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MOLYBDENITE POLYTYPES IN THEORY AND OCCURRENCE. I. THEORETICAL CONSIDERATIONS OF POLYTYPISM IN MOLYBDENITE

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Abstract

The 112 theoretically possible polytypes of molybdenite with less than seven layers have been derived. They distribute themselves as follows: 2 layers—3; 3 layers—2; 4 layers—10; 5 layers—16; 6 layers—81. The intensities of the reflections in the X-ray powder patterns for 48 of these polytypes have been calculated.

Introduction

Molybdenite (MoS_2) is hexagonal with a well-established crystal structure determined as early as 1923 by Dickinson and Pauling. Great interest was aroused when Bell and Herfert (1957) synthesized a rhombohedral modification, which later was reported by Traill (1963) from a natural occurrence at the Con mine, Yellowknife, District of Mackenzie, Canada. Takéuchi and Nowacki (1964) determined the atomic arrangement of rhombohedral MoS_2, showing that the two modifications differ only in the way the MoS_2-layers are stacked.

These discoveries suggested the possible existence of other MoS_2 polytypes in nature, and potential relationships between polytype and chemical composition, mode of occurrence, and similar problems. The present paper is a contribution to this general field.

Method of Derivation of the Polytypes

After showing that the two natural modifications of molybdenite known to date differed only in the way the MoS_2-layers were stacked, Takéuchi and Nowacki (1964) derived the simple polytypes, *i.e.* those which could be obtained by using only one of the two stacking operations: screws and translations. They found, using Ramsdell's (1947) nomenclature, three 2-layer structures, $2H_1$, $2H_2$, $2T$; and one 3-layer structure, $3R$. (See comments on the nomenclature on p. 1846.)

Independently, Zvyagin and Soboleva (1967) derived those polytypes which satisfy what in the cover-to-cover translation is called "the conditions of periodicity and uniformity". They found five structurally distinct polytypes: those mentioned above and one 6-layer structure, which shall be called 6*R*.

An extensive investigation of molybdenite seemed in order to establish those polytypes which existed in nature. The best way to examine each sample would be by single crystal X-ray techniques, but most molybdenite is not suitable for single crystal study. It thus was necessary to resort to powder diffraction techniques. In order to use powder methods effectively, it was considered useful to calculate the intensity distributions that would be expected for each of the possible polytypes. Because of the possibility of mixtures of two and three layer polytypes giving patterns resembling six layer polytypes, it was necessary to generate the six layer polytypes and calculate their powder intensities also. The generation of these polytypes and their powder patterns is the subject of Part I of this present investigation. In Part II the examination of natural samples is described.

The molybdenite polytypes are derived by stacking the double layers of MoS_2 in different sequences following the rules of close-packed structures. Within an individual double layer the Mo atoms are surrounded by six S atoms forming a trigonal prism. The idealized layer can be visualized as a net constructed from these prisms. Figure 1 shows a part of such a layer in projection with the S atoms located at the corners of the triangles in the projection, one above and one below the plane. All the Mo atoms are in the plane and occupy the center of either all shaded or all white triangles. The S atoms of a layer thus form two sheets where

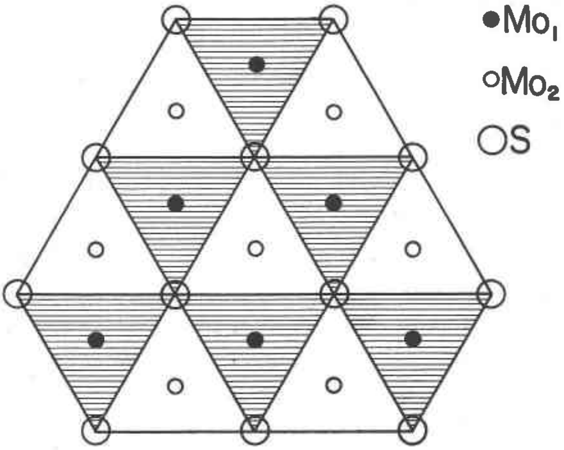

FIG. 1. Projection of one layer of the molybdenite structure. The three possible origins are the S position and the two Mo positions.

the S atoms are exactly above each other and the double layer, therefore, can be treated as a single unit in a discussion of stacking sequences.

To describe the arrangements the designations A, B and C will be used for three possible (x,y)-positions of the S sheets. These positions are shown in the column of the S positions in the table below. In the same way α,β and γ refer to the three possible positions of the Mo sheets, and they are given in the column of Mo positions in the table. A complete layer can therefore be written symbolically as a Greek letter between two identical Latin letters, *e.g.* $A\beta A$. The two possible positions of the Mo atoms for a given S position are such that the Greek and Latin letter cannot be equivalent. The six possible kinds of stacking layers are as shown:

Short symbol of layer	*Complete symbol of layer*	*Mo position*	*S positions*
A_1	$A\beta A$	$\frac{1}{2}\ \frac{2}{3}\ 0$	$00, \pm z$
A_2	$A\gamma A$	$\frac{2}{3}\ \frac{1}{3}\ 0$	$00, \pm z$
B_1	$B\gamma B$	$\frac{2}{3}\ \frac{1}{3}\ 0$	$\frac{1}{3}\ \frac{2}{3}, \pm z$
B_2	$B\alpha B$	$0\ 0\ 0$	$\frac{1}{3}\ \frac{2}{3}, \pm z$
C_1	$C\alpha C$	$0\ 0\ 0$	$\frac{2}{3}\ \frac{1}{3}, \pm z$
C_2	$C\beta C$	$\frac{1}{3}\ \frac{2}{3}\ 0$	$\frac{2}{3}\ \frac{1}{3}, \pm z$

where z indicates that the S atoms are not in the same plane as the Mo atoms; the absolute distance between the planes is 1.5775 Å according to Takéuchi and Nowacki (1964).

