

data cannot be obtained from a single diffraction photograph. The sample-holder of the small-angle camera must allow the sample a possibility of turning about the axis parallel to the beam direction. The measurement of integrated intensities is simplified by adopting the geometrical arrangement in such a way that the vertical extension of the measured diffuse pattern does not exceed the height of the counter entrance-slit, corresponding to the constant radial sensitivity of the counter. The integration of the intensity along the various t -axes is then performed automatically. The total amount of the measured data necessary for carrying out the mathematical operations

involved in (7) with sufficient accuracy is in this case practically the same as with the frequent point-by-point intensity measurements.

I wish to thank my colleague J. Loos CSc for valuable discussions.

References

- GUINIER, A. & FOURNET, G. (1955). *Small-Angle Scattering of X-rays*. New York: Wiley. London: Chapman & Hall.
 KRANJC, K. (1954). *Acta Cryst.* **7**, 709.
 SYNEČEK, V. (1960). *Acta Cryst.* **13**, 378.

Acta Cryst. (1962). **15**, 644

The Crystal Structure of the Zeolite, Phillipsite

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The crystal structure of phillipsite has been determined from the $0kl$, $h0l$, and $hk0$ electron density projections and has been refined by means of a three dimensional least-square procedure. The unit cell is orthorhombic, $B2mb$, $a = 9.96_5$, $b = 14.25_2$, $c = 14.25_2$ Å and there are two formula weights of probable composition $(K_xNa_{1-x})_5Si_{11}Al_5O_{32} \cdot 10H_2O$ in the unit cell. The silicate framework can be described as consisting of a fundamental unit of two tetrahedra linked head to head through an apical oxygen atom. Ten of these double units are then linked together by sharing corners into an S shaped configuration which is approximately 14 Å long and 7 Å wide. The open ends of this S configuration link to other S units through the oxygen atoms of the upper and lower bases of the double unit into a three dimensional network. Adjacent S units are $\frac{1}{2}a$ apart so that large channels exist both parallel to a and to b . The channel parallel to a is octagonally shaped and has an open passage with a 12 Å² cross section. The channel parallel to b has a rectangular cross section which is approximately 9 Å². The locations of the exchangeable ions and of the water molecules are discussed.

Introduction

The crystal chemical investigations of the zeolite minerals have received a sharp stimulus because of the almost simultaneous recognition that these compounds can participate in many industrially useful physico-chemical reactions and that they also frequently constitute an important fraction of sedimentary rocks in which they occur both as a diagenetic product and also as accessory authigenic crystals. The general features of zeolite structures were established by many of the early workers in X-ray crystallography (Bragg, 1937) and recently many zeolite structures have been redetermined by modern methods (Nowacki & Bergerhoff, 1957; Meier, 1960). Little attention had been devoted to the naturally occurring

lamellar type zeolites. Strunz (1957) investigated the lattice constants of phillipsite and reports

$$a = 10.02, b = 14.28, c = 8.64 \text{ \AA}; \beta = 125^\circ 40'$$

and Wyart (1938) reports similar values for the mineral christianite. The minerals phillipsite and offretite also have similar unit cells and compositions. All these minerals probably have an almost identical silicate framework and may differ only in the type of exchangeable ion which is present.

The mineral phillipsite was chosen for this investigation because of its widespread occurrence in sediments; it is considered to have a structural relationship to some of the synthetically produced molecular sieves and it is a member of a group of zeolites whose structure until recently (Sadanaga *et al.*, 1960) had not been studied in detail. The material which was used in this investigation was supplied by Dr. G. Arrhenius of the Scripps Institution of Ocean-

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ography who found the phillipsite crystals in the pelagic sediments of the Pacific Ocean. They are probably authigenic and consist of very complexly twinned specimens approximately 5 mm long and 2–3 mm. in cross section.

Experimental

The X-ray diffraction data were collected from a single crystal fragment of phillipsite which was cut from one of the branches of the cross twins. The dimensions of the fragment used were approximately $0.4 \times 0.2 \times 0.1$ mm. with the long dimension of the crystal parallel to the short axis of the unit cell. The diffraction data which were obtained from the single crystal fragment showed definite orthorhombic symmetry with extinctions hkl , $h+l=2n$; $hk0$, $k=2n$, which is consistent with the space groups $Bmmb$, $B2mb$ and $Bm2b$. The orthorhombic cell dimensions are

$$a = 9.965, \quad b = 14.252, \quad c = 14.252 \text{ \AA},$$

and the non-standard labelling of the cell was chosen so as to keep the relationship to the reported monoclinic cell $c_o = 2c_m + a_m$. The intensities were obtained from Weissenberg multiple films using $\text{Cu } K\alpha$ radiation as well as from precession photographs using $\text{Mo } K\alpha$ radiation. The intensities were not corrected for absorption or extinction errors.

Wyart (1938) surveyed fourteen chemical analyses reported for christianite of hydrothermal origin and presents the formula $\text{K}_2\text{Ca}_2\text{Si}_{10}\text{Al}_5\text{O}_{32} \cdot 12\text{H}_2\text{O}$, where the potassium and calcium ions are presumably exchangeable. A qualitative spectrochemical analysis of the material from the pelagic sediment showed no calcium, only sodium and potassium were present which may reflect the environmental condition in which the mineral was deposited or perhaps in which it crystallized. A determination of the base exchange capacity on a very minute sample by means of a radioactive tracer technique indicated 377 m.e.q./100 g or 5 exchangeable ions for the above formula. The measured density of the specimen is 2.10 g.cm.^{-3} corresponding to two formula weights of 1278 g. The weight of the silicate framework and the 12 water molecules leaves only 106 g to be assigned to the exchangeable ions, corresponding to about 4.5 Na^+ or 2.5 K^+ . It is more likely that the assumption of $12\text{H}_2\text{O}$ is too high for this specimen and there are probably no more than 10 H_2O associated with the framework. If this assumption is correct, then the formula for this specimen is $(\text{K}_x\text{Na}_{1-x})_5\text{Si}_{11}\text{Al}_5\text{O}_{32} \cdot 10\text{H}_2\text{O}$.

