11th Scientific Conference &12th Annual General Meeting
of the ELECTRON MICROSCOPY SOCIETY OF MALAYSIA

Transmission Electron Microscopy Investigation on Defect Structures of Molybdenum Oxides

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Johore Bahru 17 December 2002

Why I come here ?

born in China.

Ph.D in Austria

work in Germany

look like Malay

Reduction/Oxidation of Mo Oxides

◆ **XRD and XAS studies on reduction of MoO_3**

T<698K $MoO_3+H_2 \longrightarrow MoO_2+H_2O$

T>698K $3MoO_3+MoO_2 \longrightarrow Mo_4O_{11}$

$Mo_4O_{11}+3H_2 \longrightarrow 4MoO_2+3H_2O$

No Crystalline intermediates is formed

(T. Ressler, etc., J. Phys. Chem. B (2000) **104**, 6360)

◆ **XAS studies on reduction/oxidation of MoO_{3-x}**

Presence of edge-shared octahedra with short Mo-Mo distance in MoO_{3-x}

(T. Ressler, etc., J. Catalysis (2000) **191**, 75)

Short range order defect structure forms molybdenium suboxide ?
Visualisation and detection by means of HREM and electron diffraction ?

Homologous series of Mo suboxides

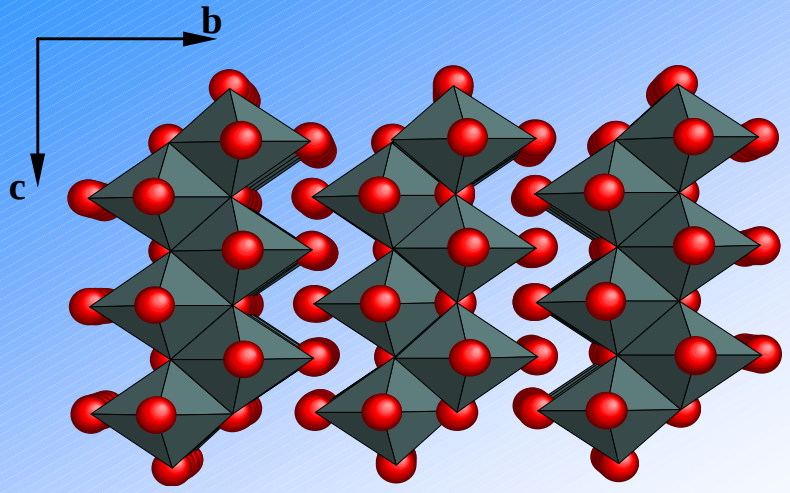
Shear Structures

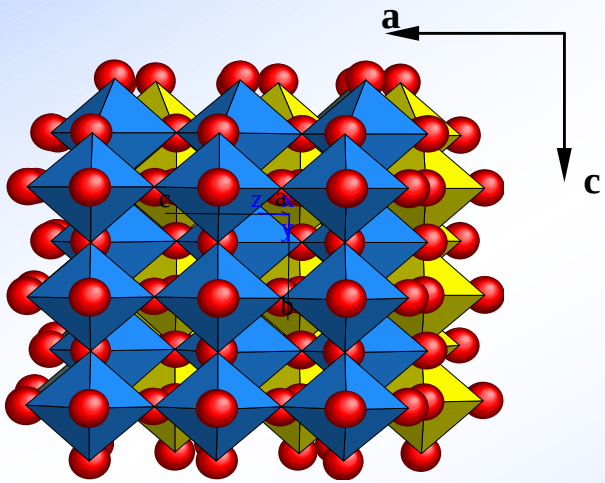
- **Mo_nO_{3n-2} (17£ n £25)**
  $Mo_{18}O_{52}$, ¼ derived from MoO_3 (layered structure)
- **Mo_nO_{3n-1} (n<10)**
  Mo_8O_{23} , ¼ derived from ReO_3-type structure