There are several methods which can be used in the derivation of the n-layer polytypes. In this paper all possible sequences will be considered and identical or impossible stackings are eliminated by the following rules.

(1) *Adjacent layers in a stacking must have different letters; the sequences* AA, BB *and* CC *are forbidden.* This rule is a direct consequence of the atomic arrangment in the two known polytypes.

(2) *Any layer can be used as the first layer of the* N*-layer unit.*

(3) *The* N*-layer unit can be read both from the left to the right and from the right to the left.*

Rules (2) and (3) follow from the observation that no layer differs from any other layer; they are all alike.

(4) *Two stackings are identical if one can be obtained from the other by permutation of the letters* A, B *and* C *without changing the subscripts of the short symbols.* The origin of the unit cell can be chosen in several ways in a layer. The rule follows from the observation that translations $+(\frac{1}{3}\ \frac{2}{3}\ 0)$ and $+(\frac{2}{3}\ \frac{1}{3}\ 0)$ give two other possible origins.

(5) *Two stackings are identical if they can be transformed into each other by the rules*

$$A_1 \rightarrow A_2 \qquad B_1 \rightarrow C_2 \qquad C_1 \rightarrow B_2$$
$$A_2 \rightarrow A_1 \qquad B_2 \rightarrow C_1 \qquad C_2 \rightarrow B_1$$

This rule is based on the observation that a 120° rotation around the c-axis gives identity, whereas a rotation of 60° gives an alternative description.

Using the Greek letters α, β and γ as defined above, the positions of the Mo atoms of two adjacent layers can be expressed by a combination of two letters. It is seen then that there are two different kinds of arrangements, since the letters can be the same, *e.g.* $\alpha\alpha$, or different, *e.g.* $\alpha\beta$. An arrangement such as $\alpha\alpha$ means that the Mo atoms are above each other and that the interatomic distance is shorter than in the arrangement $\alpha\beta$. The following sequences have the metal atoms above each other: A_1C_2, A_2B_1, and B_2C_1. Those stackings where the Mo atoms occur above each other will be indicated by a number in parentheses after the period. In the following polytype derivations and listings the stacking sequence will always begin with an A_1-layer.

THE 2-LAYER POLYTYPES

The following stackings are possible: A_1B_1; A_1B_2; A_1C_1; and $A_1C_2(1)$. According to the rules, A_1B_1 and A_1C_1 are identical. The three remaining polytypes are the same as the simple polytypes derived by Takéuchi and Nowacki (1964). A_1B_2 is their $2H_1$[1], and $A_1C_2(1)$ is their $2H_2$; both having space group $P6_3/mmc$–$D^4_{6h}\cdot A_1B_1$ is their $2T$; space group $P\bar{6}m2 - D^1_{3h}$. This polytype presents a problem of nomenclature, because the $\bar{6}$ axis is considered as hexagonal by most crystallographers and the space group is listed in the International Tables as hexagonal. It is suggested that this polytype be renamed $2H_3$, because (1) it is consistent with current usage; (2) no synthetic or natural example is known, so little confusion will arise; and (3) the nomenclature of the International Tables is followed for the 6-layer polytypes. Inconsistencies would result, therefore, if the name remained unchanged. The coordinates of the polytypes are given in Table 1.

THE 3-LAYER POLYTYPES

The following 3-layer stackings are possible:

$A_1B_1C_1$	$A_1B_2C_1$	$A_1C_1B_1$	$A_1C_2B_1$
$A_1B_1C_2$	$A_1B_2C_2$	$A_1C_1B_2$	$A_1C_2B_2$.

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[1] The sulfur coordinates in Table 3 of the paper by Takeuchi and Nowacki contain printing errors; the projection in their Figure 6 is correct.

TABLE 1. THE 2-LAYER POLYTYPES OF MOLYBDENITE[a]

Space group	Polytype	Atomic positions	
		Mo	S
$P6_3/mmc-D^4_{6h}$	A_1B_2 $(=2H_1)$	2 (*c*)	4 (*f*); 0.8785
	$A_1C_2(1)$ $(=2H_2)$	2 (*b*)	4 (*f*); 0.8785
$P\bar{6}m2-D^1_{3h}$	A_1B_1 $(-2H_3)$[b]	1 (*c*) 1 (*f*)	2 (*g*); 0.1285 2 (*h*); 0.6285

[a] The atomic positions refer to the International Tables; the number following the position is the parameter value.

