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Anisotropic Mean-Square Displacements (MSD) in Single Crystals of 2H- and 3R-MoS₂

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Abstract

Integrated intensities for *h0l* reflections in single crystals of 2H- and 3R-MoS₂ have been measured both to refine the *c*-axis structural parameter (*z*) and to determine the vibrational amplitude for the Mo and S atoms. It was found that the MSD for the Mo atom along the *c* axis is distinctly larger than for the S atom ($7.6 \times 10^{-3} \text{ \AA}^2$ versus $5.0 \times 10^{-3} \text{ \AA}^2$), independent of the polytype studied. Within the basal plane the amplitudes of 2H-MoS₂ are both smaller and more equal ($4.8 \times 10^{-3} \text{ \AA}^2$ for Mo and $3.8 \times 10^{-3} \text{ \AA}^2$ for S). Both polytypes gave a *z* parameter for the S atom of $z = 0.127_4$.

I. Introduction

MoS₂ belongs to the layered dichalcogenides of transition metals of Groups IVb, Vb and VIb, which have attracted interest on account of their highly anisotropic properties. A review of these materials may be found in Wilson & Yoffe (1969). The metal dichalcogenide layer consists of one plane of hexagonally packed metal atoms between two planes of

chalcogenide atoms. In these layers the chalcogen array around each metal atom is typically octahedral or trigonal prismatic and MoS₂ belongs to the latter group. The metal dichalcogenide layers may be stacked in different ways (polytypism). Thus, MoS₂, either natural or synthetic, may be 2H or 3R or a mixture of both. In nature, 2H-MoS₂ is dominant (Frondel & Wickman, 1970). Further polytypic structures in molybdenite, other than 2H or 3R, have been derived analytically (Zvyagin & Soboleva, 1967) but have not yet been observed experimentally.

Recently, calculations to determine the mean-square displacements (MSD) of 2H-MoS₂ have been made by Feldman & Boyer (1981). In the present paper, we compare these calculations with experimental findings and refine the structural *z* parameter which is half the height of the MoS₆ prism studied earlier by Dickinson & Pauling (1923) and Takéuchi & Nowacki (1964).

II. Theory

The structures of the 2H and 3R polytypes of MoS₂ are easily visualized by starting from the unit structure of an MoS₂ plane sandwich (Zvyagin & Soboleva, 1967). This unit structure is shown in Fig. 1, with the S atoms at (0, 0, ±*z*), the Mo atom at ($\frac{2}{3}, \frac{1}{3}, 0$) and with the nomenclature for the different lattice sites *A*, *B* and *C*. We obtain the 2H polytype by stacking this unit structure along the *c* axis (leaving a van der Waals gap

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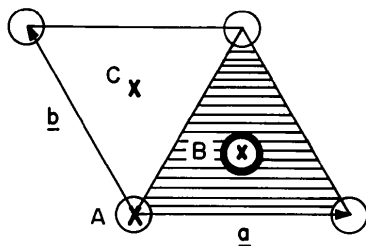


Fig. 1. Projection on the (00.1) plane of the MoS_2 unit repeat structure; \circ S atoms, \bullet Mo atoms, \times lattice origins: A, B, C. The unshaded triangle represents the antiparallel orientation to the MoS_6 prism (shaded).

in between) with a position sequence $AB'AB' \dots$ for the S atoms, where the prime refers to the antiparallel orientation of the MoS_6 prism (shaded triangle of Fig. 1). If the stacking sequence is $ABCABC \dots$, i.e. the MoS_6 prisms are oriented parallel, we obtain the $3R$ polytype. Obviously, the unit cell for $3R\text{-MoS}_2$ will be larger by a factor of about 1.5 along the c axis when compared with $2H\text{-MoS}_2$. This is observed experimentally together with a nearly unmodified a parameter [see Murray & Evans (1979) for a recent review on $2H\text{-MoS}_2$ and Takéuchi & Nowacki (1964) for $3R\text{-MoS}_2$].

