

LATTICE DYNAMICS

X-ray absorption near edge spectroscopy of thermochromic phase transition in CuMoO_4

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Thermochromic phase transition was studied in CuMoO_4 using the Cu and Mo *K*-edge x-ray absorption spectroscopy in the temperature range of 10–300 K. The hysteretic behavior has been evidenced from the temperature dependence of the pre-edge shoulder intensity at the Mo *K*-edge, indicating that the transition from brownish-red γ - CuMoO_4 to green α - CuMoO_4 occurs in the temperature range of 230–280 K upon heating, whereas the α -to- γ transition occurs between 200 and 120 K upon cooling. Such behavior of the pre-edge shoulder at the Mo *K*-edge correlates with the change of molybdenum coordination between distorted tetrahedral in α - CuMoO_4 and distorted octahedral in γ - CuMoO_4 . This result has been supported by *ab initio* full-multiple-scattering x-ray absorption near edge structure (XANES) calculations. *Published by AIP Publishing.*
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Introduction

Molybdates and tungstates find a wide range of practical applications due to their ability to adopt different crystallographic structures, whose physical properties can be further modified by a chemical composition.^{1,2} In particular, these materials are used as scintillators, down-conversion phosphors, white light-emitting diodes, laser host materials, catalysts, sensors and pigments.^{3–12}

Copper molybdate CuMoO_4 is a functional oxide material exhibiting thermochromic and piezochromic properties.^{13–15} It attracts much attention because of its potential applications for temperature sensing in the ranges where majority of organic compounds and liquid crystals are unstable. Possible chromic-related applications extend from the user-friendly temperature and pressure indicators^{14–17} to “smart” inorganic pigments.¹⁸ Besides, copper molybdate has also promising catalytic properties.^{19–23}

Structural, optical, electrical and magnetic properties of CuMoO_4 were previously studied in Refs. 13 and 24–27. Currently six different structural phases of CuMoO_4 are known.^{24,28} In this study, we focus on two of them—green α - CuMoO_4 and brownish-red γ - CuMoO_4 phases that are stable at high and low temperatures, respectively (Fig. 1).

At ambient pressure and room temperature, CuMoO_4 has α -phase with triclinic structure (space group *P*-1).^{24,29} It is composed of distorted CuO_6 octahedra, CuO_5 square-pyramids and MoO_4 tetrahedra. By decreasing temperature

tetrahedra. below ~ 200 K (or by applying pressure above 0.2 GPa at room temperature) reversible first order phase transition from α - CuMoO_4 to γ - CuMoO_4 occurs.²⁴ Low-temperature γ modification also has triclinic lattice (space group *P*-1) built up of distorted CuO_6 and MoO_6 octahedra.²⁵ The α -to- γ phase transition is accompanied by color change (from green to brownish-red) and volume reduction of 12%–13%²⁴ that makes the two phases easily distinguishable. However, the presence in both phases of three non-equivalent Cu and Mo atoms with different local environment makes structural analysis challenging.²⁴

The α -to- γ phase transition occurring below room temperature was studied previously using x-ray diffraction²⁴ and optical spectroscopy,^{14,26} differential scanning calorimetry and magnetic susceptibility¹⁴ measurements. It was found that the transition has hysteretic behavior, so that lower temperature is required to promote the α -to- γ transition than γ -to- α .

Chromic properties of CuMoO_4 are associated with the interplay between two optical absorption bands: the one in the blue range (around 3 eV) is due to the interband transition across the band gap of the crystal and the second one in the red (around 1.49 eV) originates due to the intraband *d*-*d* transition at copper.^{13,14,26} Note that the thermochromic phase transition is strongly affected by chemical composition: for example, an addition of tungsten to CuMoO_4 results in a formation of solid solutions $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ ($x \leq 0.12$) and shifts the transition temperature by up to 100 K.^{14,18,24}

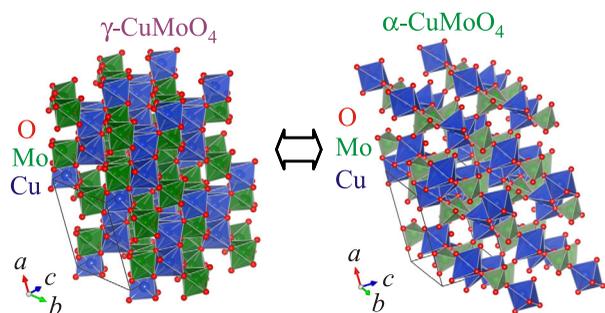


Fig. 1. Crystalline structures of high-temperature α -CuMoO₄ and low-temperature γ -CuMoO₄ phases.²⁴

