Detailed crystal structure of rhombohedral MoS2 and systematic deduction of possible polytypes of molybdenite

Detailed Crystal Structure of Rhombohedral MoS₂ and Systematic Deduction of Possible Polytypes of Molybdenite[1])

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With 9 figures in the text and 3 tables

Abstract

The rhombohedral modification of molybdenite which was recently found in Binnatal (Switzerland) has the lattice constants: $a_0 = 3{,}166 \pm 0{,}005$ Å and $c_0 = 18{,}41 \pm 0{,}02$ Å. The space group is C_{3v}^5—$R3m$. There are three formula units in the cell. The crystal structure was investigated by Fourier methods and a trigonal prismatic coordination of Mo atoms was established. The Mo-S distances are $2{,}41 \pm 0{,}02$ Å.

Possible polytypes with simple structures were theoretically derived. The results give one rhombohedral, two hexagonal and one trigonal structures. They are respectively designated by $3R$, $2H_1$, $2H_2$ and $2T$. A comment on the stacking operations of the $2T$ structure is given.

1. Introduction

The crystal structure of molybdenite, MoS₂, was first investigated by Dickinson and Pauling (1923). It is hexagonal and the structure is characterized by MoS₂ layers in which the Mo atoms have trigonal prismatic coordination of six sulfur atoms. In 1957, Bell and Herfert artificially obtained a rhombohedral modification of MoS₂ and they proposed, by qualitative study of (00*l*) reflexions, a similar layer structure but the Mo atoms having octahedral coordination. Jellinek et al. (1960) studied synthetic rhombohedral modifications of MoS₂ and pointed out that the coordination polyhedra of the Mo atoms are trigonal

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[1]) Contr. no. 142; paper no. 9 on sulfosalts and sulfides from Binnatal (Switzerland).

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prisms. It has been reported that another possible new modification of MoS_2 was obtained by ZELIKMAN et al. (1961), though the structure of the modification has not been established.

In Nature, since the work by DICKINSON and PAULING, molybdenite seemed to exist only in the hexagonal form until quite recently GRAESER (1963) found by X-rays a non-hexagonal form of natural molybdenite in Binnatal and TRAILL (1963) identified the same modification, found in Con mine, Yellowknife, District of Mackenzie (Canada), as rhombo- · hedral.[3] GRAESER kindly gave us his material for further investigation. In view of these circumstances, it seemed worthwhile to make a theoretical derivation of possible polytypes of this particular layer structure and, on the other hand, to establish the detailed configuration of the MoS_2-layers. This investigation was undertaken as part 9 of researches on sulfides and sulfosalts from Binnatal (Part 8, see NOWACKI et al., 1963, 1964).

2. Experimental

The crystals of rhombohedral molybdenite are well developed and a suitable specimen for X-ray work was successfully prepared. It is practically free from distortion and has a cross section 0.15×0.02 mm. To minimize the effect of absorption, $MoK\alpha$ radiation ($\lambda = 0.7107$ Å) was used with Zr metal filter throughout this work. For $MoK\alpha$, the linear absorption coefficient of MoS_2 was found to be as low as 73.5 cm^{-1} (calculated from μ_a). Lattice constants found in precession photographs are:

$$a_0 = 3.166 \pm 0.005 \text{ Å}, \quad c_0 = 18.41 \pm 0.02 \text{ Å}$$

The possible space group $C_{3v}^5 - R3m$ was confirmed by the later stage of structure analysis. There are three formula units in the hexagonal cell. These lattice constants give the calculated density 4.99 ± 0.01 g/cm^{-3} which should be compared with the density 5.022 ± 0.002 g/cm^{-3} for the synthetic rhombohedral MoS_2 (BELL and HERFERT, 1957). By a chemical treatment, it has been proved that the molybdenite is practically pure MoS_2 (GRAESER, 1963).

The intensities of 104 $(h0l)$ reflections were measured from the integrated Weissenberg diagrams with the help of a Joyce-Loebl-densitometer. Transmission factors for each reflection were graphically estimated (TAKÉUCHI, 1958), by assuming a rectangular cross section.

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[3] Recently A. H. CLARK [Miner. Soc., Notice No. 126, Meeting on 30 January 1964 in London] gave a paper on "Rhombohedral molybdenite from Minas da Panasqueira, Beira Baixa, Portugal" (Occurrence in greisenized granite).

3. Analysis

There are three Mo and six S atoms in the hexagonal cell. It is, therefore, expected that they are distributed over the $3(a)$ positions of the space group. The problem ist then to determine three z-parameters of the atoms. The zero-layer reflections about one of the hexagonal a-axes were indexed based upon an oblique cell as shown in Fig. 1. The cell has the plane symmetry p_1. Calculations of structure factors and Fourier syntheses were performed on the basis of this oblique cell. The number of parameters were, then, increased to six because of lower symmetry of the cell. Indices of reflections were finally transformed to those of hexagonal axes.

