Acta Cryst. (1966). **21**, 200

The Crystal Structure of Neptunite*

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(*Received* 16 *November* 1965)

When this work was begun the following chemical and crystallographic data of neptunite were available: formula $KNa_3Fe_2Ti_2(Si_4O_{12})_2$; lattice parameters: $a=16{\cdot}46$, $b=12{\cdot}50$, $c=10{\cdot}01$ Å, $\beta=115°26'$, space group $C2/c$, $Z=4$. A new chemical analysis showed the presence of some lithium that had been determined as sodium in previous analyses. On this basis the crystal structure analysis was carried out by the use of three-dimensional Patterson and Fourier syntheses, direct methods and least-squares refinement of atomic parameters (final $R=0{\cdot}117$). The structure is based upon a new three-dimensional network of SiO_4 tetrahedra. When the structure determination was nearly accomplished a piezoelectric effect was detected. A crystal structure with space group Cc is postulated which is fairly similar to the centrosymmetrical one and could explain the piezoelectricity. Chemical and crystallographic considerations suggest the following formula for neptunite: $LiNa_2K(Fe,Mg,Mn)_2(TiO)_2[Si_8O_{22}]$.

Introduction

Neptunite was first found at Julianehaab (Greenland) by Flink (1895) who studied it from an optical and morphological point of view. He pointed out also a kind of morphological relationship between neptunite and titanite (sphene). Subsequently neptunite was found at San Benito (California) and studied by Ford (1909); Bradley (1909) and Louderback (1910) gave chemical analyses of Californian neptunite. In 1926 Fersman studied and analysed a manganese-rich (MnO 9·95%) neptunite from the Kola Peninsula. At the same time Gössner (1925) noticed a crystallographic analogy between neptunite and aegirine. Gössner & Mussgnug (1928) first reported the cell parameters of neptunite from San Benito. Nockolds (1950) re-examined the optical properties of neptunite and Heinrich & Quon (1963) found the mineral at Seal Lake, Labrador, and summarized the properties, particularly the optical ones, of neptunites studied up to that time. Further values of the cell data were given by Berry (1963) together with X-ray powder data.

Strunz (1957) considers neptunite as a silicate with rings of four SiO_4 tetrahedra while Belov (1963), on the basis of theoretical considerations, suggests that a particular kind of chain of tetrahedra, extended around a pseudo fourfold screw axis, is present.

The present study was started with the following data: chemical formula: $KNa_2Ti_3(Fe,Mg,Mn)_2(Si_4O_{12})_2$; cell parameters: $a=16{\cdot}46$, $b=12{\cdot}50$, $c=10{\cdot}01$ Å (all $\pm 0{\cdot}01$), $\beta=115°26'$; space group $C2/c$, $Z=4$.

Experimental

The X-ray diffraction data were collected from a single-crystal fragment of neptunite from San Benito which was made nearly cylindrical; the radius of this cylindrical sample was 0·011 cm and the *c* axis was parallel to the axis of the cylinder. Multiple film Weissenberg photographs of the integrated reflexions *hkl* (*l* from 0 to 5) were taken with Cu $K\alpha$ radiation and precession pictures of the reflexions *h*0*l* were recorded with Mo $K\alpha$ radiation. The intensities were measured with a Nonius microdensitometer. The corrections applied to the intensities were concerned with absorption, incipient but incomplete $\alpha_1-\alpha_2$ spot doubling (Sakurai, 1962) and Lorentz-polarization. The linear absorption coefficient of neptunite is $\mu=281$ cm^{-1} for Cu $K\alpha$ and the transmission factors varied from 0·12 to 0·91. A secondary extinction correction was applied during the refinement (see below).

Structure analysis

Patterson projections along [010] and [001] were first calculated. While the latter projection did not yield any immediate information, the former [Fig. 1(*a*)] showed nearly all the maxima aligned on directions parallel to [100] at *w* ranges of $\frac{1}{6}$ (*i.e.* at $w=0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}$). On the basis of this observation, four Patterson sections normal to [001] at the *w* levels given above were calculated. In addition, in order to record the Patterson maxima with a different *w*, [001] Patterson projected slabs $\frac{1}{6}$ *c* thick, with the middle part at the same levels, were computed. The two kinds of Patterson syntheses did not appear appreciably different.

A rough computation showed that the heights of the Patterson peaks defining distances between equivalent points were too low to be useful, even for the Fe–Fe distances, so that the high maxima actually present in the Patterson sections must be related to distances between non-equivalent atoms occurring many times. This prevents the determination of the crystal structure considering Fe and Ti as heavy atoms.

According to the assumed space group $C2/c$, an arrangement of Patterson maxima with *w* coordinates like those observed could be obtained only if the *z*

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* Paper presented at the XXI Congress of the Società Mineralogica Italiana, Pisa, Italy, October 1964. Cannillo, Mazzi & Rossi (1965).

coordinates of most of the atoms were: (*a*) 0, $\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, $\frac{5}{6}$ or (*b*) $\frac{1}{12}$, $\frac{1}{4}$, $\frac{5}{12}$, $\frac{7}{12}$, $\frac{3}{4}$, $\frac{11}{12}$. From the four Patterson sections [Fig. 1(*b*)] one can remark that while on the sections at $w=0$ and $\frac{1}{3}$ the highest maxima are at $v=0$, $v=\frac{1}{4}$ and $v=\frac{1}{2}$, on the section at $w=\frac{1}{6}$ and $w=\frac{1}{2}$ the most relevant ones are at $v=\frac{1}{8}$, $v=\frac{5}{8}$ *etc.* The coordinates of the equivalent points suggest that an arrangement like that mentioned above is consistent with the z coordinates of type (*b*), while with coordinates of type (*a*) the positions of the maxima on the Patterson sections at $w=\frac{1}{6}$ and $w=\frac{1}{3}$ must be interchanged. On the Patterson sections at $w=0$ and $w=\frac{1}{6}$ two large maxima are present, namely: A ($u=0{\cdot}133$, $v=0$) and B ($u=0{\cdot}050$, $v=0{\cdot}117$). This pair offers a clue for the resolution of the structure because it gives rise to vectors with a modulus of about 2 Å. Such vectors could be referred only to (Fe,Ti)–O distances; moreover the maxima are arranged in such a way that they correspond to the six vectorial distances of a nearly perfect octahedron. The further consideration that the A and B maxima are fairly high, although they are due to distances from oxygen atoms, leads to the conclusion that all the (Fe,Ti)–O octahedra have the same orientation in the unit cell.