Structure determination

The structure determination was begun by applying the statistical tests to the $0kl$ and $h0l$ reflections (Lipson & Cochran, 1953). The experimental points closely followed the centrosymmetric distribution and

space group $Bmmb$ was used in the initial stages of the determination.

The three Patterson projections were calculated and their interpretations were undertaken on the assumption that the aluminosilicate framework consisted only of tetrahedra. The peaks appearing in the $0kl$ projection were consistent with a slightly distorted octagonal arrangement of silicon atoms and y, z coordinates for the two asymmetric tetrahedral ions in general 16-fold positions could be derived. In space group $Bmmb$ the plane $x=0$ is a mirror so that an atom at xyz has a related atom at $\bar{x}yz$. The $h0l$ Patterson projection showed a very strong interaction of approximately 3 Å which was quite clearly due to the distance between tetrahedral atoms connected through an apical oxygen. Thus the model with which the structure determination was begun consisted of an octahedral ring formed by SiO_4 tetrahedra with the apical oxygen atoms in the mirror planes $x=0$ and $x=\frac{1}{2}$. This mirror plane reflects the octagonal arrangement of the tetrahedra so that the basic unit of the structure in projection consisted of a double layer of tetrahedra arranged in an octagonal unit.

The signs for the $0kl$ structure factors were calculated on the basis of the above model and the electron density projection on (100) showed that the assumptions were essentially correct. Peaks on the mirror plane at $y=\frac{1}{4}$ appeared which were due to water molecules and to the exchangeable cations. It was possible to refine this projection to an R value of 20%, but not below it.

With the y and z values from the projection on (100) and x values derived from the assumption that the tetrahedra were linked through the apical oxygen to form a unit twice the height of one tetrahedron, signs were calculated for $F(h0l)$ and electron density projections were calculated. The projections confirmed that the silicate framework was essentially correct, but at the same time the heights of the oxygen peaks were very uneven and extraneous peaks appeared in locations which could not be related to peaks in the $0kl$ projection. In both projections the peaks due to water molecules and exchangeable cations, were very much lower than they should have been, and it became obvious that the scattering power in those locations was less than one ion. Difference syntheses of the two projections also indicated that the assumption of full scattering power in those locations was erroneous. The $0kl$ difference syntheses also showed that the superpositions of oxygens due to the mirror related atoms at xyz and $\bar{x}yz$ were incorrect. The observed feature in this region of the map indicated that the atoms were placed too closely together. Space group $Bmmb$ demands exact superposition and it was therefore concluded that one of the non-centrosymmetric space groups $B2mb$ or $Bm2b$ was correct. Space group $B2mb$ does not demand superpositions of atoms in the projection on (100) but does preserve its centrosymmetric character. The continued

