APPENDIX

Photometer measurements on spots of non-uniform density

In the following, the clear-base transparency is taken as unity.

Suppose the spot is divided into areas $A_1, A_2, \ldots, A_r, \ldots, A_n$ with corresponding transparencies $t_1, t_2, \ldots, t_r, \ldots, t_n$. The total X-ray intensity causing this spot is proportional to (area × density) and is given by $T = \Sigma A_r \log(1/t_r)$, where r has the values 1 to n. Assuming that density variation across the spot is small, we may write $t_r = t_1+\Delta_r$, where Δ_r is small. Then

$$\log\frac{1}{t_r} = \log\frac{1}{t_1+\Delta_r} = \log\frac{1}{t_1} - 2{\cdot}3\frac{\Delta_r}{t_1}\,,$$

if we ignore terms in $(\Delta_r)^2$ etc. Thus

$$T = \Sigma A_r\left(\log\frac{1}{t_1} - 2{\cdot}3\frac{\Delta_r}{t_1}\right) = A\log\frac{1}{t_1} - 2{\cdot}3\,\Sigma\frac{A_r\Delta_r}{t_1}\,,$$

where A is the total spot area.

The photometer reading β corresponds to an effective mean transparency for the spot given by $\bar{t} = \Sigma A_r t_r/\Sigma A_r$ and hence to a mean density $\bar{D} = \log(1/\bar{t})$. Thus

$$\bar{D} = \log\left(\frac{\Sigma A_r}{\Sigma A_r t_r}\right) = \log\left(\frac{\Sigma A_r}{\Sigma(A_r t_1 + A_r\Delta_r)}\right)\,,$$

which reduces on expansion, ignoring terms in $(\Delta_r)^2$ etc., to

$$\bar{D} = \log A - \log A t_1 - 2{\cdot}3\,\frac{\Sigma A_r\Delta_r}{A t_1}$$
$$= \log\frac{1}{t_1} - 2{\cdot}3\,\frac{\Sigma A_r\Delta_r}{A t_1}\,.$$

Thus the product of total area and mean density, $A\bar{D}$, is equal to T above.

Hence, under the above conditions, the transmission reading β is based upon a mean transparency which would lead to a true value of X-ray intensity, and thus the arguments in § 2 for a uniform spot are valid also for one across which the density variation is small.

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An X-ray Study of Na_2SO_4 III

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The determination of the crystal system of Na_2SO_4 III was made directly from the powder pattern. Na_2SO_4 III was found to belong to the tetragonal system with $a = b = 13{\cdot}45$ Å and $c = 7{\cdot}879$ Å, with 16 molecules in the unit cell.

Introduction

Of the five forms of Na_2SO_4 indicated by the thermal analysis, Kracek & Kasanda (1930) studied the spacing of only three by the X-ray diffraction method, namely (1) Na_2SO_4 V or thenardite, stable at ordinary temperatures, (2) Na_2SO_4 I, stable only above 245°C., and (3) Na_2SO_4 III, stable below 185°C. Colby (1931) found Na_2SO_4 V to belong to the orthorhombic space-group *Fddd*. However, no definite information about the other two forms can be found. It was seen by us that Fravel's (1940) suggestion that Na_2SO_4 III is orthorhombic is not consistent with all the lines of the powder pattern, and Lipson's (1949) method applied by us further showed that it certainly does not belong to the orthorhombic system. The main difficulty in finding the actual crystal class of Na_2SO_4 III lies in the fact that no single crystal of appreciable size can be obtained so that standard methods cannot be applied.

Recently Hesse (1948) suggested a novel method for indexing powder photographs. Stosick (1949) made some modifications of Hesse's idea and treated the case in the general way. He showed that if there be any equation of the type $m_1q_1 = m_2q_2$, where q's are the $\sin^2\theta$ values and m's are integers, the crystal system must be either (*a*) tetragonal, (*b*) hexagonal or (*c*) cubic, of which the last can be recognized immediately from the pattern itself. When $m_1q_1 = m_2q_2$ one can have $m_1M_1 = m_2M_2$ (l being zero), where $M = h^2+k^2$ or

h^2+hk+k^2 for tetragonal and hexagonal crystals respectively; and actually the ratio $m_1:m_2$ determines whether the crystal is tetragonal or hexagonal. The system having been determined, the constants A and C in the equation $q = AM+CN$ (where $N = l^2$) can be found and all the lines can then be indexed.