A Patterson projection along one of the a-axes was first prepared by the aid of the von Eller machine. This is shown in Fig. 2. From this vector-map it is immediately seen that the Mo-atoms should have a trigonal prismatic coordination of sulfur atoms. The pairs of peaks
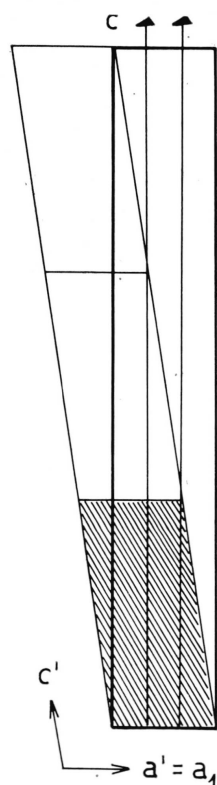

Fig. 1. The relation of the oblique cell (shaded) and rhombohedral cell as projected along the a_2-axis. The rhombohedral cell is outlined by heavy lines. Three fold axes are indicated.
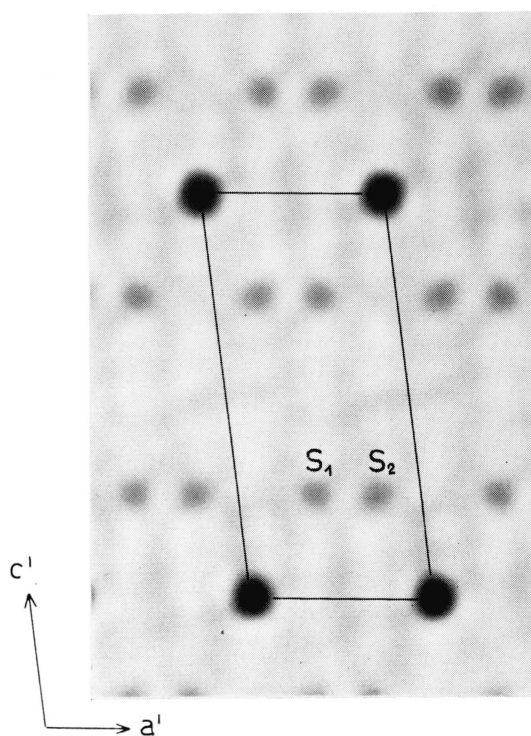
Fig. 2. Patterson projection of rhombohedral MoS₂ along a_2-axis.

Table 1. *Comparison of F_0 and F_c of rhombohedral molybdenite*

h'	k'	l'	h	l	F_0	F_c	A_c	B_c
0		1	0	3	33,7	38,2	38,2	0
		2		6	8,4	12,1	12,1	0
		3		9	30,8	31,5	31,5	0
		4		12	39,9	40,4	40,4	0
		5		15	17,1	18,4	18,4	0
		6		18	5,0	6,7	6,7	0
		7		21	11,4	19,7	19,7	0
		8		24	20,2	22,8	22,8	0
		9		27	12,0	9,2	9,2	0
1		0	1	1	27,1	28,8	24,1	−15,9
		1		4	36,6	37,9	36,7	9,3
		2		7	35,9	37,4	35,2	12,4
		3		10	18,1	21,6	19,9	−8,5
		4		13	16,8	18,9	16,4	−9,4
		5		16	22,8	24,9	23,7	7,7
		6		19	21,0	22,1	21,0	6,8
		7		22	12,7	12,9	11,2	−6,3
		8		25	10,0	11,2	10,2	−4,5
		9		28	12,2	14,6	13,8	4,8
		10		31	12,5	11,4	11,1	2,8
2		0	2	2	20,1	20,4	19,4	6,2
		1		5	29,4	31,6	28,9	−11,3
		2		8	23,4	24,3	23,8	−4,9
		3		11	17,1	17,0	13,3	10,4
		4		14	17,1	16,2	15,8	3,3
$\bar{1}$		1	$\bar{1}$	2	28,2	29,1	27,9	8,5
		2		5	39,2	41,6	38,8	−14,8
		3		8	31,1	30,8	30,2	−5,7
		4		11	20,4	20,7	16,5	12,5
		5		14	19,4	19,2	18,8	3,7
		6		17	24,0	26,6	24,5	−10,3
		7		20	17,8	17,7	17,5	−2,1
		8		23	12,9	12,5	9,7	7,8
		9		26	12,4	11,7	11,7	0,9
		10		29	14,8	14,8	13,7	5,6
		11		32	7,8	9,1	9,1	0,2
$\bar{2}$		1	$\bar{2}$	1	19,7	20,1	16,7	−11,2
		2		4	25,6	27,7	26,8	7,1
		3		7	26,9	28,9	27,2	9,9
		4		10	19,5	17,3	15,8	−7,2
		5		13	15,8	15,8	13,7	−7,9
		6		16	21,2	21,4	20,3	6,6
		7		19	19,9	19,0	18,1	5,7
		8		22	12,4	11,2	9,8	−5,4
		9		25	12,4	9,9	9,1	−3,8
		10		28	15,3	13,0	12,3	4,2
		11		31	11,3	10,2	9,9	2,4
$\bar{3}$		1	$\bar{3}$	0	27,2	28,7	28,7	−0,0
		2		3	18,1	16,4	16,4	0,0
		3		6	5,9	5,6	5,6	0,0

h = $\overline{3}$

k	l				
4	9	17,7	17,2	17,2	− 0,0
5	12	25,8	24,1	24,1	− 0,0
6	15	14,9	11,5	11,5	0,0
7	18	—	4,7	4,7	0,0
8	21	15,3	13,1	13,1	− 0,0
9	24	16,3	15,3	15,3	− 0,0