The $2H$ and $3R$ polytypes are experimentally distinguished from one another in a straightforward fashion. In Table 1, the structure factors are given for the sets of Bragg reflections that we later employ. The f_x^t values give the scattering amplitude of atom x with the inclusion of the thermal Debye-Waller factor (DWF). For the $3R$ polytype the same DWF has been tacitly assumed for both S sites. In Table 1, we see that the factor of 2 for $2H\text{-MoS}_2$ and 3 for $3R\text{-MoS}_2$ may be taken out, which simply reflects the number of MoS_2 units per unit cell. It is then clear that the $00.l$ reflections may not be used to differentiate between the $2H$ and $3R$ polytypes. $h0.0$ reflections, however, allow us to decide whether $2H$ is present or not: the reflections $3h' \pm 1 0.0$ are only allowed for $2H\text{-MoS}_2$. Finally, the presence of $3R\text{-MoS}_2$ can be determined from the $h0.l$ reflections. Although all the 2θ values for low- l reflections are close to one another ($c \gg a$), the

Table 1. Structure factors $|F|$ for the $2H$ and $3R$ polytypes of MoS_2

In comparing $|F|$ with those of Zvyagin & Soboleva (1967), care must be taken because they based their evaluation of F on an expression that neglects dispersion effects in the atomic scattering factors.

$hk.l$	$ F (2H\text{-MoS}_2)$	$ F (3R\text{-MoS}_2)$
$h0.l$	$2l(f_{\text{Mo}}' + 2f_{\text{S}}' \cos 2\pi lz) \cdot \cos \pi h/3l$ $l = 2l'$	$3l f_{\text{Mo}}' \exp(-2/3\pi hi) + 2f_{\text{S}}' \cos 2\pi lz$ $h = 3h'$ and $l = 3l'$
	$2l(f_{\text{Mo}}' - 2f_{\text{S}}' \cos 2\pi lz) \cdot \sin \pi h/3l$ $l = 2l' + 1$	$h = 3h' + 1$ and $l = 3l' + 1$ $h = 3h' - 1$ and $l = 3l' - 1$ otherwise
		0

differences separating the ω values of the $h0.0$ and $h0.l$ reflections, stemming from the different c parameters of the unit cell for $3R$ - and $2H\text{-MoS}_2$, still permit a clear distinction to be made.

The thermal DWF, and thus the MSD $\langle u_x^2 \rangle = B_x/8\pi^2$ of atom x , has so far been included in the scattering amplitudes without any specification. To account for the two atom types involved and the layered structure of the compound, four thermal DWF's are sufficient to describe MoS_2 : B_{Mo}^\perp , B_{S}^\perp , B_{Mo}^\parallel and B_{S}^\parallel . Here, \perp refers to the displacements along the c direction and \parallel to those within the basal plane as in James (1958). Thus, the f_x^t values for $h0.l$ reflections can be written as

$$f_x^t = f_x \exp [-(B_x^\perp \cos^2 \varphi + B_x^\parallel \sin^2 \varphi) S^2],$$

where $S^2 = (\sin \theta/\lambda)^2$ and φ is the angle between the c axis and the direction of the scattering vector. Separately, B_x^\perp and B_x^\parallel can be found from $00.l$ and $h0.0$ reflections, respectively.

III. Experimental details

Two synthetic MoS_2 single-crystal flakes, one of the $2H$, the other of the $3R$ polytype, of irregular lateral form were used. They had been prepared by Dr A. Wold for the Exxon Corporate Science Research Laboratories, Linden, New Jersey, by chemical vapor deposition and were kindly given to us by Dr R. R. Chianelli. Both samples had a $[00.l]$ surface normal in common. Their thicknesses varied from $d = 120$ to $200 \mu\text{m}$ as determined from X-ray absorption measurements (using $\mu_i = 74 \text{ cm}^{-1}$). For the $00.l$ reflections the ω scans, or rocking curves, had a FWHM of $\sim 0.15^\circ$, whereas for the basal-plane reflections, a larger FWHM of $\sim 0.30^\circ$ was found. Their lattice parameters as determined by the Bond method were $a = 3.161$ and $c = 12.295 \text{ \AA}$ for $2H\text{-MoS}_2$ and $a = 3.163$ and $c = 18.37 \text{ \AA}$ for $3R\text{-MoS}_2$, with an error of $\sim 0.05\%$. For the $3R\text{-MoS}_2$ crystals, no indication of the $2H$ polytype was found. The $2H\text{-MoS}_2$ sample, however, showed a small amount of the $3R$ polytype (about 5%).

