

OPEN ACCESS

Optical absorption and Raman spectroscopy of CuWO_4

To cite this article: J Ruiz-Fuertes *et al* 2010 *J. Phys.: Conf. Ser.* **215** 012048

View the [article online](#) for updates and enhancements.

You may also like

- [A detailed de Haas–van Alphen effect study of the overdoped cuprate \$\text{Ti}_{1-x}\text{Ba}_x\text{CuO}_{6-x}\$](#)
P M C Rourke, A F Bangura, T M Benseman *et al.*
- [Electronic structure of \$\text{CuWO}_4\$: dielectric-dependent, self-consistent hybrid functional study of a Mott–Hubbard type insulator](#)
Ho Viet Thang, Elisa Albanese and Gianfranco Pacchioni
- [Comparative description of magnetic interactions in \$\text{Sr}_2\text{CuTeO}_6\$ and \$\text{Sr}_2\text{CuWO}_6\$](#)
Yuanhui Xu, Shanshan Liu, Nianrui Qu *et al.*



PRIME
PACIFIC RIM MEETING
ON ELECTROCHEMICAL
AND SOLID STATE SCIENCE

HONOLULU, HI
Oct 6–11, 2024

Abstract submission deadline:
April 12, 2024

Learn more and submit!



Joint Meeting of

The Electrochemical Society
•
The Electrochemical Society of Japan
•
Korea Electrochemical Society

Optical absorption and Raman spectroscopy of CuWO_4

J. Ruiz-Fuertes¹, M. N. Sanz-Ortiz^{2§}, J. González², F. Rodríguez², A. Segura¹ and D. Errandonea¹

¹ MALTA Consolider Team, Física Aplicada-ICMUV, Universidad de Valencia, Burjassot, Spain

² MALTA Consolider Team, DCITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

E-mail: sanzmn@unican.es

Abstract. The electronic absorption and Raman spectra of CuWO_4 are studied as a function of pressure in the 0 – 20 GPa range. The below-gap absorption bands at 1.15, 1.38 and 1.56 eV correspond to Cu^{2+} d-transitions split by the Jahn-Teller distortion of CuO_6 ($R_{eq} = 1.98 \text{ \AA}$; $R_{ax} = 2.39 \text{ \AA}$; $Q_0 = 0.47 \text{ \AA}$). Pressure induces a strong reduction of the JT distortion up to 10 GPa. Above this pressure we observe, by optical absorption and Raman spectroscopy, a first-order phase transition at 11 GPa with phase coexistence in the 10-12 GPa range, as it is confirmed by Raman spectroscopy. The absorption spectra suggest that two different Cu^{2+} sites are formed in the high pressure phase, each having rather different CuO_6 distortion. The more JT distorted CuO_6 centre is stable up to 20 GPa. Rather than JT reduction, pressure induces reorientations of the CuO_6 octahedra in the high-pressure phase.

1. Introduction

Copper tungstate (CuWO_4) is a new type of wide-gap ($E_g = 2.3 \text{ eV}$) and magnetic ($T_N = 24 \text{ K}$) semiconductor with attractive opto-magneto-electrical applications [1-4]. The band gap and the related optical, electrical and magnetic properties strongly depend on the structure of WO_6 and CuO_6 octahedra and on how they are coupled [3,4]. Despite the importance of WO_6 complex in the band gap, the optical and magnetic properties of CuWO_4 are mainly governed by the corner-linked CuO_6 octahedra [4]. In particular, such properties are related to the electronic structure of the axially elongated CuO_6 by the Jahn-Teller (JT) effect, and the oxygen-mediated Cu-Cu exchange interaction, which is modulated both by the JT distortion and the octahedron tilting [5]. Due to this, a correlation study between CuWO_4 crystal structure and the associated vibrational and electronic properties is essential to understand and eventually control its properties.