The strongest Patterson peak (C) occurs at $u=\frac{1}{4}$, $v=\frac{1}{4}$, $w=0$ and it is clearly due to a vectorial distance repeated many times: if all the octahedra have the same orientation this peak may represent distances between homologous atoms of the octahedra, particularly between the (Fe,Ti) cations. If also the high peaks D ($u=0{\cdot}166$, $v=0{\cdot}117$) and E ($u=0{\cdot}416$, $v=0{\cdot}416$) are thought to be due to distances between the same atoms, two kinds of chains of octahedra may be found consistent with the coordinates of the equivalent points in the chosen space group and with the considerations made on the Patterson sections. One of the two following sets of approximate parameters could therefore be assigned to (Fe,Ti):

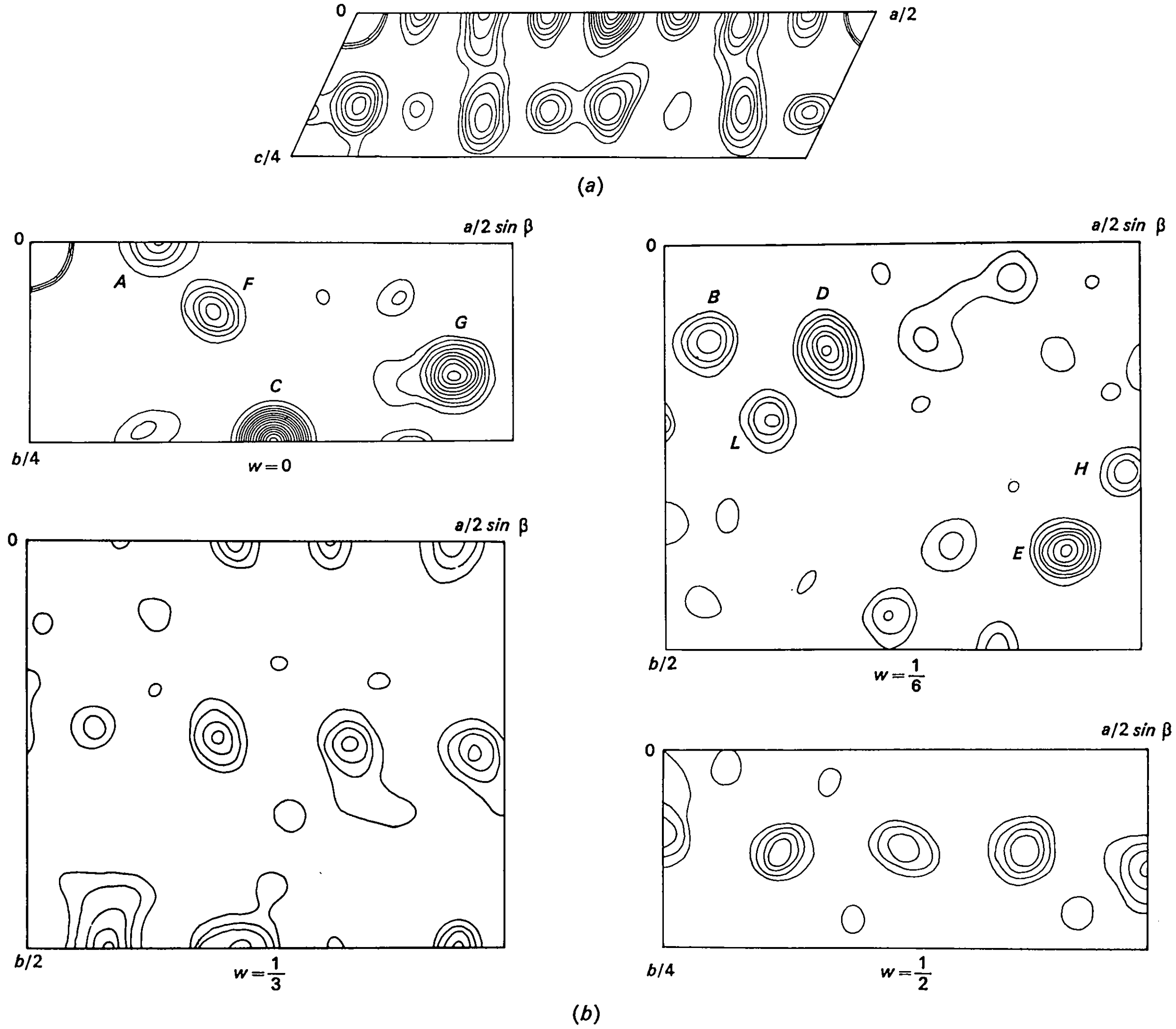

Fig. 1. (*a*) Patterson projection normal to [010]. (*b*) Patterson sections normal to [010]. Contours are drawn at equal but arbitrary levels.

		x/a	y/b	z/c
(*a*)	(Fe,Ti)(1)	0·208	0·187	0·083
	(Fe,Ti)(2)	0·458	0·437	0·083
(*b*)	(Fe,Ti)(1)	0·333	0·310	0·083
	(Fe,Ti)(2)	0·083	0·062	0·083

Some more Patterson peaks remained, apparently not due to (Fe,Ti)–(Fe,Ti) and (Fe,Ti)–O distances, namely the F and G maxima on the section at $w=0$ and the L and H maxima on the synthesis at $w=\frac{1}{6}$. These peaks are consistent with the supposition of pairs of silicon atoms lying on lines parallel to [110] and [$\bar{1}$10] at opposite sides of the chains of the (Fe,Ti)–O octahedra. In such a way, bearing in mind the alternative pairs of coordinates of (Fe,Ti), two sets of equivalent points could be assigned to silicon atoms, the approximate parameters of which are, for model (*a*):

	x/a	y/b	z/c
Si(1)	0·375	0·062	0·083
Si(2)	0·042	0·312	0·083
Si(3)	0·625	0·312	0·083
Si(4)	0·292	0·562	0·083

and for model (*b*):

Si(1)	0·166	0·437	0·083
Si(2)	0·500	0·187	0·083
Si(3)	0·250	−0·062	0·083
Si(4)	−0·083	0·187	0·083

Both models can be derived from a close-packed arrangement of the oxygen atoms. Taking the atomic diameter of oxygen to be a little more than 3 Å, the cell dimensions allow the distribution of the oxygen atoms on a nearly tetragonal body centered lattice whose unit cell has the following dimensions: $a'=3\cdot02$ Å (normal to the (001) plane), $b'=3\cdot13$ Å (parallel to **b**), $c'=4\cdot12$ Å (parallel to **a**). If some series of octahedra and tetrahedra are built up with oxygen atoms in a way consistent with Patterson syntheses, model (*a*) is obtained by putting some oxygen atoms on the twofold axes, and model (*b*) results from putting no oxygen atoms on them. In both cases the condition was fulfilled that each SiO_4 tetrahedron shared only a corner with other polyhedra (SiO_4 tetrahedra, (Fe,Ti)O_6 octahedra). The two structural models are rather similar as far as the linking of SiO_4 tetrahedra in directions nearly parallel to [110] and [$\bar{1}$10] is concerned, but are different in the linking of such polyhedra along [001]. The same consideration is true for the linking of (Fe,Ti)O_6 octahedra. From this point of view both models seem to be possible and the real structural arrangement cannot be decided.