h = $\overline{4}$

k	l				
1	$\overline{1}$	11,5	10,8	9,0	6,0
2	2	14,1	11,0	10,6	− 3,2
3	5	18,7	16,7	15,6	6,1
4	8	13,4	13,3	13,1	− 2,4
5	11	9,8	9,7	7,8	5,7
6	14	10,9	9,5	9,4	1,7
7	17	14,6	13,2	12,3	− 4,9
8	20	10,3	9,3	9,2	1,0
9	23	7,2	6,9	5,6	− 3,9

h = $\overline{5}$

k	l				
1	$\overline{2}$	10,6	7,7	7,3	− 2,2
2	1	8,9	7,5	6,4	− 3,8
3	4	10,5	10,4	10,0	2,5
4	7	11,3	10,9	10,4	3,4
5	10	7,7	7,0	6,5	− 2,6
6	13	8,1	6,6	6,0	− 2,8
7	16	7,3	7,5	7,3	2,2
8	19	8,1	7,7	7,4	2,0

h = $\overline{6}$

k	l				
1	$\overline{3}$	6,1	5,9	5,9	0,0
2	0	8,2	8,1	8,1	− 0,0
3	3	5,1	4,7	4,7	0,0
4	7	—	2,2	2,2	0,0

h = 2

k	l				
5	17	21,4	22,7	21,1	− 8,7
6	20	14,5	15,4	15,3	− 1,9
7	23	11,9	10,8	8,5	6,7
8	26	10,4	10,3	10,3	0,9
9	29	13,4	13,1	12,2	− 4,9

h = 3

k	l				
0	3	18,6	16,7	16,7	− 0,0
1	6	5,6	5,6	5,6	− 0,0
2	9	16,8	16,9	16,9	0,0
3	12	22,4	24,2	24,2	0,0
4	15	13,1	11,7	11,7	− 0,0
5	18	—	4,6	4,6	− 0,0
6	21	13,0	13,0	13,0	0,0
7	24	15,3	15,3	15,3	0,0

h = 4

k	l				
0	4	16,9	14,8	14,3	3,6
1	7	18,6	15,8	14,9	5,4
2	10	12,5	9,9	9,2	− 3,8
3	13	10,7	9,2	8,1	4,4
4	16	13,2	12,3	11,8	3,5
5	19	13,1	11,4	10,9	3,3

h = 5

k	l				
0	5	13,5	11,5	10,9	− 3,9
1	8	11,3	9,5	9,3	1,8
2	11	8,1	6,8	5,7	3,7
3	14	7,1	6,9	6,8	1,2
4	17	8,5	8,5	7,9	− 2,9

h = 6

k	l				
0	6	—	2,6	2,6	− 0,0
1	9	5,1	4,9	4,9	0,0
2	12	7,0	7,0	7,0	0,0

marked by S_1 and S_2 in the map can be explained only by that particular coordination of S atoms, thus confirming the results obtained by JELLI-NEK et al. (1960). If octahedral, only one of the pair peaks should appear in the projection.

It is clear that the Mo atoms should be located at $z = 0$; the rest of the z-parameters of the S atoms found in this map were refined by Fourier methods. The final parameters for the oblique cell are:

	x'	z'
Mo	0	0
S_1	0,752	0,257
S_2	0,582	0,743

Between the z-parameters of the S atoms, $z(S_1)$ and $z(S_2)$, there should be a relation, $z(S_1) = 1 - z(S_2)$, if the MoS_2 layer has a mirror plane passing through the Mo atoms. It appeared, in the course of refinement, that the above relation was not held, but showed a deviation of about 0,003. However, the deviation was reduced to less than 0,001 at a final
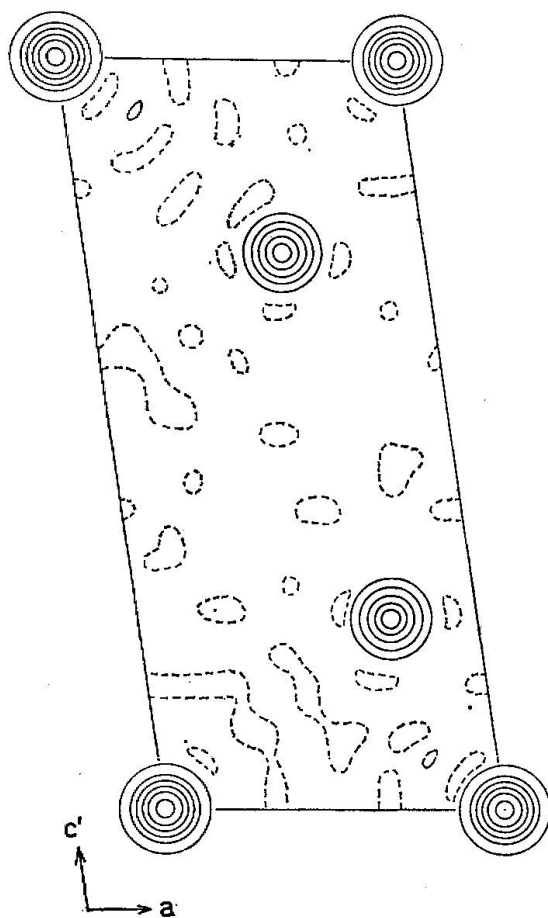

Fig. 3. Final Fourier projection of rhombohedral MoS_2. Contours are drawn at intervals of 10 e·A^{-2} for S and 30 e·A^{-2} for Mo, starting from 10 e·A^{-2}. Zero contours are shown by broken lines.

