CRYSTAL STRUCTURE OF NARSARSUKITE

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The complete crystal structure investigation of narsarsukite Na_2 (Ti, Fe) (O, OH)-[Si_4O_{10}] has been undertaken. It was found that narsarsukite is tetragonal, the unit cell dimensions being a = = 10.72, c = 7.99 A. Atomic arrangement was determined by Patterson and Fourier syntheses. Narsarsukite represents a new structure type with [Si_4O_{10}] $_\infty$ chains stretching along $\underline{c}$.

Narsarsukite is a rare titanosilicate found in alkali pegmatites in Greenland, the USA, and the USSR. Its composition is $Na_2(Ti,Fe)Si_4O_{11}$, with the Ti and Fe in the ratio 3:1 (by number of atoms, approximately); some (about $\frac{1}{2}$) of the O atoms are replaced by OH [1]. The mineral is tetragonal (Laue class 4/m) [1, 2] and the parameters are a = 10.80 and c = 8.01 A. The systematic absences correspond to the possible space groups $C_{4h}^5 - I4/m$, $C_4^5 - I4$ and $S_4^2 - I\bar{4}$. The morphology makes the first (centrosymmetric) group very probable [2], but difficulties have been encountered in further studies of the structure.

We have used specimens given to us by I. P. Tikhonenkov to record patterns from transparent fragments about 0.3×0.3 mm in cross section extended along $\underline{c}$ and terminated by perfect cleavage surfaces [on (100)].

The Laue class was confirmed as 4/m by means of an RKOP camera; the lattice parameters were found from oscillation photographs used in conjunction with pinacoid reflections recorded with an x-ray goniometer; they are: a = 10.72 ± 0.04, c = 7.99 ± 0.02 A. The density is 2.779 and the molecular weight is 384.3, so N = 3.99 ≈ 4.

A KFOR camera (retigraph) was used to record the O layer lines (by rotation on $\underline{c}$, and also on 0kl). Rotation on $\underline{c}$ gave very good patterns, whereas that on 0kl gave rather few (about 60) spots, which were subject to very uneven absorption. The perfect cleavage on (001) prevented us from making isometric pieces for use in examination along $\underline{a}$.

The only spots were those corresponding to $h + k + l = 2n$. The result is that the x-ray group is 4/mI, $-/-$, i.e., is I4/m, I4 or $I\bar{4}$.

The atoms to be located in the cell are eight Na, 4(Ti + Fe), 16 Si, and 44 O. It is difficult to make any reasonable assumption about OH, but we may suppose that the Ti + Fe atoms are randomly distributed in one position. The Ti: Fe ratio is nearly 3:1, and these body-centered groups contain no position of multiplicity one or three.

The positions available in these space groups are such that the four Ti* atoms can lie only 4, $\bar{4}$, or 4_2 axes. It was difficult at this early stage to locate the other atoms (particularly on account of the choice of space groups), so we had recourse to analysis of the intensities. A 30-point blackening scale ($I_{min} : I_{max} =$ = 1:300) was used. The Lorentz and polarization factors were allowed for in calculating the F^2. The small size of the fragments (less than 0.3×0.3 mm) made absorption corrections unimportant.

First we constructed a Patterson projection along $\underline{c}$, which contained a few sharp peaks whose positions were such as to indicate that the heavy (Ti) atoms must be duplicated in the xy projection on one of the two