At this stage of the work an attempt was made to settle the question by means of direct methods. The 131 strongest reflexions were examined and the determination of the signs of the corresponding structure factors was tried by the application of Sayre's (1952) relation:

$$S_{hkl}=S_{h'k'l'},\ S_{h+h',\ k+k',\ l+l'}\ .$$

Owing to the rather high value of the unitary structure factor of these reflexions, there was a very high probability of a correct identification of their phases. Using the Woolfson (1961) method, a coherent set of signs was given to 98 reflexions (among which were those with $h=2n$, $l=2n$); for the remaining ones, two alternative self-consistent sets of signs were possible. Electron density projections permitted the rejection of one of these sets of signs because it disagreed with the above models; the other gave a result in full agreement with model (*b*) of the structure.

All previous considerations made and some electron density syntheses permitted the identification of the positions of the oxygens, of the potassium atoms (on fourfold series of equivalent points) and of two-thirds of the sodium atoms (on an eightfold series of equipoints). The positions of the remaining sodium atoms were not detected, but they obviously could be only on a fourfold series of equivalent points. The electron density syntheses showed a low peak on a twofold axis, but sodium could not be put in that position because it would have been surrounded by six oxygen atoms at distances of little more than 2 Å. However there was no place, besides the one above mentioned, where it was possible to put an atom.

Then the possibility that the chemical formula might be incorrect was considered. Actually all the chemical analyses of neptunite give a total percentage of oxides greater than 100, and three of them in a rather significant way (Table 1). Besides this the chemical formula

Table 1. *Chemical analyses of neptunite**

	1	2	3	4	5	6
SiO_2	51·53	51·93	52·87	53·44	52·68	52·29
TiO_2	18·13	17·45	17·83	17·18	18·21	17·35
FeO	10·91	10·23	11·69	11·23	5·16	11·92
MnO	4·97	5·32	0·85	1·78	9·95	2·27
MgO	0·49	—	1·44	1·82	0·12	1·55
CaO	—	0·71	1·56	0·25	0·43	0·62
K_2O	4·88	5·71	5·08	5·39	4·94	5·58
Na_2O	9·26	9·63	9·56	9·14	9·16	6·81
Li_2O	—	—	—	—	—	1·63
Total	100·17	100·98	100·88	100·23	100·65	100·02

* 1. Julianehaab (Flink, 1895), 2. Julianehaab (Sjöström, 1895), 3. San Benito (Bradley, 1909), 4. San Benito (Louderback, 1910), 5. Kola (Fersman, 1926), 6. San Benito (this paper).

computed from each analysis gives a figure for the number of sodium atoms less than 3 (ranging from 2·67 to 2·85) against a constant number of 1 for potassium. This sodium defect could be partially or totally balanced by the presence of a little calcium replacing some sodium. However, these considerations and the results of the structural analysis led to the opinion that all the discrepancies would disappear if some lithium were present. This lithium could have been considered as sodium in the chemical analyses because sodium was determined as the difference between the total chlorides and the potassium chloride. A new chemical analysis of neptunite was carried out and lithium chloride was separated by treating the chlorides with alcohol-ether, in which only the lithium chloride is soluble. The result is given in Table 1.

The refinement was carried out by means of some cycles of least-squares (full matrix, isotropic temperature factor for each atomic species, equal weight for all reflexions). The structure factors were calculated by using the atomic scattering factors obtained from Moore's constants (1963) and considering iron and titanium as replaceable cations. All the calculations were carried out with an ELEA 6001 digital computer. A plot of ln I_c/I_o against I_c for the most intense reflexions showed a conspicuous secondary extinction effect. A linear relation between ln I_c/I_o and I_c was assumed and a least-squares secondary extinction coefficient derived. This was applied to all the F_o's by means of the formula:

$$(F_o)_{\text{corr}}=(F_o)_{\text{ext.}}\ \exp(\tfrac{1}{2}\varepsilon I_c)\ \text{where}\ \varepsilon=1\cdot76\times10^{-6}\ .$$

The refinement lowered the discrepancy index from 0·40 to 0·117 for the observed reflexions and 0·155 for all the reflexions (giving to the unobserved ones a value half of the least observed intensity).

The atomic parameters and their standard deviations (Cruickshank, 1949) are given in Table 2. The isotropic thermal parameters are: $B_{\text{Fe,Ti}}=1\cdot52$, $B_{\text{Na}}=2\cdot06$, $B_{\text{K}}=1\cdot72$, $B_{\text{Li}}=4\cdot47$, $B_{\text{Si}}=0\cdot80$, $B_{\text{O}}=1\cdot44$ Å^2. The observed and calculated structure factors are compared in Table 3.

At this stage of the work, when the determination of the crystal structure seemed accomplished in the space group $C2/c$, the opportunity was offered to subject neptunite to a test for piezoelectricity, which gave a positive effect. It seemed rather improbable that a completely wrong structure could give such good agreement with experimental data, so an attempt was made to see whether it was possible to obtain, from the centric model, an acentric structure so as to justify the rather strong piezoelectric effect. In the next section, after the description of the 'centrosymmetrical' structure, a suggestion will be made as to what might be the real structural model.

Description of the structure

The basic structure of neptunite is a three-dimensional network of SiO_4 tetrahedra. This network is different from that of framework silicates because each tetrahedron shares only two or three oxygen atoms with its neighbours. This arrangement is built up (Fig. 2) by two series of chains of tetrahedra extended roughly along [110] and [$\bar{1}$10]; these chains, sharing some oxygen atoms, give rise to other chains along [001]. The network can be imagined as the repetitition by translation of a 'cage' built up from two rings of 18 SiO_4 tetrahedra and four rings of 14 SiO_4 tetrahedra. The 'cage' represents a stoichiometric unit corresponding to $[Si_{16}O_{44}]^{24-}$ (Fig. 3). Actually there are two identical systems of 'cages'; they are interlaced and tied together by the $(Fe,Ti)O_6$ octahedra that are connected in such a way as to determine a further network which has dimensions comparable to those of the 'cages' of tetrahedra. Each octahedron shares two edges with its two

Table 2. *Atomic coordinates and their standard deviations* (*standard deviations of fractional coordinates in parentheses*)