stage. Since the deviation of the x' coordinates from the threefold axes were found to be slightly less than 0,001, the above deviation in the z-parameters is not significant. The errors in coordinates, thus, do not likely to exceed more than $\pm 0,01$ for the hexagonal true cell, for which the above coordinates are expressed as:

$$\text{Mo at } 3(a) \text{ with } z = 0$$
$$\text{S}_1 \text{ at } 3(a) \text{ with } z = 0,247_7$$
$$\text{S}_2 \text{ at } 3(a) \text{ with } z = 0,419_0$$

The final coordinates give $R = 8,6\%$ for the $(h0l)$ reflections. The wrong structure with octahedral coordination gives $R = 30,4\%$. For the atomic scattering factors, approximations by VAND et al. (1957) were used with parameters later given by FORSYTH et al. (1959), and computations were performed by a Bull-machine. The temperature coefficients $B = 0,5$ were estimated by trial and error. The final Fourier map is shown in Fig. 3. Comparison of F_0's and F_c's is given in Table 1.

4. Description of the structure

The MoS₂ layers consist of trigonal prisms of MoS₆ groups. The detailed configuration of the group is shown in Fig. 4a. The dimensions of the cell edges of the trigonal prism are equal within the limits of experimental errors. Bond distances and angles found for the groups are:

Mo–S	2,41	$\pm 0,02$ Å
S₁–S₁	3,166	$\pm 0,005$
S₁–S₂	3,15	$\pm 0,02$
S₁–Mo–S₁	82,1	$\pm 0,5°$
S₁–Mo–S₂	81,8	$\pm 0,5°$

Mo–S bond distances reported for other compounds are 2,36 Å and 2,57 Å. They were found in Mo₂S₃ by an analysis of powder data (JELLINEK, 1961). The Mo atoms in this compound have distorted octahedra of S atoms. Sulfur atoms between successive layers are at close packed positions. Distances of S–S between layers are $3,50 \pm 0,02$ Å and slightly smaller than the sum of van der Waals radii. Each sulfur atom is surrounded by three S atoms and three Mo atoms (Fig. 4b).

The structure of rhombohedral MoS₂ is illustrated in Fig. 5a ($3R$) and Fig. 6a ($3R$). The difference from the hexagonal modification is merely in the way of layer stackings and it is best explained by the
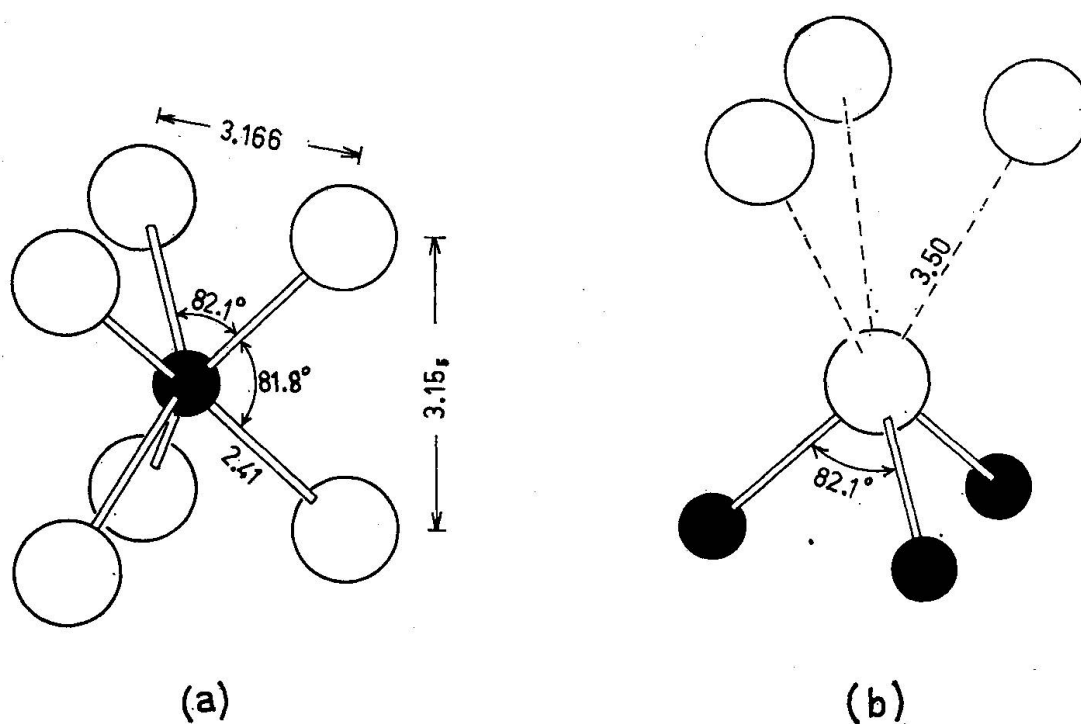
Fig. 4. (a) Configuration of MoS_6 trigonal prism.
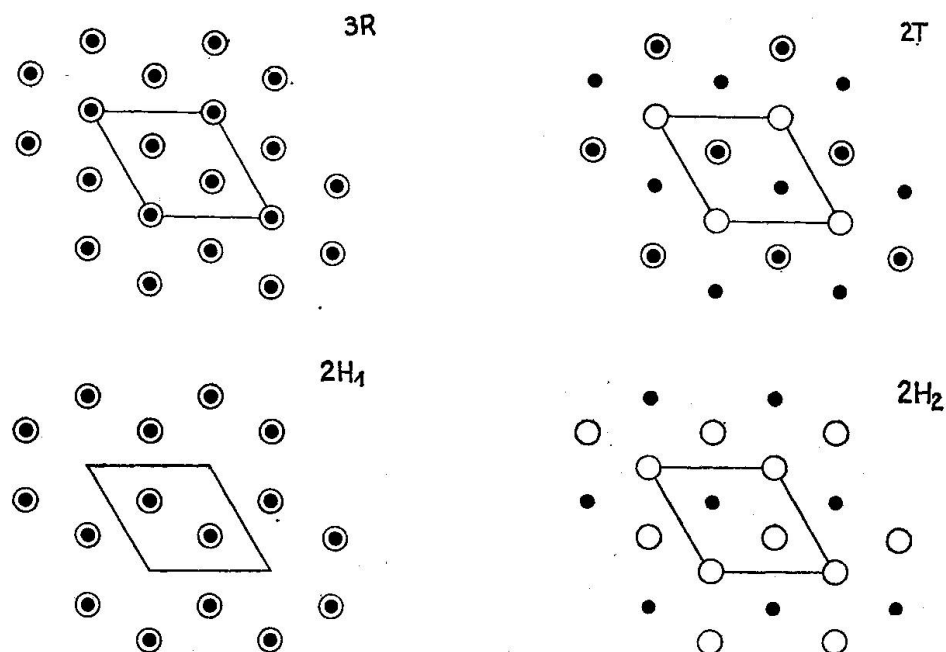(b) Surroundings of sulfur atom. Mo and S are respectively shown by solid and open circles.