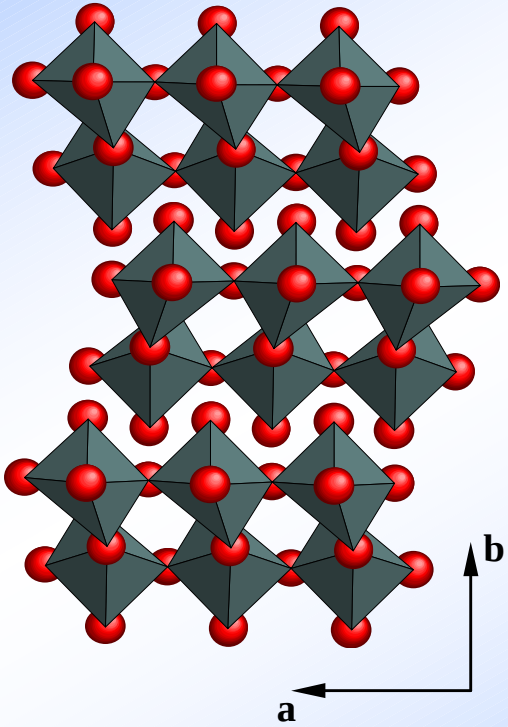
Other structures

- **Mo_4O_{11} ,**
- **Mo_5O_{14} , ¼**

Structure Model of MoO_3





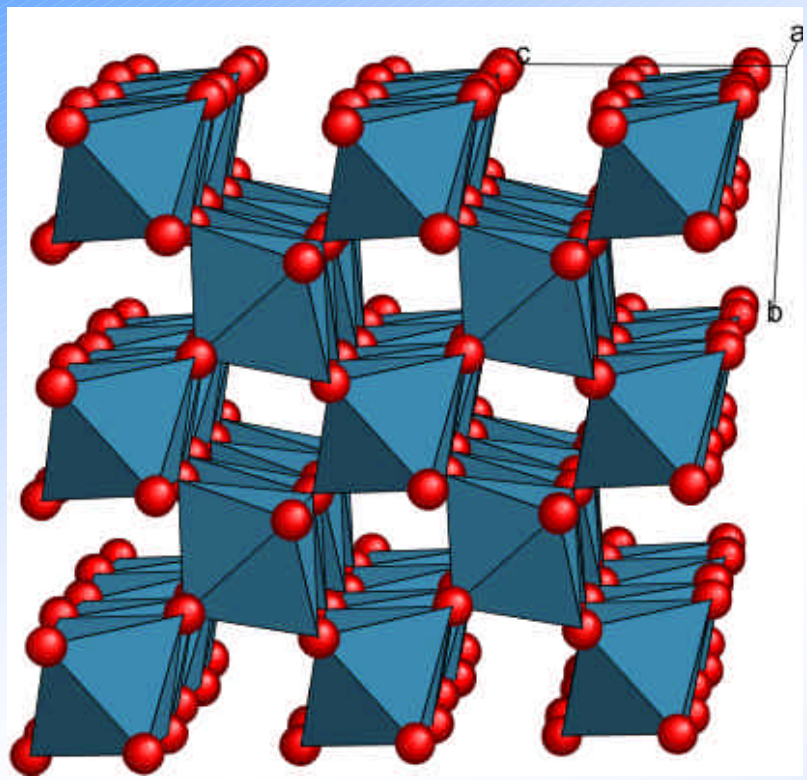


Space group: Pbnm

Structure type: Orthorhombic

a=3.92 Å
b=13.94 Å
c=3.66 Å

Structure Model of MoO_2