This work reports results on CuWO_4 electronic and vibrational structure obtained by means of polarized optical absorption and Raman spectroscopy as a function of pressure and temperature. The aim is to correlate variations of the band gap, Cu^{2+} d-d transitions and vibrational mode frequencies with the corresponding changes of the crystal structure and, particularly, the local JT distortion and orientation of CuO_6 . The knowledge of how the coordination geometry of JT-active transition metal ions changes with pressure is difficult to achieve through x-ray diffraction (XRD) or absorption (XAS) studies since these systems often display antiferrodistortive-like structures, twinning or preferential orientation that hidden CuO_6 local structure information from XRD. Whereas, XAS spectra at the Cu K-edge in a diamond anvil cell (DAC) are difficult to exploit due to the low symmetry of the Cu site

and the existence of several Cu-O distances close to each other. Earlier, high-pressure optical absorption studies on Cu^{2+} [6] and Mn^{3+} [7,8] JT systems showed the feasibility of this technique as a local probe to detect changes of local structure at high pressure. In particular, crystal-field (CF) spectroscopy under pressure provides valuable information on the local symmetry and bond distances associated with MX_6 systems. This is an interesting study for JT Cu^{2+} systems since their corresponding optical spectrum provides complete information on the JT energy, electron-lattice coupling coefficients and the associated structural changes [5-8] and their variation with pressure. These values are not known in oxides like CuWO_4 . Throughout this work attention is paid to the dynamics of JT CuO_6 with pressure in each phase and in the structural phase transition (PT) induced by pressure. Their effects on the optical spectra will be analyzed in terms of changes of structural variations.

2. Experimental

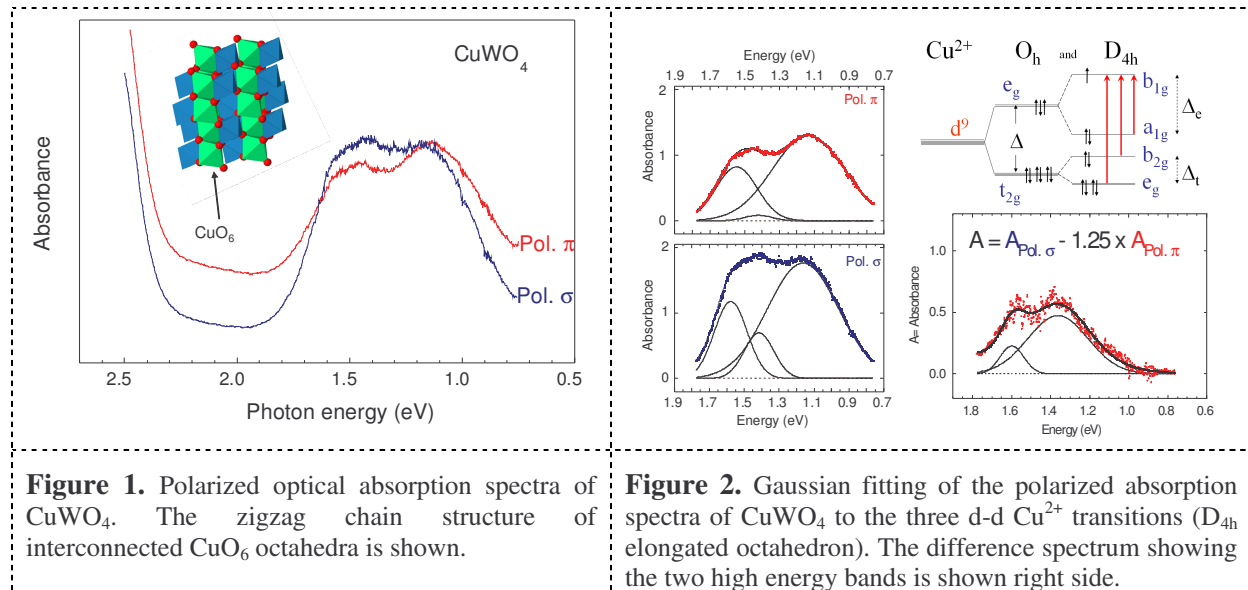
The triclinic crystal structure, space group $\text{P}\bar{1}$, of CuWO_4 was checked by XRD. The lattice parameters, $a = 4.709(7)$ Å, $b = 5.845(9)$ Å, $c = 4.884(7)$ Å, $\alpha = 88.3(2)^\circ$, $\beta = 92.5(2)^\circ$, and $\gamma = 97.2(2)^\circ$ are in good agreement with the literature [9]. The single crystal orientation was accomplished through a polarizing microscope. The extinction directions were selected parallel and perpendicular to the chains for optical absorption in a (010) cleaved sample.

