figure numbers as percentages of the 9.4 Å spacing. Oxygen atoms are denoted by open circles and silicon, aluminium atoms by small solid circles.

A three-dimensional analysis was contemplated, but since the extra data, although increasing the precision of the determination and eliminating the overlap of the peaks, would give further irregular peaks of doubtful significance, a more profitable method was investigated, as is described in Part V. So refinement was carried as far as practicable and the structure determination terminated at this unsatisfactory point. The final co-ordinates of the peaks referred to the x_m and y_m axes are in Table 3 and the co-ordinates in $R\bar{3}m$ deduced from them in Table 1. Table 2 lists the observed and calculated structure amplitudes: the final R -factors are 0.21 (room temp.) and 0.19 (low temp.) for all reflections, and 0.13 (room temp.) and 0.15 (low temp.) for observed reflections only. As for the first crystal it was necessary to use two positions separated by 0.3 Å to satisfy the elongated peak for the calcium atom. Only the centres of the chlorine peaks are listed in Table 1. The rhombohedral c -axis projection of the structure is shown in Fig. 3. Each chlorine is shown by a quadrilateral formed from the four positions that were used to approximate the electron density (Table 3). The calcium atom is denoted by a single symbol at the centre of the two partial atoms used to represent it in

Fig. 2. Interatomic distances using the averaged co-ordinates of crystal 2 at low and room temperature are listed in Table 4.

TABLE 4.

Interatomic distances using average co-ordinates.

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Si-O ₁	1.61 (1)	O ₂ -O ₃	2.63 (1)	Cl-O ₃	3.04 (1)
Si-O ₂	1.60 (1)	O ₂ -O ₄	2.63 (1)	Cl-O ₂	3.26 (2)
Si-O ₃	1.67 (1)	O ₃ -O ₄	2.68 (1)	Cl-Ca	3.59 (1)
Si-O ₄	1.64 (1)	Ca-O ₄	2.95 (3)	Cl-Cl	3.95 (2)
O ₁ -O ₂	2.64 (1)	Ca-O ₃	3.32 (3)	O ₁ -O ₁ ¹	6.86 *
O ₁ -O ₃	2.71 (1)	Ca-Cl	3.59 (3)	O ₂ -O ₂ ¹	7.44 *
O ₁ -O ₄	2.71 (1)	Cl-Cl	2.85 (2)	O ₃ -O ₃ ¹	6.03 *

* These three distances are diameters of the eight-membered ring.

The numbers in parentheses are the multiplicities with respect to the first atom.

DISCUSSION

We first discuss three simple, but valuable, conclusions. First, sorption of chlorine markedly changes the cell dimensions and the shape of the framework. The inter-axial angle changes 3° during chlorination, and the atoms in the aluminosilicate framework

