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THE CRYSTAL STRUCTURE OF MOLYBDENITE

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The mineral molybdenite, MoS_2, is described[2] as occurring in hexagonal crystals with a very complete basal cleavage. A study of its crystal structure has been carried out using X-ray spectral photographs and Laue photographs treated as previously described.[3] Since the crystals bend very easily and inelastically, some difficulty was experienced in obtaining good Laue photographs. However, the following procedure resulted in very satisfactory photographs: a crystal considerably thicker than the desired section was selected and one surface cleaved away; the cleavage face was then cemented to a cover glass and the specimen thus supported cleaved to the desired thickness and photographed without removal from the glass. A Laue photograph taken with the incident beam normal to the basal plane possessed a hexagonal axis and 6 symmetry planes. Several photographs were made with the beam somewhat inclined to this position.

The Unit of Structure

Angles of reflection of the molybdenum $K\alpha$ radiation from the faces (0001), $(10\bar{1}0)$, and $(11\bar{2}0)$ are given in Table I. The reflections from the last two faces were obtained by transmission of the beam through the crystal; in these cases the α doublet was not resolved. A density determination carried out with a pycnometer using benzene gave the value 4.92 g./cc. From this the number of molecules in a unit having $d_{0001} = 6.15$ Å. and $d_{10\bar{1}0} = 2.73$ is found to be 0.988. The axial ratio of this unit is 1.95; correspondingly the angle between the faces $(20\bar{2}1)$ and (0001) should be 77° 28.6′. Direct observations[2] have given values from 70° 28′ to 77° 13′, the last being the usually accepted value.

TABLE I

REFLECTION DATA FROM MOLYBDENITE

$h\,i\,k\,l$	λ	Observed angle of reflection	$\frac{1}{n} \times d_{hikl}$	Relative intensities	S u = 0.621
(0001)	0.7078	3° 18′	½ × 12.32	strong	5.05
....	....	6° 37′	¼ × 12.28	weak	1.27
....	....	9° 56′	⅙ × 12.32	medium	5.85
....	....	13° 19′	⅛ × 12.28	med. strong	9.17
....	....	16° 43′	1/10 × 12.30	med. weak	4.26
$(10\bar{1}0)$	0.7085	7° 27′	1/1 × 2.73	....	..
$(11\bar{2}0)$	0.7085	13° 25′	1/1 × 1.53	....	..

When indices were assigned to the Laue spots on a basis of this unit, values of $n\lambda$ as low as 0.13 Å. were found. As the minimum wave length

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[1] National Research Fellow in Chemistry.

[2] Hintze, "Handbuch der Mineralogie," Viet and Co., Leipzig, **1904**, vol. 1, p. 410.

[3] Dickinson, THIS JOURNAL, **44**, 276 (1922).

present was about 0.24 Å., this unit is not possible. A unit having d_{0001} = 12.30 Å. and an axial ratio 3.90 and containing, therefore, 2 MoS_2 gave no impossible values of $n\lambda$; this unit is the smallest one possible and all of the indices used in the remainder of this paper refer to its axes.

The Arrangement of the Atoms

Reference to a tabulation[4] of the coördinates of equivalent points in space groups isomorphous with the point-groups D_{3h}, C_{6v}, D_6, and D_{6h} shows that there is a variety of ways of arranging 2 MoS_2 in an hexagonal unit in such a way that the molybdenum atoms are in equivalent positions, and likewise the sulfur atoms. Some of these arrangements can be obtained by placing 1 MoS_2 in the smaller unit shown to be impossible. Excluding these, the following distinct arrangements remain.

	Mo at	S at
1.	$(\frac{1}{3}\frac{2}{3}0)$ $(\frac{2}{3}\frac{1}{3}0)$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{1}{3}\frac{2}{3}\bar{u})$ $(\frac{2}{3}\frac{1}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$
2.	$(00v)$ $(00\bar{v})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{1}{3}\frac{2}{3}\bar{u})$ $(\frac{2}{3}\frac{1}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$
3.	(000) $(00\frac{1}{2})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$
4.	$(00\frac{1}{4})$ $(00\frac{3}{4})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$
5.	$(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$	$(00u)$ $(00\bar{u})$ $(0,0,\frac{1}{2}+u)$ $(0,0,\frac{1}{2}-u)$
6.	$(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$

Arrangements 1 and 2 make it difficult to account for the absence of odd orders from (0001), and the absence of all first orders from planes having $\frac{1}{3}(h + 2i)$ integral and l odd. Any of the remaining arrangements accounts for the above observations.

