The Crystal Structure of Sulphohalite.

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(With 1 Figure.)

The structure of sulphohalite, $2Na_2SO_4 \cdot NaCl \cdot NaF$, has been determined from a powder pattern. The structure is cubic face-centered and there are four formular units in the unit cell, $a_0 = 10.08 \pm 0.01$ Å. From a consideration of atomic radii positions can be assigned to all atoms which give good agreement of observed and calculated intensities.

Through the courtesy of Dr. A. A. Fitch the writer obtained crystals of sulphohalite from Searles Lake, California. The crystals are pale yellow, clear, octahedrons, from 2 to 10 mm. in diameter. They occur about 65 feet below the surface.

Thanks to the kindness of Mr. W. H. Dore of the Division of Plant Nutrition, University of California, the writer was able to obtain a powder diffraction pattern of sulphohalite. Molybdenum radiation was used with zirconium oxide filter. The casette used was of the standard type furnished by the General Electric Company. It was calibrated from a pattern of calcite and found to have a radius of exactly 8 inches.

Table I gives the measurements of the powder pattern. From the average value of $\sin^2 \theta / h^2 + k^2 + l^2$, 0.001248, the length of the edge of the unit cube is calculated to be 10.08 ± 0.01 Å. The proper formula for sulphohalite, $2Na_2SO_4 \cdot NaCl \cdot NaF$, was established by Penfield[1]). He also gave the density as 2.500. From these data it can be shown that there are four (4.038 calc.) formular units of sulphohalite in the unit cube.

Table I. Powder pattern of sulphohalite.

2θ	$\sin^2 \theta = (h^2 + k^2 + l^2)q$	hkl	2θ	$\sin^2 \theta = (h^2 + k^2 + l^2)q$	hkl
6.98°	3×0.001237	111	27.13	44×0.001251	2(311)
7.99	4×0.001215	2(100)	28.32	48×0.001247	4(111)
11.47	8×0.001247	2(110)	29.24	51×0.001249	711, 551
13.42	11×0.001241	311	30.67	56×0.001248	2(321)
14.07	12×0.001250	2(111)	31.46	59×0.001246	731, 553
16.24	16×0.001247	4(100)	32.85	64×0.001249	8(100)
18.17	20×0.001247	2(210)	34.85	72×0.001246	4(211), 6(110)
19.94	24×0.001248	2(211)	35.87	76×0.001247	2(331)
21.18	27×0.001251	3(111), 511	36.85	80×0.001249	4(210)
23.06	32×0.001248	4(110)	40.49	96×0.001247	4(211)
24.53	36×0.001252	6(100), 2(221)	42.21	104×0.001246	2(510)
25.91	40×0.001254	2(310)			

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[1]) Penfield, S. L., On the Chemical Composition of Sulphohalite. Am. J. Sci. (4) **9** (1900) 425.

From the indices assigned to the lines in table I it is clear that the lattice is face-centered. The occurrence of the lines 2(100), 2(210), 311 and 711 or 551 excludes all space groups based on a face-centered lattice except the groups O_h^5, O^3, T_h^3, T_d^2 and T^2. The first three of these offer the following positions[1]):

4b.	000;	24c.	$\frac{1}{4}\frac{1}{4}0$;	24a.	$u00$;	32a.	uuu;
4c.	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$;		$\frac{3}{4}\frac{1}{4}0$;		$\bar{u}00$;		$\bar{u}u\bar{u}$;
8e.	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$;		$\frac{1}{4}0\frac{1}{4}$;		$0u0$;		$\bar{u}\bar{u}u$;
	$\frac{3}{4}\frac{3}{4}\frac{3}{4}$;		$\frac{3}{4}0\frac{1}{4}$;		$0\bar{u}0$;		$u\bar{u}\bar{u}$;
			$0\frac{1}{4}\frac{1}{4}$;		$00u$;		$\bar{u}uu$;
			$0\frac{3}{4}\frac{1}{4}$;		$00\bar{u}$;		$u\bar{u}u$;
							$uu\bar{u}$;
							$\bar{u}\bar{u}\bar{u}$.

To each position stated must be added three more positions obtained by the translations $\frac{1}{2}\,\frac{1}{2}\,0$, $\frac{1}{2}\,0\,\frac{1}{2}$ and $0\,\frac{1}{2}\,\frac{1}{2}$.

It is necessary to place in the unit cube 24 *Na*, 8 *S*, 32 *O*; 4 *Cl* and 4 *F*. Whether *F* or *Cl* is put at 000 merely amounts to a choice of origin. Putting *F* at 4b, *Cl* goes into 4c. Then there is only one position possible for *S*, namely 8e and only one for *O*, namely 32a. There are now two possibilities for *Na*, either 24c or 24a. Putting *Na* in 24c and assuming the distance *S—O* to be 1.50 Å (it cannot be much less, the smallest reported value being 1.49 Å) it may be calculated that the distance *Na—O* would be 2.05 Å. From ionic radii[2]) this distance cannot be much less than 2.35 Å. The discrepancy is considered to rule out this arrangement.

The other possibility in these groups is putting *Na* in 24a. If this is done a parameter may be found that is in harmony both with ionic radii and the intensity of diffraction lines, as will be shown in detail.