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*Here and in future we denote (Ti, Fe) by Ti alone, for brevity.
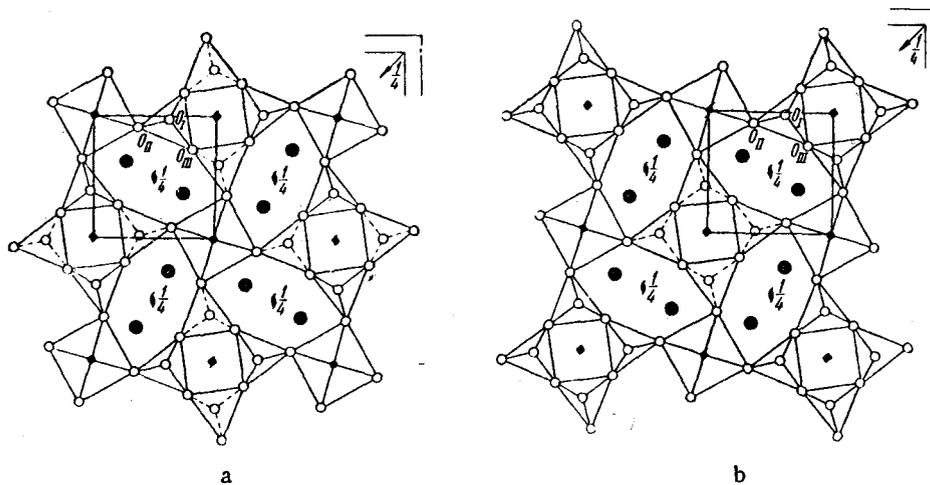
Fig. 1. Two possible models of the structure of narsarsukite.
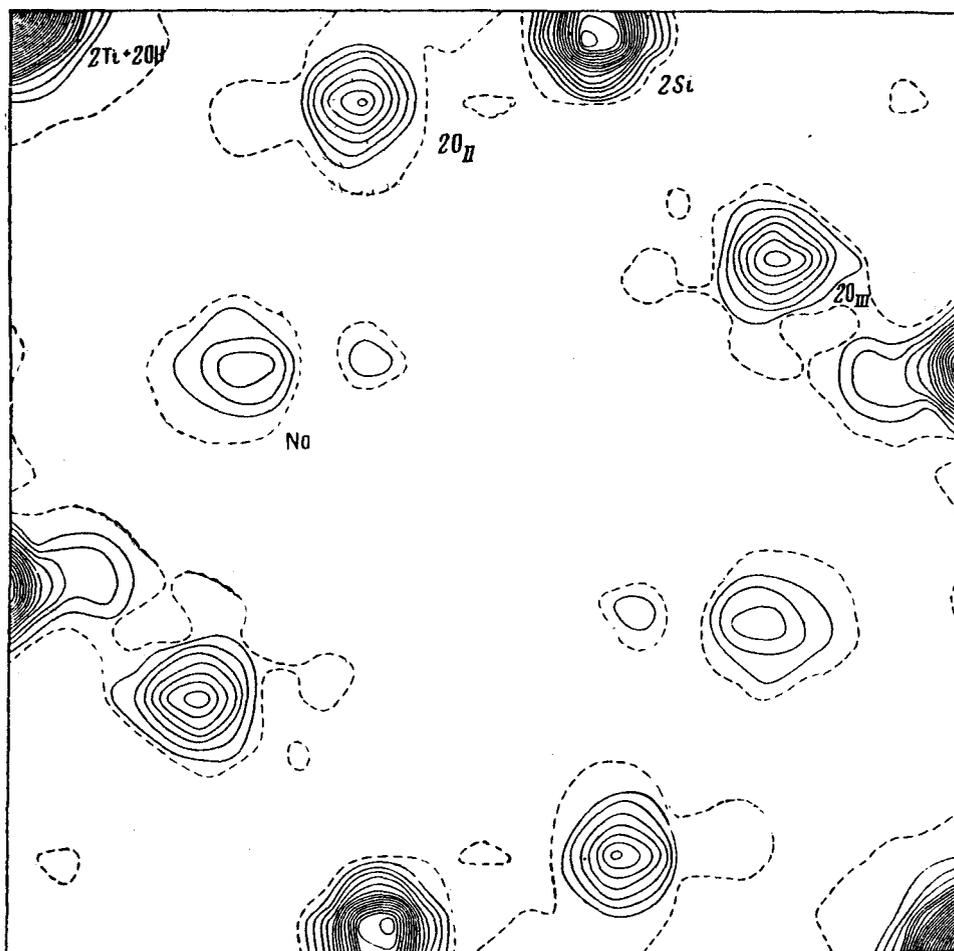
Fig. 2. Pattern (1/4 cell) for $\rho_2(xy)$.

