separation of potassium and sodium perchlorates, two extractions with intermediate solution of potassium perchlorate being required; (2) the extraction separation of potassium and lithium perchlorates, one extraction only being required; and (3) the separation of sodium and lithium subsequent to their extraction from potassium, following the procedure of Willard and Smith[2] in which sodium chloride is precipitated from solution in *n*-butyl alcohol, by a hydrogen chloride solution in the same solvent. The sodium was determined volumetrically by Mohr's method.

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THE CRYSTAL STRUCTURE OF BARITE

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Introduction

Barite, $BaSO_4$, a member of a large class of isomorphous crystals, is described by Groth[1] as orthorhombic bipyramidal, with axial ratios $a:b:c = 0.8152:1:1.3136$. This crystal has been recently investigated by Allison[2] by means of X-rays. The axial ratios were redetermined by goniometric measurements, using X-rays instead of visible light, and the values 0.8148:1:1.3131 were obtained. Spectrometric measurements were made from thirteen planes, using a tungsten tube operated at 90,000 volts; and values of d/n were then calculated from the angles of reflection of the tungsten lines and the barium K absorption edge. The conclusions drawn from the data as to the structure of the crystal seem, however, to be clearly erroneous. For the author bases the determination of the unit of structure upon the assumption that the unit must have the crystallographic axial ratios, which in fact result from an arbitrary choice of a parametral plane from among the many permitted by the crystallographic data. Moreover, his derived unit of structure is inconsistent with his data, in that he gives in Table IV for plane (102) $d_{\text{calcd.}} = 2.792$ and $d_{\text{obs.}} = 5.562$; yet his observation shows that $d/n = 5.562$; and this obviously requires that $d = 5.562\ n$, where n is an integer, and hence does not permit that $d = {}^1/_2 \times 5.562$ as calculated (approximately) from his unit of structure.[3] The

[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1908**, Vol. II, p. 388.

[2] S. K. Allison, *Am. J. Sci.*, [5] **8**, 261 (1924).

[3] The author is aware that there is a difficulty here, for he states that this result from (102) may be due to some "accidental" arrangement of atoms; however, it is not possible with any arrangement of atoms in his unit to explain the observed reflection. The analogy suggested to (100) of succinic acid and (010) of succinic anhydride [Yardley, *Proc. Roy. Soc.*, **105A**, 451 (1924)] is not pertinent, for in these cases $d_{\text{calcd.}}$ is twice $d/n_{\text{obs.}}$, not one-half of it.

author's conclusion as to the space group involved is also invalidated, since it is based on his unit of structure.

It has seemed to us desirable, therefore, to investigate anew the crystal structure of this substance, utilizing data obtained from Laue as well as from spectral photographs. This research was made with the help of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our appreciation.

The Experimental Method

Spectral photographs were taken of the K-radiation of molybdenum reflected from the faces (100), (010) and (001) of a natural crystal. These faces were previously roughened by grinding with fine carborundum and oil; the face (100), which was not developed, was ground normal to the other two pinacoids. Reflections from (100) of calcite were taken at the same time for calibration. The data are given in Table I. The lines have the following wave lengths in Ångström units: molybdenum $K\alpha_1$, 0.7078; α_2, 0.7121; β, 0.6311; γ 0.6197.

TABLE I

SPECTRAL PHOTOGRAPHIC DATA FROM BARITE

(*hkl*)	Order of reflection	Line	Angle of reflection	*d*/*n* Å.	Estimated intensity[a]
(100)	*n*	γ	4° 1.0′	4.429	vw
	n	β	4 6.0	4.411	m
	n	α_1	4 35.4	4.425	s
	n	α_2	4 37.0	4.422	ms
	2*n*	γ	8 3.5	4.420	vvw
	2*n*	β	8 12.7	4.419	vw
	2*n*	α_1	9 12.5	4.425	mw
	2*n*	α_2	9 16.4	4.420	w
	3*n*	β	12 22.4	4.414	vvw
	3*n*	α_1	13 52.5	4.429	mw
	3*n*	α_2	13 58.7	4.426	w
(010)	*n*	β	6 41	2.715	vvw
	n	α_1	7 30.1	2.712	s
	n	α_2	7 31.7	2.718	ms
	2*n*	β	13 27.4	2.712	mw
	2*n*	α_1	15 6.5	2.717	s
	2*n*	α_2	15 12.5	2.715	ms
(001)	*n*	γ	4 59.8	3.557	vvw
	n	β	5 5.0	3.562	mw
	n	α_1	5 42.0	3.564	s
	n	α_2	5 44.2	3.561	s
	2*n*	γ	10 2.3	3.555	vvw
	2*n*	β	10 12.3	3.562	w
	2*n*	α_1	11 27.9	3.560	m
	2*n*	α_2	11 32.1	3.551	w

[a] The abbreviations signify: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak.