Fig. 5. Structures of simple polytypes projected along the c-axis. The origin of $2H_2$ is not taken on a six-fold screw axis. To compare with Fig. 6, the origin of $2H_2$ should be shifted to ($\frac{2}{3}$, $\frac{1}{3}$, 0) and that of $2T$ to ($\frac{1}{3}$, $\frac{2}{3}$, 0). (● = Mo, o = S).

a_1-axis projection. Both structures give the same projection along the [210] axis. This is shown in Fig. 7 together with a Fourier projection obtained by 22 (hhl) reflections recorded on precession films.
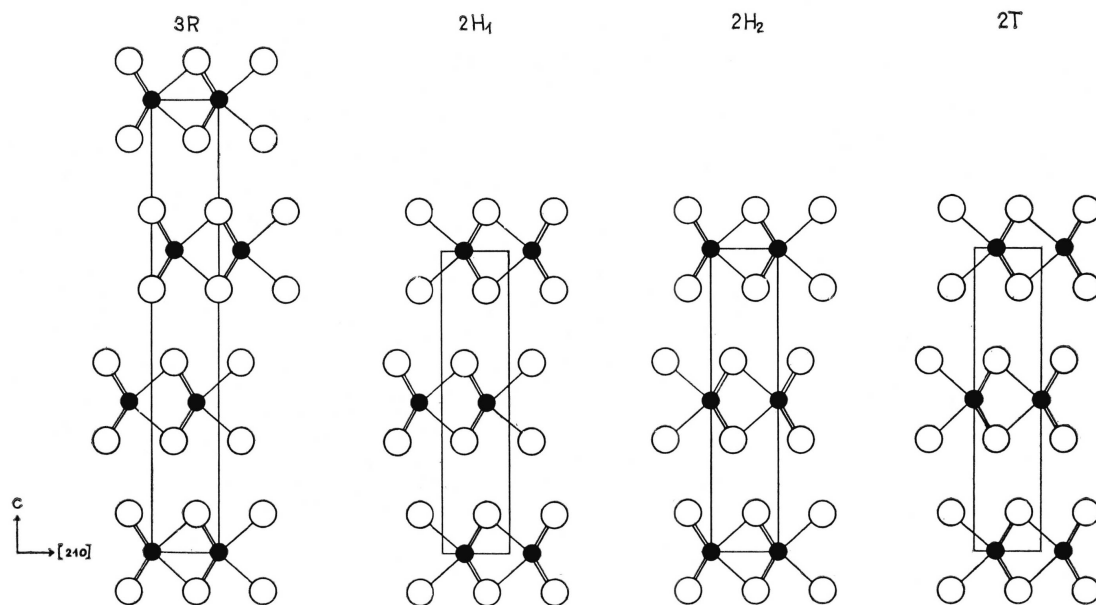