sets of fourfold axes. We took the (2Ti) atoms ($Z_{eff} > 44$) as lying at the origin of the xy projection, in order to get the peaks in P (uv) to represent the positions of most of the other atoms. The only group giving a satisfactory interpretation of this is $C_{4h}^5 - I\ 4/m$. The main argument in favor of that group is that all the peaks
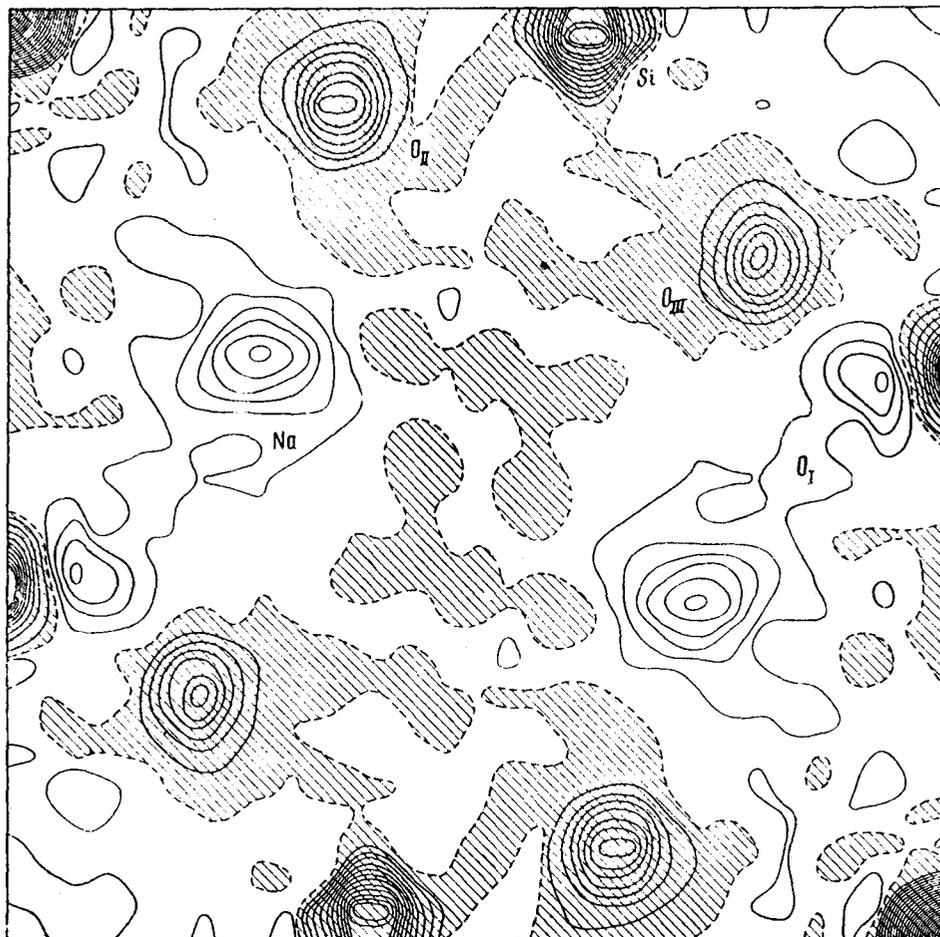
Fig. 3. Inclined projection $\sigma_2(xy)$. The negative regions are hatched.

TABLE 1

Comparison of the Horizontal Coordinates Derived from $\rho\,(xy)$ and $\sigma_2(xy)$

Атом	x		y		Coordinates adopted	
	$\rho\,(xy)$	$\sigma_2(xy)$	$\rho\,(xy)$	$\sigma_2(xy)$	x	y
Na	0.136	0.133	0.185	0.184	0.135	0.185
Si	0.307	0.307	0.013	0.013	0.307	0.013
O_I	—	0.025	—	0.299	0.025	0.299
O_{II}	0.180	0.175	0.049	0.049	0.178	0.049
O_{III}	0.401	0.402	0.133	0.134	0.402	0.134

in the xy projection can be explained only if we assume that all the atoms (not merely the Ti ones) are duplicated, i.e., that a horizontal reflection plane is present. Further evidence for group C_{4h}^5 was obtained subsequently.

The two possible positions of the Ti atoms (on the 4 or 4_2 axes in group I4/m) give rise to two models of the structure. Figure 1a, shows the model with the Ti atoms on the rotation axes. The x and y coordinates used here derive directly from the Patterson projection, O_I expected (O_I is not resolved from 2Si in this projection, so the x and y for these atoms have been taken as the same). Figure 1a, illustrates the three-dimensional network formed by Ti octahedra and rings of Si tetrahedra. The octahedra are joined at opposed vertices

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TABLE 2

Comparison of Measured and Calculated F_{hk0} (the F Include a Factor $\exp[-0.56 \times \times (\sin \vartheta/\lambda^2]$