[b] The polytype $2H_3$ is the polytype $2T$ of Takéuchi and Nowacki (1964).

The application of the rules reduces this number to only two: $A_1B_1C_1$ and $A_1B_1C_2$ (1). $A_1B_1C_1$ is the $3R$ polytype of Takéuchi and Nowacki; space group $R3m-C^5_{3v}$. $A_1B_1C_2$ (1) will be called $3T$; space group $P3m1-C^1_{3v}$. This polytype is not cited by Takéuchi and Nowacki or Zvyagin and Soboleva (1967). See Table 2 for coordinates of the two polytypes.

THE 4-LAYER POLYTYPES

Since no diffraction pattern in the investigated material indicated

TABLE 2. THE 3-LAYER POLYTYPES OF MOLYBDENITE[a]

Space group	Polytype	Atomic positions	
		Mo	S
$R3m-C^5_{3v}$	$A_1B_1C_1$ $(=3R)$	3 (*a*); 0	3 (*a*); 0.7523 3 (*a*); 0.5811
$P3ml-C^1_{3v}$	$A_1B_1C_2$ $(=3T)$	1 (*a*); 0.3333 1 (*a*); 0.6667 1 (*b*); 0	1 (*a*); 0.0856 1 (*a*); 0.9144 1 (*b*); 0.4189 1 (*b*); 0.2477 1 (*c*); 0.7523 1 (*c*); 0.5811

[a] The atomic positions refer to the International Tables; the number following the position is the parameter value.

a 4-layer structure, no detailed presentation of the 4-layer structures will be given here. The ten different stackings are:

1. $A_1B_1C_1B_1$
2. $A_1B_1C_1B_2(1)$
3. $A_1B_1C_2B_1$
4. $A_1B_1C_2B_2$
5. $A_1B_1A_1B_2$
6. $A_1B_1A_1C_2(2)$
7. $A_1B_1A_2C_2(2)$
8. $A_1B_1A_2B_1(2)$
9. $A_1B_2A_1C_2(2)$
10. $A_1B_2A_2B_1(1)$

The 5-layer Polytypes

No diffraction pattern in the material studied indicated a 5-layer structure. The 16 different polytypes are listed without further details:

1. $A_1B_1C_1B_1C_1$
2. $A_1B_1C_1B_2C_1(2)$
3. $A_1B_1C_2B_1C_1$
4. $A_1B_1C_2B_2C_1(1)$
5. $A_1B_1A_1B_2C_1(1)$
6. $A_1B_1A_1C_2B_1(1)$
7. $A_1B_1A_2C_2B_1(1)$
8. $A_1B_2A_1C_2B_1(1)$
9. $A_1B_1C_1B_2C_2(2)$
10. $A_1B_1C_2B_1C_2(1)$
11. $A_1B_1C_2B_2C_2(1)$
12. $A_1B_1A_2B_1C_2(3)$
13. $A_1B_2A_2B_1C_2(2)$
14. $A_1B_1C_2A_2C_1$
15. $A_1B_1C_1A_2B_1(1)$
16. $A_1B_1C_2A_1C_2(3)$

The 6-layer Polytypes

Because preliminary X-ray diffraction patterns indicate possible 6-layer structures might be present in the natural samples the 81 possible stackings have been derived. In Tables 3 and 4 these polytypes are listed according to space group and number of Mo atoms in adjacent layers above each other. The atomic positions are given for the 43 polytypes of higher symmetry in Table 3, whereas only the layer sequence has been listed for the 38 polytypes in Table 4. The latter belong to space group $P3m1-C^1_{3v}$, and the atoms must be in one-fold positions [(a) $0\ 0\ z$; (b) $\frac{1}{3}\ \frac{2}{3}\ z$; (c) $\frac{2}{3}\ \frac{1}{3}\ z$]. The atomic coordinates are easily derived from the stacking sequence, and it thus is not necessary to prepare a detailed list.

Calculation of Powder Pattern Intensities for the Theoretical Polytypes

Using the derived sets of atomic coordinates, it is possible to calculate the expected intensities to be observed in an X-ray powder pattern for each polytype. These patterns may then be used as standards for comparison with the measured patterns, thus making it a relatively easy task to identify individual polytypes and even mixtures. The standard

TABLE 3. SIX-LAYER POLYTYPES OF MOLYBDENITE NOT BELONGING TO SPACE GROUP $P3ml-C^1_{3v}$

The atomic positions refer to the International Tables; the number following the position is the parameter value.