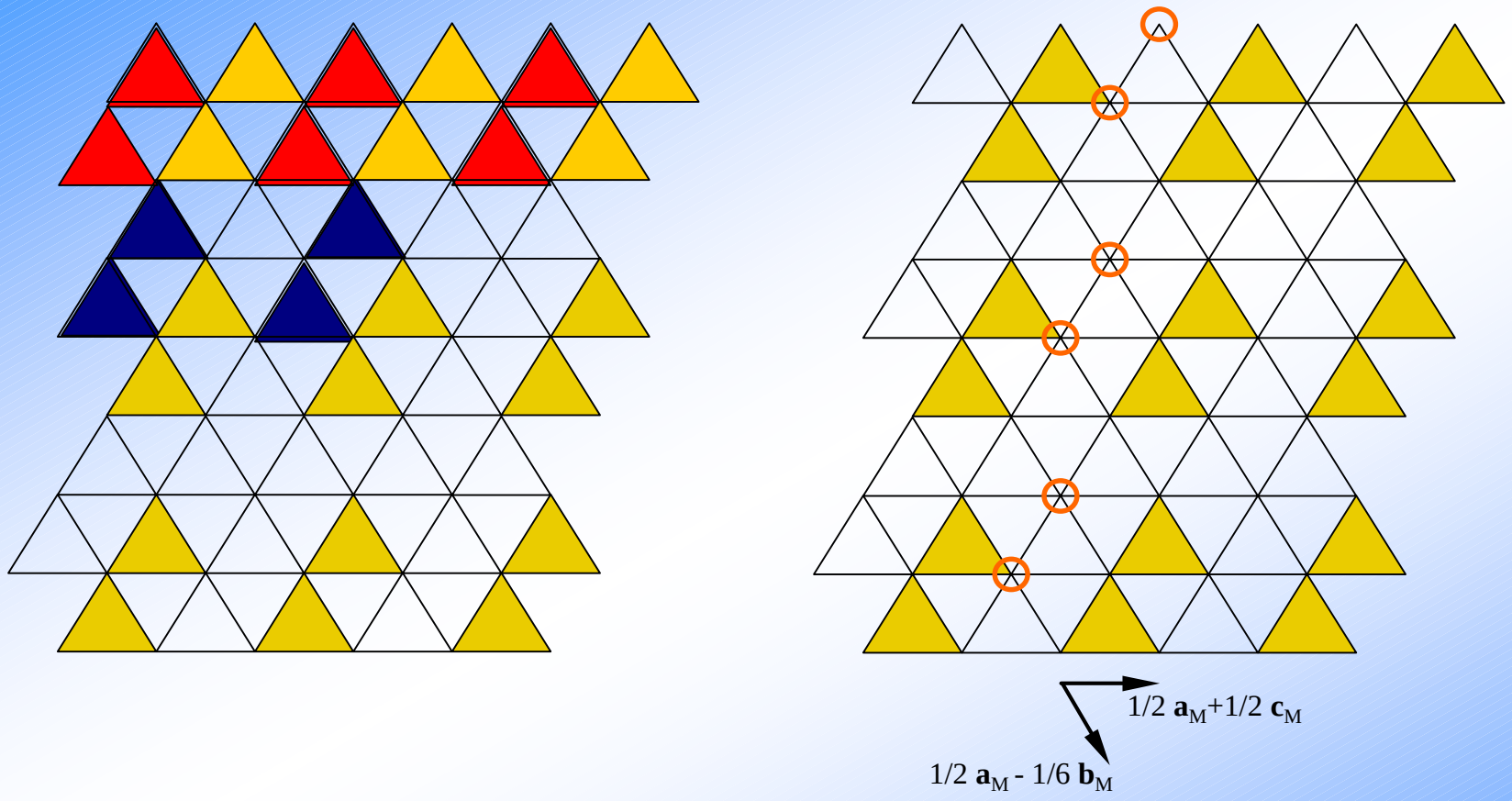


Space group: $P2_1/c$

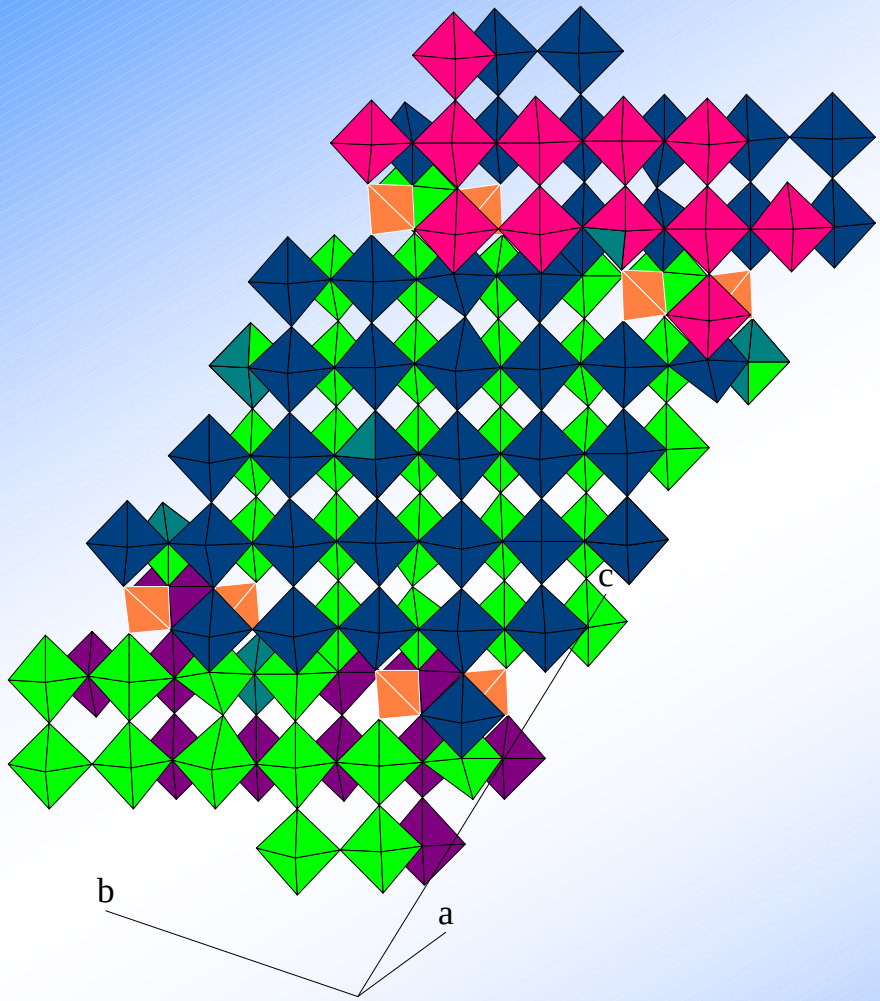
Structure type: Monoclinic

a=5.61 Å
b=4.86 Å
c=5.63 Å
β=120.9°

Principles of Shear Operation



Structure Model of $Mo_{18}O_{52}$

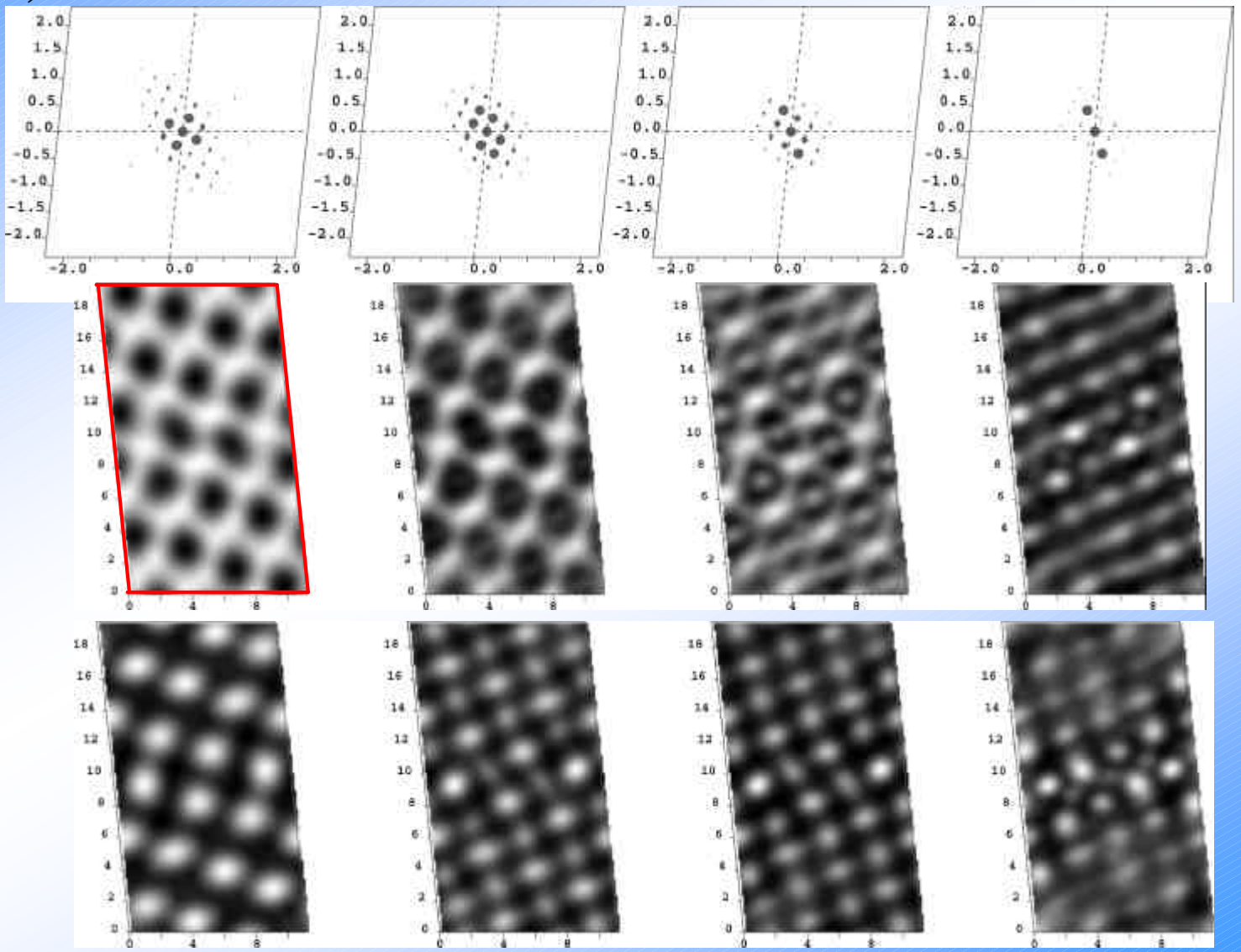


Space group: p-1