hk0	F_0	F_0	hk0	F_0	F_0	hk0	F_0	F_0	hk0	F_0	F_0
020	125	+127	1.15.0	0	—5	5.13.0	49	+58	8.12.0	19	+8
040	83	+79	1.17.0	20	+32	5.15.0	13	—10	8.14.0	24	+24
060	191	+190	1.19.0	0	+6	5.17.0	27	+39	8.16.0	0	+15
080	23	+35	220	104	—109	620	143	+135	910	25	+21
0.10.0	121	+120	240	25	—23	640	94	+94	930	132	+124
0.120	24	+20	260	38	+25	660	94	+95	950	33	+37
0.14.0	17	+18	280	0	—6	970	65	+73	12.8.0	26	+30
0.16.0	76	+63	2.10.0	122	+129	990	47	+47	12.10.0	45	+45
0.18.0	0	+5	2.12.0	0	+5	9.11.0	49	+53	12.12.0	0	+1
110	36	+42	2.14.0	17	+23	9.13.0	73	+73	12.14.0	48	+56
130	128	+125	2.16.0	94	+79	9.15.0	24	+17	13.1.0	60	+63
150	10	—5	2.18.0	24	+31	9.17.0	31	+31	13.3.0	42	+52
170	15	+6	310	125	+125	10.2.0	36	+34	13.5.0	24	+35
190	20	—32	330	185	+218	10.4.0	107	+111	13.7.0	86	+71
1.11.0	0	—4	350	59	+66	10.6.0	72	+79	13.9.0	24	+30
1.13.0	39	+39	370	160	+170	10.8.0	64	+74	13.11.0	30	+37
390	79	+75	680	0	+18	10.10.0	44	+45	13.13.0	38	+40
3.11.0	53	+69	6.10.0	73	+81	10.12.0	0	—24	14.2.0	0	0
3.13.0	156	+121	6.12.0	55	+54	10.14.0	30	+44	14.4.0	49	+49
3.15.0	0	—5	6.14.0	51	+51	10.16.0	20	+16	14.6.0	18	—8
3.17.0	25	+19	6.16.0	42	+42	11.1.0	28	+32	14.8.0	0	—5
420	91	+81	6.18.0	26	+25	11.3.0	35	+49	14.10.0	36	+50
440	148	+145	710	138	+135	11.5.0	26	—47	14.12.0	0	+12
460	136	+118	730	124	+116	11.7.0	16	+24	15.1.0	0	+5
480	11	—9	750	12	—25	11.9.0	0	0	15.3.0	0	—7
4.10.0	35	+37	770	97	+98	11.11.0	0	—9	15.5.0	23	+32
4.12.0	0	+4	790	25	+27	11.13.0	20	+25	15.7.0	57	+46
4.14.0	0	+7	7.11.0	0	+7	11.15.0	0	—14	15.9.0	0	+4
4.16.0	0	+4	7.13.0	29	+36	12.2.0	20	+31	15.11.0	25	+21
4.18.0	20	—8	7.15.0	0	+2	12.4.0	42	+45	16.2.0	0	+16
510	95	+96	7.17.0	28	+46	12.6.0	14	—11	16.4.0	95	+79
530	0	—9	820	73	—92	16.6.0	30	+35	17.7.0	0	+9
550	98	—106	840	0	+10	16.8.0	29	+32	17.9.0	0	+9
570	140	+145	860	18	—2	16.10.0	58	+49	18.2.0	26	—22
590	0	—7	880	22	—23	17.1.0	77	+63	18.4.0	20	+26
5.11.0	27	—40	8.10.0	41	+62	17.3.0	27	+32	18.6.0	17	—4
						17.5.0	0	+12	19.1.0	29	+37

into chains along z; the c period equals the length of two links in the chain. The rings are formed by SiO_4 tetrahedra facing in opposite directions in pairs. The rings are coupled vertically via their O_I atoms into infinite $[Si_4O_{10}]_{\infty}$ chains or columns. The circles in Fig. 1 denote the Na atoms.

In the second model (Fig. 1b) the Ti atoms lie on the 4_2 axes. The structure follows the same general plan, the most important difference being that the tetrahedra take up other positions in the rings; all four are oriented identically. These different rings are coupled in a different fashion; in the first model the rings formed chains, whereas in the second we have duplicated four-member rings having the same Si : O ratio in their radicals.

The two models have identical $P(uv)$, as follows from the fact that F^2_{hkl} (I) = F^2_{hkl} (II) for hk$l$ reflections having l even [3]. Later we analyzed the odd layer lines and proved conclusively that the first model represents the true structure, but even at this stage there were very strong indications that the first model was the correct one; the distances in the structures provided valuable evidence. In both models there are tetrahedra nearly regular in shape and so oriented that their heights are parallel to z. Here c = $4h_{tetr}$, so a is $\sqrt{6/8} \cdot c$ = 2.45 A. A tetrahedron of side 2.45 A is improbable; some rotation (distortion of the four-membered rings) is required in order to produce normal distances. The axis of the rings is a 4 axis in the second model, and that axis allows only one type of distortion, namely rotation of the tetrahedra about the line joining adjacent O_{III} atoms; the $O_{III}-O'_{III}$ distance remains low. But if the axis is 4_2 (first model), the symmetry allows a greater variety of rotations, which means that normal spacings can be achieved.