The polarized optical spectra were obtained in a Cary 6000i spectrophotometer operating in absorption mode, and in a homemade microspectrophotometer setup using a Hamamatsu R928 S photomultiplier and an InGaAs detector to cover the 300 – 1700 nm range. The microcrystal ($200 \times 200 \times 30$ μm^3) was mounted on a 100 μm drilled steel plate and placed in a top-illuminated metallographic microscope. The light was chopped at 80 Hz and polarized parallel and perpendicular to the extinction directions of the sample plate (parallel and perpendicular to the chains) using a Glan Taylor polarizing prism. An optical fiber collected the transmitted light and the signal was filtered with a SR400 lock in amplifier. This procedure allowed us to measure absorption coefficients beyond 10000 cm^{-1} . Optical absorption (OA) and Raman spectra at high pressure were performed using two different membrane DACs [4,10]. For the Raman spectra the crystal was excited with the 530.9 and 647.1 nm lines of a Coherent krypton laser (model Innova 300) using a Ramanor U1000 double monochromator equipped with a LN refrigerated Symphony CCD detector. The Raman spectra under pressure were obtained in second order with an attached confocal microscope. A mixture of methanol-ethanol-water was used as pressure transmitting medium in both Raman and OA high-pressure studies.

3. Results and discussion

3.1. Polarized optical absorption spectra

Figure 1 shows CuWO_4 polarized absorption spectra at ambient conditions. Although similar, the two polarized spectra confirm the presence of three absorption bands E_1 , E_2 and E_3 at 1.15, 1.38 and 1.56 eV, respectively. It must be noted that the two higher energy bands, which are hidden in the unpolarized spectrum, can be resolved by combining both spectra by $A = A_{\text{Pol},\sigma} - 1.25 \times A_{\text{Pol},\pi}$ as it is shown in the inset of figure 2. The factor 1.25 is introduced to remove the first absorption band in the difference spectrum. This procedure demonstrates the presence of two bands which are assigned to CF transitions from the B_{1g} ground state (D_{4h} notation) to the parent octahedral T_{2g} states split by the JT effect in $(E_g + B_{2g})$ according to the energy level diagram of figure 2. The first absorption band at 1.15 eV is assigned to the $a_{1g} \rightarrow b_{1g}$ electronic transition within the parent doubly degenerate e_g octahedral orbitals. This assignment is supported by the polarization behaviour of these bands. In fact the $a_{1g} \rightarrow b_{1g}$ transition exhibits an opposite polarization behaviour than $e_g \rightarrow b_{1g}$ and $b_{2g} \rightarrow b_{1g}$, the latter being the most polarized transition [11,12]. The weak polarization dependence of the spectrum is due to the zigzag character of the CuO_6 forming chains, the axial distortion of which alternates along the chain forming Cu-O-Cu angles of about 90° [9]. Interestingly, the Cu^{2+} d-orbital splitting, derived from