Space group	Polytype	Atomic positions				
		Mo		S		
$P6_3/mmc-D^4_{6h}$	$A_1B_1A_1B_2A_2B_2$ $(=6H_1)$	2 (*b*) 4 (*f*); 1/12		4 (*f*);0.293	4 (*f*);0.960	4 (*f*);0.874
$P\bar{6}m2-D^1_{3h}$	$A_1B_1C_1B_1C_1B_1$ $(=6H_2)$	1 (*c*) 1 (*f*)	2 (*g*); 1/3 2 (*i*); 1/6	2 (*g*);0.043 2 (*h*);0.543	2 (*h*);0.210 2 (*h*);0.124	2 (*i*);0.376 2 (*i*);0.290
	$A_1B_1C_2B_1C_2B_1$ $(=6H_3)$	1 (*c*) 1 (*f*)	2 (*h*); 1/3 2 (*i*); 1/6	2 (*g*);0.043 2 (*h*);0.543	2 (*h*);0.210 2 (*h*);0.124	2 (*i*);0.376 2 (*i*);0.290
	$A_1B_1C_2B_2C_2B_1$ $(=6H_4)$	1 (*b*) 1 (*c*)	2 (*h*); 1/3 2 (*i*); 1/6	2 (*g*);0.043 2 (*h*);0.543	2 (*h*);0.210 2 (*h*);0.124	2 (*i*);0.376 2 (*i*);0.290
	$A_1B_1C_1B_1A_1B_1$ $(=6H_5)$	1 (*a*) 1 (*d*)	2 (*h*); 1/6 2 (*i*); 1/3	2 (*g*);0.376 2 (*g*) 0.290	2 (*h*);0.043 2 (*h*);0.543	2 (*i*);0.124 2 (*i*);0.210
	$A_1B_1C_1B_1A_1B_2$ $(=6H_6)$	1 (*a*) 1 (*b*)	2 (*h*); 1/6 2 (*i*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*i*);0.124	2 (*i*);0.210 2 (*i*);0.543
	$A_1B_1C_2B_1A_1B_1$ $(=6H_7)$	1 (*d*) 1 (*e*)	2 (*h*); 1/6 2 (*i*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*i*);0.124	2 (*i*);0.210 2 (*i*);0.543
	$A_1B_1C_2B_1A_1B_2$ $(=6H_8)$	1 (*b*) 1 (*e*)	2 (*h*); 1/6 2 (*i*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*i*);0.124	2 (*i*);0.210 2 (*i*);0.543
	$A_1B_1A_1B_2A_1B_1$ $(=6H_9)$	1 (*b*) 1 (*c*)	2 (*h*); 1/3 2 (*i*); 1/6	2 (*g*);0.043 2 (*g*);0.290	2 (*g*);0.376 2 (*h*);0.124	2 (*h*);0.210 2 (*h*);0.543
	$A_1B_1A_1B_2A_1B_2$ $(=6H_{10})$	1 (*c*) 1 (*f*)	2 (*g*); 1/6 2 (*h*); 1/3	2 (*g*);0.043 2 (*g*);0.290	2 (*g*);0.376 2 (*h*);0.124	2 (*h*);0.210 2 (*h*);0.543
	$A_1B_1C_1B_1A_1C_1$ $(=6H_{11})$	1 (*a*) 1 (*b*)	2 (*h*); 1/6 2 (*i*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*h*);0.543	2 (*i*);0.124 2 (*i*);0.210
	$A_1B_1C_2B_1A_1C_1$ $(=6H_{12})$	1 (*b*) 1 (*e*)	2 (*h*); 1/6 2 (*i*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*h*);0.543	2 (*i*);0.124 2 (*i*);0.210
	$A_1B_2C_2B_2A_1C_1$ $(=6H_{13})$	1 (*b*) 1 (*e*)	2 (*g*); 1/6 2 (*i*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*h*);0.543	2 (*i*);0.124 2 (*i*);0.210
	$A_1B_1C_1B_2C_1B_1$ (2) $(=6H_{14})$	1 (*b*) 1 (*c*)	2 (*g*); 1/3 2 (*i*); 1/6	2 (*g*);0.043 2 (*h*);0.124	2 (*h*);0.210 2 (*h*);0.543	2 (*i*);0.290 2 (*i*);0.376
	$A_1B_1A_1B_2C_1B_2$ (2) $(=6H_{15})$	1 (*a*) 1 (*f*)	2 (*g*); 1/6 2 (*h*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.210 2 (*h*);0.543	2 (*h*);0.124 2 (*i*);0.043
	$A_1B_1A_1C_2B_1C_2$ (2) $(=6H_{16})$	1 (*a*) 1 (*b*)	2 (*h*); 1/6 2 (*h*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*h*);0.543	2 (*i*);0.124 2 (*i*);0.210
	$A_1B_2A_1C_2B_1C_2$ (2) $(=6H_{17})$	1 (*b*) 1 (*e*)	2 (*h*); 1/6 2 (*h*); 1/3	2 (*g*);0.290 2 (*g*);0.376	2 (*h*);0.043 2 (*h*);0.543	2 (*i*);0.124 2 (*i*);0.210

TABLE 3—(*Continued*)