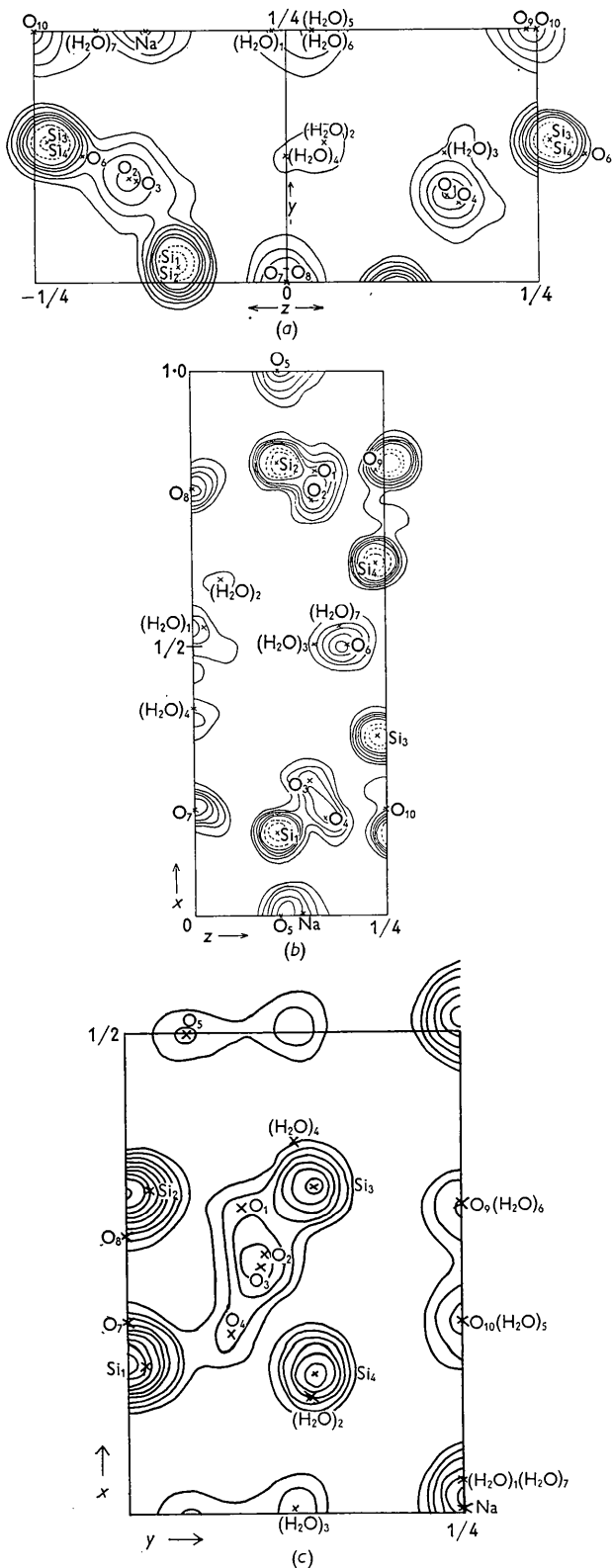


Fig. 1. (a) Electron density projection of phillipsite on (100). Contours are in intervals of approximately $5 \text{ e.}\text{\AA}^{-2}$ except for the dashed lines which are $10 \text{ e.}\text{\AA}^{-2}$. Contours start at

refinement of the structure was now based on this assumption and both electron density and difference maps of all three projections were used in the later stages of the structure work. It was now possible to refine $0kl$, $h0l$ and $hk0$ to R values of 0.106, 0.156, and 0.127 respectively. Table 1 lists the coordinates as obtained from the three projections, Fig. 1(a), (b), (c).

Table 1. Atomic coordinates and temperature factors obtained from electron-density projections

Atom	x	y	z	B
Si ₁	0.153	0.018	0.892	1.75 \AA^2
Si ₂	0.833	0.017	0.891	
Si ₃	0.335	0.861	0.238	
Si ₄	0.650	0.860	0.237	
O ₁	0.815	0.083	0.156	2.60 \AA^2
O ₂	0.773	0.104	0.840	
O ₃	0.235	0.102	0.849	
O ₄	0.178	0.075	0.174	
O ₅	0.992	0.048	0.885	
O ₆	0.509	0.874	0.205	
O ₇	0.203	0	0	
O ₈	0.796	0	0	
O ₉	0.303	0.250	0.740	
O ₁₀	0.707	0.250	0.750	
(H ₂ O) ₁	0.535	0.250	0.990	2.60 \AA^2
$\frac{1}{2}$ (H ₂ O) ₂	0.620	0.136	0.035	
$\frac{1}{2}$ (H ₂ O) ₃	0.500	0.115	0.166	
$\frac{1}{2}$ (H ₂ O) ₄	0.375	0.123	0	
$\frac{1}{2}$ (H ₂ O) ₅	0.172	0.250	0.032	
$\frac{1}{2}$ (H ₂ O) ₆	0.832	0.250	0.032	
$\frac{1}{2}$ (H ₂ O) ₇	0.500	0.250	0.830	
Na	0.010	0.250	0.865	2.60 \AA^2

The molecule designated $\frac{1}{2}$ (H₂O)₇ could not be established with certainty from the projections. The atom labelled 'Na' is probably a K⁺ which occupies this site on a statistical basis so that the scattering power is approximated by Na. Similarly some of the locations in which water molecules were placed probably represent exchangeable cations such as Na⁺ which are statistically distributed over those sites so that the scattering is approximated by that of water. The designation $\frac{1}{2}$ (H₂O) means that $\frac{1}{2}f$ (oxygen) was used to represent the contribution to the calculated structure factor from that site.

Three dimensional least squares refinement

Several of the peaks which were designated as water molecules in Table 1 had very low heights in the electron density projections and it was impossible to determine whether they represented exchangeable cations, water molecules or were of a spurious nature. They were retained in a three-dimensional least-square

approximately $5 \text{ e.}\text{\AA}^{-2}$. (b) Electron density projection on (010). Contours in intervals of $5 \text{ e.}\text{\AA}^{-2}$, beginning at approximately $10 \text{ e.}\text{\AA}^{-2}$. Dashed contours are in $10 \text{ e.}\text{\AA}^{-2}$ intervals. (c) Electron density projection on (001). Contours are in intervals of $4 \text{ e.}\text{\AA}^{-2}$ beginning at approximately $10 \text{ e.}\text{\AA}^{-2}$. Crosses mark the final atomic locations.

Table 2. *Final coordinates, standard deviations and isotropic temperature factors obtained from the least-squares refinement*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B (\AA^2)
Si ₁	0.1517	0.0011	0.0165	0.00065	0.8920	0.00065	2.0
Si ₂	0.8340	0.0012	0.0170	0.00061	0.8903	0.00061	2.0
Si ₃	0.3356	0.0012	0.8610	0.00069	0.2376	0.00056	2.1
Si ₄	0.6477	0.0011	0.8597	0.00069	0.2366	0.00061	2.0
O ₁	0.8159	0.0028	0.0854	0.0017	0.1599	0.0017	2.8
O ₂	0.7659	0.0030	0.1027	0.0019	0.8435	0.0019	3.6
O ₃	0.2519	0.0030	0.1012	0.0019	0.8514	0.0019	3.2
O ₄	0.1815	0.0026	0.0773	0.0017	0.1717	0.0017	2.4
O ₅	0.9996	0.0049	0.0469	0.0014	0.8872	0.0014	2.7
O ₆	0.5035	0.0036	0.8751	0.0014	0.2029	0.0014	3.0
O ₇	0.1945	0.0036	0	—	0	—	2.0
O ₈	0.7860	0.0039	0	—	0	—	3.0
O ₉	0.3187	0.0038	0.2500	—	0.7385	0.0026	3.2
O ₁₀	0.6972	0.0050	0.2500	—	0.7491	0.0031	4.3
(H ₂ O) ₁	0.5356	0.0049	0.2500	—	0.9848	0.0032	6.6
$\frac{1}{2}$ (H ₂ O) ₂	0.6202	0.0063	0.1377	0.0045	0.0379	0.0040	5.2
$\frac{1}{2}$ (H ₂ O) ₃	0.5030	0.011	0.1267	0.0042	0.1572	0.0040	6.6
* $\frac{1}{2}$ (H ₂ O) ₄	0.3871	0.0056	0.1242	0.0047	-0.0001	0.0047	5.5
$\frac{1}{2}$ (H ₂ O) ₅	0.2000	0.0078	0.2500	—	0.0261	0.0047	1.9
$\frac{1}{2}$ (H ₂ O) ₆	0.8205	0.0093	0.2500	—	0.0263	0.0049	3.4
$\frac{1}{2}$ (H ₂ O) ₇	0.5368	0.011	0.2500	—	0.8107	0.0060	6.6
†Na	0.0054	0.0036	0.2500	—	0.8600	0.0013	3.5