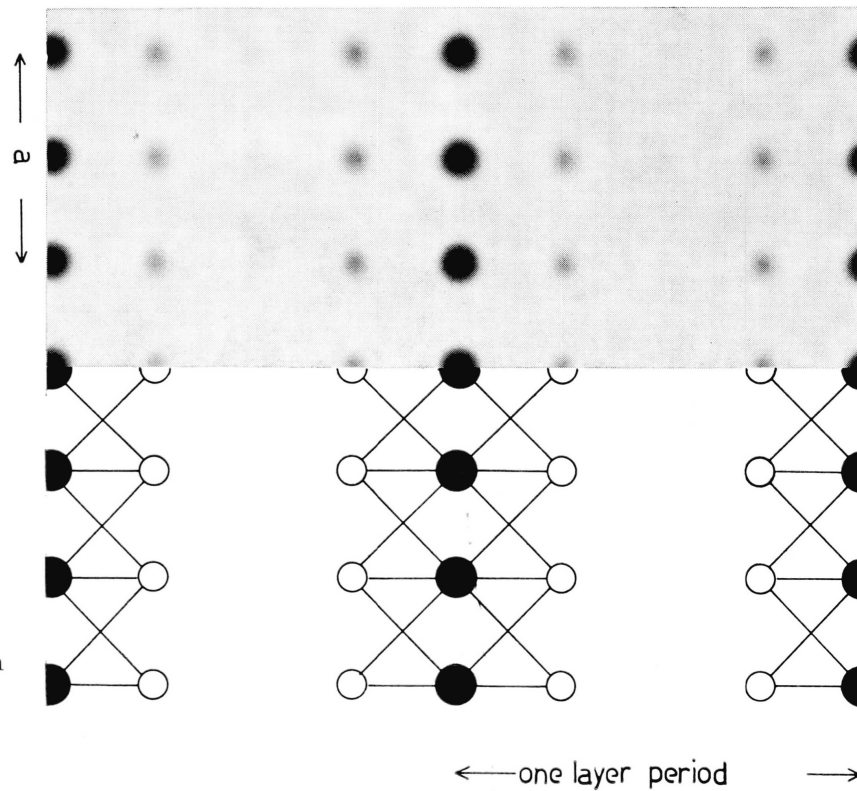Fig. 6. Structures of simple polytypes projected along the a_2-axis.

Fig. 7. Projection of rhombohedral MoS$_2$ // [210].

5. Polytypes

Rhombohedral and hexagonal structures are different only in the way of stacking of the MoS_2 layers. It is then suspected that there may be some other ways of stacking of these particular layers. To study this problem, a systematic derivation of possible polytypes of this structure was carried out.

The fundamental feature of the MoS_2 structures is the close packing of sulfur layers between two successive MoS_2 layers. A layer of MoS_2 can be brought in such a close packed position by two kinds of operations, *stacking operations*, namely *translations* and *screw operations*. Possible translation operations, T, may be expressed by the form $T_n = mt_n + t_c$, $m = 1$, 2 (mod 3), where t_n is the horizontal component of T_n (Fig. 8b), and t_c is the vertical component and equal to the one-layer period along the normal of the layers. As stacking operations, only primitive translations should be taken into account. Thus, the translations are expressed by $T_n = t_n + t_c$ where $n = 1$, 2, 3. T_1, T_2 and T_3 are equivalent by the symmetry of the MoS_2 layers.

The possible screw operations are:

axis (Fig. 8b)	rotation	translation
A	$\alpha = \pm\ 60°, 180°$	t_c
B	$\beta = \quad 180°$	t_c
C	$\gamma = \pm 120°$	t_c
D	$\delta = \pm 60°, 180°$	t_c

The structure of a polytype can be derived by a successive sequence of a stacking operation or of a combination of operations. The fundamental polytypes with ordered simple structures are those which can be derived by one kind of sequence of a stacking operation. With that condition, four polytypes are derived as follows.

1. Polytypes derived by translation operations

Among possible sequences of the translation operations, two are distinct. They are

(i) stacking sequence: T_n, $\overline{T}_n$, T_n, $\overline{T}_n$, ... (Fig. 8c)

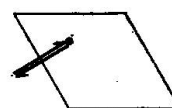The translation sequence can be rearranged in terms of translations from starting layer to each layer. This is:
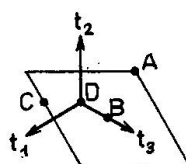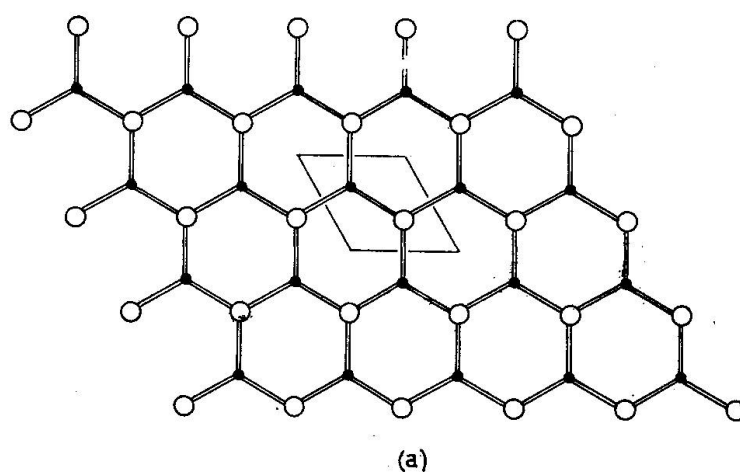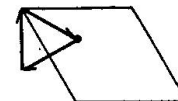
Fig. 8. One MoS₂ layer as seen along c-axis (a) and derivation of polytypes (b–e).
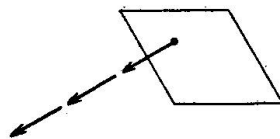
$$T_n, \; T_n \cdot \overline{T}_n, \; T_n \cdot \overline{T}_n \cdot T_n, \ldots$$
$$= [T_n, \; 2\,t_c] \bmod 2\,t_c$$

These two-layer structures have a symmetry $D^1_{3h} - P\bar{6}m2$.

(ii) The stacking sequence: $T_n, \; T_n, \; T_n, \ldots$ (Fig. 8d).

Similarly as above, the translations from the starting layer to each layer are

$$T_n, \; 2T_n, \; 3T_n, \ldots$$
$$= [T_n, \; 2T_n, \; 3\,t_c] \bmod 3\,t_c.$$

A three-layer structure with symmetry $C^5_{3v} - R3m$ results.