Space group	Polytype	Atomic positions				
		Mo		S		
$P\bar{6}m2-D^1_{3h}$	$A_1B_1C_2A_1C_2B_1$ (2)	1 (*a*)	2 (*g*); 1/6	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.124
	$(=6H_{18})$	1 (*b*)	2 (*i*); 1/3	2 (*g*); 0.376	2 (*h*); 0.543	2 (*i*); 0.210
	$A_1B_1C_1B_1A_1C_2$ (2)	1 (*a*)	2 (*h*); 1/6	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.124
	$(=6H_{19})$	1 (*f*)	2 (*i*); 1/3	2 (*g*); 0.376	2 (*h*); 0.543	2 (*i*); 0.210
	$A_1B_1C_2B_1A_1C_2$ (2)	1 (*a*)	2 (*g*); 1/6	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.124
	$(=6H_{20})$	1 (*b*)	2 (*h*); 1/3	2 (*g*); 0.376	2 (*h*); 0.543	2 (*i*); 0.210
	$A_1B_1A_1C_2A_1B_1$ (2)	1 (*a*)	2 (*g*); 1/6	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.210
	$(=6H_{21})$	1 (*b*)	2 (*h*); 1/3	2 (*g*); 0.376	2 (*i*); 0.124	2 (*i*); 0.543
	$A_1B_1A_1C_2A_2C_2$ (2)	1 (*a*)	2 (*h*); 1/6	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.210
	$(=6H_{22})$	1 (*b*)	2 (*h*); 1/3	2 (*g*); 0.376	2 (*i*); 0.124	2 (*i*); 0.543
	$A_1B_1A_2B_1A_1B_1$ (2)	1 (*e*)	2 (*h*); 1/3	2 (*g*); 0.043	2 (*g*); 0.376	2 (*i*); 0.210
	$(=6H_{23})$	1 (*f*)	2 (*i*); 1/6	2 (*g*); 0.290	2 (*h*); 0.124	2 (*i*); 0.543
	$A_1B_1A_2B_1A_1B_2$ (2)	1 (*b*)	2 (*h*); 1/3	2 (*g*); 0.043	2 (*g*); 0.376	2 (*k*); 0.210
	$(=6H_{24})$	1 (*e*)	2 (*i*); 1/6	2 (*g*); 0.290	2 (*h*); 0.124	2 (*h*); 0.543
	$A_1B_2A_1C_2A_1B_2$ (2)	1 (*a*)	2 (*g*); 1/6	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.210
	$(=6H_{25})$	1 (*b*)	2 (*i*); 1/3	2 (*g*); 0.376	2 (*i*), 0.124	2 (*i*); 0.543
	$A_1B_2A_1C_2A_2C_2$ (2)	1 (*a*)	2 (*h*); 1/6	2 (*g*); 0.124	2 (*g*); 0.543	2 (*i*); 0.290
	$(=6H_{26})$	1 (*f*)	2 (*h*); 1/3	2 (*g*); 0.210	2 (*h*); 0.043	2 (*i*); 0.376
	$A_1B_1A_2B_2A_2B_1$ (2)	1 (*b*)	2 (*i*); 1/6	2 (*g*); 0.043	2 (*g*); 0.376	2 (*h*); 0.210
	$(=6H_{27})$	1 (*c*)	2 (*i*); 1/3	2 (*g*); 0.290	2 (*h*); 0.124	2 (*h*); 0.543
	$A_1B_1A_1C_2B_2C_2$ (2)	1 (*b*)	2 (*h*); 1/6	2 (*g*); 0.124	2 (*h*); 0.043	2 (*i*); 0.290
	$(=6H_{28})$	1 (*e*)	2 (*h*); 1/3	2 (*g*); 0.210	2 (*h*); 0.543	2 (*i*); 0.376
	$A_1B_1A_1C_2A_1C_2$ (4)	1 (*c*)	2 (*h*); 1/6	2 (*g*); 0.043	2 (*g*); 0.376	2 (*i*); 0.124
	$(=6H_{29})$	1 (*f*)	2 (*h*); 1/3	2 (*g*); 0.290	2 (*h*); 0.543	2 (*i*); 0.210
	$A_1B_1A_2B_1A_1C_2$ (4)	1 (*d*)	2 (*h*); 1/3	2 (*g*); 0.043	2 (*g*); 0.376	2 (*h*); 0.210
	$(=6H_{30})$	1 (*e*)	2 (*i*); 1/6	2 (*g*); 0.290	2 (*h*); 0.124	2 (*i*), 0.543
	$A_1B_1A_2B_1A_2B_1$ (4)	1 (*d*)	2 (*i*); 1/6	2 (*g*); 0.124	2 (*g*); 0.543	2 (*h*); 0.290
	$(=6H_{31})$	1 (*e*)	2 (*i*); 1/3	2 (*g*); 0.210	2 (*h*); 0.043	2 (*h*); 0.376
	$A_1B_2A_1C_2A_1C_2$ (4)	1 (*a*)	2 (*h*); 1/6	2 (*g*); 0.124	2 (*g*); 0.543	2 (*i*); 0.290
	$(=6H_{32})$	1 (*d*)	2 (*h*); 1/3	2 (*g*); 0.290	2 (*h*); 0.043	2 (*i*); 0.376
	$A_1B_2C_1B_2A_1C_2$ (4)	1 (*a*)	2 (*g*); 1/6	2 (*g*); 0.290	2 (*h*); 0.124	2 (*i*); 0.043
	$(=6H_{33})$	1 (*d*)	2 (*h*); 1/3	2 (*g*); 0.376	2 (*h*); 0.210	2 (*i*); 0.543
$P6_3mc-C^4_{6v}$	$A_1B_1C_2B_2A_2C_1$	2 (*a*); 1/3	2 (*b*); 2/3	2 (*a*); 0.043	2 (*b*); 0.124	2 (*b*); 0.790
	$(=6H_{34})$	2 (*b*); 0		2 (*a*); 0.957	2 (*b*); 0.290	2 (*b*); 0.876
	$A_1B_1C_1B_2A_2C_2$ (2)	2 (*a*); 1/6	2 (*b*); 5/6	2 (*a*); 0.043	2 (*b*); 0.290	2 (*b*); 0.624
	$(=6H_{35})$	2 (*b*); 0		2 (*a*); 0.957	2 (*b*); 0.376	2 (*b*); 0.790

