PRESSURE DEPENDENCE ON THE ABSORPTION SPECTRUM OF *$CuMoO_4$*
STUDY OF THE GREEN→BROWN-RED PIEZOCHROMIC PHASE TRANSITION AT *2.5 kbar*

D. Hernández [a], F. Rodríguez [a], J. García Jaca [b], H. Ehrenberg [c] and H. Weitzel [c]

[a] DCITMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 SANTANDER, Spain

[b] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 MADRID, Spain

[c] Fachgebiet Strukturforschung, Fachbereich Materrialwissenschaft, TechnischeUniversität, D-64287 DARMSTADT, Germany

INTRODUCTION

- The copper oxide, $CuMoO_4$, is a triclinic compound ($P\bar{1}$ space group) exhibiting two phases at room temperature:

  1) Low pressure α-$CuMoO_4$ (green phase) 2) High pressure γ- $CuMoO_4$ (brownish red phase).
- The γ-phase is more compact than the normal α-phase. The phase transition α→γ is of first order involving a volume reduction of 13%.

  Density changes from ρ = 3.4(α) → 3.9(γ) grs/cc
- The crystal exhibits a strong piezochromism associated with this α→γ transition.
- In α-$CuMoO_4$: 2/3 of Cu^{2+} are octahedral elongated (CuO_6) and 1/3 of Cu^{2+} are square-pyramidal coordinated (CuO_5)

  In γ-$CuMoO_4$: all Cu^{2+} are octahedral elongated (CuO_6)

MAIN GOALS

- The study of the piezochromic and thermochromic properties of $CuMoO_4$.
- The aim is to understand the microscopic origin of the colour change on passing the α →γ transition

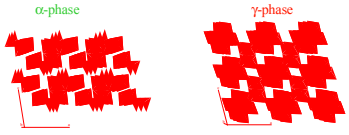
METHOD

- To obtain the electronic spectrum of single crystals of $CuMoO_4$ and its dependence with pressure.
- Correlations between electronic spectra and crystal structure.

EXPERIMENTAL

- Optical Absorption (OA) spectra were obtained from improved microespectrophotometer.
- Pressure experiments were done by mean of DAC (High Pressure Diamond Optics, Inc).
- A Closed-circuit cryostat was employed for temperature variations at atmospheric pressure.

Fig. 1 CRYSTAL STRUCTURES OF THE α AND γ PHASES



COLOUR: GREEN BROWNISH RED

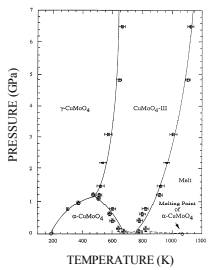
Triclinic Structure (Space Group $P\bar{1}$)

	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
α-phase	9.901	6.786	8.369	101.13	96.88	107.01
γ-phase	9.708	6.302	7.977	94.76	103.35	103.26

Coordination geometry around Cu^{2+} (average bond-distances):

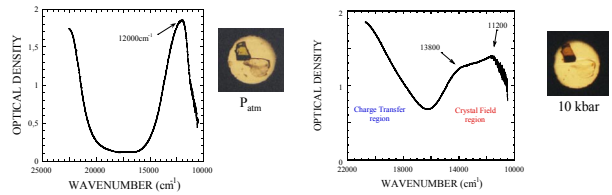
CuO_6 (D_{4h}):	Cu-O (eq) = 1.95 Å	Cu-O (ax) = 2.38 Å
CuO_5 (C_{4v}):	Cu-O (eq) = 1.93 Å	Cu-O (ax) = 2.34 Å

PHASE DIAGRAM FOR $CuMoO_4$



COMPARISON BETWEEN OPTICAL ABSORPTION SPECTRUM OF THE α– AND γ -PHASE OF $CuMoO_4$

α-$CuMoO_4$ γ-$CuMoO_4$

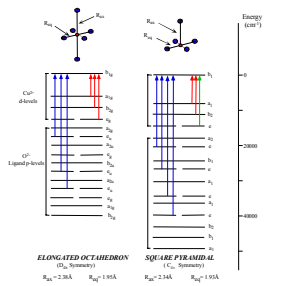


MAIN FEATURES

* The OA spectrum of both phases show two different regions:
  Crystal Field (CF) region → ~ 12000 cm^{-1} (1.5 eV)
  Charge Transfer (CT) region → ~ 25000 cm^{-1} (3.1 eV)
* The crystal colour is governed by the optical window formed by the tail of the first CT band and the CF bands.
* The intense piezochromism (green → brownish red) at the phase transition is associated with:
  1) The disappearance of the intense band at 12000cm^{-1}.
  2) The broadening of the CT band in the γ-phase.

  Both features displace the transmittance maximum towards lower energies and increase the transmittance in the red.