* Na⁺ statistically distributed over this site.† K⁺ statistically distributed over this site.

procedure, employing the IBM NYXR 1 program, using 723 independent reflections with the expectation that the values of the isotropic temperature factor would indicate the weight which should be assigned to the scattering from this site. Four refinement cycles were carried out using an isotropic temperature factor for each atom. The starting coordinates were those of Table 1 which gave an R value of 0.181. After four refinement cycles R dropped to 0.140 and the temperature factors for the atoms labelled $\frac{1}{2}$ (H₂O)₇, (H₂O)₁, and $\frac{1}{2}$ (H₂O)₃ rose to 6.6 \AA^2 . The inspection of the electron density projections shows that the peaks marked $\frac{1}{2}$ (H₂O)₇ and $\frac{1}{2}$ (H₂O)₃ are very uncertain, while the peaks marked in the projections as (H₂O)₁ are very prominent and may perhaps be due to a cation occupying this site statistically. The coordinates obtained from the least-square refinement together with the isotropic temperature factors are listed in Table 2. Table 3 lists the observed and calculated values of the structure factors.

The silicate framework

The structure of the silicate framework can be described in terms of an idealized arrangement of tetrahedra. The fundamental unit can be considered as consisting of two tetrahedra connected head on through the apical oxygen into a double unit approximately 4.5 \AA high. Ten of these double units are linked together, by sharing corners, into a S shaped configuration which is approximately 14 \AA long and 7 \AA wide as shown in Fig. 2. The open ends of this S configuration then link to other S units through the oxygen atoms of the upper and lower

bases of the double unit into a three dimensional network. The height of two of these staggered S units is approximately 9 \AA and they occupy an area of $14 \times 14 \text{\AA}^2$ in the plane perpendicular to the 9 \AA height. The observed height of the unit cell, 9.97 \AA , indicates that this idealized picture is slightly distorted in the crystal, as it should be because of the improbability of a 180° value for the Si—O—Si angle in the double unit formed by two tetrahedra connected through the apical oxygen. In the idealized description of the structure the apical oxygen atoms lie on a mirror plane and the tetrahedra of the upper half of the

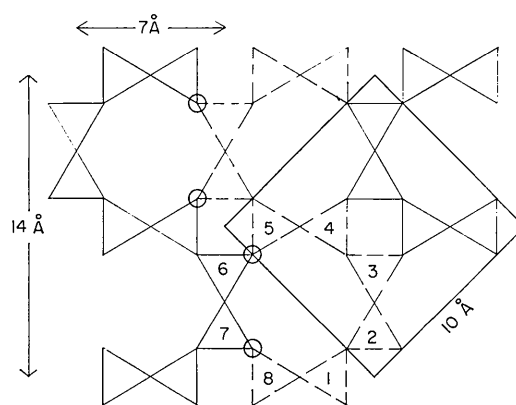


Fig. 2. The S configuration of the SiO_4 tetrahedra. Each triangle is approximately 4.5 \AA high and represents two tetrahedra linked through the apical oxygen atom. The dashed S configuration is displaced by $\frac{1}{2}a$ above the plane of the paper and lower tetrahedra of this double unit articulate with the upper tetrahedra of the double unit (solid outline) at the circled corners. The drawing is idealized. The c axis is horizontal and b is vertical.