Laue photographs[4] were made with the incident beam at small angles with the normal to (001), the crystal slips used being cleaved along (001) from the large specimen. The radiation had a minimum wave length of 0.24 Å., for the tungsten tube used was operated at a peak voltage of about 52,000 volts. Gnomonic projections were used in interpreting the photographs. Laue data are given in Tables II and III.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM BARITE: PHOTOGRAPH 1

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity[a]	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$1\bar{4}1$	1.407	0.42	a	$\bar{9}11$	0.960	0.40	0.4
$6\bar{1}1$	1.400	.34	5	$\bar{9}\bar{1}1$	.960	.38	.4
$3\bar{4}1$	1.285	.29	0.02	$\bar{1}\bar{6}2$	.931	.42	1.3
341	1.285	.42	1.6	$\bar{4}61$	.881	.30	0.01
$\bar{4}\bar{4}1$	1.199	.42	1.6	$5\bar{6}3$	.802	.42	1.0
$\bar{2}51$	1.114	.42	3	$\bar{9}\bar{4}2$	.793	.41	0.6
251	1.114	.33	0.1	$\bar{1}0.\bar{3}.2$	.785	.42	.1
$\bar{2}\bar{5}1$	1.114	.30	.05	943	.770	.42	.05
$\bar{7}\bar{3}1$	1.048	.39	.2	$\bar{9}52$	.735	.40	.1
$\bar{6}41$	1.025	.42	.3	$\bar{1}\bar{1}.3.2$	.728	.41	.8
$7\bar{3}2$	1.016	.41	1.6	$\bar{1}\bar{3}.1.2$	.664	.34	.05

[a] a signifies absent.

The Unit of Structure

Spectral data in Table I give for d/n for (100), (010) and (001), values of 4.423, 2.715 and 3.55 Å. On assigning indices on the basis of the unit obtained by putting $n = 1$ in each case and calculating values of $n\lambda$, a number of planes such as $(\bar{7}\bar{3}1)$, $(\bar{9}\bar{1}1)$, $(\bar{4}61)$, $(\bar{1}\bar{3}.1.2)$, etc., gave values less than 0.24 Å., eliminating this unit, and all units in which $n = 1$ for one or two of the pinacoids. The smallest unit which accounts for these observed reflections is obtained by taking $n = 2$ for each of the pinacoids; this unit has $d_{100} = 8.846$, $d_{010} = 5.430$, and $d_{001} = 7.10$ Å. This unit accounts completely for all Laue data obtained, and may accordingly be accepted as the correct one. The amount of data accounted for is shown by the fact that on one Laue photograph over 200 planes, belonging to 90 different forms, gave first-order reflections. Representative data are given in Table II, in which indices refer to the axes of this unit. It is to be noted that these indices may be obtained from those based on the usual crystallographic axes by doubling *h*.

The number of molecules in this unit is four, corresponding to the density 4.51, which is in good agreement with the directly determined values[1] 4.48 to 4.50. The density calculated from the values of d/n obtained

[4] A reproduction of a Laue photograph through (001) of barite has been published by Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, **1924**, p. 110.

spectrometrically by Allison[2] is 4.43. We have estimated the probable error in our spectrographic observations to be less than 0.1%; the agreement in calculated density and the directly determined values (which in general tend to be low) verifies this estimate.[5]

The Space Lattice and the Space Group

Observed first-order reflections from planes with one or two indices even, with the sum of all three indices even, and with the sum of any two indices even (Table II) require[6] that the lattice underlying the structure be the simple orthorhombic lattice Γ_0. The types of prism planes giving first-order reflections (Table III) are such as to eliminate definitely all of the holohedral space groups[7] V_h^1 to V_h^{16} (2Di−1 to 2Di−16) based on this lattice except V_h^1, V_h^5, V_h^{13} and V_h^{16}.