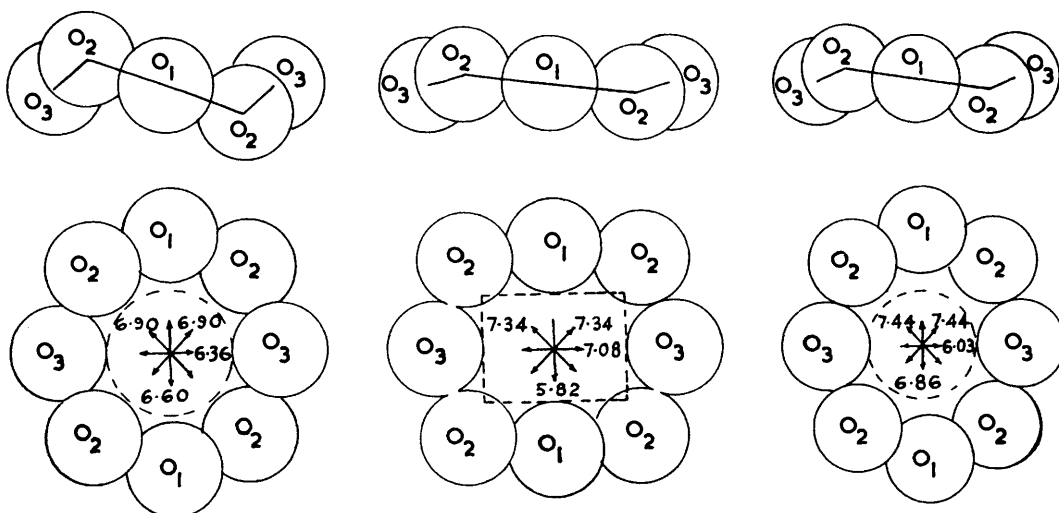


FIG. 4. Corresponding shapes of the eight-membered apertures in chabazite shown in projection and elevation for hydrated-Ca-chabazite (*left*), dehydrated (*centre*), and chlorinated (*right*). A radius of 1.35 Å has been assigned to the oxygen atoms.

move by up to 0.5 Å. There is also a considerable change between the framework for the hydrated and chlorinated varieties. Perhaps the most important change is in the size and shape of the eight-membered rings which form the apertures between the cavities (Fig. 4). In dehydrated chabazite, the aperture is elliptical (or rectangular) and nearly planar; in hydrated chabazite, it is circular and non-planar, while in chlorinated chabazite it is again elliptical, and nearly planar. However, the major and minor axes of the ellipse have been interchanged between dehydrated and chlorinated chabazites, and the chlorinated chabazite more nearly resembles hydrated. Thus the aluminosilicate framework in chabazite has considerable freedom of movement.

Secondly, chlorine molecules occupy definite positions in the unit cell. Although there is uncertainty about their orientation, there is no doubt about the location of the centres of the molecules. In addition, the close similarity between the electron-density maps of crystal 2 at the two temperatures shows that the uncertainty about the orientation does not

arise from thermal motion. The anisotropic shape of the electron density peaks for chlorine indicates that there is a preferred orientation (or orientations) for the molecules.

Thirdly, the calcium atoms change position during sorption. Those at the centres of the di-trigonal prisms move to the six-membered rings, and all of them move towards the chlorine molecules.

The remainder of the discussion is more speculative. Since the adsorption isotherm of chlorine in chabazite is not known, nor was the number of molecules adsorbed in the crystals used measured, this number is uncertain. Kington and MacLeod⁵ report that the following numbers of molecules can enter one cavity (or one unit cell) of chabazite: 5.9 atoms of argon, 6.3 molecules of oxygen, 5.4 of nitrogen, 5.7 of carbon monoxide, and 4.3 of carbon dioxide. Barrer and Wasilewski⁶ report sorption of 2 molecules of iodine per cavity. The chlorine molecule is somewhat larger than the argon atom, being approximately an ellipsoid of revolution of length 5.3 and diameter 3.3 Å in comparison with a sphere of diameter 3.5 Å. Six argon atoms easily fit into chabazite, while six chlorine molecules can be fitted by squeezing, so the observation of six electron-density peaks for chlorine in chabazite seems reasonable. However, the observed electron density is too low for one molecule per site, because the total number of electrons corresponding to the scattering factors used for the chlorine in crystal 2 is only 68 per unit cell, corresponding to 4 chlorine atoms or 2 chlorine molecules. Unfortunately this estimate of 68 electrons may be very wrong because the peaks in F_o-F_c maps can be reduced to background level by a wide range of atomic scattering factors and artificial temperature factors. The (100) reflection, on which temperature has little effect, suggests that the estimate is low.

