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Equal compressibility structural phase transition of molybdenum at high pressure

Lun Xiong(熊伦)[1,†], Bin Li(李斌)[1,2], Fang Miao(苗芳)[1], Qiang Li (李强)[1], Guangping Chen(陈光平)[1,2], Jinxia Zhu(竹锦霞)[1], Yingchun Ding(丁迎春)[3], and Duanwei He(贺端威)[4,5,‡]

[1] *School of Intelligent Manufacturing, Sichuan University of Arts and Science, Dazhou* 635000, *China*
[2] *DaZhou Industrial Technology Institute of Intelligent Manufacturing, Dazhou* 635000, *China*
[3] *College of Optoelectronics Engineering, Chengdu University of Information Technology, Chengdu* 610225, *China*
[4] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*
[5] *Key Laboratory of High Energy Density Physics and Technology of Ministry of Education, Sichuan University, Chengdu* 610065, *China*

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We have studied the high-pressure compression behavior of molybdenum up to 60 GPa by synchrotron radial x-ray diffraction (RXRD) in a diamond anvil cell (DAC). It is found that all diffraction peaks of molybdenum undergo a split at around 27 GPa, and we believe that a phase transition from a body-centered cubic structure to a rhombohedral structure at room pressure has occurred. The slope of pressure–volume curve shows continuity before and after this phase transition, when fitting the pressure–volume curves of the body-centered cubic structure at low pressure and the rhombohedral structure at high pressure. A bulk modulus of 261.3 (2.7) GPa and a first-order derivative of the bulk modulus of 4.15 (0.14) are obtained by using the nonhydrostatic compression data at the angle $\psi = 54.7^\circ$ between the diffracting plane normal and stress axis.

Keywords: molybdenum, high pressure, phase transition, radial x-ray diffraction, diamond anvil cell

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Transition metal molybdenum is a common pressure scale used in high-pressure physics, and its equation of state (EOS) is widely used for pressure calibration in diamond anvil cell (DAC) experiments. However, since the 1990s, experimental and theoretical calculations have found that the possible phase transition of molybdenum at high pressures has been controversial. Therefore, studying the phase transition of molybdenum at high pressures can contribute to a better understanding of the high-pressure physical properties of d-electron transition metals.

Hixson *et al.*[1] experimentally measured the Hugoniot sound velocity of molybdenum and found an inflection near 210 GPa pressure, suggesting that the solid-solid phase transition of molybdenum occurred before the impact melting, but the subsequent results of static and high pressure experiments[2,3] did not support this assertion. Meanwhile, Moriarty[4] and Boettger *et al.*[5] and Belonoshko *et al.*[6] computationally studied the phase stability of the body-centered cubic (bcc), face-centered cubic (fcc), and dense-row hexagonal (hcp) structures of molybdenum based on the first principles, and their results did not support a phase transition near 210 GPa. Cazorla *et al.*[7] performed calculations after considering anharmonic effects and showed that the fcc and hcp high-temperature phases of molybdenum are not more stable than the bcc phase in the range of 0–600 GPa. Wang *et al.*[8] explored the high-pressure stable structure of molybdenum based on a particle swarm optimization algorithm and predicted the bcc→dhcp phase transition at 660 GPa at zero temperature. Zhao *et al.*[9] used the generalized gradient approximation (GGA) to calculate the total energy and enthalpy of molybdenum at different volumes for body-centered cubic (bcc) and double-layer dense hexagonal (dhcp) structures within the framework of the DFT of the plane wave pseudopotential, and the calculated isothermal compression lines were in good agreement with the previous calculations. The phase transition of the structure bcc→dhcp near 620 GPa pressure is predicted by making a difference in the enthalpy values. Based on the results of the phonon spectra, it can be seen that the bcc structure may change to the dhcp or 9R structure at high pressure. The calculation of the mechanical stability further shows that dhcp-Mo is a stable phase at 620 GPa.

In order to investigate the presence of phase transition metal molybdenum at high pressure, we studied it in a DAC with synchrotron radial x-ray diffraction (RXRD) up to 60 GPa. In order to clarify the structure after the phase transition, we searched for some possible structures by theoretical calculations using the density functional theory (DFT).