The spiral sequence of stacking operations like T_1, T_2, T_3, gives the same rhombohedral structure (Fig. 8e).

It can be proved by similar treatment that other possible sequences of stacking operations are equivalent to one of the above two cases.

2. Polytypes derived by screw operations

It is evident, among possible screw operations as given above, the operation at B is equivalent to that of A with $\alpha = 180°$. Therefore, operations at A, C, and D are the cases which should be considered. To derive polytypes by screw operations, generally, we have to study two cases, one is the case where rotation occurs alternatively and the other it occurs only in one direction (SADANAGA and TAKÉUCHI, 1961). The results obtained by a similar treatment as in the case of translations are:

screw operation at	alternative	one direction
A	$[A(\alpha, t_c), 2t_c] \bmod 2t_c$ $2H_1$	$[A(\alpha, t_c), 2t_c] \bmod 2t_c$ $2H_1$
C	$[C(\gamma, t_c), 2t_c] \bmod 2t_c$ $2T$	$[C(\gamma, t_c), C(\gamma, 2t_c), 3t_c] \bmod 3t_c$ $3R$
D	$[D(\delta, t_c), 2t_c] \bmod 2t_c$ $2H_2$	$[D(\delta, t_c), 2t_c] \bmod 2t_c$ $2H_2$

The polytypes derived by screw operations at C are the same with the results of translation operations. Thus, the distinct polytypes of MoS_2 with simple structures are one three layer structure and three two layer structures.

The three-layer structure is rhombohedral and has space group $C_{3v}^5 - R3m$. Two of the two-layer structures are hexagonal and have same space group $D_{6h}^4 - P6_3/mmc$, but different structures. The rest of the two-layer structures has trigonal symmetry $D_{3h}^1 - P\bar{6}m2$. For convenience, these polytypes may be designated by $3R$, $2H_1$, $2H_2$ and $2T$ respectively just like the nomenclature of polytypes of micas (SMITH and YODER, 1956). The structure of these polytypes are compared in Fig. 5 and Fig. 6.

The $2H_1$ structure is the ordinally hexagonal molybdenite found in Nature. The $3R$ whose detailed structure is descrived above is found in Nature and also obtained by synthesis. Other polytypes of MoS_2

have not been identified. However, it should be noted that the structure proposed for hexagonal NbS_2 (JELLINEK, 1960) corresponds to $2H_2$. In view of this evidence, it may be expected that MoS_2 will also be obtained in that structure.

The missing rules of reflections are identical for $2H_1$, $2H_2$ and $2T$. The „characteristic" missing rules for $D_{3h}^1 - P\bar{6}m2$ and $D_{6h}^4 - P6_3/mmc$ are different; but by „composition" of different lattice complexes (Gitterkomplexe) $D_{3h}^1 - P\bar{6}m2$ may give the same missing rules as $D_6^4 - P6_3/mmc$. In the $2T$-structure, we have the composition of Mo_1 ($\frac{1}{3}\frac{2}{3}0$) with Mo_2 ($\frac{2}{3}\frac{1}{3}\frac{1}{2}$) and of S_1 ($z = 0,1285$, $0,8715$) with S_2 ($z = 0,6285 = 0,1285 + \frac{1}{2}$, $0,3715 = 0,8715 - \frac{1}{2}$). This gives the „compositional missing rule" [Kompositionsauslöschung]: ($hh\overline{2h}l$) only for $l = 2n$ present which is „characteristic" for $D_{6h}^4 - P6_3/mmc$ (see Int. Tabellen, v. I, p. 401, 1935, I. Laue symmetry $D_{6h} - 6/mmm$, A. II. 1.; $D_{3h}^1 - P\bar{6}m2$ is a „mögliches Raumsystem"). This effect now is called „Templeton effect" (TEMPLETON, 1956; PABST, 1959, 1961), but it is just a special case of the Kompositionsauslöschungen, recognised long ago. However, these three modifications of two-layer structures of MoS_2 can be effectively identified by comparing intensities of reflections. The structure factors $F(h0l)$ are computed for these structures and compared in Table 2. To compare with the $2T$ structure, origines of $2H_1$ and $2H_2$ are not taken at centers of symmetry. As seen in Fig. 5, the frame of S atoms is the same for these three structures while only the positions of Mo are different. The calculations of structure factors were made in a similar way as for the analysis of the rhombohedral modification.

If sequences of translation operations are not unique, infinite numbers of polytypes can be derived in a theoretical sense. The situation is quite similar for other layer structures like CdJ_2 (MITCHEL, 1962) or SiC (RAMSDEL, 1947). For the case where the sequence T_n, T_n, T_n,... is interrupted by $\overline{T}_n$ with a regular interval, various rhombohedral structures are derived. For instance, in the sequence, every third T_n is replaced by $\overline{T}_n$, a nine layer rhombohedral structure ($9R$), and if every fourth T_n is replaced by $\overline{T}_n$, a $12R$ structure will result and so on. To enumerate these kinds of complex polytypes of longer c-axis periods, to the works by RAMSDEL for SiC (1947) should be referred. The sequences of translation operations can be easily correlated with RAMSDEL's notation for SiC polytypes. Combinations of screw operations give other series of complex structures.