Experimental

Anhydrous Na_2SO_4 or thenardite was prepared as suggested by Kracek (1929) and freed from alcohol and water. This was powdered and introduced into a thin glass capillary tube, the ends being sealed after filling. After heating this stick to about 500° C. it was brought back to the original temperature, when thenardite transformed into Na_2SO_4 III. X-ray powder photographs were taken with a cylindrical camera of radius 3·92 cm., using Cu $K\alpha$ rays from a Hadding tube run at 50–60 kV. and 15 mA. The exposure was about 6 hr. The d values (Table 1) found by us are in good agreement with those found by Kracek & Kasanda (1930) and also with those found by Hanawalt, Rinn & Fravel (1938).

Determination of the crystal class

It was seen from the $\sin^2\theta$ values (Table 1) that

$$(1)\ 9q_1 = 8q_2,\quad (2)\ q_{10} = 5q_1,\quad (3)\ q_8 = 4q_1 \text{ and } (4)\ 5q_8 = 4q_{10}\,.$$

These relations are of the form $m_1q_1 = m_2q_2$. Hence the powder pattern must correspond to either the tetragonal, the hexagonal or the cubic system. That it is not cubic is definitely seen from the pattern itself. Moreover, $q_1+q_8 = q_{10}$, $q_8+q_{10} = q_{17}$, which also show that it must be either tetragonal or hexagonal (Stosick, 1949). From the observed relations it will be found that

$$(a)\ 9M_1 = 8M_2,\quad (b)\ M_{10} = 5M_1,\quad (c)\ M_8 = 4M_1\,,$$

whence the sequence of the M values (1, 4, 5, 8, 9) decides in favour of the tetragonal system. The relation (a) requires that M_1 must be equal to 8 or some multiple of it. Taking $M_1 = 8$, A becomes equal to 0·003275. Then q_4-AM_4, with $M_4 = 1$, equals 0·0382 $= q_3$. Let the M values for q_3 be taken as zero, then $Cl_4^2 = Cl_3^2$. With $l_3 = 1$, l_4 is also 1, but all the lines of the powder pattern cannot be indexed with these values. But when $l_3 = 2$, and $l_4 = 2$, C comes out to be 0·0382/4 = 0·0095. With these values of A and C, all the lines of the powder pattern of Na_2SO_4 III can be indexed. The axial lengths a and c can be found directly by solving the equation $a = \frac{1}{2}\lambda/\sqrt{A}$ and $c = \frac{1}{2}\lambda/\sqrt{C}$. The hkl values for all the lines are shown in Table 1 and the axial lengths of Na_2SO_4 III crystal come out as

$$a = b = 13{\cdot}45\ \text{Å},\quad c = 7{\cdot}879\ \text{Å}$$

Table 1. *Observed spacings, hkl values and observed and calculated* $\sin^2\theta$ *values*

d_o (Å)	$(\sin^2\theta)_o$	$M = h^2+k^2$	$N = l^2$	hkl	$(\sin^2\theta)_c$
4·757	0·0262	8	0	220	0·0262
4·477	0·0295	9	0	300	0·0295
3·941	0·0382	0	4	002	0·0382
3·780	0·0415	1	4	102	0·0415
3·410	0·0510	4	1	201	0·0510
2·804	0·0751	20	1	241	0·0751
2·630	0·0856	0	9	003	0·0855
2·376	0·1049	32	0	440	0·1048
2·239	0·1182	10	9	133	0·1182
2·125	0·1311	40	0	260	0·1310
2·074	0·1378	16	9	403	0·1379
1·954	0·1552	1	16	104	0·1553
1·877	0·1680	5	16	124	0·1682
1·743	0·1950	13	16	234	0·1948
1·690	0·2076	17	16	144	0·2076
1·614	0·2277	58	4	372	0·2277
1·585	0·2360	72	0	660	0·2360
1·559	0·2438	2	25	115	0·2440
1·528	0·2538	5	25	125	0·2538
1·480	0·2704	10	25	135	0·2704
1·443	0·2830	40	16	264	0·2830
1·398	0·3031	20	25	245	0·3031
1·369	0·3162	85	4	292	0·3165
1·310	0·3456	1	36	106	0·3457
1·290	0·3563	36	25	605	0·3566
1·224	0·3960	121	0	11,0,0	0·3962
1·205	0·4081	20	36	246	0·4081
1·170	0·4322	106	9	593	0·4321
1·124	0·4692	117	9	693	0·4692
1·089	0·4999	106	16	594	0·4999
1·059	0·5283	89	25	585	0·5286
1·050	0·5370	164	0	10,8,0	0·5371
1·039	0·5483	121	16	11,0,4	0·5483
1·007	0·5845	74	36	576	0·5844

From the axial lengths for Na_2SO_4 III given in the previous section and the density (2·69 g.cm.$^{-3}$) the unit cell contains 16 molecules. As the number of reflecting planes in a powder pattern is limited it is difficult to assign any definite space group to Na_2SO_4 III from this study.

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