31. Crystal Structure of Cancrinite from Dódó, Korea, II.

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(Comm. by S. KÔZU, M.I.A., Feb. 13, 1933.)

Arrangement of atoms:—According to P. Niggli,¹⁾ the co-ordinates of the symmetry elements relating to the orthohexagonal unit cell are given as:

Six-fold screw axis $\left(\frac{3\tau}{6}\right)$ $[001]00, [001]_{\frac{1}{2}}\frac{1}{2}$.

Three-fold rotation axis $[001]_{\frac{1}{3}}0, [001]_{\frac{5}{6}}\frac{1}{2}, [001]_{\frac{2}{3}}0, [001]_{\frac{4}{6}}\frac{1}{2}$.

Two-fold screw axis $[001]_{\frac{1}{2}}0, [001]_0\frac{1}{2}, [001]_{\frac{1}{4}}\frac{1}{4}, [001]_{\frac{3}{4}}\frac{3}{4},$
 $[001]_{\frac{1}{4}}\frac{3}{4}, [001]_{\frac{3}{4}}\frac{1}{4}$.

If we indicate these symmetry elements in reference to the unit hexagonal prism, and project them on the basal plane, they are as shown in Fig. 1.

The equivalent points belonging to this space group are:

Two equivalent positions:

a) $00u; 0, 0, u+\frac{1}{2}$. b) $\frac{1}{3}\frac{2}{3}u; \frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}$.

Six equivalent positions:

c) $xyz; y-x, \bar{x}, z; \bar{y}, x-y, z; \bar{x}, \bar{y}, z+\frac{1}{2}; x-y, x, z+\frac{1}{2}; y, y-x, z+\frac{1}{2}$.

As already mentioned in our previous papers,²⁾ the cancrinite unit cell contains one molecule with a chemical formula whose ideal form can be stated as $3(\text{Na}_2\text{Al}_2\text{O}_4 \cdot \text{Si}_2\text{O}_4) \cdot 2\text{CaCO}_3$. The atoms in the formula may be grouped as 2Ca , 2C , 3Na_I , 3Na_II , $6(\text{SiAl})_\text{I}$, $6(\text{Si}, \text{Al})_\text{II}$, 6O_I , 6O_II , 6O_III , 6O_IV , and 6O_V .

To determine the co-ordinates of these atoms, the following consideration was made. From the experimental result $c_0=5.18\text{\AA}$, which is practically double the O—O distance ($2.6\text{\AA}$) in the edge of the tetrahedral group $(\text{Si}, \text{Al})\text{O}_4$, we may reasonably consider that two tetrahedrons are linked so that one edge of a tetrahedron is directly connected with O in common with one edge of another tetrahedron and that their direction is parallel to the c-axis. In order to satisfy the symmetrical relation of this space group in arranging 12 groups of tetrahedrons linked in this manner in a unit cell with $a_0=12.72\text{\AA}$, the grouping of $(\text{Si}, \text{Al})_{12}\text{O}_{36}$ around the six-fold screw axis alone is con-

ceivable. From the dimensions of the unit cell, from the radii of ions, and from Pauling's principle, we may consider that Na (rarely Ca) must be placed in the space between the (Si, Al)₆O₁₈ groups. From the symmetrical relation, it is evident that CaCO₃ must be put at the position of the three-fold rotation axis. The arrangement of ions, thus constructed, are shown diagrammatically in Fig. 2. If we indicate the co-ordinates of all the ions included in a unit cell by $\theta_1=2\pi x$, $\theta_2=2\pi y$ and $\theta_3=2\pi z$, the results are as seen in Table I.

Fig. 1. Elements of symmetry in the space group C_6^h .

Fig. 2. Basal projection of the unit cell of cancrinite.

TABLE I.
Co-ordinates of Atoms in Cancrinite.

Atom	n	θ_1	θ_2	θ_3	x	y	z
Ca	2	240°	120°	— 50°	0.67	0.33	— 0.14
C	2	240	120	130	.67	.33	.36
Na _I	3	180	180	80	.50	.50	.22
Na _{II}	3	180	180	—100	.50	.50	— .28
Si	6	12	94	93	.33	.26	.26
Al	6	94	82	85	.26	.23	.24
O _I	6	18	130	5	.05	.36	.01
O _{II}	6	130	115	— 10	.36	.32	— .03
O _{III}	6	60	98	93	.17	.27	.26
O _{VI}	6	— 37	56	88	— .13	.16	.24
O _V	6	72	230	130	.20	.64	.36

Examination of reflections:—The intensity formula in reference to the space group C_6^2 may be given as:

$$I \propto \sum 4 \{ f \sin(h\theta_1 + k\theta_2) \sin l\theta_3 \}^2 + \sum 4 \{ f \sin(h\theta_1 + k\theta_2) \cos l\theta_3 \}^2, \text{ when } l = \text{odd},$$

$$I \propto \sum 4 \{ f \cos(h\theta_1 + k\theta_2) \cos l\theta_3 \}^2 + \sum 4 \{ f \cos(h\theta_1 + k\theta_2) \sin l\theta_3 \}^2, \text{ when } l = \text{even},$$

in which, f is the scattering power of the atom.

TABLE II.

hkl	Sin θ	$\frac{\text{Sin } \theta}{\lambda}$	I (calc.)/100	I (obs.)
100	0.074	0.045	5	W.M.
200	0.145	0.090	2	W.
300	0.210	0.135	64	S.
400	0.277	0.185	107	V.S.
500	0.351	0.230	4	W.M.
600	0.422	0.275	16	W.M.
700	0.490	0.320	37	S.
800	0.559	0.365	16	W.M.
900	0.628	0.410	1	V.W.
1000	0.702	0.465	5	W.
1100	0.770	0.500	2	W.
1200	0.843	0.545	9	W.
1300	0.910	0.582	1	V.W.
1400	0.982	0.635	4	W.M.
001	0.149	0.097	0	Abs.
002	0.298	0.105	313	V.V.S.
003	0.446	0.290	0	Abs.
004	0.595	0.385	145	S.
005	0.750	0.485	0	Abs.
006	0.897	0.580	35	V.W.

For f of Si etc., Bragg's values³⁾ were used, and for f of C, Pauling's value⁴⁾ was adopted for our calculation. For f of Ca, a slight modification was made, taking into account the influence of H₂O.

Using these values, the intensities of reflections obtained by calculation for ($h00$) and ($00l$) are shown in Table II, in which the corresponding observed intensities are given for comparison.

From the fairly good agreement between the calculated and observed intensities, we see that the cancrinite structure derived by the present study may be taken as the most probable one.

References.

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