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# Pressure-induced structural changes in $\alpha$ -MoO<sub>3</sub> probed by X-ray absorption spectroscopy

Inga Jonane<sup>1</sup>, Andris Anspoks<sup>1</sup>, Lucie Nataf<sup>2</sup>, François Baudalet<sup>2</sup>, Tetsuo Irifune<sup>3</sup> and Alexei Kuzmin<sup>1</sup>

<sup>1</sup> Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia

<sup>2</sup> Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France

<sup>3</sup> Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

E-mail: inga.jonane@cfi.lu.lv

**Abstract.** Energy-dispersive X-ray absorption spectroscopy at the Mo K-edge was used to study pressure-induced (up to 36 GPa) changes in the local atomic structure of 2D layered oxide  $\alpha$ -MoO<sub>3</sub>. A linear combination analysis based on the low and high-pressure X-ray absorption near edge structure (XANES) spectra shows clear evidence of two high-pressure phases, existing at 18-25 GPa and above 32 GPa. The first transition is due to gradual decrease of the interlayer gap, whereas the second one – to its collapse and oxide structure reconstruction. The local atomic structure around molybdenum atoms at 0.2, 18.5 and 35.6 GPa was determined from the extended X-ray absorption fine structure (EXAFS) using reverse Monte Carlo calculations.

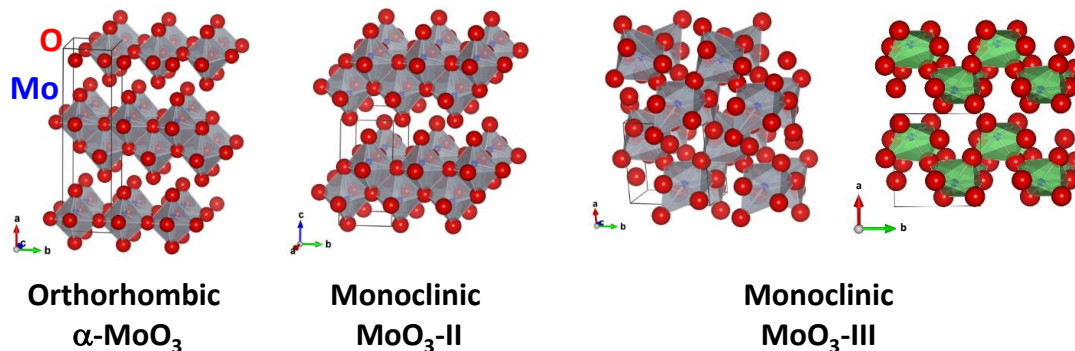
## 1. Introduction

After the discovery of graphene, other members of 2D layered materials family, including molybdenum trioxide (MoO<sub>3</sub>), have been intensively investigated due to their unique properties [1]. MoO<sub>3</sub> is known to exist in six different phases:  $\alpha$ -MoO<sub>3</sub>, h-MoO<sub>3</sub>,  $\beta$ -MoO<sub>3</sub>,  $\beta'$ -MoO<sub>3</sub>, MoO<sub>3</sub>-II and MoO<sub>3</sub>-III [2, 3]. Only orthorhombic  $\alpha$ -phase (space group *Pbnm*) is the thermodynamically stable at ambient conditions. The structure of  $\alpha$ -MoO<sub>3</sub> (Fig. 1) is composed of strongly distorted MoO<sub>6</sub> octahedra, which share edges and form chains linked into layers stacked on top of each other with rather weak van der Waals forces [4]. The oxidation state of molybdenum ions is +6, corresponding to the electronic configuration 4d<sup>0</sup>, which is responsible for their displacement from the octahedron centre due to the second-order Jahn-Teller effect [5].

$\alpha$ -MoO<sub>3</sub> attracts much attention because of its electrochromic and photochromic properties [6, 7]. Layered structure makes it prospective for applications in solar cells [8], catalysis [9, 10] and gas sensing devices [11, 12, 13]. At the same time, technologically relevant electric and optical properties can be affected when high pressure is applied.

