

# X-ray diffraction study of molybdenum disulfide to 38.8 GPa

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## Abstract

The high-pressure behavior of molybdenum disulfide ( $\text{MoS}_2$ ) has been investigated using an energy dispersive synchrotron X-ray diffraction method in a diamond anvil cell to 38.8 GPa at room temperature. It is found that the  $c$ -axis compression ratio is about three times larger than  $a$ -axis at pressures below 10 GPa. It gradually decreases with increasing pressure, and reduces to two times above 28.9 GPa. The reduction of  $c$ -axis with pressure displayed a discontinuity between 20.5 and 28.9 GPa. This may result from a phase transformation. The experimental pressure–volume data below 20.5 GPa were fitted with the third-order Birch–Murnaghan equation of state, and the bulk modulus was obtained as  $K_{0T} = 53.4 \pm 1$  GPa and its pressure derivative as  $K'_{0T} = 9.2 \pm 0.4$ .

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## 1. Introduction

Solid lubricants have been attracting attention because of meeting a vast range of industrial requirements such as minimizing friction and protecting from surface corrosion under high-pressure conditions. In several industrial applications of solid lubricants, friction affects power loss, fuel consumption, and service life of machineries. Molybdenum disulfide ( $\text{MoS}_2$ ) with a high-load capability has been used either as a solid lubricant or as a supplement to liquid lubricants to decrease the friction as surfaces move against each other [1]. For engineering applications, such as in vacuum and space technologies, where liquid lubricants do not function properly,  $\text{MoS}_2$  has been recognized as one of the most important solid lubricants [2]. Another advantage of  $\text{MoS}_2$  is that it can work under high pressure, whereas others fail to perform adequately or rupture due to high pressure when surfaces make contact [3]. Although the shear stress of  $\text{MoS}_2$  is about 25 MPa, it can be employed to lubricate sliding surfaces at high contact stresses (on the order of 1 GPa) [4]. Therefore  $\text{MoS}_2$  is one of the best means to control friction and wear for applications involving severe tribological environments.  $\text{MoS}_2$  has a 2H hexagonal layered crystal structure

(P63/mmc) with an inherently low shear stress. Each Mo atom is surrounded by a trigonal prism of S atoms at a distance of 0.241 nm. The forces holding atoms together in each S:Mo:S layer are strong covalent bonds. However, weak Van der Waals bonding exists in the neighboring planes of S atoms which vibrate along  $c$ -axis [5]. Its crystal structure consists of two-dimensional layers of S–Mo–S sandwiches that are weakly bonded to one another along the third dimension ( $c$ -axis) [6]. These layers can slide over each other at the molecular level, allowing the surfaces of metals to move smoothly, even under severe pressures. The structure of  $\text{MoS}_2$  is also plotted in Fig. 1 [7]. Analysis of  $\text{MoS}_2$  has been also performed to clarify its morphology as a catalyst [8,9].

Studies regarding compression and tribological behaviors of solid lubricant nanoparticles have been performed up to 0.7 GPa [10,11]. The properties of  $\text{MoS}_2$ , such as its structural stability and compressibility are particularly important at higher pressures. In this paper, we present X-ray diffraction measurements of  $\text{MoS}_2$  using diamond anvil cell technique [12] to 38.8 GPa.

## 2. Experiment

A symmetric diamond anvil cell was used to generate pressures. The diamond anvils had flat culets with diameters of 300  $\mu\text{m}$ . A rhenium alloy selected as the

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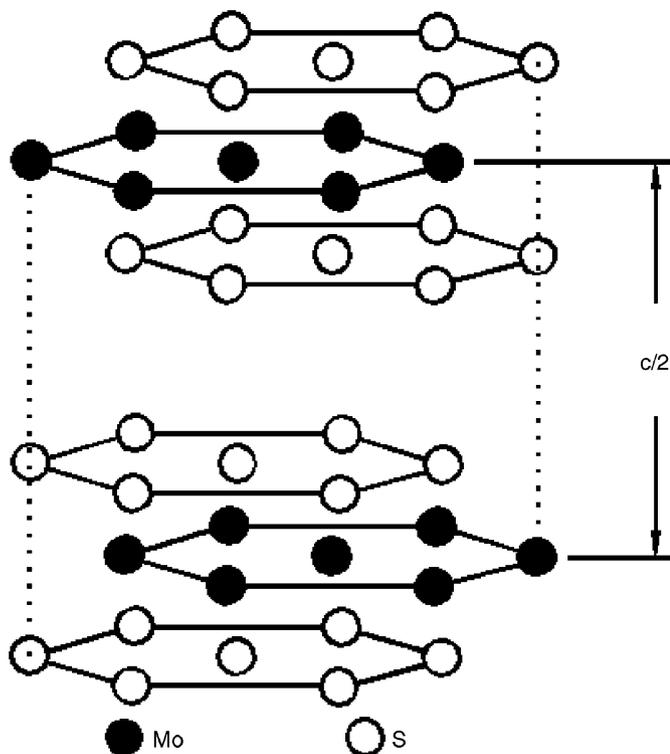