TABLE 3—(*Continued*)

Space group	Polytype	Atomic positions	
		Mo	S
$R\bar{3}m-D^5_{3d}$	$A_1B_1C_1A_2B_1C_2$ (3) (=$6R$)	6 (*c*); 1/12	6 (*c*); 0.207 6 (*c*); 0.293
$P3m1-D^3_{3d}$	$A_1B_1C_2A_2C_1B_2$ (2) (=$6T_1$)	2 (*c*); 5/12 2 (*d*); 11/12 2 (*d*); 1/4	2 (*c*); 0.207 2 (*d*); 0.040 2 (*d*); 0.374 2 (*c*); 0.293 2 (*d*); 0.126 2 (*d*); 0.460
	$A_1B_2A_2B_1A_1B_2$ (1) (=$6T_2$)	2 (*c*); 5/12 2 (*d*); 11/12 2 (*d*); 1/4	2 (*d*); 0.040 2 (*d*); 0.374 2 (*d*); 0.707 2 (*d*); 0.126 2 (*d*); 0.460 2 (*d*); 0.793
	$A_1B_1C_1A_2B_2C_2$ (1) (=$6T_3$)	2 (*c*); 1/12 2 (*d*); 3/4 2 (*d*); 5/12	2 (*c*); 0.207 2 (*d*); 0.040 2 (*d*); 0.541 2 (*c*); 0.293 2 (*d*); 0.126 2 (*d*); 0.627
	$A_1B_1C_2A_1B_2C_2$ (2) (=$6T_4$)	2 (*c*); 1/12 2 (*d*); 3/4 2 (*c*); 5/12	2 (*c*); 0.207 2 (*d*); 0.040 2 (*d*); 0.541 2 (*c*); 0.293 2 (*d*); 0.126 2 (*d*); 0.627
	$A_1B_1C_2A_2B_1C_2$ (2) (=$6T_5$)	2 (*d*); 1/4 2 (*d*); 11/12 2 (*d*); 5/12	2 (*c*); 0.207 2 (*d*); 0.040 2 (*d*); 0.541 2 (*c*); 0.293 2 (*d*); 0.126 2 (*d*); 0.627
	$A_1B_2A_2B_1A_2B_1$ (3) (=$6T_6$)	2 (*c*); 1/4 2 (*d*); 11/12 2 (*c*); 5/12	2 (*d*); 0.040 2 (*d*); 0.374 2 (*d*); 0.707 2 (*d*); 0.126 2 (*d*); 0.460 2 (*d*); 0.793
	$A_1B_2C_1B_1A_2C_2$ (3) (=$6T_7$)	2 (*c*); 5/12 2 (*d*); 11/12 2 (*d*); 3/4	2 (*c*); 0.207 2 (*d*); 0.040 2 (*d*); 0.374 2 (*c*); 0.293 2 (*d*); 0.126 2 (*d*); 0.460