Molecular Orbitals diagram based on Extended-Hückel calculation for CuO_6 and CuO_5 complex



BAND ASSIGNMENT

Extended-Hückel calculations performed on a CuO_n (n = 5, 6) complex suggest:

1) Absorption bands at 13800 and 11200 cm^{-1} in γ-phase correspond to the $e_g \rightarrow b_{1g}$ and $b_{2g} \rightarrow b_{1g}$ CF transitions (calculated at 15000 cm^{-1} and 13800 cm^{-1}) of the CuO_6 complex.

The 12000 cm^{-1} in α-phase must correspond to the $e \rightarrow b_1$ CF transition of the CuO_5 1/3-complexes. The CF bands of the remainder 2/3 CuO_6 are masked by this intense band.

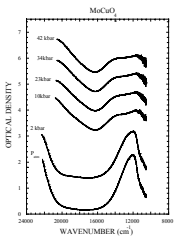
Estimated Oscillator Strength $CuO_5 \rightarrow f = 8\ (3) \times 10^{-4}$ $CuO_6 \rightarrow f = 7\ (3) \times 10^{-5}$

2) The first $O^{2-} \rightarrow Cu^{2+}$ Charge Transfer transition: $e_u \rightarrow b_{1g}$ (CuO_6) and $e \rightarrow b_1$ (CuO_5), are placed around 20000 cm^{-1} for both complexes:

⇒ *The intense band at 12000 cm^{-1} correspond to the $e \rightarrow b_1$ CF transition and not to CT transition.*

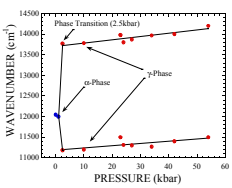
The CF-transition oscillator-strength in α-$CuMoO_4$ is higher than in γ-$CuMoO_4$ by the different symmetry of the copper complexes: $e \rightarrow b_1$, is electric dipole allowed in CuO_5.
$e_g \rightarrow b_{1g}$ is electric dipole forbidden in CuO_6.

VARIATION OF THE OPTICAL ABSORPTION SPECTRUM OF $CuMoO_4$ WITH PRESSURE



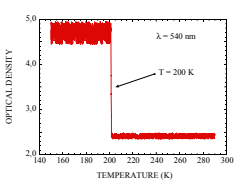
* There is an abrupt jump in the optical spectrum at the α→γ phase transition.
* The spectrum does not change significantly with pressure in each phase.
  → *Pressure induces minor variations of local structure around Cu^{2+}.*
* Piezochromism is associated with the displacive character of the phase transition:
  Rearrangement of CuO_n units → *Change of coordination number:* $CO_5 \rightarrow CuO_6$

DETERMINATION OF THE PHASE-TRANSITION PRESSURE



* The diagram shows the variation of the peak energy corresponding to the e→b_1 CF band in α-phase, and to the $e_g \rightarrow b_{1g}$ and $b_{2g} \rightarrow b_{1g}$ CF bands in γ-phase.
* The measured transition pressure is P_c = 2.5 kbar.

DETERMINATION OF THE TRANSITION-PHASE TEMPERATURE

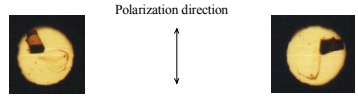


* The α→γ phase transition can also be induced by temperature at atmospheric pressure (*Thermochromism*).
* The thermochromic transition is detected through changes in the optical density at 540 nm upon varying temperature.
* The measured transition temperature is T_c = 200K.

DICHROISM IN γ-$CuMoO_4$

Single crystal observed with polarized light along the two extinction directions

Polarizing Microscope view



* The OA spectrum in γ-phase is strongly polarized.
* The increase of optical density upon changing polarization reduces the transmitted light intensity in more than one order of magnitude (**black crystal**).
* The strong dichroism is associated to the ordering of CuO_6 complexes in γ-phase.
  The equatorial planes of CuO_6 are oriented in the same direction forming layers (Fig. 1).
* The first $e_u \rightarrow b_{1g}$ CT transition is *completely* polarized in the equatorial-plane of the CuO_6 complex.
  ⇒ The maximum crystal absorption is attained when the light polarization is within the layer.

CONCLUDING REMARKS

- The band at 12000 cm^{-1} is assigned to the e→b_1 Crystal Field transition of CuO_5 in α-$CuMoO_4$, and not to a Charge Transfer transition.
- The piezochromic transition pressure at room temperature is at P_c = 2.5 kbar and the thermochromic transition temperature is T_c = 200 K at atmospheric pressure.
- The piezochromism is explained by the disappearance of the intense CF band at 12000cm^{-1} and the broadening of the first CT band on passing the α→γ structural phase transition.
- The dichroism observed in γ-$CuMoO_4$ is associated with the orientation of the CuO_6 complexes within the layers.