The high-pressure behaviour of microcrystalline  $\alpha$ -MoO<sub>3</sub> has been investigated in the past by angle-dispersive synchrotron X-ray powder diffraction and Raman spectroscopy techniques up to 43 GPa [3]. Two phase transitions were found at room temperature – to monoclinic MoO<sub>3</sub>-II phase (*P2<sub>1</sub>/m*) at ~12 GPa and to monoclinic MoO<sub>3</sub>-III phase (*P2<sub>1</sub>/c*) at ~25 GPa (Fig. 1). Note that MoO<sub>3</sub>-II phase was observed before only at high-pressure and high-temperature in [14].





**Figure 1.** Structures of molybdenum trioxide: orthorhombic  $\alpha$ -MoO<sub>3</sub> ( $Pbnm$ ) [4], monoclinic MoO<sub>3</sub>-II phase ( $P2_1/m$ ) and monoclinic MoO<sub>3</sub>-III phase ( $P2_1/c$ ) [3, 14]. Two ways of structure representation are shown for MoO<sub>3</sub>-III using MoO<sub>7</sub> (left) and MoO<sub>6</sub> (right) polyhedra.

While the first two phases,  $\alpha$ -MoO<sub>3</sub> and MoO<sub>3</sub>-II, are quite similar from the local environment point of view, a collapse of the interlayer gap occurs in MoO<sub>3</sub>-III phase [3].

In this study, we report on the pressure-dependent X-ray absorption spectroscopy (XAS) study of  $\alpha$ -MoO<sub>3</sub> up to  $\sim 36$  GPa to evaluate the influence of pressure on the local atomic and electronic structure. Since XAS is extremely sensitive to the distortions in the local environment around the absorbing atom, its spectral features in X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions can be used to monitor and identify structural changes during compression.

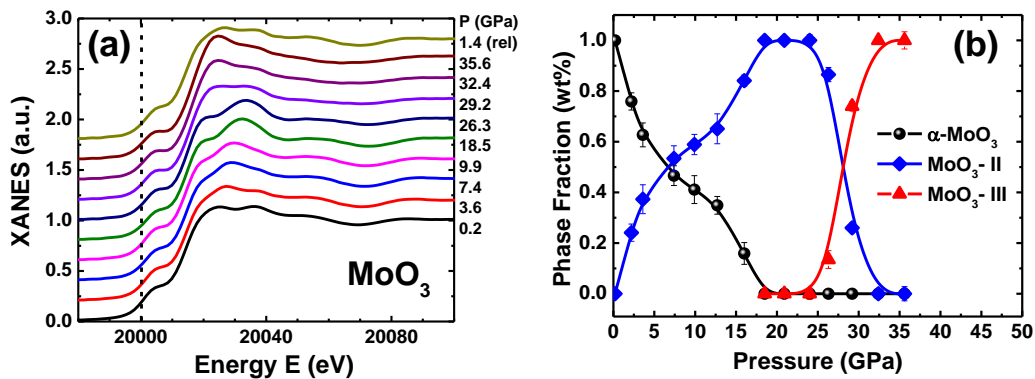
## 2. Experimental

Pressure-dependent Mo K-edge (20000 eV) X-ray absorption spectroscopy of microcrystalline  $\alpha$ -MoO<sub>3</sub> was performed at room temperature using energy-dispersive setup of bending-magnet ODE beamline [15] located at SOLEIL synchrotron facility. The SOLEIL synchrotron operated in the top-up mode with the energy  $E=2.75$  GeV and current  $I=450$  mA. A dispersive polychromator Si(311) was employed to focus X-rays, and the X-ray intensity was measured by a Princeton Instruments PIXIS-400 CCD camera coupled with a scintillator. A membrane-type nano-polycrystalline diamond anvil cell (NDAC) [16] was used to control the sample pressure up to 36 GPa. The silicon oil was used as a pressure transmitting media. The pressure in the cell was determined from a position of the  $R_1$ -line of ruby fluorescence excited at 473 nm.