Since thermochromic and piezochromic properties of CuMoO₄ are connected with its local structure, x-ray absorption spectroscopy (XAS) is an obvious choice to probe structural changes during the phase transition. XAS provides information complementary to other techniques and, in the case of CuMoO₄ can probe the local environment around Cu and Mo atoms independently by detecting two different absorption edges. Therefore, we have performed the temperature-dependent (10–300 K) Cu and Mo *K*-edge XAS study of thermochromic phase transition in CuMoO₄ at the new P65 beamline (HASYLAB at DESY, Hamburg) using the synchrotron radiation from the PETRA-III storage ring. The obtained results allowed us to confirm the hysteretic nature of phase transition and to explain the influence of structural changes on the x-ray absorption near edge structure based on *ab initio* full-multiple-scattering calculations.

Experimental and data analysis

Polycrystalline CuMoO₄ powder was synthesized using solid-state reaction method by heating a mixture of CuO and MoO₃ powders at 650 °C in air for 8 h followed by cooling down to room temperature. The as-prepared powder corresponded to α -CuMoO₄ phase and had green color.

Temperature-dependent (from 10 to 300 K) x-ray absorption experiments were conducted at the HASYLAB PETRAIII P65 undulator beamline. The PETRA-III storage ring operated at $E = 6.08$ GeV and current $I = 95$ mA in top-up 40 bunch mode. The harmonic rejection was achieved by uncoated (Cu edge) and Rh-coated (Mo edge) silicon plane mirrors. Fixed exit Si(311) double-crystal monochromator was used in all experiments. The x-ray absorption spectra were collected at the Cu (8979 eV) and Mo (20 000 eV) *K*-edges in transmission mode using two ionization chambers. The Oxford Instruments liquid helium flow cryostat was used to maintain the sample temperature. The CuMoO₄ powder was gently milled in agate mortar and deposited on Millipore membrane.

The Cu and Mo *K*-edge XANES parts of the x-ray absorption spectra were isolated and used in the further analysis. It was observed that the Cu *K*-edge XANES spectra do not vary significantly upon temperature change indicating some stability of the copper environment. Therefore, they will not be discussed further. At the same time, the Mo *K*-edge XANES was significantly affected by temperature variation. The experimental Mo and Cu *K*-edge XANES spectra corresponding to γ -CuMoO₄ at 10 K and α -CuMoO₄ at 300 K are shown in