Table 3. *Observed and calculated structure factors*
(Signs for the centrosymmetric $0kl$ reflections are shown)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	2	195	-206	1	0	7	106	100	2	6	8	58	60	3	13	7	103	94	5	4	1	57	57
		4	171	-221			9	128	124			10	50	56			11	12	19	18		6	30	29
		6	149	-241			11	149	149			12	33	33			13	14	28	28		7	16	16
		8	250	-238			13	66	66			14	16	17			15	14	38	38		5	3	3
		10	28	-6		1	13	153	158			16	11	6			17	9	24	19		5	3	3
		12	59	-55			15	136	107			17	24	27			18	15	68	76		5	7	7
		14	39	-44			17	19	18			18	22	22			19	21	24	24		5	9	9
		16	36	-55			19	24	24			19	22	22			20	21	24	24		5	7	7
		18	79	-113		1	22	15	15			20	67	60			21	17	86	86		1	11	11
		20	78	-83			23	24	15			21	18	18			22	15	74	86		1	13	13
		22	27	-6		2	26	144	25			22	25	25			23	27	24	24		6	3	3
		24	79	-73			27	58	58			23	61	61			24	27	94	100		5	5	5
		26	74	-73			29	78	78			24	14	14			25	16	16	16		6	3	3
		28	53	-53			31	77	77			25	12	12			26	14	78	78		6	3	3
		30	20	-22			33	80	80			26	14	17			27	14	62	62		7	7	7
		32	25	-22			35	33	33			27	14	17			28	14	57	62		7	7	7
		34	143	-181		2	37	33	33			28	14	17			29	14	57	62		7	7	7
		36	104	-107			39	33	33			29	14	17			30	14	57	62		7	7	7
		38	246	-256			41	108	86			30	14	17			31	14	57	62		7	7	7
		40	18	-46			43	22	22			31	14	17			32	14	57	62		7	7	7
		42	10	-12			45	22	22			32	14	17			33	14	57	62		7	7	7
		44	14	-18			47	22	22			33	14	17			34	14	57	62		7	7	7
		46	14	-18			49	22	22			34	14	17			35	14	57	62		7	7	7
		48	14	-18			51	22	22			35	14	17			36	14	57	62		7	7	7
		50	14	-18			53	22	22			36	14	17			37	14	57	62		7	7	7
		52	14	-18			55	22	22			37	14	17			38	14	57	62		7	7	7
		54	14	-18			57	22	22			38	14	17			39	14	57	62		7	7	7
		56	14	-18			59	22	22			39	14	17			40	14	57	62		7	7	7
		58	14	-18			61	22	22			40	14	17			41	14	57	62		7	7	7
		60	14	-18			63	22	22			41	14	17			42	14	57	62		7	7	7
		62	14	-18			65	22	22			42	14	17			43	14	57	62		7	7	7
		64	14	-18			67	22	22			43	14	17			44	14	57	62		7	7	7
		66	14	-18			69	22	22			44	14	17			45	14	57	62		7	7	7
		68	14	-18			71	22	22			45	14	17			46	14	57	62		7	7	7
		70	14	-18			73	22	22			46	14	17			47	14	57	62		7	7	7
		72	14	-18			75	22	22			47	14	17			48	14	57	62		7	7	7
		74	14	-18			77	22	22			48	14	17			49	14	57	62		7	7	7
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		140	14	-18			143	22	22			81	14	17			82	14	57	62		7	7	7
		142	14	-18			145	22	22			82	14	17			83	14	57	62		7	7	7
		144	14	-18			147	22	22			83	14	17			84	14	57	62		7	7	7
		146	14	-18			149	22	22			84	14	17			85	14	57	62		7	7	7
		148	14	-18			151	22	22			85	14	17			86	14	57	62		7	7	7
		150	14	-18			153	22	22			86	14	17			87	14	57	62		7	7	7
		152	14	-18			155	22	22			87	14	17			88	14	57	62		7	7	7
		154	14	-18			157	22	22			88	14	17			89	14	57	62		7	7	7
		156	14	-18			159	22	22			89	14	17			90	14	57	62		7	7	7
		158	14	-18			161	22	22			90	14	17			91	14	57	62		7	7	7

double SiO_4 unit are reflection images of the lower tetrahedra. In the actual structure this mirror plane at $x=0$ does not exist but the deviations are small as can be seen from the final coordinates in Table 2. The pseudo centrosymmetric character of the framework explains why the distribution of the intensities followed so closely the centric curve for the intensities.

Adjacent S units are always at different levels so that a large channel exists next to a chain of tetrahedra. Also octagonal shaped channels run through the structure parallel to the short axis. The stereographic views of Fig. 3(a) and (b) show the silicate framework as seen along the a axis and the b axis, although the distortions of the model are unfortunately due to its construction and do not reflect actual distortion of tetrahedral linkages in the framework.

The structure can also be described as consisting of an octagonal arrangement of tetrahedra, 12 being linked head to head through apical oxygen atoms and they constitute $\frac{1}{2}$ of the S unit which has been described. The four remaining tetrahedra of the octagonal unit point in opposite directions; the two tetrahedra linked at the bottom half point downward and the two tetrahedra linked at the upper half point upward and thus become part of the S chains above and below.

The structure of phillipsite proposed by Barrer *et al.* (1959) from considerations of powder diffraction data of synthetic zeolites which displayed characteristics similar to phillipsite and based also on considerations of the structures of Linde Sieve A synthetic zeolites, consists of two rings of four tetrahedra joined head to head through apical oxygens into a basic building block of the structure. This basic unit is then arranged on a body centered cubic lattice which has a 10 Å repeat distance. Fig. 2 can be used to show the differences between Barrer's proposed phillipsite structure and the structure determined in this investigation. The tetrahedra labelled 1, 2, 5, 6 surrounding origins of the cubic cell shown by the solid outline, can be considered as pointing in one direction while the tetrahedra marked 3, 4, 7, 8 point in the opposite

direction. The structure determined in this investigation has the six tetrahedra, 8, 1, 2, 3, 4, 5 point in one direction while 6 and 7 point in the opposite direction. Even though Barrer's proposed structure for the natural mineral phillipsite is incorrect it may well be the structure of the synthetic cubic phases reported in that investigation.

The aluminum ions which substitute for silicon within the framework and thus give rise to the exchange capacity of this zeolite could not be located. No meaningful differences in bond lengths exist within the silicate framework when the 3σ test is applied to them. Within the precision of this determination the aluminum ions appear to be statistically distributed over the tetrahedral sites and the observed length of 1.64 Å indicates approximately 0.2 Al per site. The assumed value for the aluminum substitution shown in the chemical formula for the mineral and based on indirect evidence is 0.3 Al ion per site.

