A Method of Obtaining Fibrous Arrangements of the Micro-Crystals of Some Substances

By

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Abstract

The writer first dissolved some crystals in water and then soaked a stretched bundle of rayon threads in it. When the crystals were in the act of being recrystallized the solvent was removed by evaporation. How the recrystallization takes place in the interstice of the bundle of rayon threads was the question the writer wanted to examine. He found by means of X-rays that the micro-crystals were reformed in a fibrous form similar to the interstices of the rayon threads. The materials used were potassium chromate, sodium sulphate, potassium bromide, magnesium sulphate and potato starch.

To obtain a fibrous arrangement of the micro-crystals of a substance is very important in examining the lattice form and the nature of the crystal. The writer secured fibrous arrangements of the micro-crystals of some substances which are soluble in water, by recrystallising the solute by evaporating the solvent in the narrow interstices of a stretched bundle of rayon threads. The fibrous arrangement of the micro-crystals thus obtained was examined by means of X-ray diffraction.

The bundle of rayon threads used in the experiment consisted of 400–500 threads, each of which was 7–8μ in diameter. They were fixed on a frame to keep them tense, in the manner shown in Fig. 1, Plate I. After being soaked in an aqueous solution of the substance, the superfluous liquid was removed by stretching the threads as tense as possible, and by means of filter paper. The recrystallization took place slowly by the evaporation of the water solvent in the narrow interstices of the threads. Then the stretched bundle was fixed on the slit of the X-ray camera, and a diffraction photograph was taken by means of a K_α line of copper.

The diffraction pattern due to the rayon threads was of course superposed on the photograph with the impression of the recrystallised substance. But the broadly diffused pattern of the rayon threads was easily discriminated from that of the recrystallised substance.

The materials used were potassium chromate, sodium sulphate, potassium bromide, magnesium sulphate and potato starch. Potato starch was dissolved in water by the Salomon method[1] at ordinary temperature, and the others were all dissolved in water at a temperature of 45–50°C at a concentration of about 2–5%.

Fig. 2, Plate I is the X-ray photograph thus obtained with crystallised potassium chromate, and it is evidently a fibre diagram. The plate distance was 27.6 mm. in this case.

Table I

Layer line	Spots	sin ϕ	I Å	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
0	A_1			.0107	.0097	(110)	st.
	A_2			.0349	.0362	(310)	st.
	A_3			.0671	.0703	(230)	st.
	A_4			.0856	.0869	(330)	m. st.
	A_5			.1019	.1014	(040)	m. st.
1st	I_1	.2641	5.83	.0352	.0355	(021)	st.
	I_2	.2635	5.75	.0688	.0672	(331)	st.
	I_3	.2626	5.87	.1222	.1182	(431)	w.
2nd	II_0	.5122	6.01	.0707	.0705	(302)	st.
	II_1	.5230	5.89	.0951	.0959	(322)	w.
	II_2	.5256	5.86	.1206	.1191	(422)	w.
	II_3	.5306	5.80	.1297	.1300	(512)	st.

Mean value of I=5.88 Å

As shown in Table I, the identity period in the axial direction of the fibre is 5.88 Å, which completely agrees with a-axis of the potassium chromate crystal. The lattice form of this crystal belongs to the orthorhombic system, having the size $a=5.88$ Å, $b=10.30$ Å and $c=7.45$ Å, and the micro-crystals nestle in the narrow interstices between the stretched rayon threads by keeping their a-axis parallel to the direction of the threads. In the table ϕ is the layer angle and θ is the glancing angle.

Fig. 3, Plate I is the fibre photograph obtained with the crystals of sodium sulphate prepared by the above method. The plate distance was 32.5 mm. in this case.