The crystal structure of molybdenum at room temperature and room pressure is a body-centered cubic structure. The space group is *Im*-3*m*. The molybdenum samples for high-pressure RXRD experiments were purchased from Alfa Aesar (99.9% purity) and have cell parameters of $a = b = c =$

†Corresponding author. E-mail: 1094129778@qq.com
‡Corresponding author. E-mail: duanweihe@scu.edu.cn

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5.5942(0.0021) Å and $\alpha = \beta = \gamma = 90°$, respectively. We performed RXRD experiments using a two-fold panoramic DAC with a culet diameter of 300 μm to study the compression behavior of molybdenum under differential stress compression. A beryllium (Be) gasket was firstly precompressed to approximately 20 GPa, at which pressure the thickness was ~ 25 μm. A 60 μm diameter hole was then drilled in the middle of the indentation. A ruby chip of ~ 10 μm diameter was placed at the center above the sample chip as the pressure standard.[10] In order to generate a large differential stress, we did not add a pressure transmission medium. The DAC was tilted to an angle of 28° to minimize the effect of the diffraction peaks of the Be gasket on the diffraction signal of the sample.

The *in situ* high-pressure RXRD experiments were conducted at the Beijing Synchrotron Radiation Facility (BSRF) 4W2 beam line. The wavelength of synchrotron radiation used at the beam line is 0.6199 Å. The spot size after focusing with a Kirkpatrick–Baez mirror is 30 μm×8 μm (FWHM). The powder diffraction signal (Fig. 1) was received by a Mar345 detector and integrated with Fit2D software[11] (Fig. 2). The diffraction spectra for each pressure were collected for 20 minutes after 30 minutes stress relaxation.

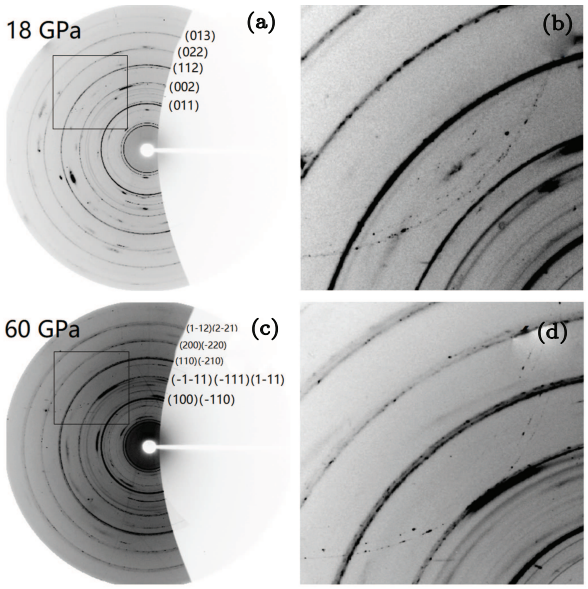


Fig. 1. (a) The diffraction pattern of molybdenum recorded on an image plate at 18 GPa under nonhydrostatc compression. The index based on a bcc lattice. (b) The enlarged image of the square area in (a). The diffraction pattern of molybdenum at 60 GPa. The index based on a rhombohedral lattice. (d) The enlarged image of the square area in (c).

Integrating the diffraction pattern, we can obtain the *d*-spacings for different *hkl* crystal planes, and then derive the cell parameters. The maximum pressure of the experiments is 60 GPa, and the pressure values of the experiments are obtained from the ruby pressure sensor.[10] We found that the diffraction peaks of the body-centered cubic structure split at 27 GPa, (011) diffraction peak split as (100) and (-110) peaks, (002) split as (-1-11), (-111) and (1-11) peaks, (112) split as (110), (-210) and (-211) peaks, (022) split as (200) and (-220) peaks, and (013) splits into (1-12) and (2-21) peaks. We believe that a phase transition from a body-centered cubic structure to a rhombohedral structure has occurred. Figure 2(a) represents the diffraction spectra of 12 GPa, 56 GPa, and 5 GPa (decompression), and Fig. 2(b) represents the RXRD patterns at pressures near 27 GPa with phase transition of 18 GPa, 27 GPa and 31 GPa. The structures of the body-centered cubic structure (*Im*-3*m*) and the rhombohedral structure (*R*-3*m*) are shown in the insets in Fig. 2. The rhombohedral structure can be described as one-atomic cell with $a = b = c$ and $\alpha = \beta = \gamma$. Similarly, the one-atom body-centered cubic cell can be described as a special one-atom rhombohedral cell where $a = \sqrt{3a_0}$, $\alpha = 109.47°$, and a_0 is the cell parameter of an ordinary 2-atom body-centered cubic cell. The volume of the rhombohedral unit cell can be expressed as $V = a^3(1-\cos\alpha)\sqrt{1+2\cos\alpha}a = \sqrt{3}a_0/2$. The phase transition from the body-centered cubic to the rhombohedral structure under high pressure corresponds to the displacement deformation of the body-centered cubic structure along the diagonal [111] on the $a_1 \times a_2$ plane.[12] The derived cell parameters of rhombohedral structure at 27 GPa after phase transition are $a = 2.6544(61)$ Å, $\alpha = 109.47°$, and $V = 14.3978(131)$ Å^3.