Fig. 4. Comparison of experimental (———) and calculated (— — — —) F_{hk0}.
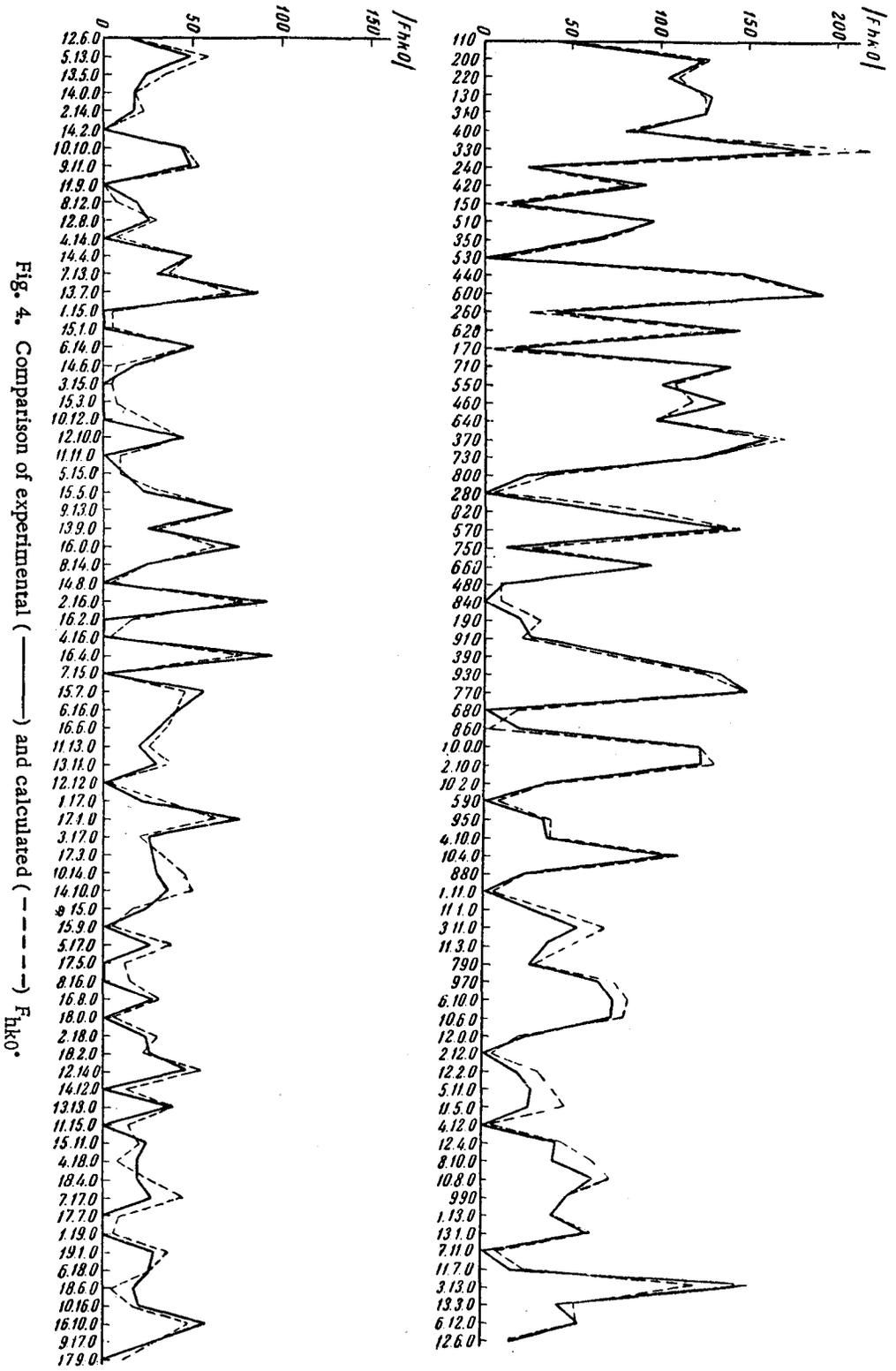