TABLE 4. SIX LAYER POLYTYPES OF MOLYBDENITE BELONGING TO SPACE GROUP $P3m1-C^1_{3v}$

Polytype	Ramsdell symbol	Polytype	Ramsdell symbol
$A_1B_1C_2B_1C_1B_1$	$6T_8$	$A_1B_1C_1B_2A_1C_1$ (1)	$6T_{27}$
$A_1B_1C_2B_1C_2B_2$	$6T_9$	$A_1B_1C_1A_1B_2C_2$ (1)	$6T_{28}$
$A_1B_1C_2B_2C_2B_2$	$6T_{10}$	$A_1B_1C_2B_2C_1B_2$ (2)	$6T_{29}$
$A_1B_1C_2A_2C_1B_1$	$6T_{11}$	$A_1B_1A_2C_2B_1C_2$ (2)	$6T_{30}$
$A_1B_1A_1B_2A_2C_1$	$6T_{12}$	$A_1B_1A_2B_1C_2B_1$ (2)	$6T_{31}$
$A_1B_1C_1B_1C_1B_2$ (1)	$6T_{13}$	$A_1B_1C_1A_2B_1C_2$ (2)	$6T_{32}$
$A_1B_1C_2B_1C_1B_2$ (1)	$6T_{14}$	$A_1B_1C_2A_1C_2B_2$ (2)	$6T_{33}$
$A_1B_1C_2B_2C_1B_1$ (1)	$6T_{15}$	$A_1B_1C_1B_1A_2C_2$ (2)	$6T_{34}$
$A_1B_1A_1B_2C_1B_1$ (1)	$6T_{16}$	$A_1B_1C_1B_1A_2B_1$ (2)	$6T_{35}$
$A_1B_1A_1C_2B_1C_1$ (1)	$6T_{17}$	$A_1B_1C_1B_2A_2B_1$ (2)	$6T_{36}$
$A_1B_1A_2C_2B_1C_1$ (1)	$6T_{18}$	$A_1B_1A_1B_2A_1C_2$ (2)	$6T_{37}$
$A_1B_2A_1C_2B_1C_1$ (1)	$6T_{19}$	$A_1B_1A_1C_2A_2B_1$ (2)	$6T_{38}$
$A_1B_1C_1B_2C_2B_2$ (1)	$6T_{20}$	$A_1B_1A_2C_2A_1B_2$ (2)	$6T_{39}$
$A_1B_2A_2B_1C_2B_1$ (1)	$6T_{21}$	$A_1B_2C_1B_1A_2C_1$ (2)	$6T_{40}$
$A_1B_1C_1A_2B_1C_1$ (1)	$6T_{22}$	$A_1B_1C_1B_2C_1B_2$ (3)	$6T_{41}$
$A_1B_1C_1B_2A_1B_2$ (1)	$6T_{23}$	$A_1B_1C_1B_2A_1C_2$ (3)	$6T_{42}$
$A_1B_1A_1B_2A_2C_2$ (1)	$6T_{24}$	$A_1B_2A_2B_1A_1C_2$ (3)	$6T_{43}$
$A_1B_1A_1B_2A_2B_1$ (1)	$6T_{25}$	$A_1B_2A_2B_1A_2C_2$ (3)	$6T_{44}$
$A_1B_1A_1C_2A_2C_1$ (1)	$6T_{26}$	$A_1B_1A_2C_2A_1C_2$ (4)	$6T_{45}$

patterns were calculated using the program of Smith (1967) modified for the IBM 360.

The use of calculated patterns as identification standards has been well substantiated, for example in Borg and Smith (1970). Briefly, the calculation involves determining the set of relative integrated intensities, I_{hkl}, from the atomic coordinates of the ideal crystal structure, and then distributing the intensity over a Cauchy distribution of appropriate half width centered at the ideal 2θ position. Summing the individual contributions results in an intensity versus 2θ curve which closely approximates the diffractometer trace including the effects of overlap of closely spaced maxima. From this trace it is possible to determine effective peak intensity values. More detail on the calculations may be found in Smith (1968).

Powder patterns have several inherent difficulties which were encountered in this study. Preferred orientation was a problem because of the platy character of molybdenite. In addition, the large unit cells, especially in the 6-layer polytypes, resulted in closely spaced diffraction maxima, and overlap of adjacent maxima became a problem at moderate values of 2θ. It was possible to define a region of the pattern from $2\theta = 29°$ to $2\theta = 59°$ that was characteristic of each polytype except for the pairs $6H(2)$—$6H(5)$ and $6T(4)$—$6T(5)$. These pairs, although not identical, are indistinguishable within experimental error. They afford interesting examples of a pseudohomomorphic pair. The chosen range contains $(10\bar{1}l)$ reflections, $l = 0$ to 19. These reflections are most sensitive to the stacking sequence and, though they would be affected systematically by the preferred orientation, the sequence of intensities still should be recognizable. Those reflections with high values of l will be enhanced over the ones with low l.

Figure 2–4 graphically presents the calculated powder patterns for the 2- and 3-layer polytypes and the 43 6-layer polytypes which showed the higher symmetry. The calculated powder patterns are listed in detail in Table 5[1]. It is a simple task to compare the measured pattern with these charts. The most useful reflections lie in the 2θ ranges 32°–43° and 46°–56°.

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[1] To obtain a copy of Table 5, order NAPS Document Number 01224 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N. Y., 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC NAPS.