The value of $S = \sqrt{A^2 + B^2}$ for planes having $\frac{1}{3}(h + 2i)$ not integral and l odd is always 2 $\overline{\text{Mo}}$ for Arrangement 3; therefore, at a given wave length such planes should always reflect more weakly the smaller the value of d/n. This is not at all in accord with the Laue photographic data, hence Arrangement 3 is impossible.

From (0001) the eight order was slightly stronger than the sixth and much stronger than the fourth. Assuming that a molybdenum atom has at least twice the reflecting power of a sulfur atom (the respective atomic numbers are 42 and 16) it can readily be shown that these (0001) intensities necessitate giving u a value between 0.11 and 0.15 or between 0.61 and 0.65 in Arrangements 4, 5, and 6. On Laue photographs, planes of the forms $\{31\bar{4}5\}$ and $\{31\bar{4}3\}$ were found to reflect much more strongly than $\{31\bar{4}1\}$ in spite of their smaller spacings. The value of S for these planes is given by $S = 2\,\bar{S}[\cos 2\pi(\frac{1}{3} + lu) + \cos 2\pi(\frac{1}{3} - lu)]$ for either Arrangment 4 or 5. The possible values of u make S differ only moderately for these 3 forms and never in such a way that the first 2 are both greater than the third. Hence Arrangements 4 and 5 are impossible.

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, **318** (1922).

For Arrangement 6 the values of S are given by the following equations.

Class 1: $\frac{1}{3}(h + 2i)$ integral, l even.

$$n = 1;\ S = 2\,\overline{\mathrm{Mo}} + 4(-1)^{\frac{l}{2}}\,\bar{\mathrm{S}} \cos 2\pi l\,\mathrm{u}$$

Class 2: $\frac{1}{3}(h + 2i)$ not integral, l even.

$$n = 1;\ S = \overline{\mathrm{Mo}} - 2(-1)^{\frac{l}{2}}\,\bar{\mathrm{S}}\,[\cos 2\pi(\tfrac{1}{3} + l\,\mathrm{u}) + \cos 2\pi(\tfrac{1}{3} - l\,\mathrm{u})]$$

Class 3: $\frac{1}{3}(h + 2i)$ integral, l odd.

$$n = 1;\ S = 0.$$

$$n = 2;\ S = 2\,\overline{\mathrm{Mo}} - 4\,\bar{\mathrm{S}} \cos 4\pi\, l\,\mathrm{u}$$

Class 4: $\frac{1}{3}(h + 2i)$ not integral, l odd.

$$n = 1;\ S = \sqrt{3}\,\overline{\mathrm{Mo}} + 2(-1)^{\frac{l+1}{2}}\,\bar{\mathrm{S}}\,[\cos 2\pi(\tfrac{1}{3} + l\,\mathrm{u}) - \cos 2\pi(\tfrac{1}{3} - l\,\mathrm{u})]$$

For $0.11 < \mathrm{u} < 0.15$ the calculated value of S for $\{31\bar{4}1\}$ is much greater than for $\{31\bar{4}5\}$ and $\{31\bar{4}3\}$, but is much less in the range $0.61 < \mathrm{u} < 0.65$; this range, then, contains the only possible values of u. The value of u may be more closely fixed by the consideration of other data.

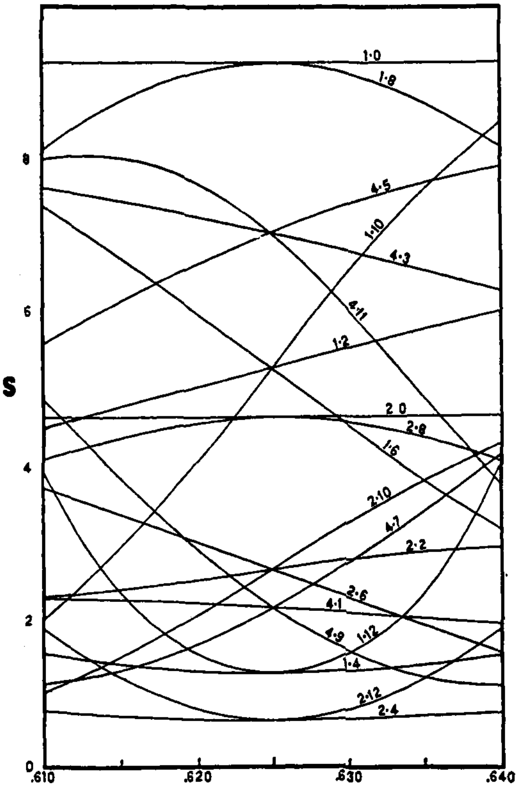

Fig. 1.—Values of S for values of u between 0.61 and 0.64 calculated for Arrangement 6, placing $\bar{\mathrm{S}} = 1$. The first number on each curve indicates the class of plane and the second the value of l. Thus 4 – 5 is the curve for any plane of Class 4 having $l = 5$.