Fig. 5. Comparison of experimental (————) and calculated (– – – –) F_{hk2}.
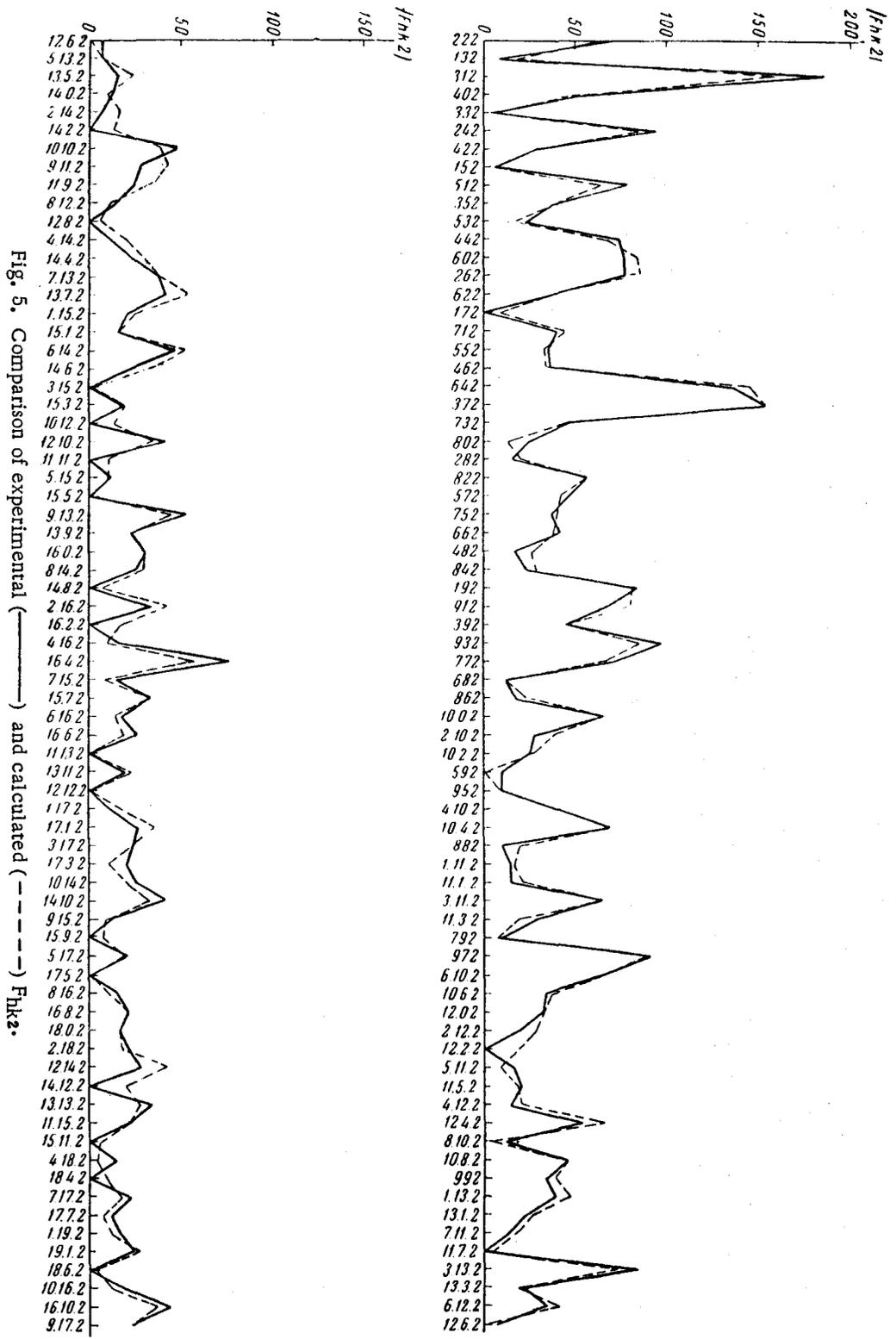
TABLE 3