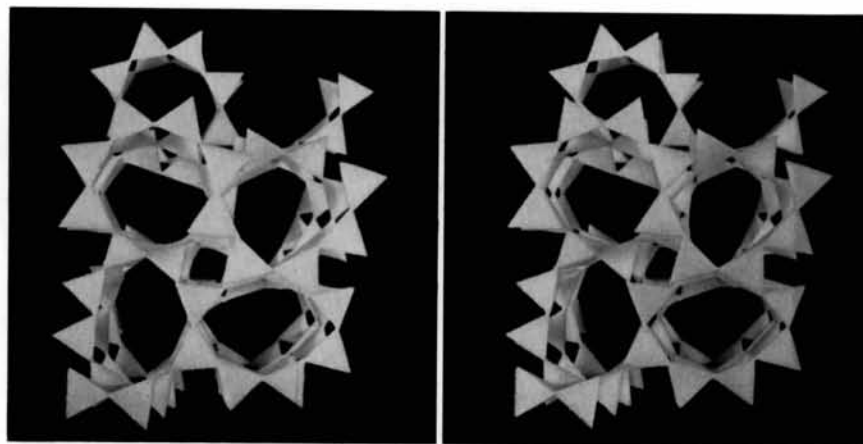
The distance in the (y, z) plane from the center of the octagonally shaped channel to the eight surrounding oxygen atoms varies from 3.1 to 3.6 Å. If an average radius of 3.3 Å is assumed and the diameter of an oxygen ion is considered to be approximately 2.7 Å then an open passage with about a 12 Å² cross section is available parallel to the short axis of the unit cell. The rectangular shape of the channel parallel to the b axis has an average unobstructed height along the a axis of 2.3 Å and an unobstructed width of approximately 4 Å so that the available area is approximately 9 Å². It can be expected that molecules with a cross sectional area of about 12 Å² or less will be absorbed by this zeolite while the larger ones will be rejected, provided the channels are not blocked by cations. The presence of cations within the channel would decrease the available volume for an absorbed molecule and thus limit the maximum size even further.

The angles $\text{Si}_1\text{-O}_5\text{-Si}_2$ and $\text{Si}_3\text{-O}_6\text{-Si}_4$ which are the angles formed by the head on articulation of two tetrahedra in the S unit are respectively 150° and 144°. These are the angles that would be 180° for the

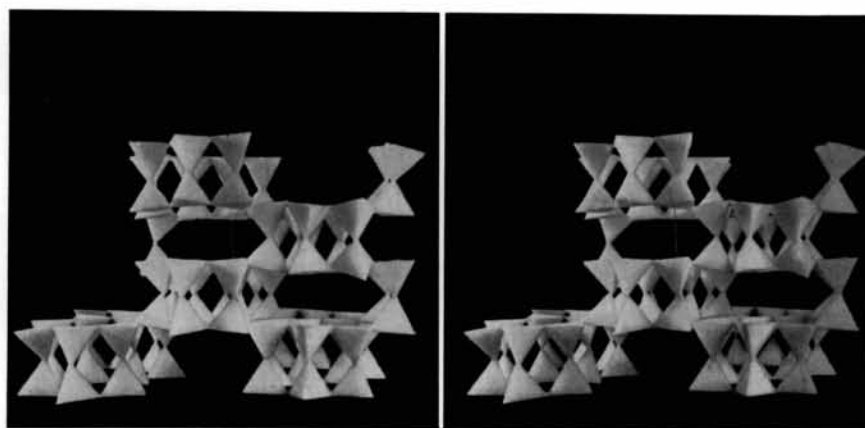
Table 4. Bond lengths within the silicate framework

(The atomic subscripts also refer to the symmetry equivalent atoms in the framework)

$\sigma(\text{Si-O}) = 0.055 \text{ \AA}$							
$\text{Si}_1\text{-O}_3$	1.670 Å	$\text{Si}_2\text{-O}_1$	1.635 Å	$\text{Si}_3\text{-O}_3$	1.610 Å	$\text{Si}_4\text{-O}_2$	1.725 Å
$\text{Si}_1\text{-O}_7$	1.614	$\text{Si}_2\text{-O}_5$	1.706	$\text{Si}_3\text{-O}_6$	1.756	$\text{Si}_4\text{-O}_6$	1.532
$\text{Si}_1\text{-O}_5$	1.578	$\text{Si}_2\text{-O}_2$	1.548	$\text{Si}_3\text{-O}_1$	1.660	$\text{Si}_4\text{-O}_{10}$	1.652
$\text{Si}_1\text{-O}_4$	1.643	$\text{Si}_2\text{-O}_8$	1.652	$\text{Si}_3\text{-O}_9$	1.627	$\text{Si}_4\text{-O}_4$	1.621
Average $\text{Si}_1\text{-O}$ 1.626		Average $\text{Si}_2\text{-O}$ 1.635		Average $\text{Si}_3\text{-O}$ 1.663		Average $\text{Si}_4\text{-O}$ 1.633	
$\sigma(\text{O-O}) = 0.073 \text{ \AA}$							
$\text{O}_3\text{-O}_7$	2.625 Å	$\text{O}_1\text{-O}_5$	2.712 Å	$\text{O}_3\text{-O}_6$	2.646 Å	$\text{O}_2\text{-O}_6$	2.717 Å
$\text{O}_3\text{-O}_5$	2.680	$\text{O}_1\text{-O}_2$	2.726	$\text{O}_3\text{-O}_1$	2.812	$\text{O}_2\text{-O}_{10}$	2.585
$\text{O}_3\text{-O}_4$	2.659	$\text{O}_1\text{-O}_8$	2.601	$\text{O}_3\text{-O}_9$	2.744	$\text{O}_2\text{-O}_4$	2.613
$\text{O}_7\text{-O}_5$	2.608	$\text{O}_5\text{-O}_2$	2.535	$\text{O}_6\text{-O}_1$	2.763	$\text{O}_6\text{-O}_{10}$	2.716
$\text{O}_7\text{-O}_4$	2.687	$\text{O}_5\text{-O}_8$	2.750	$\text{O}_6\text{-O}_9$	2.696	$\text{O}_6\text{-O}_4$	2.608
$\text{O}_5\text{-O}_4$	2.670	$\text{O}_2\text{-O}_8$	2.674	$\text{O}_1\text{-O}_9$	2.600	$\text{O}_{10}\text{-O}_4$	2.702
Average O-O 2.655		Average O-O 2.666		Average O-O 2.710		Average O-O 2.657	