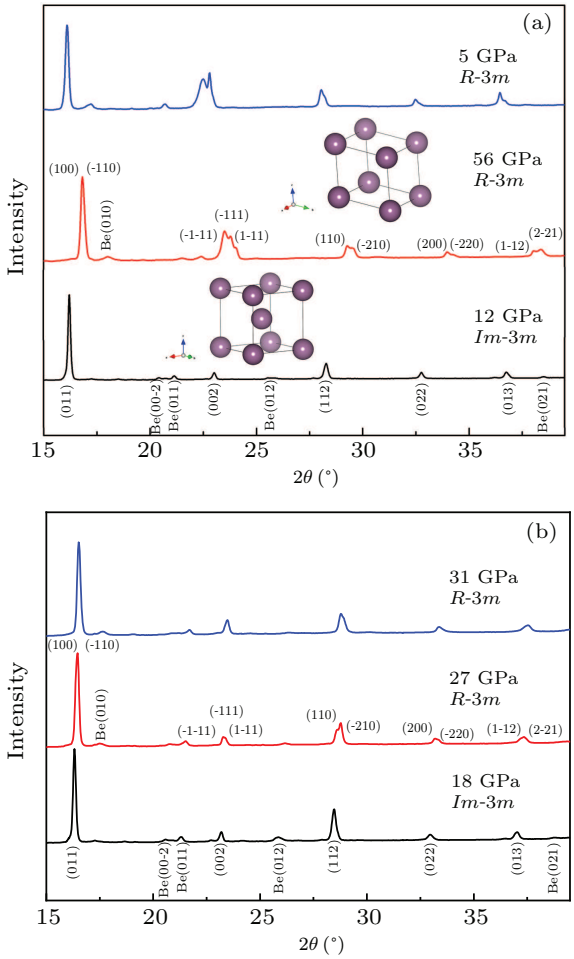


Fig. 2. (a) Nonhydrostatic RXRD patterns of molybdenum at 12 GPa, 56 GPa and 5 GPa (decompression). The insets are cubic and rhombohedral structures, respectively. (b) The RXRD patterns at pressures near 27 GPa with phase transition of 18 GPa, 27 GPa and 31 GPa.

The enlarged diffraction images of (002) and (112) at different pressures are shown in Fig. 3. It can be seen that at low pressures, the diffraction peaks of molybdenum are always single peaks and no split occurs. At high pressures, the splitting occurs, and the diffraction peak remains split after decompression to low pressure. Conventional axial x-ray diffraction (XRD) is on the minimum stress direction ($\psi = 90°$), when the stress is less than the hydrostatic $\psi = 54.7°$ direction.[13] The result is that the compression curve observed by conventional XRD is distinguished from the compression curve at hydrostatic pressure. We used RXRD to study the compression behavior of molybdenum at high pressure and found a structural phase transition from body-centered cubic to rhombohedral (all diffraction peaks appear splits), but no structural phase transition was found in the previous axial XRD experiments, possibly because the differential stress of axial XRD is not sufficient or RXRD can observe diffraction spectra in the direction of larger differential stress. In the past, although the axial diffraction pressure was as high as one hundred of GPa, the ratio of differential stress to confining pressure (ambient pressure or average pressure) was low because of the pressure transmission medium. Therefore, no such structural phase transition was observed. There are many similar phenomena. For example, hBN can be transformed into wBN under the action of shear stress (rotational diamond anvil cell, RDAC) under the confining pressure of about 6.7 GPa. However, conventional DAC experiments may not be able to observe such a structural phase transition up to 52.8 GPa.[14] In addition to the increase of pressure, the high deviatoric stress will also produce additional thermodynamic driving force, which makes the possibility of lattice reconstruction to high-pressure phase and additional atomic transformation path.[14]