A 2 kW Mo anode sealed X-ray tube ($0.4 \times 8 \text{ mm}$) and a Johann (111) Ge monochromator were used, which yielded essentially pure $\text{Mo } K\alpha_1$ ($\lambda = 0.70926 \text{ \AA}$). A small sample spot of $\sim 1 \text{ mm}$ height was employed, and an incoming-beam divergence of $\sim 5'$ in the scattering plane was used. Special care was taken to ensure the selection of a homogeneous sample area. ω scans (conventionally performed by scanning ω at fixed 2θ) with an open counter were performed in a semifocusing set-up to determine the integrated Bragg intensities at room temperature (RT). To separate Bragg intensity and background, the intensities at both ends of the ω scans were linearly interpolated through the Bragg reflection. It is known, however, that the

thermal diffuse scattering (TDS) also peaks beneath the Bragg reflection. For a rapid estimation of its contribution to the measured integrated intensities, we employed a method outlined by Jennings (1970). We used average sound velocities in his spherical approximation that were determined from the known elastic data (Feldman & Boyer, 1981).

In the evaluation of the MSD and z parameter from the integrated intensities, the function $\sum w(|F_o| - |F_c|)^2$ was minimized where w is the statistical weight, F_o and F_c are the observed and calculated structure factors, and the residual $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $|F_o|$ was obtained after intensity corrections for background, Lorentz-polarization and absorption. $|F_c|$ was calculated from the scattering factors for Mo and S of Doyle & Turner (1968) and Cromer & Liberman (1970), reflecting that the bonding within an MoS₂ layer is predominantly covalent. [The fractional ionic character of the bonding is discussed by Gamble (1974).]

IV. Results

In the following, our measurements at $h0.l$ reflections will be presented in two groups: those at $00.l$ reflections and those at $h0.0$, because they exclusively depend on B_x^\perp and B_x^\parallel respectively. In the latter group we also included the $h0.l$ reflections with low l on account of their weak dependence on B_x^\perp .

1. $00.l$ reflections

Reflections ranging from 00.6 to 00.34, the highest reflection order attainable with Mo $K\alpha_1$, were measured with 2H-MoS₂ and 00.9 to 00.48 with 3R-MoS₂ (Table 2). For 2H-MoS₂ it was checked that no $00.l$ reflections with odd l were present as these had been previously seen in measurements with crystals of natural 2H-MoS₂ (Huang, 1981) and were probably due to its contamination with metallic impurities and water.

In the fitting procedure, B_{Mo}^\perp , B_S^\perp , and z were taken as free parameters and their final values are given in Table 3. For the final data fit presented in Table 2, the two lowest reflections were not included, because their ω scans indicated surface-related problems with lower ω values. The R value was 1.9% for the 2H-MoS₂ data and 2.6% for the 3R-MoS₂ data. Three conclusions can be drawn from Table 3. First, both polytypes show good agreement between all three fitting parameters B_{Mo}^\perp , B_S^\perp and z . Second, the B^\perp value of the Mo atoms is distinctly larger than that of the S atoms. This is somewhat unexpected, for the Mo atoms are heavier than the S atoms. Third, B_{Mo}^\perp and B_S^\perp increase only slightly when we consider the TDS corrections according to Jennings (1970) without changing the first two conclusions.

Table 2. Observed $|F_o|$ and calculated $|F_c|$ structure factors for 2H- and 3R-MoS₂

2H-MoS ₂			3R-MoS ₂		
$hk.l$	$ F_o $	$ F_c $	$hk.l$	$ F_o $	$ F_c $
00.6*	46.74	62.85	00.9*	80.55	93.74
00.8*	67.18	84.13	00.12*	101.6	126.1
00.10	39.36	39.21	00.15	57.37	59.42
00.12	12.36	13.59	00.18	19.22	20.54
00.14	38.42	38.05	00.21	58.63	56.56
00.16	48.41	48.05	00.24	71.97	72.14
00.18	20.54	20.08	00.27	31.12	30.94
00.20	7.79	8.48	00.30	12.71	13.02
00.22	21.93	22.06	00.33	34.22	32.76
00.24	24.70	24.58	00.36	37.02	37.01
00.26	10.12	9.39	00.39	15.04	14.77
00.28	5.00	4.88	00.42	7.60	7.60
00.30	11.37	11.22	00.45	17.66	16.69
00.32	11.17	11.41	00.48	16.19	17.29
00.34	3.80	3.95			
10.0	58.09	56.49			
20.0	42.73	40.20			
30.0	56.42	61.18			
40.0	23.47	23.06			
50.0	16.56	16.79			
60.0	24.62	23.98			
70.0	8.42	8.44			
10.±1	29.90	30.11			
20.±1	23.78	23.26			
40.±1	13.60	13.83			
50.±1	10.63	10.88			
70.±1	6.19	6.19			

* Reflections not included in the final refinement due to surface effects at low ω .

Table 3. Positional and thermal parameters of 2H- and 3R-MoS₂

⊥ refers to vibrations normal to the basal plane (along the c axis).
 ∥ refers to in-plane vibrations.