Fig. 1. The crystal structure of the hexagonal MoS<sub>2</sub>, showing the arrangement of sulfur (solid circles) and molybdenum atoms (open circles).

gasket was preindented to 20 GPa. A 100- $\mu\text{m}$  hole serving as a sample chamber was drilled in the center of the indentation by an electric discharge machine. The sample chamber was large enough to avoid any peaks from gasket. The sample, 99% MoS<sub>2</sub> powder, was from Alfa Easer Co. The mixture of methanol ethanol at a 4:1 volume ratio (M–E) was used as a pressure medium. Ruby chips were loaded in the sample chamber at different positions to calculate the pressure by measuring the wavelength shift of the  $R_1$  ruby fluorescence line [13]. X-ray diffraction experiments were conducted at beam lines X17C and X17B3 at the national synchrotron light source (NSLS), Brookhaven National Laboratory. The energy dispersive X-ray diffraction (EDXRD) method for a diamond anvil cell was employed [14]. The X-ray beam was focused on the sample by a pair of mirrors to increase the incident photon density to a dimension of  $18 \times 25 \mu\text{m}^2$  with the  $2\theta$  angles set at  $8^\circ$ . X-ray diffraction measurements were performed to 38.8 GPa.

### 3. Results and discussion

Up to 14 GPa, the pressures measured across the sample chamber by the rubies were almost identical. They showed a continuous increase reaching 2 GPa at 20.5 GPa, and a maximum of about 4 GPa at 38.8 GPa. This indicated that the homogenous pressure below 14 GPa was reached and

the non-homogeneity is limited below 4 GPa with the pressure range reached.

EDXRD spectra of MoS<sub>2</sub> at different pressures up to 38.8 GPa are shown in Fig. 2. With increasing pressure, the peaks shift to higher energies due to reduction of the crystal lattice. The conversion from energy to  $d$ -spacings was based on the formula of  $E \times d = 6.1993/\sin(\theta)$ , where  $E$  is the energy of the X-ray in keV, and  $d$  is the  $d$ -spacing in  $\text{\AA}$ , and  $\theta$  is the diffraction angle in degree [15]. The structural refinement was performed using the ‘REFINE’ program (R. Downs, University of Arizona). The cell parameters with their cell volumes at different pressures are listed in Table 1. At all pressures,  $d$ -spacings can be refined to the 2H structure of MoS<sub>2</sub>.

Fig. 3 shows the change of  $d$ -spacings with increasing pressure. All of the  $d$ -spacings consistently decreased almost linearly with increasing pressure except the (006)