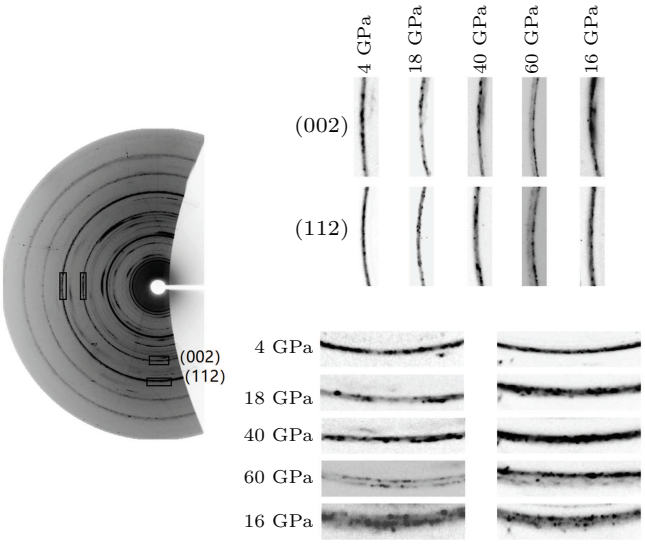


Fig. 3. Enlarged views of diffraction peaks of (002) and (112) at different positions of diffraction images at different pressures.

The normalized compression curve for $\psi = 54.7°$ are shown in Fig. 4. We fitted the body-centered cubic structure and the rhombohedral structure before and after 27 GPa, respectively. The derived bulk modulus is 260.6 (0.9) GPa and 260.4 (3.8) GPa, respectively. From Fig. 4, it can be seen that the volumes of the rhombohedral structure and the volume of the body-centered cube are continuous at different pressures, indicating that the phase transition may be related to the softening of the C_{44} triangular elastic tensor, which originates from a combination of Fermi surface nesting, band Jahn–Teller distortion and electronic topological transition combination.[15] Fitting both the body-centered cubic structure data and the rhombohedral structure data, we obtained a bulk modulus of 261.3 (2.7) GPa with its first-order derivative as 4.15 (0.14).

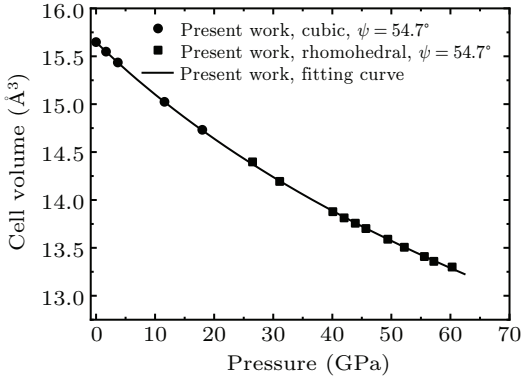


Fig. 4. Pressure–volume compression curve for molybdenum. The line represents the results of fitting by the third-order Birch–Murnaghan EOS for both body-centered cubic structure and the rhombohedral structure.

In summary, we have studied the compression behavior of molybdenum to 60 GPa in a nonhydrostatic environment in a diamond anvil cell using RXRD. We found that the all of the diffraction peaks of molybdenum split at 27 GPa, and we believed that molybdenum undergoes a structural phase transition from a body-centered cubic structure to a rhombohedral structure. DFT calculations revealed that the rhombohedral structure is most stable structure at high pressures. The transition could be associated with a soft-mode phonon induced C_{44} instability that originates from the Fermi surface nesting, band Jahn–Teller distortion and electronic topological transition combination. We fitted the pressure-volume data of both of the body-centered cubic structure and the rhombohedral structure to obtain their bulk modulus and its first-order derivative as 261.3 (2.7) GPa and 4.15 (0.14), respectively.

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