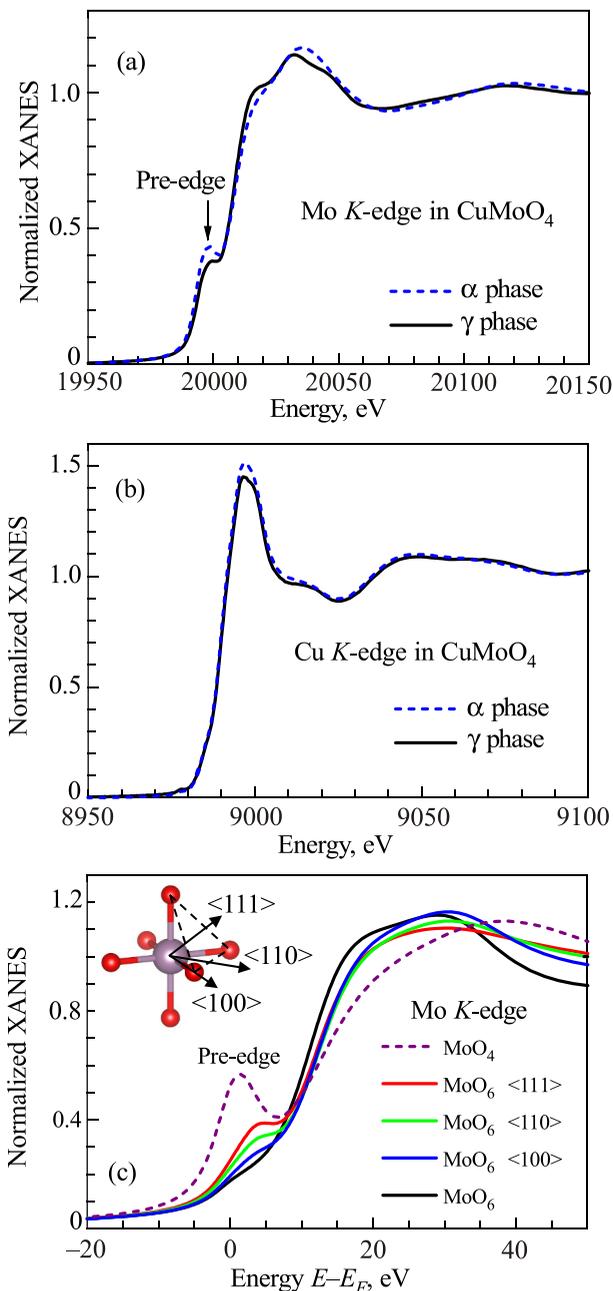


Fig. 2. (a) and (b) Experimental Mo and Cu *K*-edge XANES of α -CuMoO₄ (at 300 K) and γ -CuMoO₄ (at 10 K) phases. (c) Calculated Mo *K*-edge XANES for regular MoO₄ tetrahedron, distorted and regular MoO₆ octahedra. Numbers in brackets indicate the direction of molybdenum ion off-center displacement. See text for more details.

Figs. 2(a) and 2(b). The pre-edge shoulder at the Mo *K*-edge is clearly visible around 20 000 eV, and its change can be related to a transition from MoO₄ tetrahedra to MoO₆ octahedra upon cooling. At the same time, the Cu *K*-edge XANES does not change significantly upon phase transition.

A fraction of α -CuMoO₄ phase was evaluated at each temperature during heating from 10 to 300 K and cooling from 300 down to 100 K using a linear combination of the lowest temperature (10 K) and highest temperature (300 K) Mo *K*-edge XANES. The analysis was performed using Athena package³⁰ in the energy range from 19980 to 20010 eV with the aim to sample a variation of the pre-edge shoulder. The obtained results are shown in Fig. 3, where the hysteretic behavior is well observed.

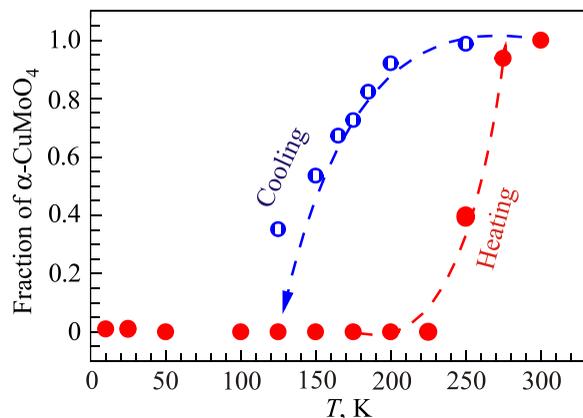


Fig. 3. Temperature dependence of the fraction of α -CuMoO₄ phase upon heating (solid circles) and cooling (open circles).

XANES calculations

Full-multiple-scattering (FMS) XANES calculations were performed using *ab initio* real-space FDMNES code^{31,32} employing muffin-tin (10% overlap) self-consistent potential. The dipole and quadrupole transitions were taken into account, and the energy-dependent real Hedin–Lundqvist exchange-correlation potential was used.^{33,34} The calculated XANES spectra were broadened to account for the core-hole level width (5.8 eV at the Mo *K*-edge³⁵) and other multielectronic phenomena. The energy origin was set at the Fermi level E_F .

The results of FMS XANES calculations for five MoO_x clusters are shown in Fig. 2(c). They correspond to regular MoO₄ tetrahedron [$R(\text{Mo–O}) = 1.78$ Å], regular MoO₆ octahedron [$R(\text{Mo–O}) = 1.98$ Å] and distorted MoO₆ octahedra with molybdenum ion being displaced in the direction of octahedron apex by 0.2 Å ($\langle 100 \rangle$), to the octahedron edge by 0.28 Å ($\langle 110 \rangle$) and to the octahedron face by 0.35 Å ($\langle 111 \rangle$).