Specimen	Anhydrous	Crystal 1	Crystal 2 (room temp.)	Crystal 2 (low temp.)
$ F_o $	118	79	42	44
F_c	+120	+79	+64	+64

The chlorine atoms in chabazite give a negative contribution while the aluminosilicate framework gives a positive one. For the anhydrous specimen¹ the agreement between calculated and observed amplitudes is excellent. For crystal 2, F_c is too large, and can be brought into agreement with $|F_o|$ by increasing the chlorine contribution by two-fifths. Consequently we assume that the number of chlorine molecules in the chabazite cell is about 3, giving half-occupancy for each site. For crystal 1 a similar calculation suggests that there are about 2 molecules per cell. A related problem arises with the calcium atom, for the number of electrons deduced from the scattering curve corresponds to 1.1 atoms per cell instead of 1.95. The value of 1.1 is again thought to be low because the calcium was approximated by two half-positions. (In dehydrated chabazite¹ there was a similar deficiency of calcium atoms in positions 1 and 2, and it was suggested that some of the calcium occurred in a third site whose electron density was near the background fluctuations; the electrons in positions 1 and 2 were possibly underestimated as for Ca-Cl₂-chabazite.) Consequently we may conclude that there are at least three molecules of chlorine per unit cell of crystal 2.

We now examine the assumption that all the chlorine occupies fixed positions and exists as molecules. That some may not be held fixed seems to be ruled out by the close similarity in the diffraction patterns obtained for crystal 2 at room temperature and -150°. Dissociation to atoms would readily explain the electron density but cannot be expected because of the energy involved (*ca.* 60 kcal./mole). Hydrolysis of chlorine to hydrogen chloride by reaction with residual water cannot be ruled out even though dehydration was quite severe. Hoss and Roy⁷ found that 90% of the water in Ca-chabazite was removed in 24 hours at 300° under 1 atmosphere pressure and 18 mm.

⁵ Kington and MacLeod, *Trans. Faraday Soc.*, 1959, **55**, 1799.

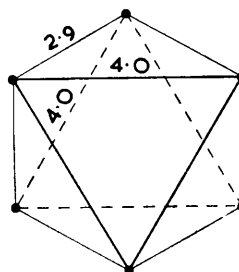
⁶ Barrer and Wasilewski, *J.*, 1958, 3817.

⁷ Hoss and Roy, *Heidelberger Beiträge zur Mineralogie*, 1960, **7**, 389.

partial pressure of water and Barrer and Langley⁸ have given additional data. Our conditions were more severe, and it seems safe to conclude that at least 95% of the water was removed. Subsequent leakage of water through the capillary walls can be ruled out by the similarity of the two sets of data collected for crystal 2, and their difference from the data for hydrated chabazite. If 5% of water remained, this could convert about one molecule of chlorine into two molecules of hydrogen chloride and half a molecule of oxygen if oxygen were released, or half a molecule of chlorine into one molecule of hydrogen chloride and one of hydroxyl if the reaction were different; therefore at least two-thirds of the chlorine in the crystals is molecular. Because the peaks for chlorine in crystal 1 are as much elongated as those of crystal 2, despite less dehydration, we conclude that all, or nearly all, the chlorine is in the form of chlorine molecules (hydrogen chloride is essentially spherical).

Assuming that chlorine sites are mainly occupied by molecules, the co-ordination and interatomic distances can be examined. The Si,Al-O distances show that there is reasonable accuracy in the atomic co-ordinates, for the observed variation of the four independent bonds is only from 1.60 to 1.67 Å. Moreover the two longer bonds of 1.64 and 1.67 Å are to oxygen atoms in contact with calcium and chlorine, while the shorter bonds of

FIG. 5. The shape of the trigonal antiprism, at whose corners lie the centres of the chlorine molecules, viewed down the inverse triad axis.



1.60 and 1.61 Å are for atoms not so bonded. The mean value of 1.63 Å agrees reasonably well with the value of 1.64, expected for a framework aluminosilicate with this Si : Al ratio.⁹