	B_{Mo}^\perp (Å ²) ($\langle u_{Mo}^\perp \rangle \times 10^3 \text{ Å}^{-2}$)	B_S^\perp (Å ²) ($\langle u_S^\perp \rangle \times 10^3 \text{ Å}^{-2}$)	z
2H-MoS ₂	0.61 (7.7) 0.62*	0.39 (4.9) 0.40*	0.127 ₃ 0.127 ₃
3R-MoS ₂	0.59 (7.5) 0.61*	0.40 (5.1) 0.41*	0.127 ₃ × $\frac{2}{3}$ 0.127 ₄ × $\frac{2}{3}$
	B_{Mo}^\parallel (Å ²) ($\langle u_{Mo}^\parallel \rangle \times 10^3 \text{ Å}^{-2}$)	B_S^\parallel (Å ²) ($\langle u_S^\parallel \rangle \times 10^3 \text{ Å}^{-2}$)	
2H-MoS ₂	0.38 (4.8) 0.40*	0.30 (3.8) 0.32*	

* Data were corrected for TDS according to Jennings (1970). The final values of $\langle u^2 \rangle$ are not altered within the allowed error.

2. $h0.0$ and $h0.±1$ reflections

Reflections that mainly yield the MSD within the basal plane were measured with both crystals. In the case of 3R-MoS₂, however, a large R value was obtained, most probably arising from stacking faults in the crystal used. For this reason we will only present the results for 2H-MoS₂.

All $h0.0$ and $h0.±1$ reflections obtainable with Mo $K\alpha_1$ were measured (Table 2). In our analysis the

$h0.\pm 1$ reflections were averaged after the absorption corrections. $B_{\text{Mo}}^{\parallel}$ and B_{S}^{\parallel} were used as free parameters with the above results for B_{Mo}^{\perp} , B_{S}^{\perp} and z . The fit gave $R = 3.6\%$. The result for B_x^{\parallel} is smaller than B_x^{\perp} for the Mo and S atoms. In addition, their B values differ less within the basal plane than along the c axis. This would seem to reflect the closer packing within these planes.

V. Discussion

Our determination of the MSD for both $2H$ - and $3R$ - MoS_2 shows the following characteristics:

(i) the MSD along the c axis for the Mo atoms is larger than that for the S atoms and does not depend on the polytype;

(ii) both atoms have smaller and more comparable MSD's within the basal plane.

These results may be compared with calculations for the MSD of $2H$ - MoS_2 by Feldman & Boyer (1981). At RT they calculated $B_{\text{Mo}}^{\perp} \simeq 0.47$, $B_{\text{S}}^{\perp} \simeq 0.51$, $B_{\text{Mo}}^{\parallel} \simeq 0.29$ and $B_{\text{S}}^{\parallel} \simeq 0.44 \text{ \AA}^2$. Thus the measured and the calculated data fall within the same range and the anisotropy parameters $A = B_x^{\perp}/B_x^{\parallel}$ for the Mo atoms (1.6 measured, 1.60 calculated) and for the S atoms (1.3 measured, 1.15 calculated) also agree reasonably well. However, the calculated ratio between the two atom types is not in agreement with the experimental findings; in particular, the calculated MSD along the c axis is smaller for the Mo atoms than for the S atoms. Analogous experimental findings have also been seen with other layered dichalcogenides, independent of the details of their structures: TiS_2 , which has a CdI_2 structure (Chianelli, Scanlon & Thompson, 1975), and $3R$ - NbS_2 (Morosin, 1974) both show a larger MSD along the c axis for the metal atoms than for the S atoms, but by a smaller amount of 10–15%.

The reason for the larger c -axis MSD for Mo over S is not obvious. It is perhaps related to the tendency in the trichalcogenides, such as NbSe_3 (Fleming, Moncton & McWhan, 1978), towards dimerization of the metal

atoms which may be connected to a (general) longitudinal softness along c of the metal atom in a sixfold chalcogen-coordinated site.

Finally, the z parameter may be compared with the literature values. Our results of 0.127_5 for $2H$ - MoS_2 and $\frac{2}{3} \times 0.127_3$ for $3R$ - MoS_2 with synthetic crystals are quite close to $z = 0.129 \pm 0.004$ for $2H$ - MoS_2 reported by Dickinson & Pauling (1923) and $z = \frac{2}{3} \times 0.128_5$ for $3R$ - MoS_2 found by Takéuchi & Nowacki (1964) with natural samples.

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