FMS XANES calculations were also performed for α - and γ -CuMoO₄ structural models created using diffraction data from.²⁴ The total calculated Mo *K*-edge XANES spectra and separate contributions from non-equivalent molybdenum atoms (Mo1, Mo2 and Mo3) are compared with the experimental data in Fig. 4.

Results and discussion

The Mo *K*-edge XANES spectra of CuMoO₄ at two temperatures (10 and 300 K) are shown in Fig. 2(a). The pre-edge shoulder at ~ 20 000 eV corresponds to the $1s(\text{Mo}) \rightarrow 4d(\text{Mo}) + 2p(\text{O})$ transition. Note that the final state of the electron is the relaxed excited state in the presence of the core hole at the $1s(\text{Mo})$ level screened by other electrons. The transition is forbidden in the dipole approximation for a regular MoO₆ octahedron, having an inversion center, but becomes allowed when inversion symmetry is broken as in distorted octahedron^{36,37} or in tetrahedron³⁸ [Fig. 2(c)]. The amplitude of the pre-edge shoulder depends on the degree of the MoO₆ octahedra distortion and $4d(\text{Mo})/2p(\text{O})$ orbital mixing and is the largest for tetrahedral MoO₄ coordination.³⁹ Therefore, it can be used to monitor the γ -to- α phase transition in CuMoO₄.

Since accurate separation of the pre-edge shoulder from the main absorption edge is tricky, we employed a different approach: the experimental XANES spectrum at each temperature was approximated by a linear combination of the

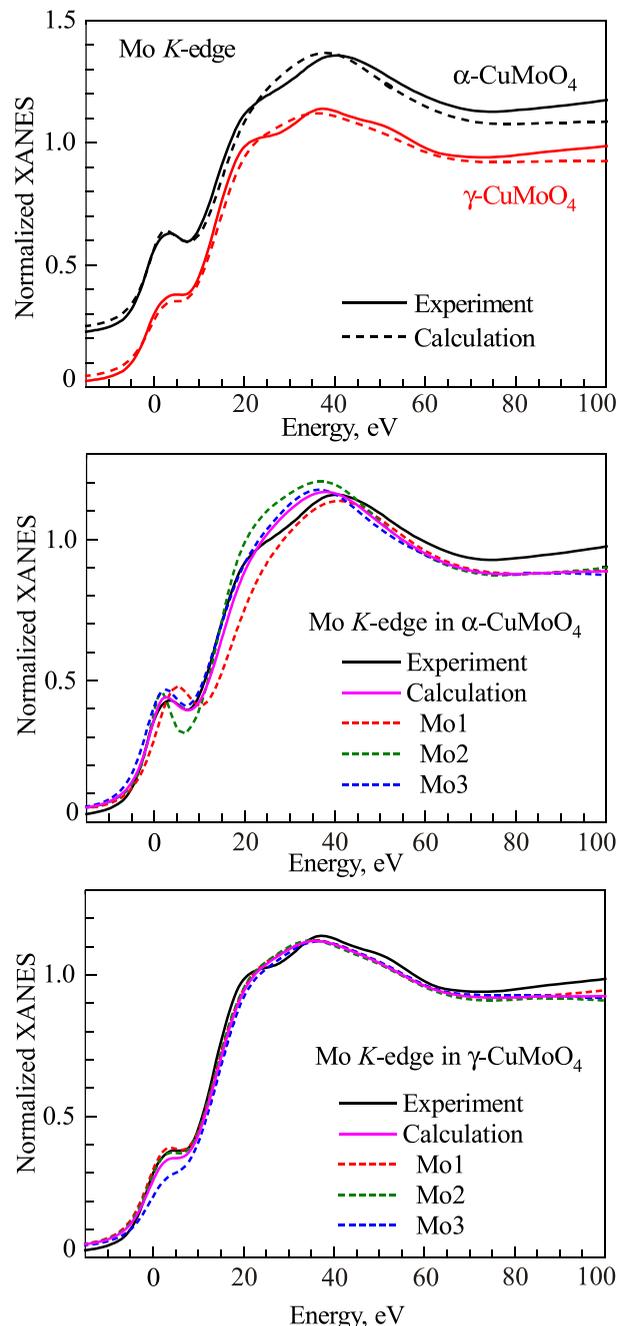


Fig. 4. Comparison of the experimental and calculated Mo *K*-edge XANES of α -CuMoO₄ and γ -CuMoO₄ phases (upper panel). Contributions from three non-equivalent molybdenum atoms (Mo1, Mo2, Mo3) to the Mo *K*-edge XANES are also shown in the middle and lower panels for α -CuMoO₄ and γ -CuMoO₄ phases, respectively.