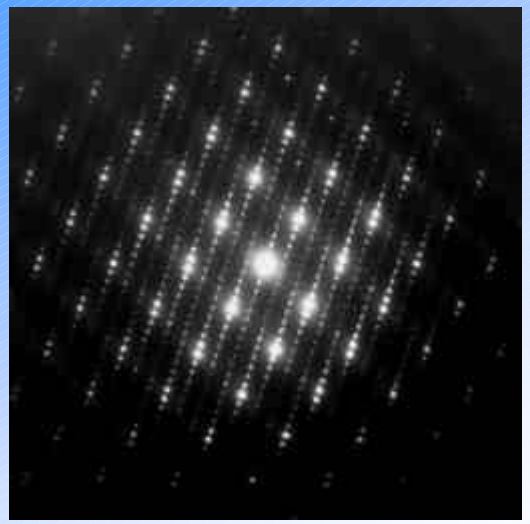
Structure type: triclinic

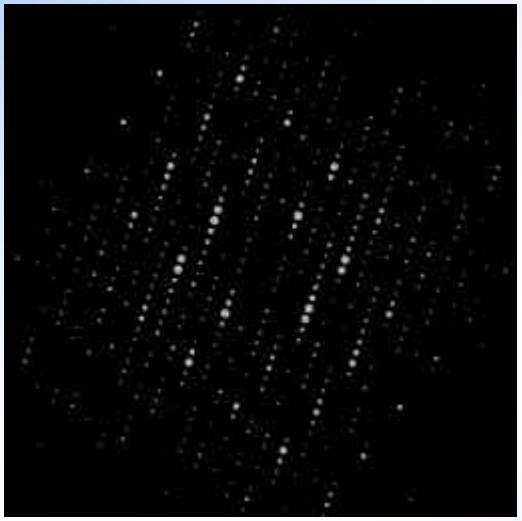
a=8.15 Å
b=11.89 Å
c=21.23 Å
α=102.7°
β=67.8°
γ= 110.0°

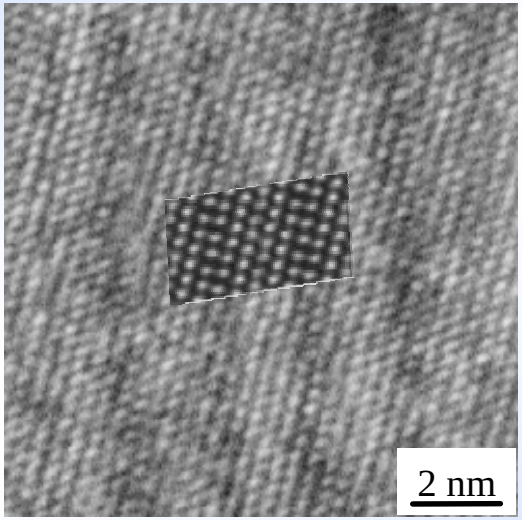
Simulated EDP and HREM images of $Mo_{18}O_{52}$ on [100] projection