Atomic Coordinates for Narsarsukite

Atom	x	y	z	Atom	x	y	z
Na (8)	0.135	0.185	(0)	O_{II} (16)	0.178	0.049	0.225
(Ti, Fe) (4)	(0)	(0)	0.250	O_{III} (16)	0.402	0.134	0.302
Si (16)	0.307	0.013	0.298	$(O, OH)_I$ (2)	(0)	(0)	(0.500)
O_I (8)	0.025	0.299	(0.500)	$(O, OH)_{II}$ (2)	(0)	(0)	(0)

TABLE 4

Interatomic Distances in Narsarsukite

Polyhedron	Interatomic distances		Limits of variation
1	2	3	4
Ti-octahedron	$Ti - (O, OH)_I = 2.00$ $Ti - (O, OH)_{II} = 2.00$	$Ti - O_{II} = 1.98$	1.98—2.00
	$O_{II} - O'_{II} = 2.80$ $O_{II} - (O, OH)_{II} = 2.68$	$O_{II} - (O, OH)_I = 2.96$	2.68—2.96
Si-tetrahedron	$Si - O_I = 1.67$ $Si - O_{II} = 1.55$	$Si - O_{III} = 1.65$ $Si - O'_{III} = 1.57$	1.55—1.67
	$O_I - O_{II} = 2.67$ $O_I - O_{III} = 2.58$ $O_I - O'_{III} = 2.64$	$O_{II} - O_{III} = 2.64$ $O_{II} - O'_{III} = 2.57$ $O_{III} - O'_{III} = 2.65$	2.57—2.67
Na-octahedron	$Na - O_{II} = 2.36$ $Na - O'_{II} = 2.67$	$Na - O_{III} = 2.54$ $Na - (O, OH)_{II} = 2.46$	2.36—2.67
	$O_{II} - O'_{II} = 2.80$ $O_{II} - O''_{II} = 3.60$ $O_{II} - (O, OH)_{II} = 2.68$	$O'_{II} - O''_{III} = 2.57$ $O_{III} - O''_{III} = 3.51$ $O_{III} - O'''_{III} = 3.16$	2.57—3.60

The x and y of the first model were used to establish the signs of the F_{hk0} (identical coordinates were adopted for O_I and Si). We used 135 independent reflections in the Fourier synthesis for $\rho_1(xy)$; this synthesis showed that the coordinates of Na had been chosen wrongly, but that the model was otherwise reliable. Fresh coordinates were used to find the signs of the F_{hk0} again and to construct $\rho_2(xy)$ (Fig. 2). Although the pattern was very sharp, it was not possible to establish the coordinates of O_I; the only useful point was that the peak was unsymmetrical, so O_I does not lie exactly above Si. The peak heights (in el/A^2) are ρ (2Ti + 2OH) = = 229.6, ρ (Na) = 29.4, ρ (2Si) = 99.8, ρ (2O_{II}) = 47.2 and ρ (2O_{III}) = 51.6. The x and y were used to calculate theoretical F_{hk0} (B = 0.6 A^2), and were compared with the F_0.

Here R (with allowance for all visible reflections up to $\sin\theta/\lambda \leq 1.1$) was 17.1%.

Next we used P(vw) in an attempt to find the z coordinates. The patterns to be used contained only about 60 spots, so we could not expect to get a sharp pattern by projection along the long (10.72 A) $\underline{a}$ axis.
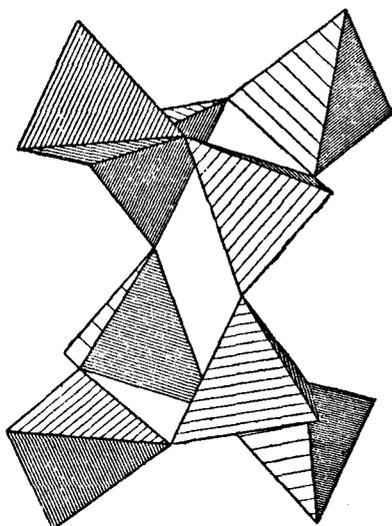
Fig. 6. Two links in the $[Si_4O_{10}]_\infty$ chains.
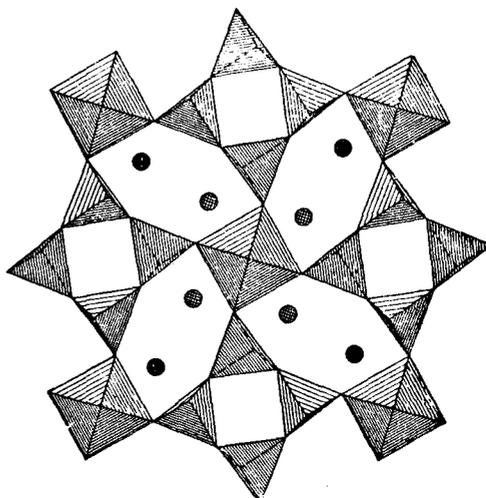
Fig. 7. Projection of the structure of nar-sarsukite along $\underline{c}$. (The circles denote Na atoms at various heights.)