TABLE III

LAUE PHOTOGRAPHIC DATA FROM BARITE. PRISM PLANES

Photograph 1				Photograph 2			
hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$\bar{3}10$	2.630	0.38	a	$\bar{2}10$	3.520	0.34	6.0
$\bar{4}10$	2.070	.32	2.5	120	2.770	.36	a
$0\bar{4}1$	1.430	.45	a	130	1.896	.38	a
051	1.150	.40	0.4	140	1.439	.29	a
902	0.994	.39	1.0	701	1.245	.38	0.05
10.0.3	.829	.46	0.02	052	1.110	.44	a
072	.811	.38	a	801	1.094	.39	0.2
11.0.2	.784	.46	a	061	0.962	.43	a
11.0.3	.733	.37	1.0	$0\bar{7}4$	.753	.46	a
				11.0.3	.733	.43	1.5

The observed data show that all types of planes with $k = 0$ give first-order reflections, those with $h = 0$ do so only if $k + l$ is even, and those with $l = 0$ only if h is even. These data render space groups V_h^1, V_h^5 and V_h^{13} improbable, for these space groups require the absence of first-order reflections from certain planes in no prism zone, or in only one, and accordingly do not account for all the observed absences. Space group V_h^{16} permits first-order reflections from all types of planes with $h = 0$, from those with $k = 0$ only if $h + l$ is even, and from those with $l = 0$ only if k is even. This space group, which completely explains the experimental observations, is accepted as correct. It is to be noted that to change from indices (hkl) used in this paper to those $(hkl)_{SG}$ based on the assignment

[5] The agreement between $d_{calcd.}$ and $d_{obs.}$ given in Table IV of the previous research is such as to indicate a probable error somewhat greater than 0.1% in the spectrometric observations reported.

[6] Pauling and Dickinson, THIS JOURNAL, **46**, 1615 (1924).

[7] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. 318, **1922**.

of axes to V_h^{16} in the course of the development of the theory of space groups, the transformation $h = k_{SG}$, $k = h_{SG}$, $l = l_{SG}$ is required.

A complete determination of the atomic arrangement is impracticable at this time, because of the number of parameters involved. An attempt was made to determine the location of barium atoms alone, using the statistical treatment of intensities successfully applied to uranyl nitrate hexahydrate.[6] This treatment should be applicable, since the structure factors for barite are made up mainly of the barium term, on account of the large relative reflecting power of this heavy atom. The possible arrangements of the four barium atoms in the unit are[7]

(a) $\frac{1}{4}\,\frac{1}{4}\,0,\ \frac{3}{4}\,\frac{1}{4}\,0,\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{2},\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{2}$;
(b) $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{2},\ \frac{3}{4}\,\frac{1}{4}\,\frac{1}{2},\ \frac{3}{4}\,\frac{3}{4}\,0,\ \frac{1}{4}\,\frac{3}{4}\,0$;
(c) $0\,u\,v,\ \frac{1}{2}\,\frac{1}{2}-u\,\bar{v},\ 0\,u+\frac{1}{2}\,\frac{1}{2}-v,\ \frac{1}{2}\,\bar{u}\,v+\frac{1}{2}$.

For arrangements (a) and (b) the structure factor in the first order is $4\overline{Ba}$ for planes with h_{SG} even and $k_{SG} + l_{SG}$ even, and 0 for all other planes. These arrangements are definitely eliminated by the experimental data; for example, $(\bar{4}11)_{SG}$ is absent, and $(5\bar{2}1)_{SG}$, with smaller interplanar distance, reflects very strongly at the same wave length. Such wide discrepancies cannot be explained as due to the effect of sulfur and oxygen atoms. The barium atoms are, therefore, located as in (c). Because of the presence of other atoms no attempt was made to determine the two parameters involved.

Summary

It is shown by Laue and spectral photographs, interpreted with the aid of the theory of space-groups, that the unit of structure of the orthorhombic crystal barite ($BaSO_4$) has $d_{100} = 8.846$, $d_{010} = 5.430$ and $d_{001} = 7.10$ Å., and contains $4BaSO_4$. These conclusions are not in accord with those previously drawn by Allison. The data further require that the structure be based on the simple orthorhombic lattice Γ_0. A consideration of prism reflections led to the assignment of this crystal to space group V_h^{16}. The general arrangement of the four barium atoms was determined, but the two parameters defining their exact locations were not evaluated.

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