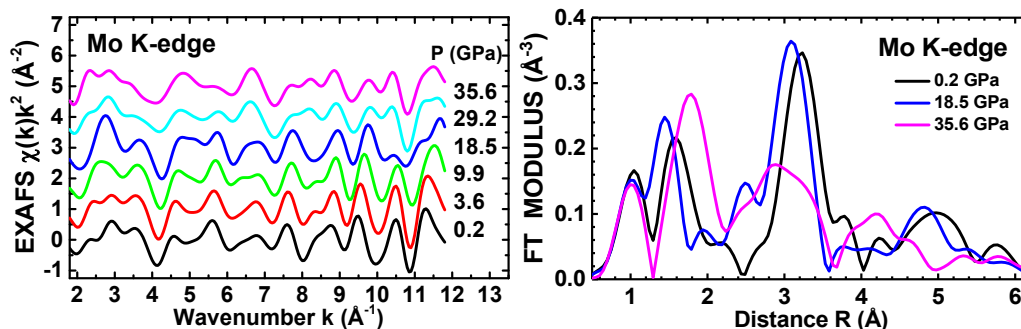
## 3. Results and discussion

Pressure dependence of the Mo K-edge XANES in Fig. 2(a) indicates the presence of three phases with transition points above 9.9 GPa and 26.3 GPa. After the pressure is released, the system returns back to the  $\alpha$ -phase. A phase fraction was evaluated from XANES in the energy range from 19985 to 20075 eV at each pressure using a linear combination analysis (LCA). The experimental XANES spectra at  $P=0.2$ , 18.5 and 32.4 GPa were selected as a reference spectra corresponding to pure  $\alpha$ -MoO<sub>3</sub>, MoO<sub>3</sub>-II, MoO<sub>3</sub>-III phases, respectively. The obtained results are plotted in Fig. 2(b) and are in good agreement with X-ray diffraction data [3]. In the pressure range between  $\sim 10$  and 15 GPa, the two phases,  $\alpha$ -MoO<sub>3</sub> and MoO<sub>3</sub>-II, coexist in a close ratio, whereas MoO<sub>3</sub>-III phase appears above  $\sim 26$  GPa, leading to a change of the XANES.

These findings are also supported by a behavior of the Mo K-edge EXAFS (Fig. 3). The transition from MoO<sub>3</sub>-II to MoO<sub>3</sub>-III phase is accompanied by a change of the Mo–O–Mo angles between neighbouring molybdenum-oxygen polyhedra from  $\sim 144^\circ$  and  $\sim 169^\circ$  in MoO<sub>3</sub>-II [14] to  $\sim 149^\circ$  in MoO<sub>3</sub>-III [3]. The absence of the Mo–O–Mo angle equal to  $169^\circ$  is responsible for a



**Figure 2.** (a) Pressure dependence of the Mo K-edge X-ray absorption near edge structure (XANES) in molybdenum trioxide. (b) Variation of the phase fraction as a function of applied pressure obtained from XANES by the linear combination analysis.

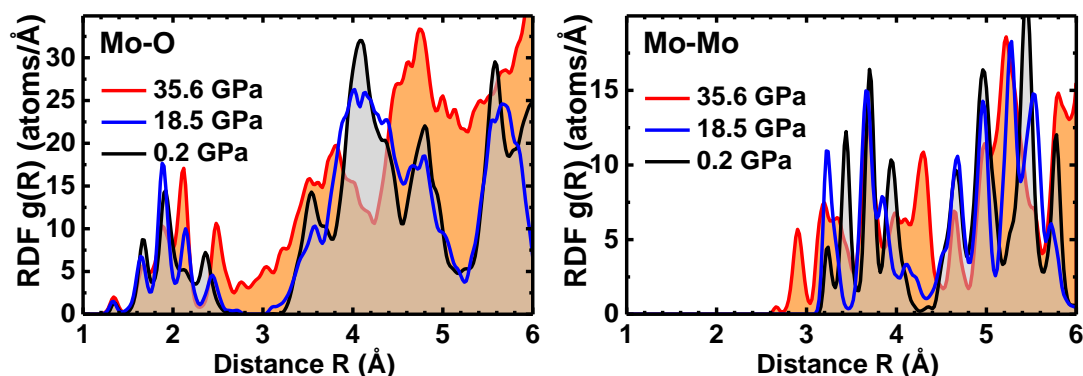


**Figure 3.** Pressure dependence of the Mo K-edge EXAFS spectra  $\chi(k)k^2$  and their Fourier transforms (FTs) in molybdenum trioxide.