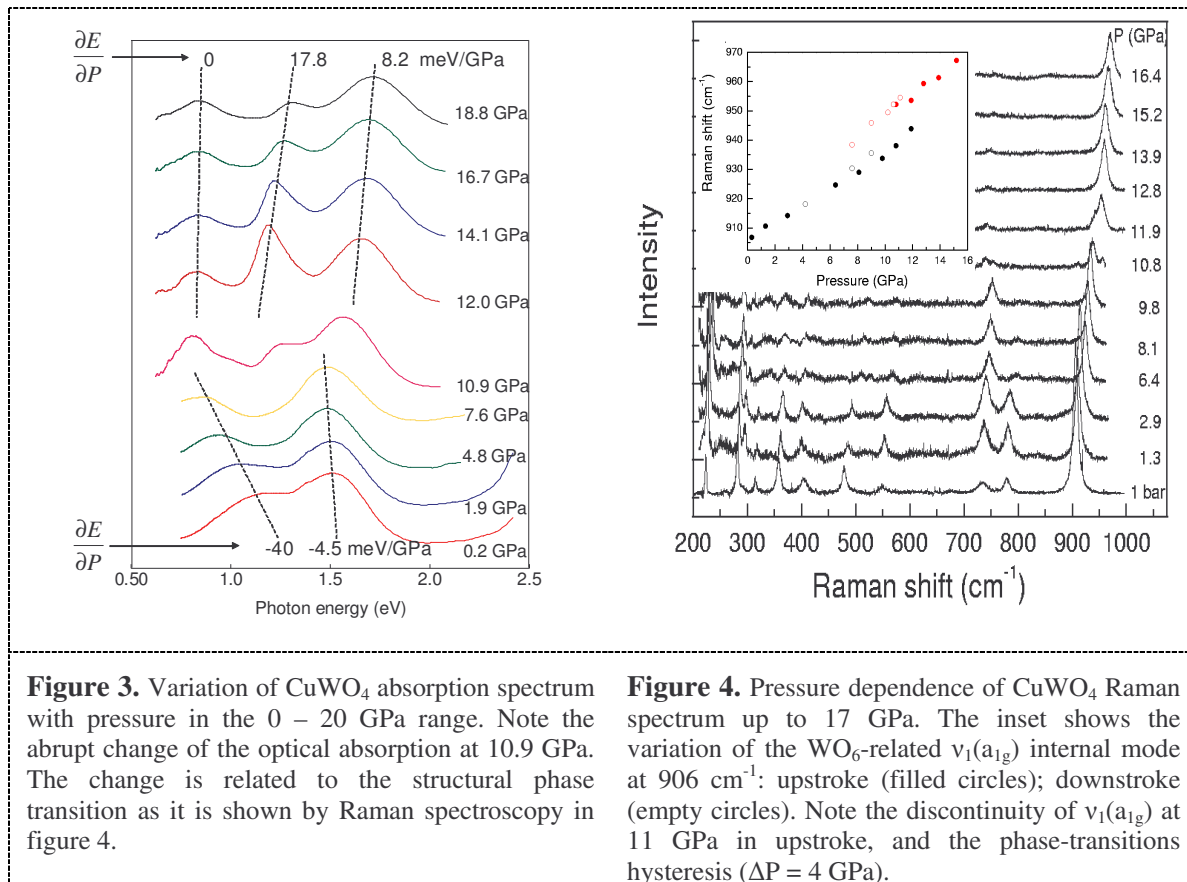


polarized absorption spectroscopy, is consistent with the actual elongated distortion of the CuO_6 octahedron (average bond distances: $R_{eq} = 1.98 \text{ \AA}$; $R_{ax} = 2.39 \text{ \AA}$).

The transition energies directly provide the splitting of Cu^{2+} t_{2g} and e_g octahedral orbitals due to the JT effect: $\Delta_t = 0.18 \text{ eV}$ and $\Delta_e = 1.15 \text{ eV}$, respectively. Following structural correlations established elsewhere [6-8] the JT energy is $E_{JT} = \Delta_e/4 = 0.29 \text{ eV}$, and the ratio between Δ_t and Δ_e and the tetragonal distortion $Q_0 = 0.47 \text{ \AA}$ [$Q_0 = 2/\sqrt{3}(R_{ax} - R_{eq})$] is 0.4 and 2.4 eV/\AA , respectively. These values are similar to those measured for other Cu^{2+} systems of CuCl_6^{4-} and CuF_6^{4-} [6,13,14] but are about the half of those measured for Mn^{3+} in fluorides MnF_6 and oxides MnO_6 [7,8,15,16]. In fact, $\Delta_e = 0.97 \text{ eV}$ in K_2CuF_4 ($Q_0 = 0.34 \text{ \AA}$) whereas $\Delta_e = 0.72 \text{ eV}$ in CsAlCuF_6 ($Q_0 = -0.28 \text{ \AA}$), the CuF_6 displaying an elongated and compressed octahedron geometry, respectively. Their associated Δ_e/Q_0 ratio is 2.8 and 2.6 eV/\AA , respectively. A similar ratio was obtained for Cu^{2+} chloride series with elongated CuCl_6 : $\Delta_e/Q_0 = 2.3 \text{ eV/\AA}$ [6]. These values compare well with $\Delta_e/Q_0 = 2.4 \text{ eV/\AA}$ derived from CuWO_4 spectroscopic data of figures 1 and 2. However, it must be noted that Δ_e/Q_0 for Cu^{2+} is about half the ratio for Mn^{3+} and Co^{3+} with $\Delta_e/Q_0 = 5.1 \text{ eV/\AA}$ [14,15], thus pointing out that, similarly to the CF strength (Δ), the tetragonal splitting to distortion ratio (Δ_e/Q_0) for trivalent JT transition metal ions is twice as large as the obtained for divalent JT ions. This explains why D_{4h} distortions producing a similar JT splitting Δ_e are larger in divalent ions. K_2CuF_4 with $\Delta_e = 0.97 \text{ eV}$ ($Q_0 = 0.34 \text{ \AA}$) and K_2NaMnF_6 with $\Delta_e = 1.1 \text{ eV}$ ($Q_0 = 0.23 \text{ \AA}$) are examples of this behaviour.