(a)



(b)

Fig. 3. (a) Stereographic view of the structure looking along the a axis.
 (b) Stereographic view of the structure looking along the b axis.

idealized picture of the silicate framework. The O-Si-O angles are tetrahedral. The values for the Si-O-Si angles which exist in the octahedral rings are given in Table 5.

Table 5. *Angles within the octahedral configuration of the double unit*

(a) Upper part of double unit

Si ₃ -O ₉ -Si ₃	152°	Angle formed by the two tetrahedra related by the mirror plane at $y = \frac{1}{4}$
Si ₃ -O ₃ -Si ₁	145	Angle formed between tetrahedra pointing in opposite directions
Si ₁ -O ₇ -Si ₁	149	Angle formed by the two tetrahedra related by $\bar{1}$ in the $0kl$ projection
Si ₁ -O ₄ -Si ₄	150	
Si ₄ -O ₁₀ -Si ₄	143	Angle formed by the two tetrahedra related by mirror plane at $y = \frac{1}{4}$

(b) Lower part of double unit

Si ₄ -O ₂ -Si ₂	146°	Angle formed between tetrahedra pointing in opposite directions
Si ₂ -O ₈ -Si ₂	146	Angle formed by the two tetrahedra related by $\bar{1}$ in the $0kl$ projection
Si ₂ -O ₁ -Si ₃	141	

The water molecules and exchangeable cations

The peaks of the electron density projections which represent sites which are not part of the silicate framework were usually lower than expected. These sites which contain the exchangeable cations and water molecules must be occupied on a statistical basis so that the effective scattering power is lowered. A qualitative spectrochemical analysis of this material had shown the presence of potassium and sodium so that these cations must be in sites which are labelled as H₂O and Na in Table 2. The heights of the peaks do not indicate with certainty what type of occupant is present and it was hoped that the observed bond lengths would show what kind of atom is located in a particular site.

Table 6. *Bond lengths from 'Na' site to oxygen ions of the framework and water molecules*

*Na-O ₅ '	} 2.92 Å	Na-O ₃ '	} 3.25 Å	Na-(H ₂ O) ₅	3.06 Å
Na-O ₅		Na-O ₃		Na-(H ₂ O) ₆	3.00
Na-O ₂ '	} 3.19	Na-O ₁₀	} 3.46	Na-(H ₂ O) ₃ '	} 3.38
Na-O ₂		Na-O ₉		Na-(H ₂ O) ₃	

* O' are atoms related by the mirror at $y = \frac{1}{4}$.

The bond lengths between the occupant of the site labelled Na and the oxygen ions of the framework and the water molecules are shown in Table 6 and the coordination around the site is pictured in Fig. 4. The interatomic distances and the number of neighbors strongly suggest that the ion is not sodium and is most likely potassium. The oxygens O₂, O₅, O₃ and the atoms related by the mirror plane at $y = \frac{1}{4}$ are coplanar with the cation while the two water molecules are approximately 2 Å above this plane and the oxygen

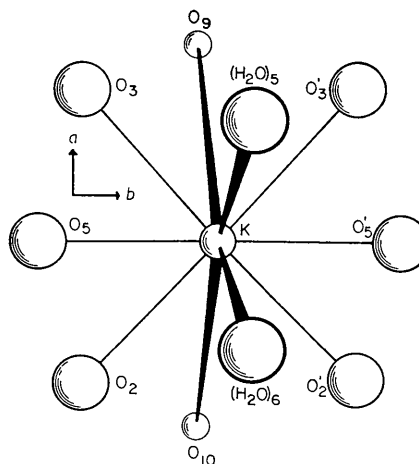


Fig. 4. Coordination around the site labelled 'Na' which is probably occupied by K⁺. Projection along [001]. O₉, O₁₀ are about 2 Å below the plane and (H₂O)₅, (H₂O)₆ are about 2 Å above the plane containing the cation and the other oxygen atoms.

atoms O₉ and O₁₀ are about 2 Å below the plane. The molecule labelled (H₂O)₃ does not appear to be a water molecule. It is not clearly resolved in any of the three electron density projections although they, together with the difference maps, do indicate that electron density exists there. The very high temperature factor and large value of $\sigma(x)$ obtained in the least-squares refinement might indicate that (H₂O)₃ is a low atomic number exchangeable ion such as Li which would be difficult to locate accurately. This assumption is strengthened by the 2.1 Å distance between sites labelled (H₂O)₃ and (H₂O)₂. If this is the case then 'Na'-(H₂O)₃ does not represent a bond and the coordination number around the potassium ion is 10.