In Fig. 1 are shown values of S for various planes plotted against values of u in the range $0.61 < \mathrm{u} < 0.65$; in the calculation of these, $\overline{\mathrm{Mo}}$ and $\bar{\mathrm{S}}$ have been taken proportional to the respective atomic numbers. It was found that $\{33\bar{6}.10\}$ reflected considerably more strongly than $\{14\bar{5}.12\}$; therefore, u is appreciably greater than 0.614. Also $\{23\bar{5}9\} \geqq \{23\bar{5}7\}$; therefore, u is probably slightly less than 0.625. From these and similar data the value of u is taken as 0.621 ± 0.004. All of the Laue photographic data treated in the above manner were found to be in agreement with the values of S calculated using u = 0.621; when, however, comparisons were made between planes of different classes, requiring a more accurate knowledge of $\overline{\mathrm{Mo}}$ and $\bar{\mathrm{S}}$, the agreement was not so good, although on the whole satisfactory. The extent of this agreement is illustrated by typical data given in Table II.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM MOLYBDENITE

Incident beam 8° 20′ from normal to (0001). Crystal thickness 0.23 mm.

h i k l	Class	$n\lambda$	*d*	Estimated intensity	*S* u = 0.621
$\bar{2}021$	4	0.37	1.36	3.2	2.17
$\bar{1}\bar{2}31$	4	.40	1.03	1.4	2.17
$3\bar{1}\bar{2}2$	2	.38	1.02	0.8	2.53
$\bar{3}213$	4	.34	1.00	6.0	7.18
$\bar{2}3\bar{1}4$	2	.37	0.98	0.15	0.64
$03\bar{3}5$	3	.37	.85	0.0	0
$4\bar{2}\bar{2}3$	3	.36	.77	0.0	0
$3\bar{4}12$	2	.38	.75	0.3	2.53
$\bar{4}225$	3	.39	.75	0.0	0
$\bar{3}\bar{1}43$	4	.36	.74	2.6	7.18
$31\bar{4}5$	4	.34	.72	2.0	6.68
$24\bar{2}7$	3	.40	.72	0.0	0
$\bar{4}316$	2	.38	.71	0.3	2.93
$\bar{1}4\bar{3}7$	4	.36	.70	0.3	1.70
$2\bar{5}33$	4	.36	.62	1.0	7.18
$5\bar{3}\bar{2}5$	4	.37	.61	1.0	6.68
$1\bar{5}43$	3	.34	.59	0.0	0
$\bar{5}237$	4	.37	.59	0.15	1.70
$\bar{1}\bar{4}54$	1	.37	.59	0.15	1.27
$\bar{5}328$	2	.37	.58	0.2	4.58
$\bar{4}\bar{1}56$	1	.37	.57	0.6	5.85
$23\bar{5}9$	4	.36	.57	0.2	2.71
$\bar{5}147$	3	.36	.56	0.0	0
$41\bar{5}8$	1	.34	.56	0.8	9.17
$\bar{4}5\bar{1}.10$	1	.34	.54	0.3	4.26
$\bar{1}5\bar{4}.12$	1	.39	.52	faint	0.72
$3\bar{6}35$	3	.36	.51	0.0	0
$2\bar{6}45$	4	.35	.50	0.3	6.68
$\bar{6}33.10$	1	.34	.48	0.15	4.26
$\bar{6}24.11$	4	.37	.47	0.2	7.58

Discussion of the Structure

The arrangement found to account for X-ray data from molybdenite is shown in Fig. 2. This arrangement is derivable from the space group D_{6h}^4 as well as from the space groups D_{3h}^4, D_6^6, C_{6h}^2, and D_{3d}^2. Considering the atoms as points or spheres, the structure then has holohedral hexagonal symmetry.

Small, very thin crystals of molybdenite may be made by fusing together ammonium molybdate, sulfur and potassium carbonate.[5] We have ex-

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[5] Guichard, *Ann. chim. phys.*, [7] **23**, 552 (1901). Hintze, Ref. 2, p. 418, also mentions trigonal artificial crystals.

amined crystals made by this method and have found them to be frequently triangular rather than hexagonal plates. Such a face development is not to be expected if the symmetry is that of the hexagonal holohedry. Several explanations of this apparent discrepancy are possible: (1) The artificial crystals may have a structure different from that of the natural mineral; satisfactory Laue photographs from the artificial crystals were not obtainable to decide this point. (2) The structure may be the same in both cases and the natural crystals twinned so as to simulate the higher symmetry; however, we have not found it possible to account for the X-ray data on this hypothesis. (3) Although the structure found has holohedral symmetry for the positions of the atoms, it may have a 3-fold symmetry axis when the shapes of the atoms or the bonds between them are considered. That this is a possible explanation follows immediately from the fact that the structure is derivable from the space group D_{3h}^4 or D_{3d}^2.