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
(Fe,Ti)(1)	0·3402 (1)	0·3211 (2)	0·0983 (4)	0·002 Å	0·003 Å	0·004 Å
(Fe,Ti)(2)	0·0883 (1)	0·0561 (2)	0·1128 (4)	0·002	0·003	0·004
Na	0·2640 (4)	0·1983 (6)	0·3094 (11)	0·007	0·007	0·011
K	0·0000	0·4204 (3)	0·2500		0·004	
Li	0·5000	0·4353 (18)	0·2500		0·023	
Si(1)	0·1452 (2)	0·4060 (3)	0·0566 (7)	0·003	0·004	0·007
Si(2)	0·5233 (2)	0·2280 (3)	0·0855 (7)	0·003	0·004	0·007
Si(3)	0·7698 (2)	0·4741 (3)	0·1083 (7)	0·003	0·004	0·007
Si(4)	0·8942 (2)	0·1491 (3)	0·0816 (8)	0·003	0·004	0·008
O(1)	0·9538 (5)	0·0446 (10)	0·0688 (18)	0·008	0·012	0·018
O(2)	0·4549 (5)	0·3253 (7)	0·0666 (16)	0·008	0·009	0·016
O(3)	0·1099 (13)	0·1673 (9)	0·2664 (18)	0·021	0·011	0·018
O(4)	0·3723 (6)	0·4387 (10)	0·2348 (16)	0·010	0·012	0·016
O(5)	0·2050 (6)	0·0796 (10)	0·0888 (19)	0·010	0·012	0·019
O(6)	0·7122 (11)	0·3677 (12)	0·0427 (19)	0·018	0·015	0·019
O(7)	0·2088 (6)	0·3077 (10)	0·0707 (16)	0·010	0·012	0·016
O(8)	0·8339 (5)	0·4919 (9)	0·0239 (19)	0·008	0·011	0·019
O(9)	0·1592 (4)	0·4505 (7)	0·2143 (15)	0·007	0·009	0·015
O(10)	0·3975 (6)	0·2104 (7)	0·2541 (15)	0·010	0·009	0·015
O(11)	0·4613 (7)	0·1173 (7)	0·0239 (19)	0·011	0·009	0·019
O(12)	0·9291 (5)	0·2562 (8)	0·0316 (14)	0·008	0·010	0·014

Table 3. *Structure factors of neptunite*

Reflexions marked * were unobservably weak; in these cases F_{obs} are derived from 0·5 $I_{obs\ min}$.