Table 7. *Interatomic bond distances from non-framework atoms*

(H ₂ O) ₄ -(H ₂ O) ₅	2.61 Å	(H ₂ O) ₃ -(H ₂ O) ₂	2.07 Å
(H ₂ O) ₄ -(H ₂ O) ₂	2.39	(H ₂ O) ₁ -(H ₂ O) ₂	1.97
(H ₂ O) ₄ -O ₇	2.61	(H ₂ O) ₁ -(H ₂ O) ₄	2.11
(H ₂ O) ₄ -O ₃	2.53	(H ₂ O) ₁ -(H ₂ O) ₇	2.48
(H ₂ O) ₄ -(H ₂ O) ₃	2.66	(H ₂ O) ₇ -O ₉	2.37
(H ₂ O) ₂ -O ₈	2.62	(H ₂ O) ₇ -O ₁₀	1.82
(H ₂ O) ₂ -O ₁	2.72	(H ₂ O) ₇ -O ₂	3.14
(H ₂ O) ₂ -(H ₂ O) ₆	2.56	(H ₂ O) ₇ -O ₄	3.48

There are five neighbors around (H₂O)₄ at distances varying from 2.39 Å to 2.66 Å as shown in Table 7. The configuration around '(H₂O)₄' is shown in Fig. 5 and can be described as a trigonal bipyramid which is sharply skewed to one side. This coordination is not inconsistent with the assumption that '(H₂O)₄' represents an exchangeable sodium ion which is statistically distributed over this site.

The bond distances from the site labelled $\frac{1}{2}$ (H₂O)₂ are 2.56, 2.72, 2.62, and 2.39 Å respectively and then

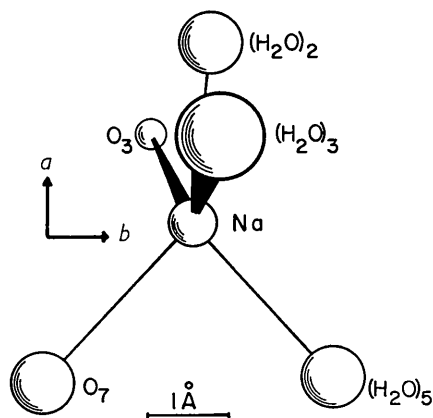


Fig. 5. Coordination around site labelled '(H₂O)₄' which is probably occupied by Na⁺. Projection along [001].

there are two very short distances of 1.97 and 2.07 Å. This site is probably occupied by a water molecule. The 2.39 Å distance is to the Na⁺ which is located in the position labelled '(H₂O)₄'. The very short distances to the positions marked (H₂O)₁ and (H₂O)₃ reinforce the assumption that these sites are occupied by an exchangeable cation and not by water molecules. Hydrogen bonding exists between O₁ and O₈ of the framework and to the site (H₂O)₆ which seems to be also occupied by a water molecule.

The very low value of the temperature factor of $\frac{1}{2}$ (H₂O)₅ indicates that the scattering power in this site should be higher than that which was assumed and that this location contains a molecule of water.

Twinned structures

The crystals of phillipsite were complexly twinned and a branch broken off from one of the cruciform twins gave a diffraction pattern displaying tetragonal symmetry with the same unit cell dimensions as the untwinned crystal. A possible mechanism to account for the tetragonal cell of the twin can be postulated by assuming that during the formation of the *S* unit one section of two double tetrahedra such as 3, 4 (Fig. 6), instead of continuing in the correct manner by linking at point *A* will articulate instead at point *B*. This results in a 90° turn of the whole structure. The *S* units are no longer vertical but horizontal as can be

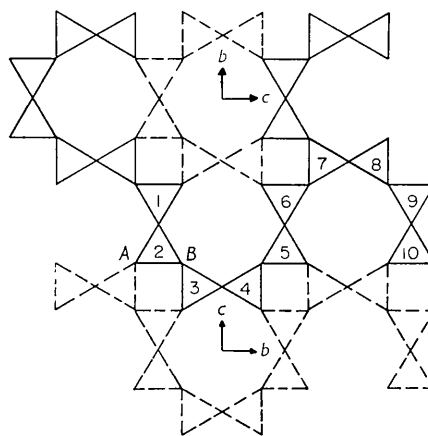


Fig. 6. Twinned structure of phillipsite.

seen from the *S* unit formed by the double tetrahedra 1–10. The double tetrahedra 1, 2, 6, 5, 7, 8, 9, and 10 are part of both the vertical and horizontal *S* structure. A specimen twinned by this mechanism will give rise to a tetragonal diffraction pattern.

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References

- BARRER, R. M., BULTITUDE, F. W. & KERR, I. S. (1959). *J. Chem. Soc.*, p. 1521.
 BRAGG, W. L. (1937). *Atomic Structure of Minerals*. Ithaca: Cornell University Press.
 LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*. London: Bell.
 MEIER, W. M. (1960). *Z. Kristallogr.* **113**, 430.
 NOWACKI, W. & BERGERHOFF, G. (1957). *Acta Cryst.* **10**, 761.
 SADANAGA, R., MARUMO, F. & TAKEUCHI, Y. (1960). *Acta Cryst.*, **13**, 1003.
 STRUNZ, H. (1957). *Mineralogische Tabellen*. Leipzig: Akademische Verlagsgesellschaft.
 WYART, J. & CHATELAIN, P. (1938). *Bull. Soc. Franç. Minér.* **61**, 121.