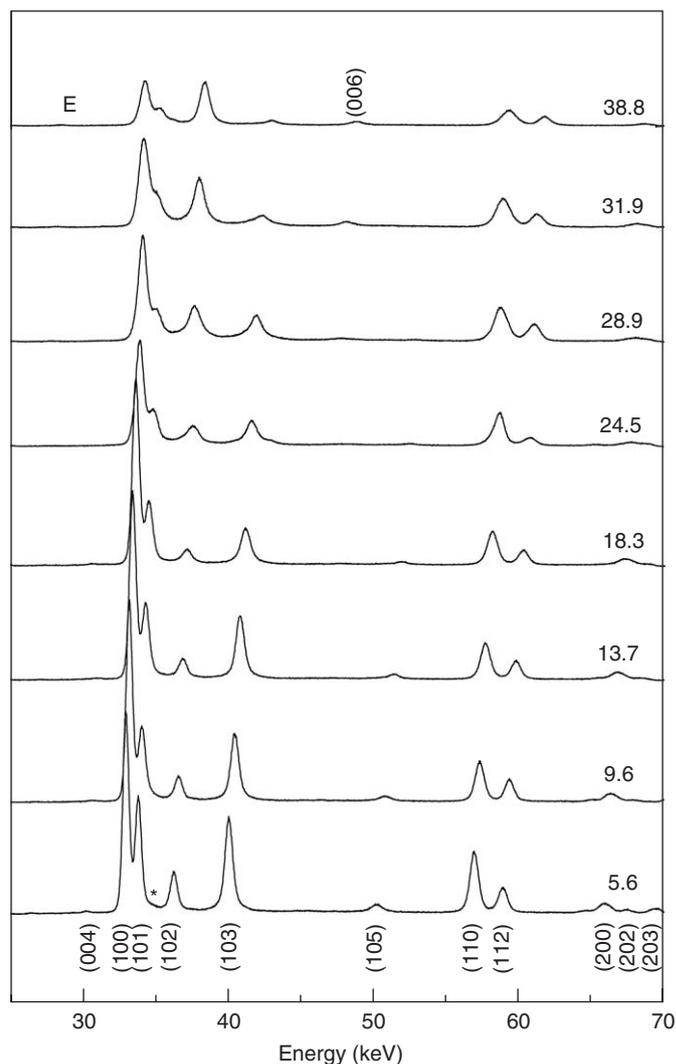


Fig. 2. Energy dispersive X-ray diffraction patterns of MoS<sub>2</sub> at selected pressures. The numbers in parenthesis under the first pattern are the corresponding Miller index of MoS<sub>2</sub>. Asterisk on the first pattern marks the diffraction from ruby. The (006) peak and the escape peak marked by ‘E’ are shown on the pattern at 38.8 GPa.

Table 1  
Cell parameters of MoS<sub>2</sub> with pressures

Pressure (GPa)	Cell parameter: $a$ (Å)	Cell parameter: $c$ (Å)	Unit cell volume: $V$ (Å <sup>3</sup> )
5.6	3.116	11.758	98.9±0.2
7.8	3.101	11.603	96.6±0.1
9.6	3.094	11.520	95.5±0.1
11.8	3.081	11.456	94.2±0.1
13.7	3.075	11.333	92.8±0.3
16.0	3.055	11.251	91.0±0.2
18.3	3.047	11.180	90.0±0.2
20.5	3.034	11.095	88.5±0.2
24.5	3.018	11.061	87.3±0.4
28.9	3.008	10.905	85.5±0.3
31.9	3.006	10.657	83.4±0.4
35.0	3.000	10.502	81.9±0.4
38.80	2.996	10.386	80.8±0.6

The cell parameters of MoS<sub>2</sub> after 20.5 GPa are obtained by assuming the 2H hexagonal structure.

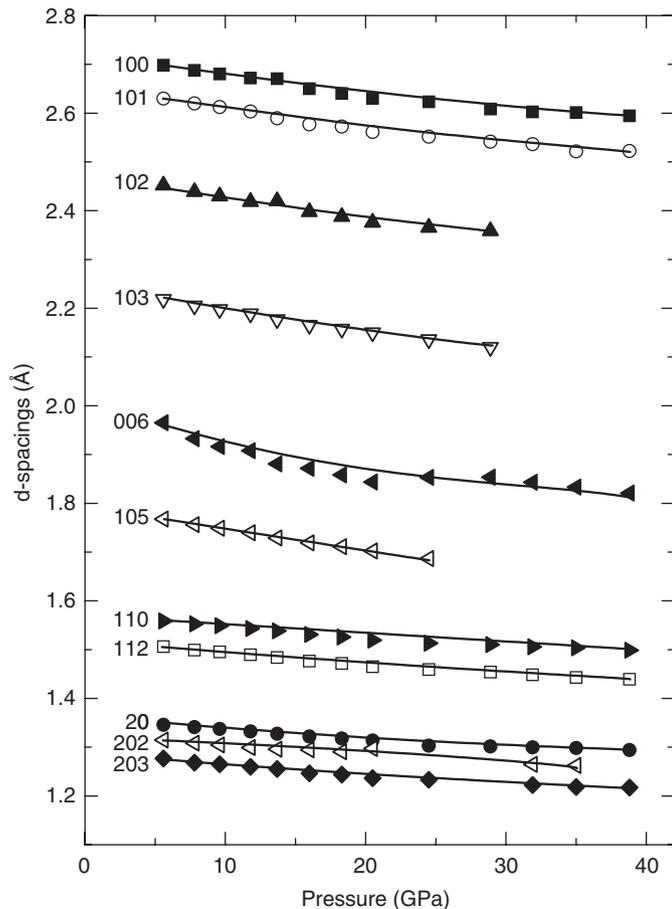


Fig. 3. The change in  $d$ -spacings observed as a function of pressure. The solid lines show the fitting to first or second order of pressure.