The two calcium atoms lie on the body diagonal displaced towards the centre of the cavity from the middle of the six-membered rings, lying at 2.95 Å from three of the oxygen atoms and 3.3 Å from the other three. Three chlorine peaks lie with their centres at 3.6 Å on the other side of the calcium atom. In dehydrated-chabazite, calcium atoms are statistically arranged¹ at the origin of the cell and near the centres of the six-membered rings. Sorption of chlorine thus causes calcium to move from the origin to the six-membered rings, and to displace all the calcium away from the centres of the six-membered rings so that contact is made with the chlorine molecules. This displacement results in Ca-O distances about 0.5 Å greater than the usual range of 2.2–2.6 Å. The values for the Ca-O and Ca-Cl distances depend on the actual positions occupied by the calcium and chlorine in the elongated peaks. The calcium atom was approximated by two half-atoms 0.6 Å apart along the diagonal, while the existence of chlorine as molecules composed of two atoms at a distance of 2.0 Å has an even larger effect on the distances. In calcium chloride¹⁰ the calcium ion lies in a distorted octahedron of chlorine ions at 2.70 and 2.86 Å. Because the chlorine in chabazite is assumed to exist as molecules, the Ca-Cl distances should be longer; thus 3.6 Å from the centres of the molecules to the calcium atoms is in the right range.

The six chlorine concentrations lie at the corners of a distorted octahedron (or more accurately, trigonal antiprism) in which the two end faces have edges of 4.0 Å and the six linking edges are 2.9 Å long (Fig. 5). In addition to the four chlorine neighbours,

⁸ Barrer and Langley, *J.*, 1958, 3817.

⁹ Smith and Bailey, *Acta Cryst.*, 1963, **16**, 801.

¹⁰ van Bever and Nieuwenkamp, *Z. Krist.*, 1935, **90**, 374.

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each chlorine is near to three oxygen atoms at 3.0, 3.3, and 3.3 Å and to the calcium atom at 3.6 Å. A packing model shows that the trigonal antiprism is the most reasonable pattern for six large atoms or molecules, thus confirming this interpretation. However, the details of the molecular orientations are far from clear. Each chlorine concentration has been represented by four partial atoms lying in projection at the corners of a quadrilateral about 0.5 Å apart, instead of two atoms lying at 2.0 Å in three dimensions. If the chlorine is molecular, the quadrilaterals must result from either a space or time average. Because of the close similarity between the diffraction data at the two temperatures, the space averaging seems more likely; this could arise in two ways: all atoms and molecules could lie in the same positions with respect to the axes of a unit cell of symmetry lower than $R\bar{3}m$, or the atoms and molecules could occupy different positions in several types of unit cell. For the former, mimetic twinning would probably occur, and if it did not, the assumption of $R\bar{3}m$ for the calculations would result in the same effects in the electron density maps. The situation is the same as that concerning the position of alkali ions in feldspars with ordered and disordered Si,Al atoms (see ref. 11, and other Papers in that volume). The chabazite framework probably^{2,3} has ordered Si and Al atoms, and the true symmetry is $P\bar{1}$ (or less likely, $P1$). Such ordering would produce asymmetric electric fields which would tend to disorient chlorine molecules from positions obeying $R\bar{3}m$. Another possibility arises from the difficulty of packing the chlorine molecules into chabazite. It is not easy to pack the six ellipsoidal molecules into one cavity without distorting the aluminosilicate framework. Such distortions might reduce symmetry. Finally, the framework of chabazite might tend inherently towards a lower symmetry, perhaps to achieve a more suitable set of Si,Al–O–Si,Al bond angles. Unfortunately there are insufficient data to solve this question, but the nature of the chlorine peaks, the temperature invariance, and the large temperature factors for the oxygen atoms definitely favour the general idea of a space average. The quadrilaterals tend to be elongated in one direction. If these elongations can be presumed to represent the average orientation of a molecule, the molecules are inclined towards the triad axes at an angle less than 45°.

In addition to being in contact with molecules in the same cage, each molecule could be in contact with one in the next cage through the 8-membered rings, for the distance between molecule centres is 5.5 Å. The longer direction of the quadrilaterals is approximately along the line of centres permitting reduction of the chlorine–chlorine distance to about 3.5 Å, so the chlorine molecules could form a continuous network throughout the chabazite framework.

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¹¹ Taylor, *Norsk Geologisk Tidsskr.*, 1962, **42**, 1.