decrease of the second shell peak (at  $\sim 3.2$  Å) amplitude in the Fourier transforms of the EXAFS spectra due to a reduction of the multiple-scattering (MS) effects.

To follow pressure induced changes in details, the analysis of EXAFS spectra beyond the first coordination shell of molybdenum was performed using reverse Monte Carlo (RMC) calculations [17], including the MS effects up to the 6th order. Structural models for  $\alpha$ -MoO<sub>3</sub>, MoO<sub>3</sub>-II and MoO<sub>3</sub>-III phases based on the diffraction data from [2, 3] were used as initial atomic configurations and resulted in good agreement with the experimental EXAFS data. The atomic coordinates obtained from RMC simulations were employed to calculate the partial radial distribution functions (RDFs)  $g_{\text{Mo-O}}(R)$  and  $g_{\text{Mo-Mo}}(R)$  for  $\alpha$ -MoO<sub>3</sub> (0.2 GPa), MoO<sub>3</sub>-II (at 18.5 GPa) and MoO<sub>3</sub>-III (35.6 GPa) phases (Fig. 4). Note that the peaks in the RDFs  $g_{\text{Mo-O}}(R)$  up to about 2.6 Å correspond to the nearest oxygen atoms, forming the coordination polyhedra.

At ambient conditions, there are three groups of two oxygen atoms each at  $\sim 1.70$ , 1.96 and 2.26 Å, which form strongly distorted MoO<sub>6</sub> octahedra in  $\alpha$ -MoO<sub>3</sub>. Already a small pressure of about 0.2 GPa induces lattice contraction, leading to an increase of the MoO<sub>6</sub> octahedra distortion and splitting of some Mo-Mo peaks. In MoO<sub>3</sub>-II phase at 18.5 GPa, the layered structure persists, MoO<sub>6</sub> octahedra remain distorted and do not differ significantly from that in  $\alpha$ -MoO<sub>3</sub>, as is expected from diffraction data [2, 3]. At high pressure (35.6 GPa), the collapse of layered structure leads to an increase of molybdenum coordination. Six nearest oxygen atoms from the same layer are responsible for the peaks at  $\sim 1.68$ , 1.88 and 2.12 Å, whereas the 7th oxygen atom bridging two layers is located at  $\sim 2.48$  Å. The high pressure modifies also the



**Figure 4.** Radial distribution functions for Mo–O and Mo–Mo atom pairs in  $\alpha$ -MoO<sub>3</sub> (at 0.2 GPa), MoO<sub>3</sub>-II (at 18.5 GPa) and MoO<sub>3</sub>-III (at 35.6 GPa), reconstructed by RMC method.

Mo–Mo distribution, leading to a shortening of the distance between neighboring molybdenum-oxygen polyhedra connected by edges (peaks at 3.25 and 2.9 Å).

#### 4. Conclusions

Two phase transitions from  $\alpha$ -MoO<sub>3</sub> to MoO<sub>3</sub>-II and, next, to MoO<sub>3</sub>-III were observed by the Mo K-edge X-ray absorption spectroscopy at room temperature in the pressure range from 0 to 36 GPa. Gradual decrease of the interlayer spacing is responsible for the first transition, whereas a collapse of the interlayer gap occurs when the oxide transforms to MoO<sub>3</sub>-III phase. The change of the molybdenum local environment upon phase transitions was determined by RMC method. After the pressure is released, the oxide restores its structure back to the orthorhombic  $\alpha$ -phase.

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