According to W. H. Zachariasen and G. E. Ziegler[1] the lattice form

1. L. Vanino: Preparative Chemie, Vol. 2, p. 203 (1923).
2. Zeit. f. Krist. Bd. 81. p. 92 (1932).

Plate I

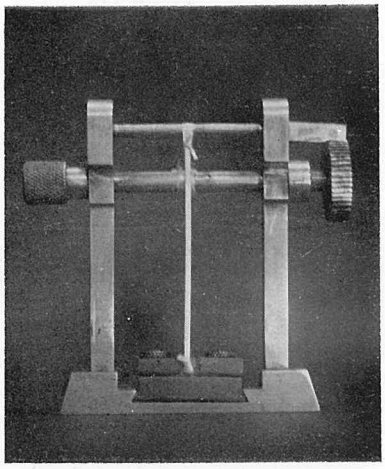

Fig. 1

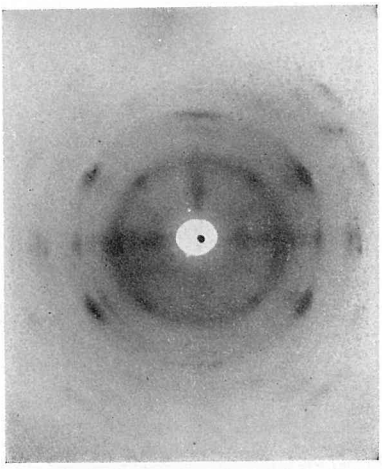

Fig. 2

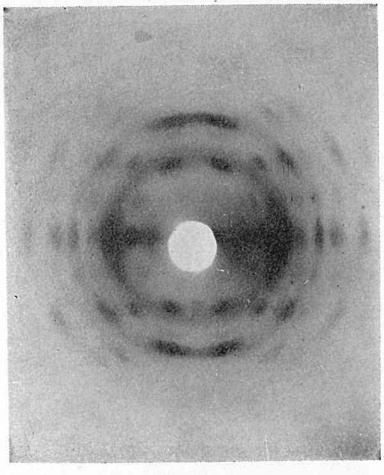

Fig. 3

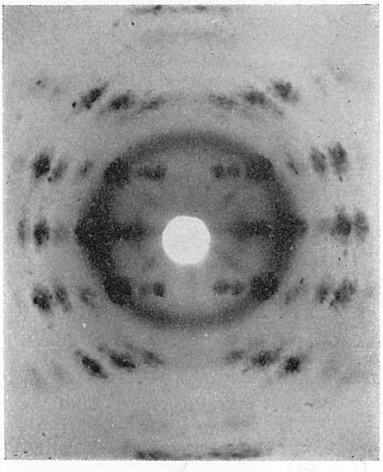

Fig. 4

Table II

Layer line	Spots	sin ϕ	I Å	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
0	A_1			.0406	.0392	(120)	w.
	A_2			.0524	.0524	(020)β	st.
	A_3			.0647	.0628	(020)α	w.
	A_4			.0877	.0862	(140)	st.
1st	I_1	.1378	11.17	.0428	.0415	(031)	w.
	I_2	.1351	11.40	.0532	.0527	(131)	st.
	I_3	.1355	11.37	.0697	.0689	(041)	w.
2nd	II_1	.2671	11.15	.0220	.0235	(102)	st.
	II_2	.2746	11.21	.0411	.0406	(022)	st.
	II_3	.2721	11.32	.0820	.0849	(222)	st.
	II_4	.2688	11.46	.1031	.1045	(232)	w.
3rd	III_1	.4065	11.37	.0477	.0460	(113)	st.
	III_2	.4125	11.20	.0711	.0716	(023)	st.
	III_3	.4085	11.31	.0788	.0793	(213)	w.
	III_4	.4056	11.39	.1118	.1107	(233)	w.
4th	IV_0	.5367	11.47	.0782	.0772	(114)	st.
	IV_1	.5460	11.28	.0891	.0889	(124)	w.
	IV_2	.5411	11.38	.1159	.1151	(024)	st.