plane, which showed different gradient and a larger decrease of up to 7.3% whereas others had decreases between 3.8% and 4.6%. The  $d$ -spacing of the (006) plane also showed a discontinuity at 20.5 GPa. The change of cell

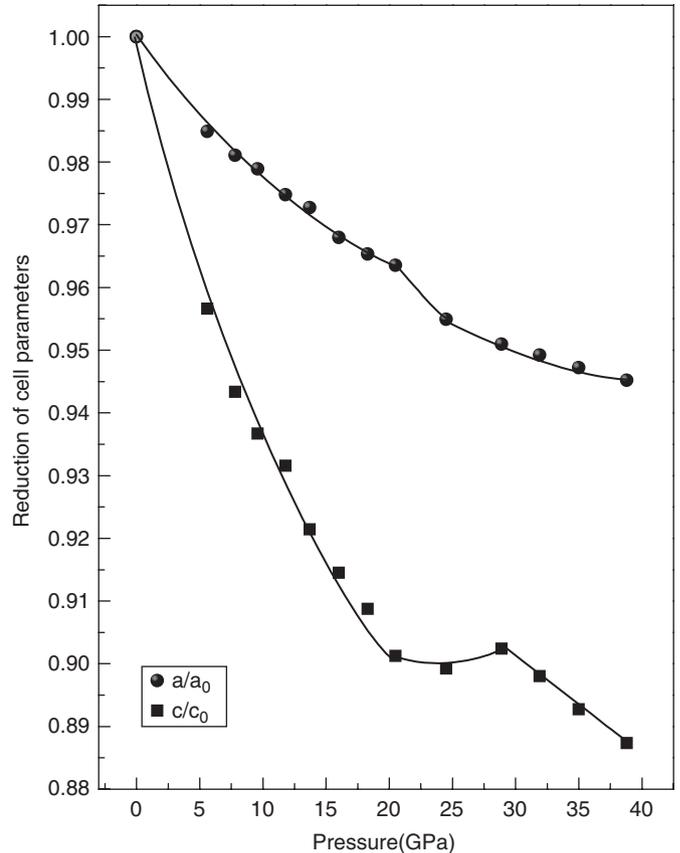


Fig. 4. Pressure dependence of the unit cell parameter. The discontinuities of  $a/a_0$ , and  $c/c_0$  are shown by the solid curve.

parameters as a function of pressure is shown in Fig. 4. The  $a/a_0$  and  $c/c_0$  decreased consistently with pressure. Their curves showed discontinuities between 20.5 and 28.9 GPa. These discontinuities with pressure is also reflected in the volume reduction as shown in Fig. 6, in which the volume changes consistently with a decreasing slope from 5.6 to 24.5 GPa. The slope also showed a discontinuity between 24.5 and 28.9 GPa. Although all the peaks can still be indexed into 2H hexagonal structure within the experimental error range, we believe that a phase transition occurred at 20.5 GPa. This transition can be either electronic or structural with a minimum distortion from the 2H structure. The ratio of axial reduction between  $a$ -axis and  $c$ -axis is shown in Fig. 5. Because the neighboring planes of the S-atoms are bonded by weak Van der Waals force along  $c$ -axis,  $c$ -axis is more compressible than  $a$ -axis with increasing pressures. The  $c$ -axis was reduced about three times more than  $a$ -axis at lower pressures. The ratio decreased with pressure down to two times at 28.9 GPa, indicating that the interaction became stronger with pressure between the adjacent sulfur layers.