k	l	$10F_o$	$10F_c$
		0 k l	
0	2	n.d.	2577
0	4	n.d.	760-
2	0	117*	213
2	1	135*	163
2	2	n.d.	258-
2	3	127*	116
2	4	389	221-
2	5	982	1035
4	0	149*	70
4	1	1453	1308
4	2	531	418-
4	3	4361	3995-
4	4	396	499-
4	5	1072	1174
6	0	169*	113
6	1	376	292-
6	2	437	390
6	3	158*	165-
6	4	731	817-
6	5	198*	191
8	0	1879	2301-
8	1	537	398
8	2	1238	1402
8	3	159*	265
8	4	926	921
8	5	497	600-
10	0	558	542-
10	1	464	567-
10	2	185*	26-
10	3	373	358-
10	4	664	717
10	5	648	879-
12	0	366	273
12	1	1014	1069
12	2	416	345
12	3	2391	2661
12	4	107*	188
12	5	135*	302
14	0	134*	227-
14	1	369	306
14	2	326	408-
14	3	413	366
14	4	295	374
14	5	75*	172-
16	0	50*	32-
		1 k l	
1	2	126*	68-
1	3	557	343
1	-3	99*	562
1	4	2809	2275-
1	-4	1548	1455-
1	5	1315	1328
1	-5	1724	1565-
3	0	754	609-
3	1	3213	3207-
3	-1	1732	1553-
3	2	3564	3365-
3	-2	3317	3143
3	3	1222	1153-
3	-3	2151	2227-
3	4	1046	1085-
3	-4	1299	1408
3	5	1031	968-
3	-5	183*	199-
5	0	497	474
5	1	735	737-
5	-1	655	629-
5	2	1229	1362
5	-2	929	860-
5	3	1035	922-
5	-3	1638	1599-
5	4	136*	169
5	-4	454	431
5	5	197*	278-
5	-5	424	526
7	0	807	862
7	1	520	492-
7	-1	193*	4-
7	2	432	396-
7	-2	172*	25-
7	3	162*	136-
7	-3	161*	284-
7	4	634	674
7	-4	478	376
7	5	653	720
7	-5	198*	230-
9	0	2424	3056-
9	1	1674	1838
9	-1	2110	2204-
9	2	1110	1247-
9	-2	717	664-
9	3	163*	62-
9	-3	704	886-
9	4	543	505
9	-4	832	904
9	5	1068	1355-
9	-5	1207	1594
11	0	169*	164-
11	1	976	1088
11	-1	195*	123
11	2	811	883
11	-2	967	972-
11	3	374	445-
11	-3	903	779
11	4	436	485
11	-4	580	744-
11	5	150*	35-
11	-5	502	567
13	0	433	388-
13	1	158*	184-
13	-1	428	406
13	2	135*	116-
13	-2	137*	37-
13	3	464	348
13	-3	919	1001
13	4	244	264
13	-4	91*	51-
13	5	367	394-
13	-5	468	611-
15	0	443	392
15	1	532	555
15	-1	651	731-
15	2	79*	173
15	-2	493	460
15	3	347	385-
15	-3	69*	216
15	-4	44*	92
		2 k l	
0	0	109*	80
0	2	138*	278
0	-2	61*	187-
0	4	1631	1442
0	-4	60*	191
2	0	770	651-
2	1	155*	318-
2	-1	843	640
2	2	3152	2727-
2	-2	631	661
2	3	996	875-
2	-3	3584	3617-
2	4	459	439-
2	-4	925	874
2	5	539	574
2	-5	1676	1596-
4	0	405	32
4	1	176*	129
4	-1	458	382-
4	2	161*	283
4	-2	1012	1077
4	3	153*	242
4	-3	766	745-
4	4	135*	58
4	-4	737	628-
4	5	779	914
4	-5	574	518
6	0	1745	1955-
6	1	2456	2660-
6	-1	1427	1422
6	2	1973	2340
6	-2	2479	2650-
6	3	1099	1119-
6	-3	1519	1597-
6	4	1650	1794
6	-4	1437	1507-
6	5	1059	1257
6	-5	1034	1150-
8	0	357	325
8	1	1021	1266-
8	-1	572	487-
8	2	468	532
8	-2	405	191-
8	3	376	261-
8	-3	353	107
8	4	139*	102-
8	-4	140*	159-
8	5	333	390
8	-5	193*	149-
10	0	1067	1194-
10	1	195*	228-
10	-1	1191	1320-
10	2	573	509-
10	-2	375	363-
10	3	893	828-
10	-3	514	309-
10	4	127*	140-
10	-4	1067	1148
10	5	762	1097-
10	-5	177*	45
12	0	447	130
12	1	168*	53
12	-1	175*	135
12	2	149*	69
12	-2	802	987-
12	3	129*	50
12	-3	133*	42-
12	4	265	299
12	-4	415	324
12	5	118*	183
12	-5	140*	164-
14	0	418	435
14	1	124*	239
14	-1	431	428-
14	2	425	525-
14	-2	320	154
14	3	247	420-
14	-3	95*	20-
14	4	479	470-
14	-4	74*	284-
14	-5	403	533
		3 k l	
1	0	132*	197-
1	1	162*	24-
1	-1	138*	200-
1	2	1488	1385
1	-2	113*	79
1	3	1588	1513
1	-3	95*	380
1	4	1279	1103
1	-4	888	938-
1	5	195*	150
3	0	2288	2688
3	1	1705	1754-
3	-1	2183	2121
3	2	665	548
3	-2	1772	1737
3	3	600	613
3	-3	1270	1130
3	4	1321	1465-
3	-4	553	362
3	5	662	610
3	-5	936	842-
5	0	393	318
5	1	187*	52-
5	-1	723	757
5	2	167*	273-
5	-2	601	618
5	3	2046	2463
5	-3	153*	133-
5	4	1243	1391
5	-4	910	884
5	5	691	779
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9	-1	141*	38-
9	2	80*	50
9	-2	727	706-
9	-3	125*	245-
9	-4	636	585
9	-5	924	891
11	0	74*	108-
11	-1	325	187-
11	-2	298	174
11	-3	443	444-
11	-4	330	204
11	-5	293	109-
		14 k l	
0	0	161*	32
0	2	137*	30-
0	-2	299	396
0	-4	389	332-
2	0	738	673
2	1	168*	61
2	-1	1764	1764
2	2	133*	311-
2	-2	435	353-
2	-3	157*	102
2	-4	136*	56-
2	-5	605	432
4	0	150*	118-
4	1	159*	80-
4	-1	180*	256-
4	2	123*	147-
4	-2	327	311
4	-3	153*	95-
4	-4	313	41-
4	-5	181*	260-
6	0	1053	1001-
6	1	864	911-
6	-1	1376	1359
6	2	827	814
6	-2	1174	1349-
6	-3	1045	978-
6	-4	1235	1227-
6	-5	1360	1486-
8	0	372	240-
8	1	441	452-
8	-1	140*	259
8	2	74*	106
8	-2	281	259-
8	-3	124*	7-
8	-4	488	530
8	-5	1070	1000-
10	0	475	466
10	-1	396	204
10	-2	290	189-
10	-3	737	646
10	-4	750	613-
10	-5	108*	80-
		15 k l	
1	0	149*	40-
1	-1	177*	201-
1	-2	435	458
1	-3	819	759-
1	-4	487	403
1	-5	936	859-
3	0	943	945
3	1	146*	295-
3	-1	1540	1533
3	-2	1174	1147
3	-3	529	502
3	-4	127*	138-
3	-5	972	874-
5	0	452	394
5	1	129*	117
5	-1	470	252
5	-2	603	545-
5	-3	139*	150
5	-4	120*	124
5	-5	594	423-
7	0	103*	114-
7	1	102*	116-
7	-1	814	823
7	-2	564	475
7	-3	124*	28-
7	-4	572	575
7	-5	144*	84-
9	0	946	895
9	-1	301	283
9	-2	258	313-
9	-3	686	592
9	-4	1090	1050-
9	-5	812	649
11	-3	368	377
11	-4	388	545-
11	-5	281	222
		16 k l	
0	0	1791	1723-
0	-2	846	932
0	-4	3239	3530
2	0	128*	84
2	-1	159*	125
2	-2	297	206
2	-3	526	536-
2	-4	120*	101
2	-5	169*	252-
4	0	116*	38-
4	-1	828	613
4	-2	411	288
4	-3	134*	89
4	-4	115*	90-
4	-5	158*	78-
6	0	472	363-
6	-1	127*	99
6	-2	121*	218
6	-3	119*	226
6	-4	101*	49-
6	-5	142*	46
8	0	444	328
8	-1	360	286-
8	-2	93*	13-
8	-3	92*	105
8	-4	1229	1002-
8	-5	111*	95
10	-3	675	751
10	-4	229	293-
10	-5	259	48
		17 k l	
1	0	685	538-
1	-1	515	455
1	-2	394	370
1	-3	128*	69-
1	-4	896	910
1	-5	155*	130
3	0	631	662-
3	-1	973	910
3	-2	1355	1177-
3	-3	1016	1033
3	-4	108*	174-
3	-5	637	445-
5	0	272	188-
5	-1	354	178
5	-2	113*	26
5	-3	243	142
5	-4	304	273
5	-5	419	233-
7	-1	65*	107-
7	-2	245	157-
7	-3	87*	12-
7	-4	76*	106
7	-5	106*	90
9	-3	893	968-
9	-4	1025	1204-
9	-5	969	903-
		18 k l	
0	0	457	351
0	-2	488	403-
0	-4	394	315
2	-1	676	570
2	-2	945	864-
2	-3	502	437
2	-4	96*	16
2	-5	133*	64
4	-1	550	464
4	-2	98*	133-
4	-3	359	249-
4	-4	308	196
4	-5	121*	204-
6	-1	398	402
6	-2	1086	1197
6	-3	737	670
6	-4	316	247-
6	-5	418	202
		19 k l	
1	-1	747	766-
1	-2	597	494
1	-3	90*	129-
1	-4	336	275-
1	-5	114*	128-
3	-1	663	633-
3	-2	80*	90-
3	-3	617	566
3	-4	370	291
3	-5	106*	9
5	-2	60*	55-
5	-3	331	342
5	-4	570	517-
5	-5	430	329
		20 k l	
0	-2	575	573-
0	-4	191	10-
2	-3	295	282
2	-4	59*	58-
2	-5	87*	215
4	-4	403	460

opposite neighbours along [110] and [$\bar{1}$10]; along [001] the connexion is due to the sharing of the opposite corners.

The alkali cations occur in the cavities left free by the chains. Lithium has a nearly perfect octahedral coordination while sodium is surrounded by seven oxygen atoms that form a sort of octahedron with a 'centered' face and potassium has an irregular coordination polyhedron made up from ten oxygen atoms (Table 4, Fig. 4).