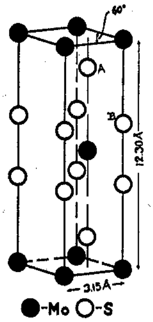

Fig. 2.—Arrangement of the atoms in molybdenite, MoS_2.

In the structure found, each sulfur atom is equidistant from 3 molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulfur atoms at the corners of a small triangular prism whose altitude is 3.17 ± 0.10 and whose edge is 3.15 ± 0.02. The distance from the molybdenum atom to these nearest sulfur atoms is then 2.41 ± 0.06. This distance is in good agreement with Bragg's hypothesis of constant atomic radii.[6] Taking the radius of molybdenum as 1.36, which is half the distance between the atoms in the metal (Wyckoff[7] has shown this to be consistent with the distances in silver molybdate, Ag_2MoO_4), and the radius of sulfur 1.05 as given by Bragg, the sum is 2.41. On the other hand, the 2 sulfur atoms marked A and B in Fig. 2, which should also be in contact on Bragg's hypothesis, are at a distance of 3.49 Å., while constant radii require 2.10. These relations are analogous to those found in cadmium iodide,[8] and in tin tetra-iodide.[9] This great distance between sulfur atoms is undoubtedly connected with the excellent basal cleavage of molybdenite.

Summary

The mineral molybdenite has been investigated by means of spectral and Laue photographs and, with the aid of the theory of space groups, the simplest structure capable of accounting for the X-ray data has been derived. This structure, which is of a new type, contains 2 MoS_2 in an hexagonal unit having d_{0001} = 12.30 Å. and an axial ratio 3.90. The molyb-

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[6] W. L. Bragg, *Phil. Mag.*, **40**, 180 (1920).

[7] Wyckoff, *Proc. Nat. Acad. Sci.*, **9**, 35 (1923).

[8] Bozorth, This Journal, **44**, 2235 (1922).

[9] Dickinson, *ibid.*, **45**, 961 (1923).

denum atoms are at $(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$ and the sulfur atoms at $(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$ where $u = 0.621 \pm 0.004$.

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NOTES

A Lecture Table Demonstration of Solubilities, or of Indicator Action.—The following procedure gives a pretty and striking lecture-table demonstration in connection with a discussion either of solubilities or of indicator action. Azolitmin, litmus, or any of the common anthocyan pigments of fruits or vegetables which are soluble in amyl alcohol when in their acid form may be used as the indicator pigment. The procedure is as follows. Place a convenient volume (25–50 cc.) of a neutral aqueous solution of the pigment in a tall, slender show glass such as a glass-stoppered cylinder or a long, slender separatory funnel, and add 4 or 5 drops of 0.1 *N* alkali (other than ammonium hydroxide). Add an equal volume of neutral amyl alcohol, shake the mixture gently and allow the liquid layers to separate. The pigment, in its alkaline color, will appear exclusively in the water layer. Add 8 or 10 drops of 0.1 *N* acid, shake and allow to separate. The pigment will now appear, in its acid color, exclusively in the alcohol layer. It is also possible, if so desired, by adding the proper amount of acid or alkali to produce exact neutrality, to get a part of the pigment in its acid color in the alcohol layer and a part in its alkaline color in the aqueous layer.

The only precaution in manipulation which is necessary is to avoid too violent shaking of the mixture, especially when alkaline, so as to break the amyl alcohol into small drops which only slowly separate from the aqueous layer.

Occasionally, by rather violent agitation, may be collected all of the alkaline pigment adsorbed at the surface interfaces of a layer of droplets between an upper clear layer of alcohol and a lower clear layer of water.

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A Post-Office Box for Keeping Analytical Weights.—A post-office box arrangement, for keeping the analytical weights used by students in quantitative analysis, was made to contain 35 small boxes provided with combination locks. The case was placed against the wall in the balance room (the back of the case being open), hung on hinges so that it might be swung out and the weights examined after every laboratory period.

The above arrangement makes it possible among other advantages to protect the weights from laboratory fumes, and to place the responsibility for the weights only upon those who use them.

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