ZELIKMAN et al. have synthetically obtained various MoS_2 by different methods (1961) and showed that some of them give powder patterns

Table 2. *Comparison of calculated structure factors $F(h\,0\,l)$ of $2H_1$, $2H_2$ and $2T$.*

h	l	$2H_1$	$2H_2$	$2T$	h	l	$2H_1$	$2H_2$	$2T$
0	4		24,2		2	0	38,2	31,1	20,3
	6		63,1			1	21,8	18,0	34,6
	8		80,9			2	22,0	46,1	23,1
	10		36,7			3	57,8	19,1	50,9
	12		13,4			4	7,4	57,8	31,5
	14		39,3			5	51,7	15,2	46,1
	16		45,6			6	22,2	38,9	19,5
						7	15,7	18,3	29,4
1	0	54,5	45,2	29,1		8	31,1	25,2	16,5
	1	31,9	25,1	49,5		9	19,6	11,5	27,2
	2	31,1	64,9	32,5		10	14,6	36,6	18,4
	3	78,3	25,1	69,3		11	43,9	15,8	38,5
	4	10,9	76,4	41,3		12	5,6	40,3	21,8
	5	66,2	18,7	59,1		13	32,7	7,8	29,6
	6	27,9	49,4	24,8					
	7	20,0	21,9	36,3	3	0		56,8	
	8	37,4	30,8	19,9		2		32,8	
	9	23,4	13,6	32,5		4		11,2	
	10	17,2	43,2	21,8		6		33,9	
	11	51,5	18,7	45,2		8		47,9	
	12	6,4	47,0	25,5		10		22,9	
	13	38,0	9,2	34,4					
	14	18,7	28,1	14,3					

These reflections are those observed on precession films by the use of Mo-radiation. The coordinates of the structures are given in Table 3.

$3R$	x	y	z
Mo	0	0	0
	$\tfrac{1}{3}$	$\tfrac{2}{3}$	$\tfrac{1}{3}$
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	$\tfrac{2}{3}$
S_1	0	0	0,2477
	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,5810
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	0,9143
S_2	0	0	0,4190
	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,7523
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	0,0856

Table 3. *Coordinates of Mo and S-atoms in the four deduced polytypes.*

$2H_1$	x	y	z
Mo	$\tfrac{1}{3}$	$\tfrac{2}{3}$	$\tfrac{1}{4}$
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	$\tfrac{3}{4}$
S	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,3785
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	$\overline{0,3785}$
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	0,8785
	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,1215

$2H_2$	x	y	z
Mo	0	0	$\tfrac{1}{4}$
	0	0	$\tfrac{3}{4}$
S	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,3785
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	$\overline{0,3758}$
	$\tfrac{2}{3}$	$\tfrac{1}{3}$	0,8785
	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,1215

$2T$	x	y	z
Mo_1	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0
Mo_2	$\tfrac{2}{3}$	$\tfrac{1}{3}$	$\tfrac{1}{2}$
S_1	0	0	0,1285
	0	0	0,8715
S_2	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,6285
	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0,3715

differing from those of $3R$ and $2H_1$. Though they concluded that these are the results of a disordering of $3R$ and $2H_1$ structures, more careful analysis is desirable to prove this hypothesis.

6. A note on the stacking operations of the 2T structure

Of the above four simple polytypes, $3R$, $2H_1$ and $2H_2$ can be derived by continuous screw operations of a MoS₂ layer in one direction, while $2T$ can not be derived in such a way. It is impressing that the stacking mechanism of layers in this polytype is completely different from those of others. However, it is possible to point out a geometrical similarity in stacking operations between $2T$ and the hexagonal structures. Namely, the $2T$ structure can also be obtained by a spiral sequence of translation operations (Fig. 9a) instead of alternative translations or alternating screw operations. The similarity of this stacking operations and hexagonal screw operations is shown in Fig. 9b, c.
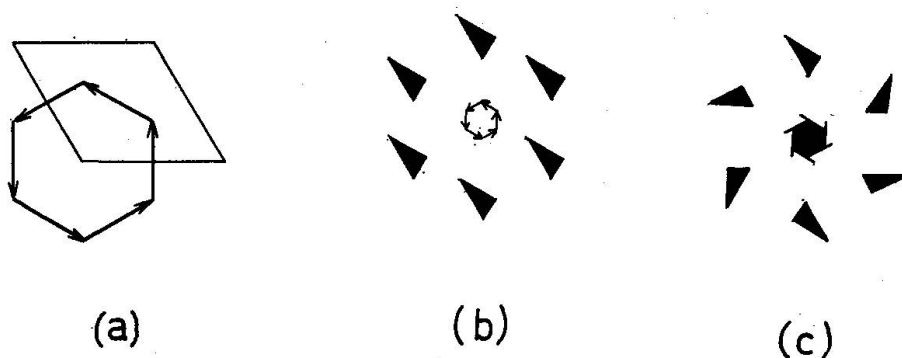

Fig. 9. Hexagonal spiral succession of translations (a). It is expressed in the similar way of screw axis (b) and compared with 6_1 (c).

This kind of spiral arrangement of translations is, in reality, an inherent property of the lattice structures and occurs in any crystal lattice. The point, however, which should be noted here, is that the individual translations in the stacking operations in $2T$ are not lattice translations, but only the products of two successive translations belong to the lattice translations.

possibility of calculation on the Bull-Gamma-machine and Mr. St. Graeser for the rhómbohedral molybdenite specimen.

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