TABLE 5

Balance of Valences in Narsarsukite

Atom	Si	Ti + Fe	Na	Sum
O_I	$2 \cdot {}^4/_4$	—	—	2
O_{II}	${}^4/_4$	${}^{15}/_4 : 6$	$2 \cdot {}^1/_7$	$2 - {}^5/_{56}$
O_{III}	$2 \cdot {}^4/_4$	—	${}^1/_7$	$2 + {}^1/_7$
$(O, OH)_I$	—	$2 \cdot {}^{15}/_4 : 6$	—	$1 + {}^1/_4$
$(O, OH)_{II}$	—	$2 \cdot {}^{15}/_4 : 6$	$4 \cdot {}^1/_7$	$2 - {}^5/_{28}$

Inclined Projections

A projection $\int$ P(uvw) cos 2π 2wdw was constructed from 140 independent hk2 reflections to test the model and to bring the hk0 and hk2 into correspondence, which is difficult in class 4/m because $F^2_{hkl} \neq F^2_{\bar{h}kl}$. The results confirmed that the model is correct; this ideal model was then subjected to analysis in order to establish the vertical coordinates more exactly (the $\underline{x}$ and $\underline{y}$ being already known).

All the spacings were brought into agreement with the standard ones quite easily; the second model did not allow of this.

The signs of the F_{hk2} were determined from the $\underline{x}$ and $\underline{y}$ derived from the final ρ (xy) and from the z derived from the model and corrected in accordance with the standard spacings. The projection

$$\sigma_2\,(xy) = \int_0^1 \rho\,(xyz)\,\cos 2\pi\,2z\,cdz$$

constructed from the F_{hk2} (Fig. 3) corresponds well with the model and with the previous syntheses. The most important result obtained from σ_2(xy) was the $\underline{x}$ and $\underline{y}$ coordinates of O_I, which were not obtainable from ρ (xy). Table 1 gives a comparison of the horizontal coordinates derived from ρ (xy) and σ_2(xy).

The new $\underline{x}$ and $\underline{y}$ were used to calculate theoretical F_{hk0}, which were compared with the F_0 (Table 2 and Fig. 4); the results are R = 13% (for $F_0 \neq 0$) and R = 17.4% for all reflections up to sin $\theta/\lambda \leq 1.1$.

Coordinates and Atomic Separations

The $0kl$ line had few spots (the axis is 10.72 A long), but the ρ (yz) constructed from 60 spots gave all coordinates except the $\underline{z}$ of O_{II}; the values are very close to those found by analysis of the model. Figure 5 compares the two sets of F_{hk2}. The results are R = 16.5% ($F_0 \neq 0$) and R = 19.3% for all hk2 up to $\sin\theta/\lambda \leq$ ≤ 1.1.

The coordinates finally adopted are given in Table 3; here $\underline{z}$ for O_{II} derives only from chemical crystallography. Four O atoms partly replaced by OH lie in positions not having parameters; the Ti atoms are defined by one parameter (00z), the Na and O_I by two parameters (xy0), and the rest (Si, O_{II}, O_{III}) are in general positions. In all, there are 14 parameters (Table 3).

Table 4 gives the interatomic distances.

Description of the Structure and Balance of Valences

The structure is based on chains of (Ti, Fe) octahedra joined by opposite vertices and on chains $[Si_4O_{10}]_\infty$ extending along $\underline{c}$. The members of the latter chains are four-membered rings composed of SiO_4 tetrahedra joined at their corners in pairs facing in opposite directions (Fig. 6). The (Ti, Fe) chains lie on fourfold rotation axes, while the axes of the $[Si_4O_{10}]_\infty$ chains are 4_2 axes. Horizontally the two kinds of chain are joined at the free vertices of octahedra and tetrahedra (Fig. 7); the octahedra and tetrahedra are almost regular. The coordination polyhedron of Na has seven corners, being a triangular prism having a pyramid on one of its faces. Polyhedra of this type have been found in ilvaite [4] and other minerals.

Table 5 gives the balance of valences, for which purpose the valence + 15/4 has been assigned to the cations at the centers of the octahedra (Ti : Fe $\approx$ 3 : 1).

The valences indicate that the OH ions are distributed over the two twofold positions of group I4/m, with a considerable preference for position 2(b): $00\frac{1}{2}$.

The properties of narsarsukite correspond well with the structure. The mineral is optically positive, and the birefringence is high (0.030-0.040); these features correspond to the chains of (Ti, Fe) octahedra and chains of silicon-oxygen figures. The large holes in the structure result in a low specific gravity (2.78). The cleavage planes pass through the O atoms at points where the chains of both sorts are joined.

The structure can be considered as of a new type. Other structures having the $[Si_4O_{10}]$ radical are layered (mica, apophyllite), but in narsarsukite that radical forms chains extending indefinitely in one dimension (compare $[Si_2O_5]$ in sillimanite).

The minerals most similar in structure to narsarsukite are those of the scapolite group, but in those minerals it is scarcely correct to separate four-membered rings, because the scapolites are silicates having extended frameworks rather than chains or rings.

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