lowest temperature (10 K) and highest temperature (300 K) XANES spectra. As a result, the fraction of the α -CuMoO₄ phase in the total XANES upon heating and cooling was estimated and is reported in Fig. 3. As one can see, only γ -CuMoO₄ is present below 150 K and only α -CuMoO₄ is observed above 280 K, as expected.

Linear combination analysis showed that upon heating, the γ -to- α phase transition occurs between ~ 230 and 280 K, whereas upon cooling, the α -to- γ transition takes place at lower temperature between ~ 120 and 200 K, showing a large hysteresis loop with the range of two phase coexistence of about 50–80 K. Following the notation from Ref. 14, two temperature $T_{1/2H}$ and $T_{1/2C}$ corresponding to about 50 mol. % of the α and

γ phases upon heating and cooling, respectively, are equal to $T_{1/2H} \approx 255$ K and $T_{1/2C} \approx 143$ K. The width of the hysteresis is defined as $\Delta T_{1/2C} = T_{1/2C} - T_{1/2H} = 112$ K.

Note that our value of $\Delta T_{1/2}$ is slightly larger than those estimated from optical reflectivity ($\Delta T_{1/2} = 72$ K), differential scanning calorimetry ($\Delta T_{1/2} = 96$ K) and magnetic susceptibility ($\Delta T_{1/2} = 80$ K) measurements in Ref. 14.

FMS Mo K -edge XANES calculations performed for α -CuMoO₄ and γ -CuMoO₄ phases are shown in Fig. 4. They are in a reasonable agreement with the experimental data. Since there are three non-equivalent molybdenum atoms in the unit cells of both molybdates,²⁴ we have calculated also their contributions into the total XANES spectrum (see two lower panels in Fig. 4).

As one can see, the three molybdenum atoms, located in distorted tetrahedral coordination with the Mo–O distances ranged between 1.70 and 1.86 Å,²⁴ produce slightly different XANES for α -CuMoO₄. At the same time, the three contributions to XANES from molybdenum atoms, located in strongly distorted octahedral environment with the Mo–O bond lengths ranged between 1.68 and 2.49 Å,²⁴ are close for γ -CuMoO₄, except for the region of the pre-edge peak. These differences are caused by an influence of outer coordination shells located above 2.5 Å, whose detailed analysis using reverse Monte Carlo approach is in progress.

Conclusions

We report the first *in situ* x-ray absorption spectroscopy study of the thermochromic phase transition between brownish-red γ -CuMoO₄ and green α -CuMoO₄ in the temperature range from 10 to 300 K. We found that the Cu K -edge XANES is weakly affected upon the phase transition because the local environment of copper atoms does not change significantly. At the same time, the analysis of the Mo K -edge XANES allowed us to follow the transition, tracing a variation of the pre-edge shoulder.

The experimental Mo K -edge XANES data were interpreted based on *ab initio* full-multiple-scattering calculations. Good agreement was found between the experimental and simulated XANES spectra, and the contribution from non-equivalent molybdenum atoms in the crystallographic unit cell was estimated. It was shown that the amplitude of the pre-edge shoulder correlates with the type and the degree of distortion of molybdenum–oxygen coordination polyhedra.

A significant variation of the experimental Mo K -edge XANES upon the thermochromic transition occurs due to the change of the local environment of molybdenum atoms from distorted tetrahedral in green α -CuMoO₄ to distorted octahedral in brownish-red γ -CuMoO₄. Moreover, the thermochromic transition has well evidenced hysteretic behavior, in agreement with the results of previous studies.¹⁴ The transition from the γ -to- α phase occurs in the temperature range of 230–280 K upon heating, whereas the α to- γ transition occurs between 120 and 200 K upon cooling. The width of the hysteresis was estimated to be about 112 K.

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