The P–V data below 20.5 GPa were fitted with the third-order Birch–Murnaghan equation of state using a ‘bulk’ software (R. Downs, University of Arizona), yielding a bulk modulus of  $K_{0T} = 53.4 \pm 1$  GPa with  $K'_{0T} = 9.2 \pm 0.4$ ,

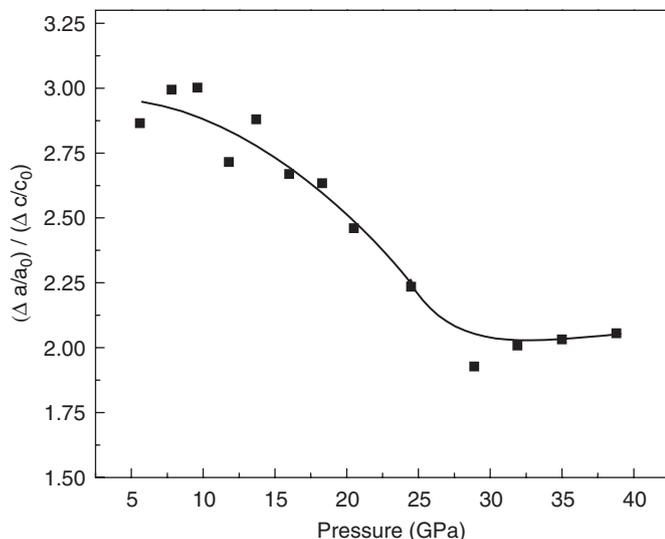


Fig. 5. The ratio axial reduction between  $c$ - and  $a$ -axis at pressures.

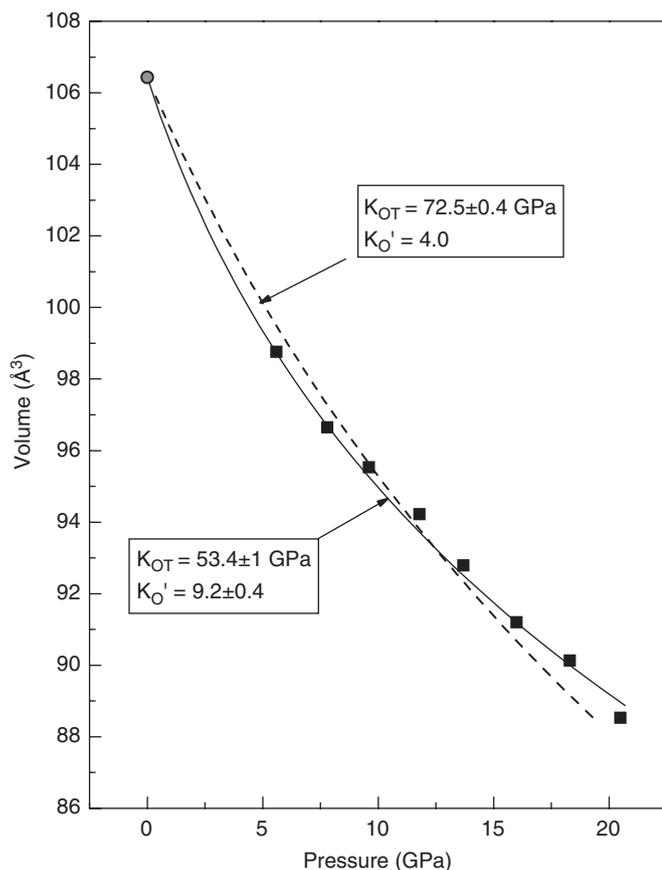


Fig. 6. Pressure dependence of the unit cell volume of  $\text{MoS}_2$  with the curve fitted both third and second order Birch–Murnaghan (B–M) Equation of state (EOS) to 20.5 GPa. Dashed line is fitting to second B–M EOS and solid line is the curve fitted to third B–M EOS.

as shown in Fig. 6. By fitting the data with the second-order Birch–Murnaghan equation of state ( $K'_{OT} = 4.0$ ),  $K_{OT} = 72.5 \pm 0.4$  GPa was obtained (Fig. 6).

#### 4. Conclusion

An X-ray-diffraction study of  $\text{MoS}_2$  has been conducted up to 38.8 GPa. The bulk modulus,  $K_{OT}$ , to 20.5 GPa was determined to be  $53.4 \pm 1$  GPa with  $K'_{OT} = 9.2 \pm 0.4$ . The  $c$ -axis decreased with pressure at a rate about three times faster than  $a$ -axis in the low-pressure range. The ratio decreased with pressure down to about two times at 28.9 GPa, indicating that the interaction becomes stronger with pressure between the adjacent sulfur layers. The discontinuities in the cell parameters and volume reduction were observed between 20.5 and 28.9 GPa. Such discontinuities were considered to be due to either an electronic or a structural phase transition with limited distortion of the 2H hexagonal structure. Further work is underway to characterize the phase transition.

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