The groups T_d^2 and T^2 lead to several other arrangements involving more than two parameters. In view of the satisfactory agreement with data shown by the structure based on O_h^5, O^3 and T_h^3, no further discussion of these is given here.

The arrangement found compatible with diffraction data and ionic radii is:

4 *F* in (4b) 000;
4 *Cl* in (4c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$;
8 *S* in (8e) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$;
24 *Na* in (24a) $u00$; $\bar{u}00$; $0u0$; $0\bar{u}0$; $00u$; $00\bar{u}$;
32 *O* in (32a) uuu; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$; $u\bar{u}\bar{u}$; $\bar{u}uu$; $u\bar{u}u$; $uu\bar{u}$; $\bar{u}\bar{u}\bar{u}$.

It is found that the distance *F—Cl*, 5.04 Å, which in this arrangement is the sum of the distances *F—Na* and *Na—Cl*, is very close to the sum of these distances, 5.10 Å, found in Zachariasen's tables. This suggests a suitable parameter for *Na*. The positions (32a) lie on the three-fold axes and are situated either between (8e) and (4b) or between (8e) and (4c).

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1) Wyckoff, R. W. G., The analytical expression etc., 1930.

2) Zachariasen, W. H., Z. Kristallogr. **80** (1931) 137.

That is, the oxygens must lie either between S and Cl or between S and F. A consideration of the radii shows that there is no room for them between S and Cl, whereas they just fit in the space between S and F. A parameter for oxygen may now be chosen from a knowledge of other sulfate structures.

A preliminary trial with the parameters 0.23 for sodium and 0.16 for oxygen showed a fair agreement of observed and calculated intensities. Other trials showed that the proper parameters must be very close to these values.

Table II. Comparison of estimated and calculated intensities.

hkl	estimated intensity	$I_{hkl}/10^6$	hkl	estimated intensity	$I_{hkl}/10^6$
111	w.	4.5	2(310)	v. w.	1.0
2(100)	v. w.	1.0	533	—	0.03
2(110)	v. s.	26.2	2(311)	w.	4.0
311	m.	11.3	4(111)	m.	5.8
2(111)	v. s.	23.7	711, 551	v. w.	2.2
4(100)	s.	16.0	2(320)	—	0.03
331	—	0.2	2(321)	m.	6.7
2(210)	m.	7.7	731, 553	m.	5.7
2(211)	w.	2.1	8(100)	v. w.	2.1
511, 3(111)	s.	15.3	2(411), 6(110)	m.	7.9
4(110)	v. s.	30.0	751, 5(111)	—	0.3
531	—	0.1	2(331)	w.	3.9
6(100, 2(221)	w.	4.0	4(210)	m.	7.6

v. s., very strong; s., strong; m., medium; w., weak; v. w., very weak.

Table II gives the estimated and calculated intensities for all lines having $h^2 + k^2 + l^2 \leqq 80$ that may occur in the pattern of a cubic crystal having a face-centered lattice. The intensities were calculated according to the formula,

$$I_{hkl} = j \cdot F^2 \cdot \frac{1 + \cos^2 2\theta}{\sin^2\theta \, \cos\theta},$$

using the f-curves of James and Brindley¹).

The parameters used in this calculation are:

sodium $u = 0.226$,
oxygen $u = 0.164$.

The agreement of observed and calculated intensities is such that these values are accepted as the best obtainable by the methods employed.

The structure leads to the following interionic distances:

$Na—Cl$	2.76 Å	$Cl—S$	4.36 Å
$Na—F$	2.28	$S—O$	1.50
$Na—O$	2.42	$O—F$	2.86.

These values are in harmony with radii given by Zachariasen²).

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1) Z. Kristallogr. **78** (1931) 470.

2) Z. Kristallogr. **80** (1931) 146, Table V.

To describe the structure it is only necessary to consider $\frac{1}{8}$ of the unit cube which is bounded by the principal symmetry planes, as shown in fig. 1. F and Cl ions are located at alternate corners of this small cube. Along each edge is one Na ion, slightly off center towards the adjoining F ion. At the center of the small cube is a tetrahedral SO_4 group so oriented that the corners of the tetrahedron point towards the F ions.

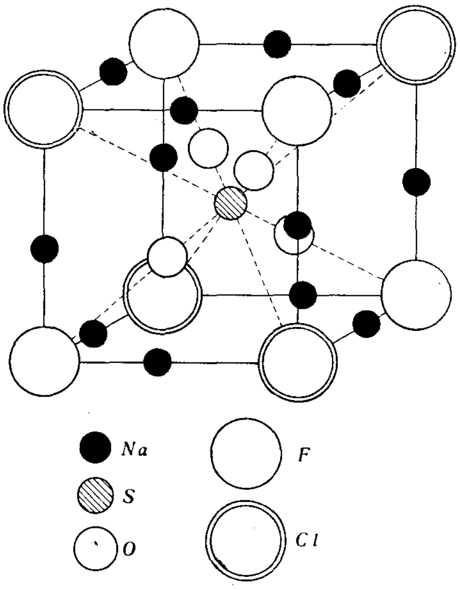

Fig. 1.

There has been some speculation as to whether sulphohalite is a distinct compound or a member of a mix-crystal series. The results here obtained provide strong support for the former view.

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