An X-ray study of schultenite

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IN 1926 schultenite from Tsumeb, Otavi, South-West Africa, was described as a new mineral by L. J. Spencer[1] and related to the compound $PbHAsO_4$. The specimen on which the original description was based is still unique in the British Museum collection and was used for the present study. There appears to be no record in the literature that the mineral has been discovered in any other locality.

For the X-ray examination rather small fragments (less than 0.1×0.05 mm.) were broken from pieces of crystals since all the available crystals were too large and the material has a high absorption to X-rays. Single crystal rotation, oscillation, and Weissenberg photographs in 6-cm. diameter cameras with Cu–$K\alpha$ radiation as well as Laue photographs (crystal-plate distance 4 cm.) with tungsten radiation were used to derive the unit-cell dimensions and space-group.

With a crystal fragment oscillated about an axis normal to the (010) cleavage face the presence of a symmetry plane parallel to (010) was confirmed and the unit-cell edge b determined from the layer-line distance. Zero, first and second layer-line equi-inclination Weissenberg photographs about the same axis gave approximate values for the unit-cell edges a and c and showed that the only systematic absences are $h0l$ with h odd leading to the space-groups C_s^2—Pa or C_{2h}^4—$P2/a$. More accurate unit-cell dimensions were subsequently obtained by measurements of indexed high-order reflections on the equatorial layer-lines of rotation photographs about the axes b and c. The angle β was measured from a Laue photograph of a crystal fragment of schultenite accurately set normal to (010) which also served to confirm the suitability of the chosen axes a and c (those of Spencer). The value of $180°-\beta$ so obtained $84\frac{1}{2}°$, is in good agreement with that determined by goniometric means $84° 36'$. Weissenberg photographs were also taken about the axis c.

The unit-cell dimensions for schultenite are therefore: a 5.83, b 6.76, c 4.85 Å., β $95\frac{1}{2}°$ giving the volume of the unit-cell 190.4 Å.[3]; space-group Pa or $P2/a$. Assuming that the theoretical formula is $PbHAsO_4$ and

[1] L. J. Spencer, Min. Mag., 1926, vol. 21, pp. 149–155.

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using the density 5·943 determined by Spencer, the number of molecules in the unit-cell is found to be 2 (calculated value 1·96).
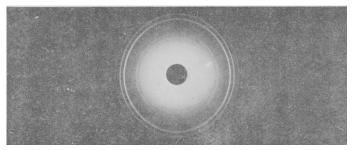

FIG. 1. Powder pattern of schultenite taken in 6 cm. diameter camera, Cu–$K\alpha$ radiation ($\lambda = 1\cdot542$ Å.).

The axial ratios calculated from the unit-cell dimensions are
$$0\cdot862 : 1 : 0\cdot717$$
and compare satisfactorily with the goniometric values
$$0\cdot8643 : 1 : 0\cdot7181 \ (\text{L.J.S.})$$
A powder photograph (6 cm. diameter camera Cu–$K\alpha$) (fig. 1) of a specimen prepared by grinding up crystal fragments in an agate mortar was measured with the results shown in Table I. Almost unambiguous indexing down to 2 Å. has been found possible by calculating spacings from the single crystal data and checking the powder diagram against indexed single crystal rotation photographs. Powder data for the artificial compound[1] are in good agreement with the stronger lines of the schultenite pattern.

In the time available it has not been possible to work out in detail the crystal structure of the mineral, but a rough model of a possible structure which appears to be in reasonable accordance with inspected intensities of the principal diffraction spectra has been constructed from space-group and crystal chemical considerations. It is intended to provide more complete data in the future.

In the more symmetrical of the two possible space-groups there are six sets of twofold special positions, four at the centres of symmetry and two on twofold axes, available for the lead and arsenic atoms. Of the $hk0$ reflections all those with h odd are weak and this precludes the

[1] Published by the American Society for Testing Materials, the American Crystallographic Association, and the (British) Institute of Physics, Joint Committee on Chemical Analysis by X-ray Diffraction Methods, Philadelphia, 1950: card no. 1488.

possibility of heavy atoms residing at the centres of symmetry but is in agreement with their being on twofold axes. It was also assumed that the oxygens are arranged tetrahedrally about the arsenics and a scale

TABLE I. X-ray powder data for schultenite.

hkl	d calc.	I	d obs.	I	d obs.
010	6·76Å.	mw	6·7Å.	w	1·643
001	4·83	vw	4·80	w	1·617
110	4·40	mw	4·37	vw	1·568
011	3·93	vvw	3·93	ms	1·546Å.
020	3·38 ⎫	vvs	3·35	mw	1·522
11$\bar{1}$	3·38 ⎭			mw	1·474
111	3·13	vs	3·13	vw	1·452
200	2·90	mw	2·90	vw	1·430
021	2·77	vw	2·76	vvw	1·411
210	2·67	vw	2·66	vw	1·393
20$\bar{1}$	2·60	vvw	2·58	vw	1·377
12$\bar{1}$	2·55	m	2·55	vw	1·348
121	2·45 ⎫	w	2·42*	vw	1·330
002	2·41 ⎭			w	1·297
211	2·25 ⎫	w	2·24	w	1·276
030	2·25 ⎭			vw	1·251*
220	2·20 ⎫	ms	2·19	mw	1·224
11$\bar{2}$	2·185 ⎭			mw	1·212
130	2·10	vw	2·10	vvw	1·197
112	2·06	mw	2·05	vw	1·180
031	2·04	vvw	2·04	vvw	1·168
		s	1·950*	vw	1·158
		mw	1·899	vvw	1·140
		w	1·859	vw	1·126
		vvw	1·820	vvw	1·110
		s	1·778*	vw	1·092
		ms	1·683	vw	1·080
			(continue next column)	vw	1·074

Order of decreasing intensity: vvs, vs, s, ms, m, mw, w, vw, vvw; broad lines are asterisked.

model of a close-packing type was constructed in which the lead and AsO_4 groups were mounted on wires representing the twofold axes. It was found possible with this model by putting lead atoms on one set of twofold axes and AsO_4 groups on the second set to arrange them in fulfilment of the space-group symmetry within the available cell space. In this arrangement (fig. 2) the lead atoms are in eightfold coordination and with y coordinates Pb = 0·80 and As = 0·21 an approximate agreement with observed intensities is achieved. A feature of this model is the layering normal to the b axis which if confirmed may be related to the extraordinarily good cleavage on (010). My thanks are

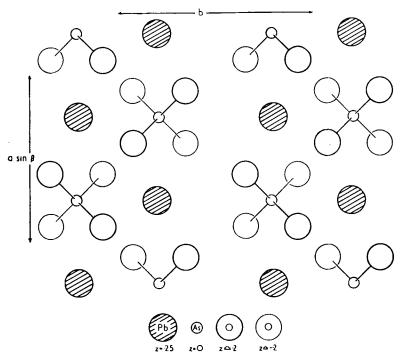due to Dr. F. A. Bannister for suggesting an examination of this mineral.

FIG. 2. View along c-axis of proposed crystal structure for schultenite ($PbHAsO_4$); positions of hydrogens not shown.