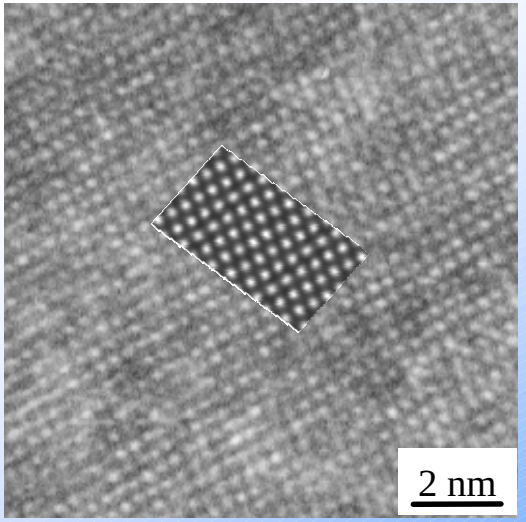


EDP and HREM of $Mo_{18}O_{52}$

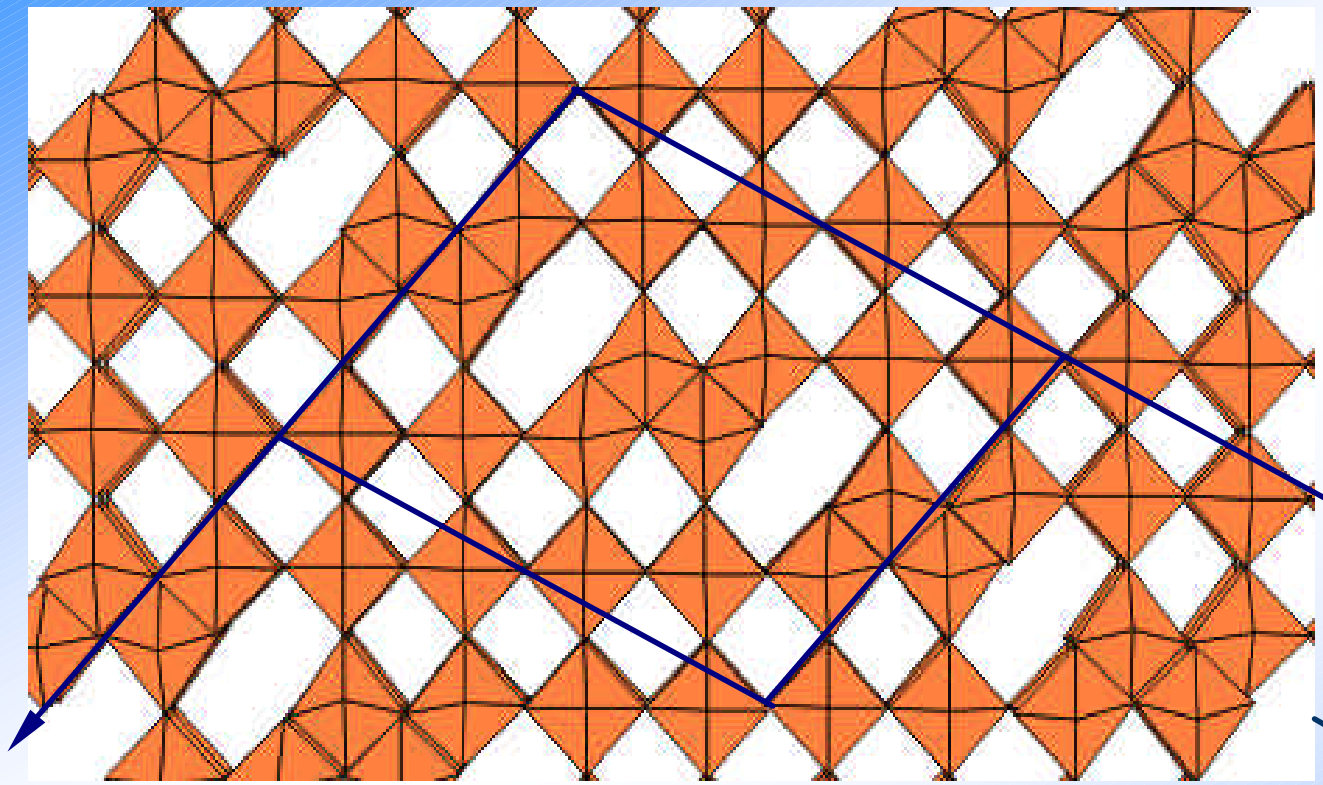








Structural Principles of Mo_8O_{23}



Space group: P2/a

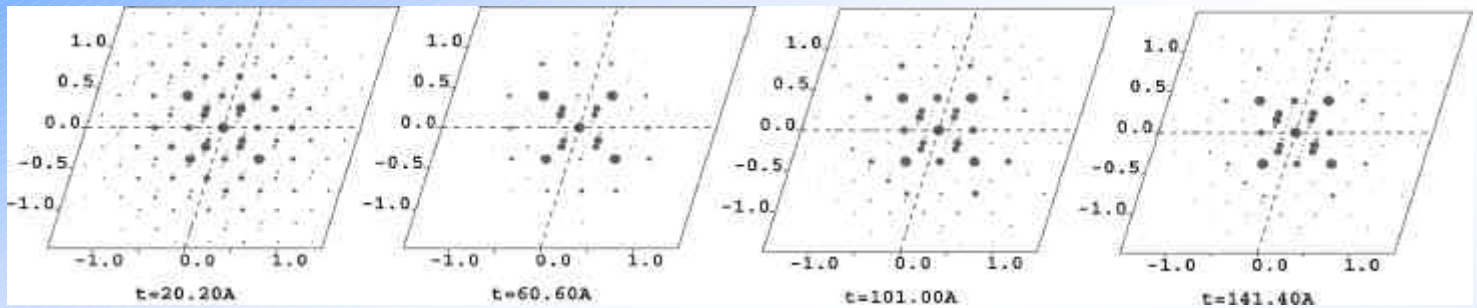
Structure type: Monoclinic

a=16.8 Å
b=4.04 Å
c=13.4 Å
β=106.5 °

Simulated EDP and HREM images of Mo_8O_{23} on [010] projection

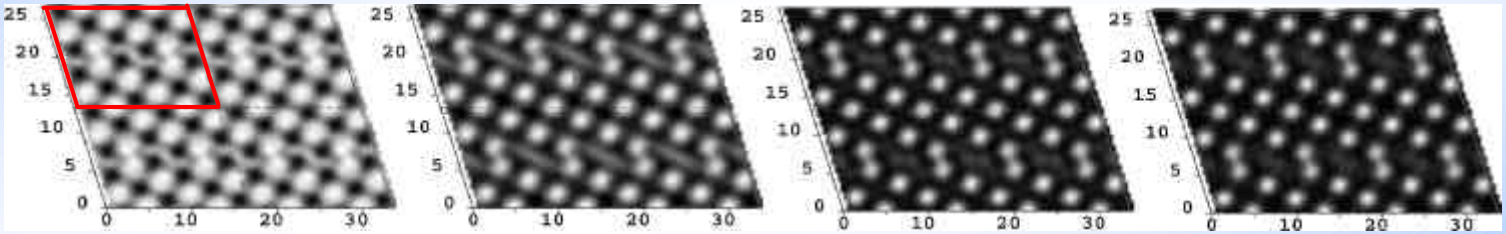
Sample Thickness(Å) 20.2 60.6 101.0 141.4