The bond distances between (Fe,Ti) and oxygen atoms have some peculiarities that permit a hypothesis of an acentric structure which would account for the piezoelectricity. All the oxygen atoms but one that take part in the octahedral coordination are shared with tetrahedra; that one is bonded only with (Fe,Ti) and Li. The bond distances between this oxygen and (Fe,Ti) in the two non-equivalent octahedra of the centrosymmetrical structure are among the shortest ones, while the distances of the oxygen atoms at the opposite side of the cations are notably longer than the average. The mean (Fe,Ti)–O distance is 2·05 Å, while these pairs of distances have the following values: 1·918 and 2·218 Å for the former octahedron and 2·010 and 2·195 Å for the latter.

An octahedron with four bonds of the same length lying on a plane and two more opposite bonds of fairly different length is a characteristic feature of Ti coordination. This ion has the tendency to bind one of the oxygen atoms of its coordination polyhedron more strongly [*cf.* piezoelectric barium and lead titanates (Jona & Shirane, 1962); titanite (Zachariasen, 1930); narsarsukite (Peacor & Buerger, 1962)].

The chemical formula derived from the cited analyses shows a remarkable constancy in the titanium content while iron is present in variable amount and it is often replaced by manganese. It may be thought that probably Fe and Ti are not replaceable cations and therefore also in the centrosymmetrical case, one series of equivalent points might be occupied by Ti only and the other by Fe and the ions that replace it. But the cited feature of pairs of bond distances with different length is present in both non-equivalent octahedra; probably this is a wrong detail introduced in the structure because it has been considered as centrosymmetrical.

In Fig. 5(*a*) there is a schematic view of the chains of the octahedra; these are distinguished in two non-equivalent series for the centrosymmetrical case. Fig. 5(*b*) shows the same chains built up by two series of non-equivalent octahedra that give rise to an acentric structure in the space group *Cc*. Considering this structure (on the hypothesis that it is the correct one) on the basis of a centrosymmetrical space group, half of the points actually occupied by Fe would be considered as occupied by Ti and *vice versa*. Owing to this fact, a coordination feature characteristic of Ti would be found in both non-equivalent octahedra.

To carry out a refinement of the non-centrosymmetrical structure, the following modifications of the centric one were made: (*a*) Fe and Ti were put alternately on the chains parallel to [110] and [$\bar{1}$10] (Table 5); (*b*) the parameters of three oxygen atoms were slightly modified in order to make the coordination around the Fe uniform and maintain the characteristic distorted octahedra around Ti (Table 5). Such an arrangement

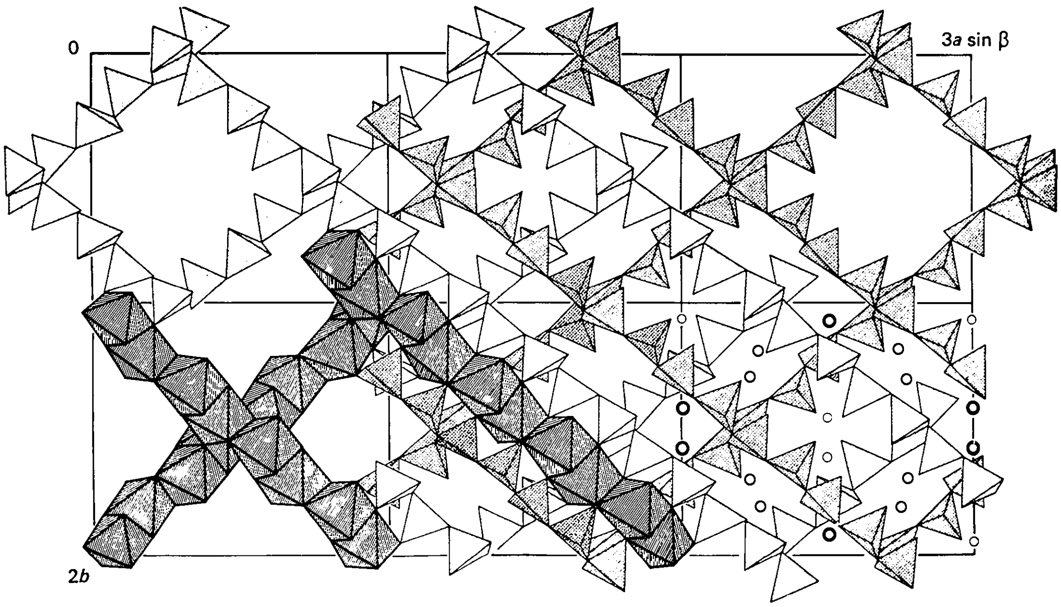

Fig. 2. The crystal structure of neptunite. Top left and right: the two systems of chains of tetrahedra and (top centre) their superposition. Bottom left: the chains of octahedra; bottom centre: their connexion with the chains of tetrahedra; bottom right: the positions of alkaline cations (for their coordination see Fig. 4).

Table 5. *Atomic coordinates in space group Cc*

	x/a	y/b	z/c
Fe(1)	0·160	0·179	−0·098
Fe(2)	0·412	0·444	−0·113
Ti(1)	0·340	0·321	0·098
Ti(2)	0·088	0·056	0·113
O(2)	0·452	0·332	0·056
O(2′)	0·045	0·175	−0·067
O(4)	0·372	0·439	0·235
O(4′)	0·128	0·054	−0·242
O(7)	0·209	0·298	0·061
O(7′)	0·291	0·192	−0·071

The parameters of the remaining atoms are unchanged from those given in Table 2.

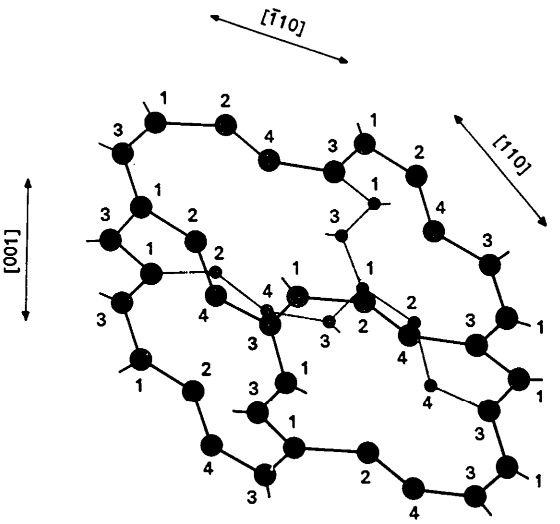

Fig. 3. Schematic view of the basic network of SiO_4 tetrahedra. Silicon atoms only are shown.

can account for piezoelectricity: in Fig. 5(*b*) it is shown that all the octahedra around Ti have their shortest bonds pointing to the positive **c** direction and their longest bonds to the negative **c** direction. Because of this the direction of **c** is polar.