Mean value of I=11.3 Å

of the crystal of sodium sulphate is monoclinic, having the size $a=5.85$ Å, $b=12.29$ Å, $c=11.38$ Å and $\beta=59°3'$. The identity period in the axial direction of the fibre, obtained from the photograph, is 11.3 Å and is equal to that in the direction of the c-axis. The positions of the diffraction spots on the photograph agree well with those calculated by taking the c-axis as the fibrous axis of the crystallites in the direction of the stretched threads. The results are tabulated in Table II.

Next, the writer experimented with potassium bromide crystals. Water, alcohol or glycerin may be used as the solvent, for the result is the same in every case. Though the diffraction spots were as not strong as in the former cases, their positions could be measured; and the results are given in Table III.

The identity period in the direction of the fibre is 9.34 Å, which is the same as that of the diagonal of the cube face of the cubic crystal of potassium bromide, whose size is $a=b=c=6.58$ Å. The results are tabulated in Table III. The fibrous arrangement was not perfect in this case, and ordinary Debye-Scherrer rings were superposed on the

Table III

Layer line	Spots	sin ϕ	IÅ	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
	A_1			.0311	.0342	(210)	w.
	A_2			.0425	.0446	(220)β	st.
0	A_3			.0551	.0548	(220)α	st.
	A_4			.0882	.0890	(320)	w.
	A_5			.1092	.1096	(400)	st.
1st	I_0	.1661	9.27	.0069	.0069	(001)	w.
	I_1	.1662	9.26	.0403	.0411	(211)	w.
	II_0	.3273	9.40	.0276	.0274	(002)	w.
2nd	II_1	.3307	9.31	.0537	.0548	(202)	st.
	II_2	.3318	9.28	.1167	.1164	(322)	st.
3rd	III_0	.4880	9.46	.0636	.0617	(003)	st.
	III_1	.4972	9.29	.1152	.1165	(223)	st.

Mean value of I=9.34 Å

photograph, which shows the presence of some crystallites oriented entirely at random.

Fig. 4, Plate I is the fibre photograph of the crystallites of magnesium sulphate recrystallised by the above method. The plate distance was 31.6 mm. in this case.

Table IV

Layer line	Spots	sin ϕ	IÅ	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
	A_1			.0164	.0164	(020)	st.
	A_2			.0217	.0208	(210)	st.
0	A_3			.0411	.0417	(310)	st.
	A_4			.0632	.0621	(330)β	w.
	A_5			.0762	.0745	(330)α	st.
	I_1	.2295	6.71	.0173	.0168	(101)	st.
	I_2	.2274	6.77	.0220	.0209	(111)	st.
1st	I_3	.2141	7.19	.0289	.0290	(021)	st.
	I_4	.2321	6.64	.0318	.0332	(121)	st.
	I_5	.2256	6.82	.0537	.0537	(131)	w.
	II_1	.4552	6.76	.0662	.0666	(022)	st.
2nd	II_2	.4584	6.72	.0734	.0710	(212)	st.
	II_3	.4636	6.64	.0892	.0871	(032)	st.
3rd	III_1	.6797	6.80	.1349	.1338	(213)	st.
	III_2	.6800	6.79	.1521	.1506	(303)	w.

Mean value of I=6.78 Å

As shown in Table IV, the identity period in the axial direction of the fibre is 6.78 Å, which agrees with that of the c-axis of the orthorhombic crystal of magnesium sulphate having the size $a=11.91$ Å, $b=12.02$ Å and $c=6.87$ Å. Thus the crystallites nestle in the interstices of the stretched rayon threads by keeping their c-axis parallel to the direction of the threads.

Lastly the writer tried to obtain a fibre photograph with soluble potato starch prepared by Salomon's method. The recrystallization of the starch was caused by adding some anhydrous ethyl alcohol to the aqueous potato solution. Though it failed to obtain a clear fibre photograph, an indication of the fibrous arrangement could be detected; and the identity period in the fibrous axis parallel to the direction of the stretched rayon threads was estimated to be about 13 Å. It is hoped that the lattice form of starch may be determined by improving this method in the near future.

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida for the interest he has taken in the present research.