EDP

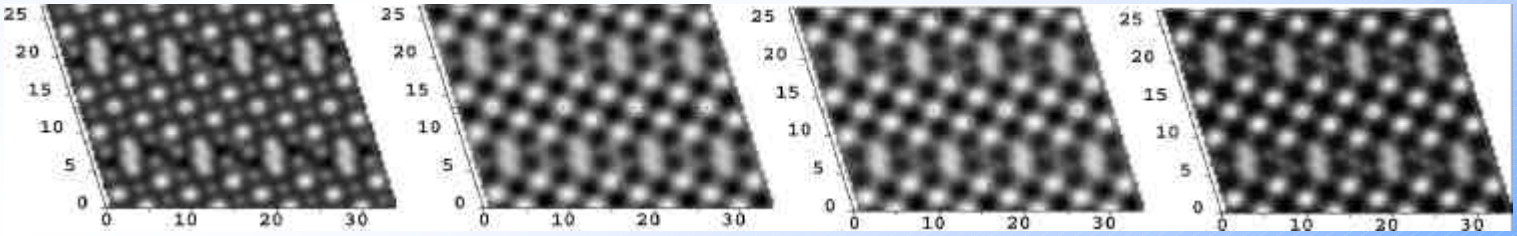


HREM Image

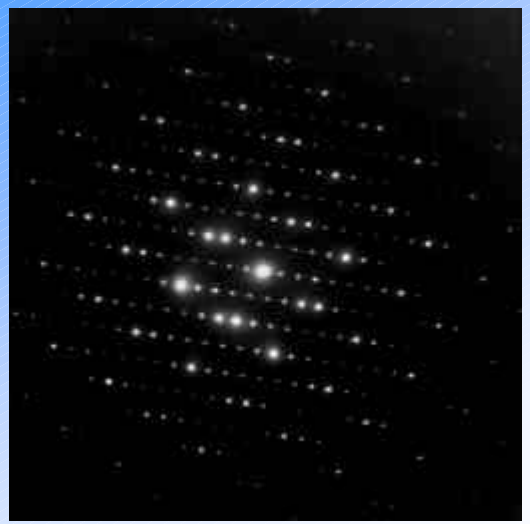
Defocus: -400 Å

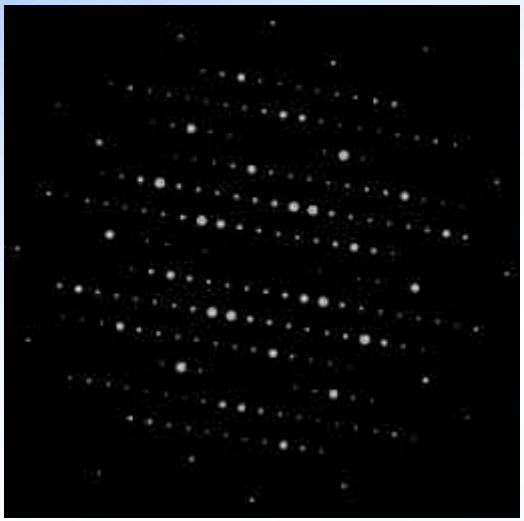


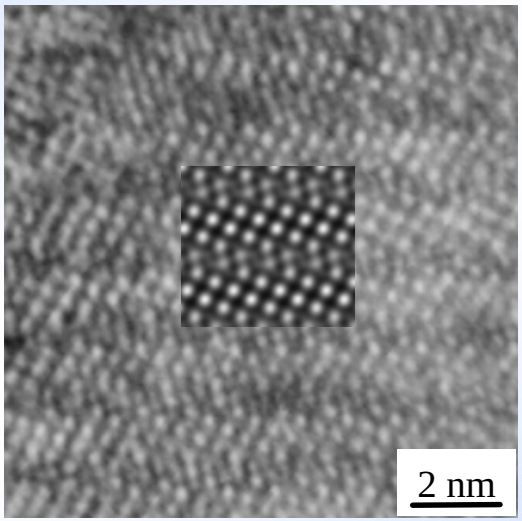
Defocus: -600 Å

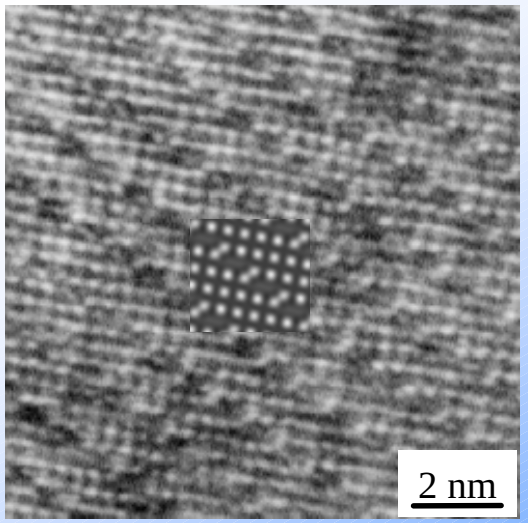


EDP and HREM of Mo_8O_{23}

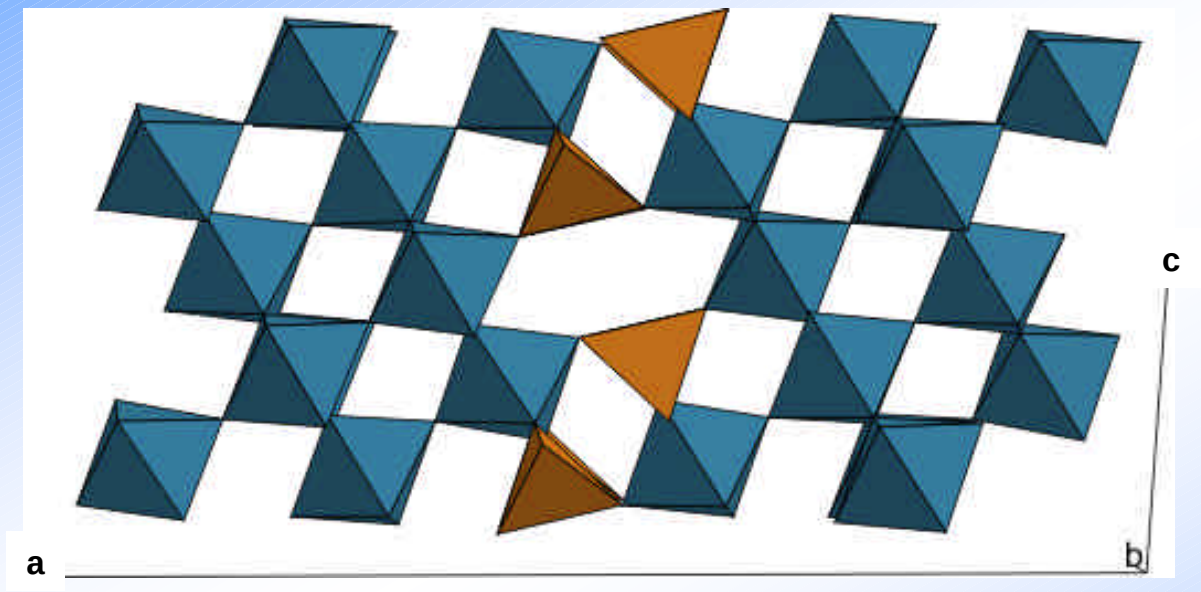








Structure Model of Mo_4O_{11}

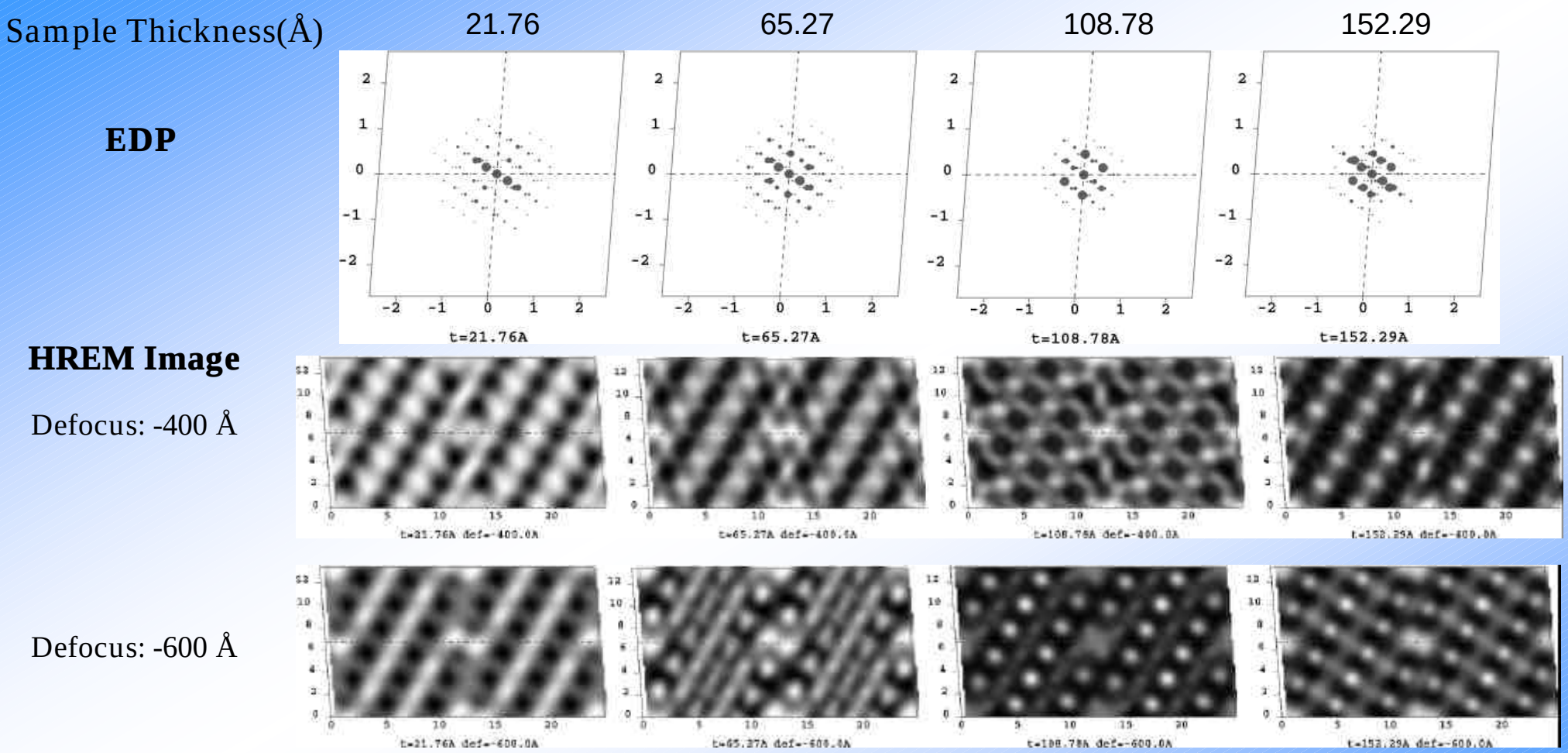


Space group: $P2_1/a$

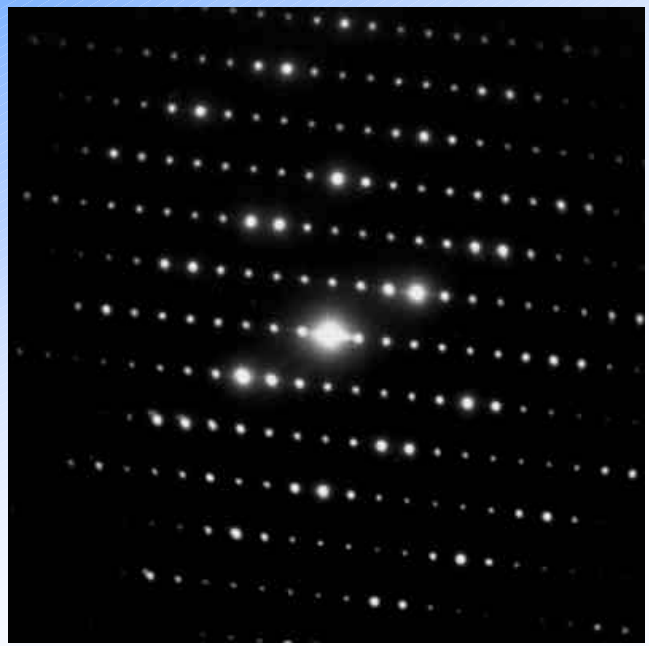
Structure type: Monoclinic

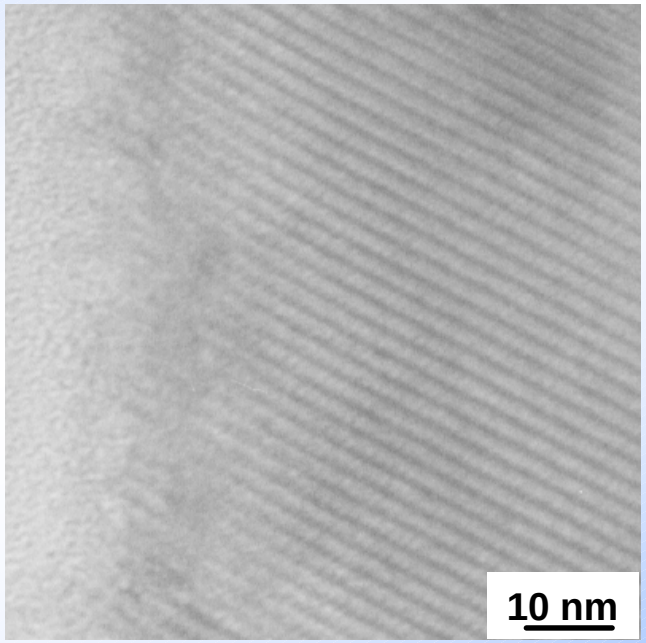