A structure factor calculation carried out with these modifications gave $R=0{\cdot}12$ (0·15 for all reflexions).

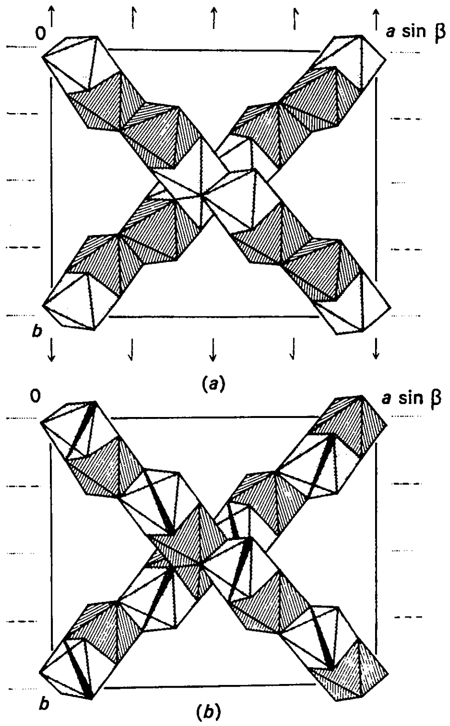

Fig. 5. Schematic view of the chains of the (Fe,Ti) octahedra in the $C2/c$ (*a*) and Cc(*b*) space groups.

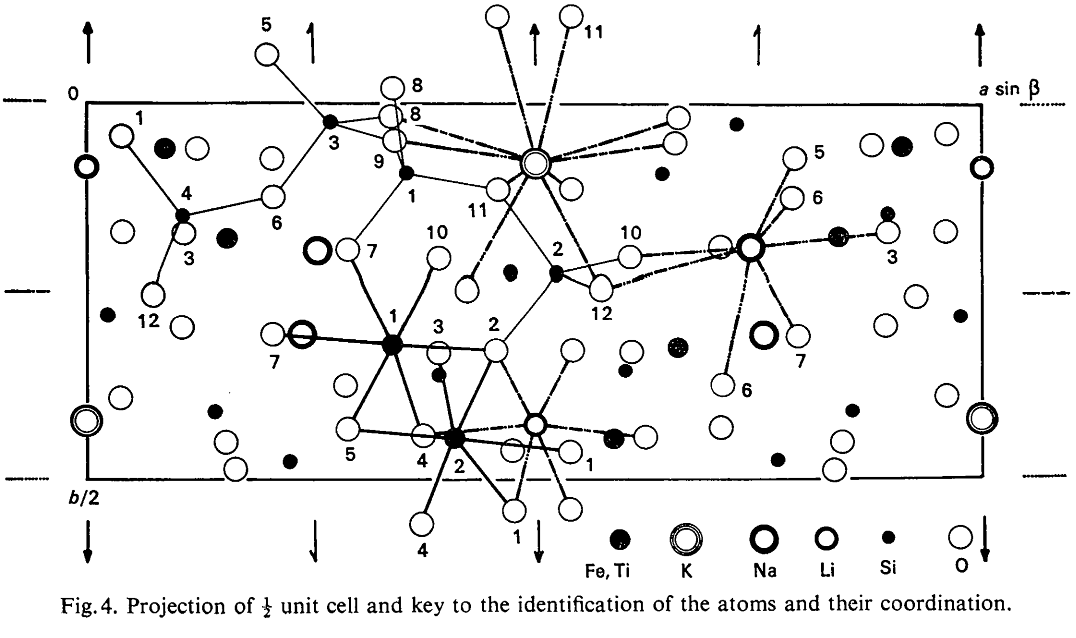

Fig. 4. Projection of ½ unit cell and key to the identification of the atoms and their coordination.

The discrepancy index, owing to the small magnitude of the shifts, the small number of the shifted atoms and the slight difference between the atomic scattering factors of Ti and (Fe,Mg), does not verify that the hypothesis is right or that it is wrong.

As a result of the above considerations we can assign to neptunite the following chemical formula:

$$LiNa_2K(Fe,Mg,Mn)_2(TiO)_2[Si_8O_{22}] .$$

Some observations can be made on the electrostatic equilibrium of the crystal structure. If we consider all the bonds as ionic and divide the charge of each cation among the anions of its coordination polyhedron, some notable deficiencies of electrostatic equilibrium are

Table 4. *Interatomic distances* (Å), *angles* (°) *and their standard deviations* (*in brackets*)

The distances preceded by an asterisk occur twice

Atoms	Bond length	Atoms	Bond angle
Si(1)O(7)	1·580 (12)	O(7)Si(1)O(8)	112·4 (8)
O(8)	1·623 (15)	O(9)	112·1 (7)
O(9)	1·597 (15)	O(11)	116·1 (6)
O(11)	1·608 (10)	O(8)Si(1)O(9)	104·3 (7)
		O(11)	108·2 (6)
		O(9)Si(1)O(11)	102·6 (8)
Si(2)O(2)	1·612 (9)	O(2)Si(2)O(10)	116·8 (7)
O(10)	1·586 (11)	O(11)	107·3 (5)
O(11)	1·671 (9)	O(12)	110·0 (7)
O(12)	1·678 (15)	O(10)Si(2)O(11)	111·3 (6)
		O(12)	107·1 (6)
		O(11)Si(2)O(12)	103·6 (8)
Si(3)O(5)	1·653 (12)	O(5)Si(3)O(6)	112·1 (7)
O(6)	1·600 (15)	O(8)	111·1 (8)
O(8)	1·625 (18)	O(9)	112·7 (8)
O(9)	1·672 (12)	O(6)Si(3)O(8)	107·7 (1·0)
		O(9)	107·9 (7)
		O(8)Si(3)O(9)	105·0 (6)
Si(4)O(1)	1·671 (13)	O(1)Si(4)O(3)	117·4 (8)
O(3)	1·566 (21)	O(6)	107·9 (8)
O(6)	1·666 (14)	O(12)	108·9 (7)
O(12)	1·618 (12)	O(3)Si(4)O(6)	105·7 (1·1)
		O(12)	110·4 (7)
		O(6)Si(4)O(12)	105·8 (7)
(Fe,Ti)(1)O(2)	2·045 (12)	O(2)(Fe,Ti)(1) O(4)	95·8 (5)
O(4)	1·918 (13)	O(5)	80·9 (5)
O(5)	2·096 (16)	O(7)	164·7 (6)
O(7)	2·065 (11)	O(7′)	87·5 (5)
O(7′)	2·218 (13)	O(10)	89·0 (5)
O(10)	1·990 (11)	O(4)(Fe,Ti)(1) O(5)	93·7 (6)
		O(7)	96·2 (5)
		O(7′)	174·8 (4)
		O(10)	94·8 (5)
		O(5)(Fe,Ti)(1) O(7)	88·9 (5)
		O(7′)	83·0 (5)
		O(10)	167·4 (6)
		O(7)(Fe,Ti)(1) O(7′)	79·9 (1·0)
		O(10)	99·4 (5)
		O(7′)(Fe,Ti)(1)O(10)	89·2 (5)
(Fe,Ti)(2)O(1)	2·067 (9)	O(1)(Fe,Ti)(2) O(1′)	81·3 (1·0)
O(1′)	2·067 (15)	O(2)	86·2 (5)
O(2)	2·195 (12)	O(3)	91·8 (8)
O(3)	1·986 (15)	O(4)	94·4 (5)
O(4)	2·010 (13)	O(5)	162·4 (7)
O(5)	2·057 (14)	O(1′)(Fe,Ti)(2)O(2)	80·0 (5)
		O(3)	170·1 (5)
		O(4)	95·6 (6)
		O(5)	87·7 (6)
		O(2)(Fe,Ti)(2) O(3)	92·6 (5)
		O(4)	175·4 (6)
		O(5)	78·3 (5)
		O(3)(Fe,Ti)(2) O(4)	91·9 (6)
		O(5)	97·2 (8)
		O(4)(Fe,Ti)(2) O(5)	100·4 (5)