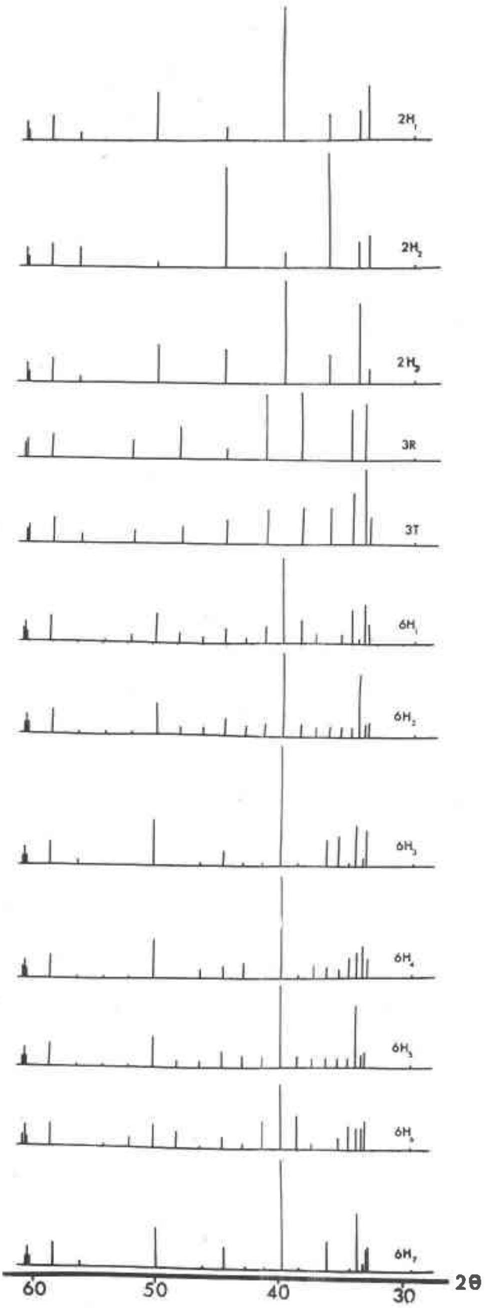

FIG. 2. Graphical representation of the 2- and 3-layer polytypes of molybdenite and 7 of the 6-layer polytypes of symmetry higher than $P3m$. All peaks are scaled to (006) $=100$.

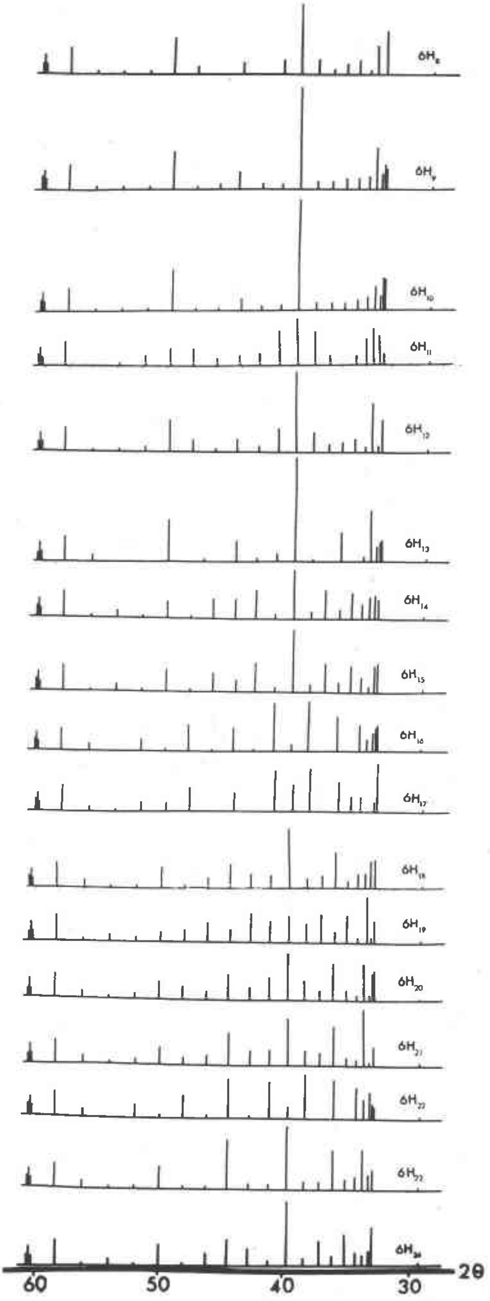

FIG. 3. Additional 6-layer polytypes of high symmetry.

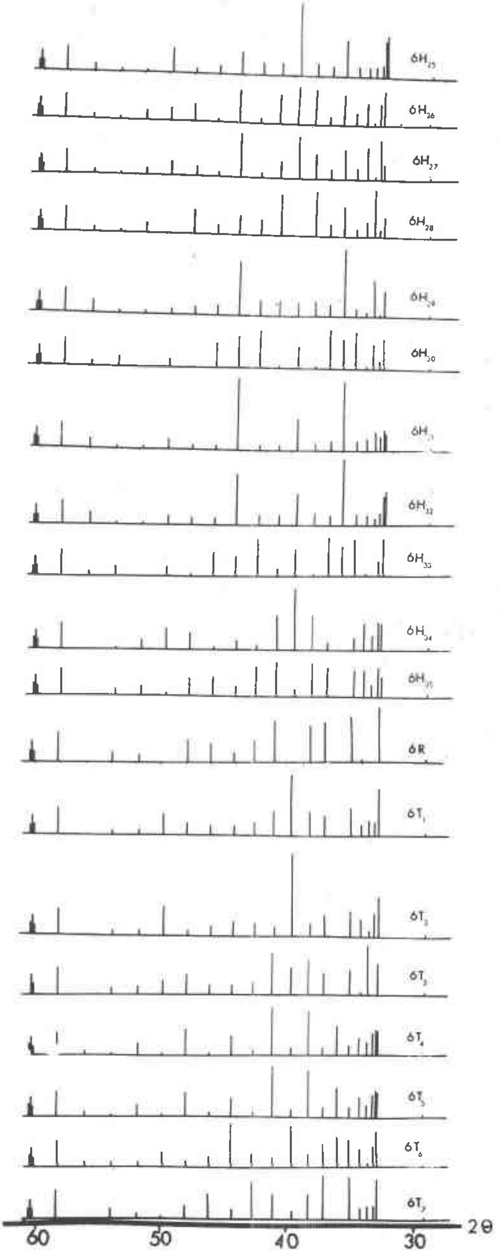

FIG. 4. Additional 6-layer polytypes of high symmetry.

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