a=24.54 Å
b=5.44 Å
c=6.70 Å
β=94.3°

Simulated EDP and HREM images of Mo_4O_{11} on [010] projection

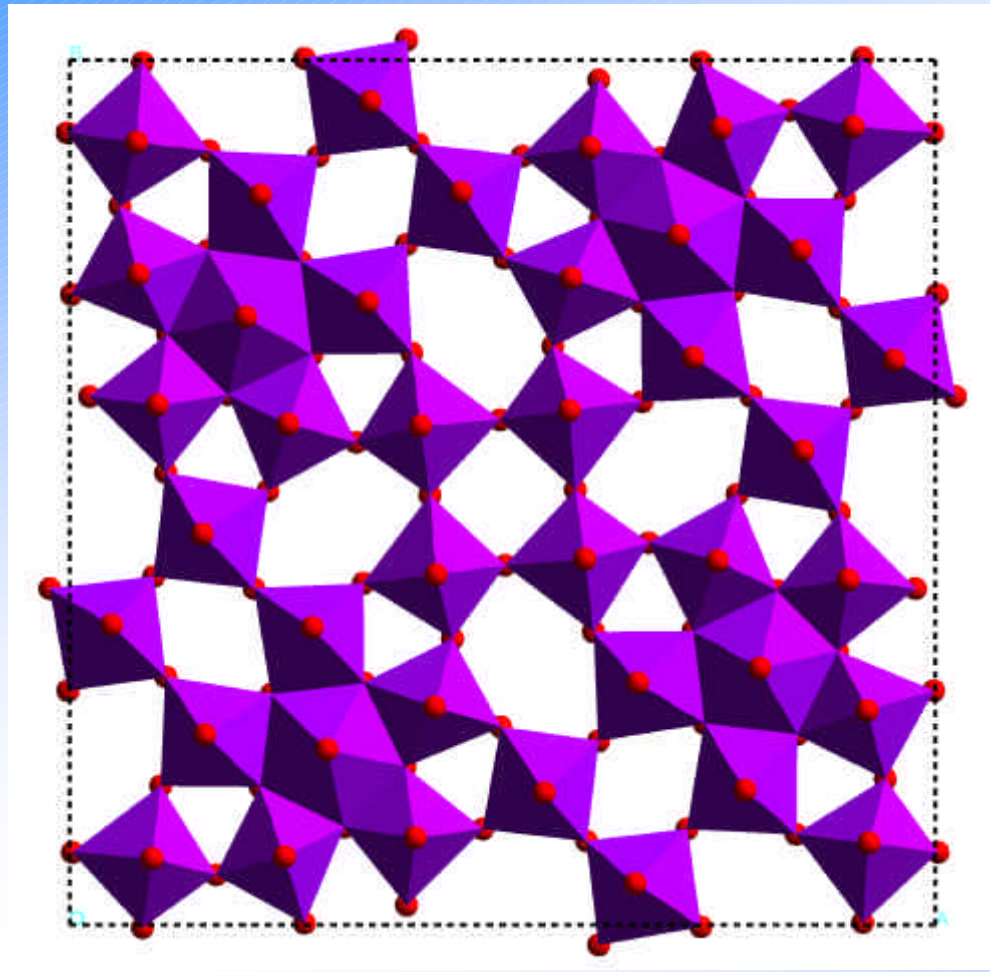


EDP and HREM of Mo_4O_{11}





Structure Model of Mo_5O_{14}



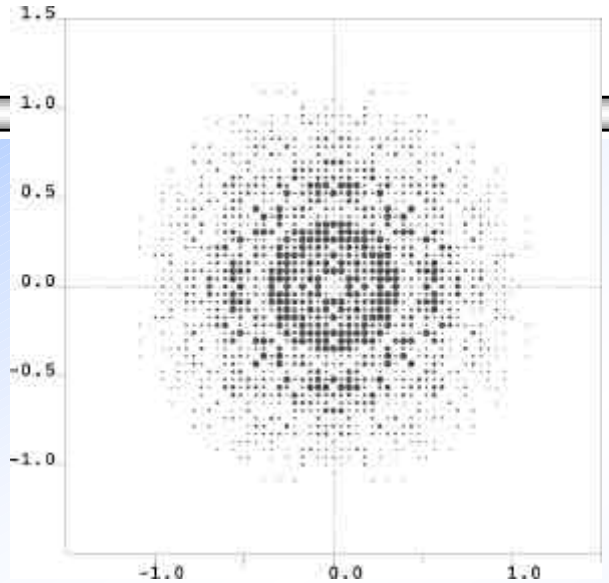
Space group: P4/mbm

Structure type: tetragonal

a=45.99 Å
b=45.99 Å
c=3.94 Å

Simulated EDP and HREM images of Mo_5O_{14} on [001] projection

EDP
Thickness: 50 Å

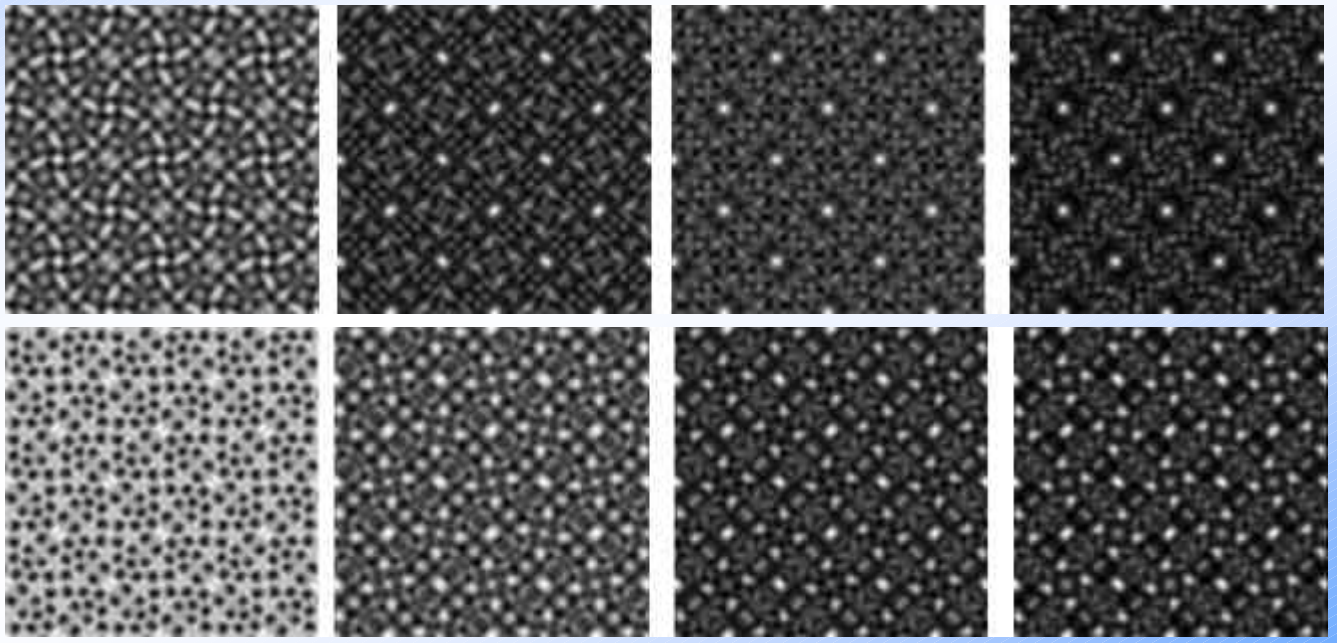


Sample Thickness(Å) 19.7 59.1 98.4 137.8

HREM Image

Defocus: -400 Å

Defocus: -600 Å



Summary

Crystallographic shearing is important in understanding the oxygen diffusion and phase transition mechanism of transition metal oxides in catalytic reactions.

CS plane produces well defined satellite spots in electron diffraction pattern → Application of TEM in the investigation of the reaction mechanism in solid state chemistry

HREM, supported by image simulation, allows the visualization of the CS structures at nanometer scale → Opens the possibility for the in-situ HREM investigation of real catalytic reaction at atomic scale.