Atoms	Bond length	Atoms	Bond angle
NaO(3)	2·414 (22)	O(3)NaO(5)	76·6 (5)
O(5)	2·482 (18)	O(6)	97·2 (6)
O(6)	2·514 (18)	O(6′)	56·7 (5)
O(6′)	2·927 (24)	O(7)	89·8 (5)
O(7)	2·553 (17)	O(10)	158·4 (7)
O(10)	2·491 (16)	O(12)	141·2 (7)
O(12)	2·726 (9)	O(5)NaO(6)	158·1 (6)
		O(6′)	113·8 (5)
		O(7)	69·2 (5)
		O(10)	83·3 (5)
		O(12)	136·0 (5)
		O(6)NaO(6′)	78·1 (1·2)
		O(7)	90·1 (5)
		O(10)	98·7 (6)
		O(12)	59·8 (4)
		O(6′)NaO(7)	141·9 (5)
		O(10)	141·5 (5)
		O(12)	86·6 (5)
		O(7)NaO(10)	75·6 (5)
		O(12)	118·5 (5)
		O(10)NaO(12)	60·2 (4)
KO(8)	*2·837 (9)	O(8)K O(9)	55·2 (4)
O(9)	*2·815 (10)	O(11)	50·8 (3)
O(11)	*3·214 (13)	O(11′)	104·9 (4)
O(11′)	*3·104 (19)	O(12)	71·4 (3)
O(12)	*2·853 (11)	O(8′)	143·3 (7)
		O(9′)	119·1 (4)
		O(11″)	98·6 (4)
		O(11‴)	80·7 (4)
		O(12′)	140·5 (3)
		O(9)K O(11)	94·2 (3)
		O(11′)	49·7 (3)
		O(12)	95·5 (3)
		O(9′)	164·6 (6)
		O(11″)	73·9 (3)
		O(11‴)	133·4 (3)
		O(12′)	95·5 (3)
		O(11)K O(11′)	133·1 (8)
		O(12)	96·9 (3)
		O(11″)	80·1 (8)
		O(11‴)	63·2 (7)
		O(12′)	168·6 (3)
		O(11′)K O(12)	113·2 (3)
		O(11‴)	162·5 (6)
		O(12′)	52·2 (3)
		O(12)K O(12′)	88·0 (7)
LiO(1)	*2·130 (20)	O(1)LiO(2)	179·2 (5)
O(2)	*2·151 (19)	O(4)	91·6 (6)
O(4)	*2·041 (11)	O(1′)	100·2 (2·1)
		O(2′)	79·6 (5)
		O(4′)	86·9 (6)
		O(2)LiO(4)	89·1 (6)
		O(2′)	100·6 (2·0)
		O(4′)	92·4 (6)
		O(4)LiO(4′)	177·6 (2·6)

evident: the positive charge for each oxygen atom is generally slightly higher than 2, but for three oxygen atoms is much lower: 1·6 for O(3) and O(10), 1·2 for O(4). This last case is represented by the oxygen not bonded with silicon and with a possible covalent bond with titanium. Generally it is rather difficult to verify the electrostatic equilibrium in a crystal containing titanium. It is very probable that the whole electrostatic equilibrium is affected by the distortion of the TiO_6 octahedron. It is a matter of fact that considering the bonds as purely ionic, potassium and, in part, also the other alkaline ions would be in contact with oxygen atoms which are apparently neutral because they are shared by two SiO_4 tetrahedra.

However, conclusive statements will be possible only after a refinement of the non-centrosymmetrical structure, by using a greater amount of experimental data.

We wish to thank Prof. F. Sgarlata, who kindly made available to us his program for three-dimensional refinement.

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A Discussion of the Distribution of Bonded Electron Density

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(*Received* 14 *December* 1965)

The final difference syntheses on a number of previously published structures are examined for evidence of bonding electrons. It is found that the aromatic C–C bond contains a residual peak of maximum height about 0·2 e.Å^{-3} with half height extensions of about 0·3 Å in, and 0·75 Å perpendicular to, the trigonal plane. In some cases direct evidence is also obtained for charge movements in the molecule. The experimental results are compared with those calculated from Slater wave functions. The agreement is generally good, but discrepancies remain which can be attributed to the neglect of σ orbital contraction and electron correlation in the theoretical calculations. It is found that refinement of structures by use of isolated atom wave functions leads to significant errors in the parameters, not only of terminal atoms, but also of trigonally bonded atoms with hydrogen substituents.

1. Introduction

The structure analysis of β-sulphanilamide (O'Connell & Maslen, 1966) has provided detailed information on the electron density distribution in the C–C, C–N and C–S bonds in this molecule. The difference synthesis shows peaks in the bonds which reach maxima near the bond centres and which extend a considerable distance above and below the plane of the molecule. The existence of such residual features in difference maps has been known for some time and detailed projection studies were carried out by Cochran (1953, 1956) and Mason (1960). However, since the advent of highly accurate three-dimensional structure analysis, remarkably little attention has been paid to features in the residual electron density maps. In fact, an extensive

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