3.2. Pressure variation of Cu^{2+} optical absorption.

Figure 3 shows the variation of CuWO_4 unpolarized absorption spectrum with pressure. It shows that the Cu^{2+} -d transitions clearly shift to lower energies in the 0 - 10 GPa range. Above 10 GPa the spectrum abruptly changes and a new band at 1.19 eV is observed. Upon increasing pressure the first absorption band do not shift significantly with pressure whereas the new band as well as the broad band at 1.66 eV shifts to higher energies. The corresponding transition energy variation for each band is shown in figure 3. The pressure dependence of the optical spectra provides information on CuO_6 local structure variation. Analysis of figures 1-3 indicates that the elongated CuO_6 octahedron decreases JT distortion towards a perfect octahedron in the 0 - 10 GPa range as it is evidenced through the reduction of the $a_{1g} - b_{1g}$ splitting (Δ_e) with pressure. Hence the JT energy decreases with pressure from 1.15 at ambient pressure to 0.86 eV at 7.6 GPa. However the CF energy, defined as $\Delta = E_2 - (1/2\Delta_e + 1/3\Delta_t)$ [8], increases from 0.96 eV to 1.10 eV in the same pressure range as it is expected for a



decrease of the average Cu-O bond distance with pressure. The appearance of a new band at 1.19 eV above 10 GPa is noteworthy. Its transition energy and intensity suggest that this band is independent of the other bands and thus it might be associated with a second Cu²⁺ site in CuWO₄ formed in the high-pressure phase as a consequence of a pressure-induced structural transition.

Although the two high energy bands could be thought to be due to the 1.5 eV band of the low-pressure phase split at the PT, the intensity and energy variations of the new 1.19 eV band suggest that it really corresponds to a distinct CuO₆ centre of the high-pressure phase. In fact, its position is close to the CF splitting at 10 GPa of the other Cu²⁺ centre ($\Delta = 1.15$ eV at 10 GPa). Its variation with pressure (17.8 eV/GPa) is similar to the Δ dependence of the low-pressure Cu²⁺ centre with pressure (19 meV/GPa). According to this, the structural PT involves a change in the CuO₆ chains yielding two different Cu²⁺ sites: centre I displaying a JT distortion similar to the low-pressure CuO₆ whereas centre II being nearly octahedral or weakly JT distorted. It is worth noting that independently of the number of Cu²⁺ sites formed at the PT, the JT distortion of centre I is preserved up to 19 GPa thus stressing the stability of the JT effect at high pressure. This result is not surprising since the JT energy per Cu²⁺ ion is $E_{JT} = \Delta_c/4 = 0.22$ eV, and therefore the pressure required to release the JT distortion would be above 20 GPa.

3.3. Pressure dependence of the CuWO₄ Raman spectrum: Phase transition effects.

The variation of the Raman spectrum with pressure confirms that CuWO₄ undergoes a structural PT at 11 GPa. Figure 4 shows the variation of the Raman spectrum with pressure. Eleven of the 18 peaks of CuWO₄ can be clearly observed at ambient conditions. Among them, we selected the one corresponding to the highest energy vibration ($\nu_1 = 906$ cm⁻¹) as a probe to explore PT phenomenon in CuWO₄. Although the PT involves slight changes of the pressure derivatives of $\nu(P)$ of all Raman peaks, we selected $\nu_1(a_{1g})$ since it corresponds to the highest intensity peak and it is located far apart

from other peaks to avoid overlapping. The plot $\nu_1(P)$ shown in the inset of figure 4 reveals a slight change of the $\nu_1(P)$ slope around 10 GPa that clearly confirms the occurrence of a structural PT. Its variations are linear with pressure as $\nu_1(\text{cm}^{-1}) = 906 + 3.0 \times P(\text{GPa})$ in the 0-12 GPa range, and $917 + 3.6 \times P(\text{GPa})$ in the 10-20 GPa range. The observed hysteresis and the intense piezochromism accompanying the PT are noteworthy. Both features together with ν_1 abrupt jump of 17 cm^{-1} at 10 GPa support a first-order PT, showing phase coexistence at 8-9 GPa (down stroke) and 11-12 GPa (upstroke). The phase coexistence is also consistent with the optical absorption measurements of figure 3, whose band structure at 10.9 GPa reveals the presence of both low- and high-pressure spectra. It is interesting to note here that the pressure evolution of the fundamental absorption edge of CuWO_4 (Fig. 3 in Ref. 4), that was interpreted as continuous non linear dependence, can also be seen as involving a change in dE_g/dP around 11 GPa. This slope change is also consistent with the occurrence of the PT here reported.

As a final remark the analysis and interpretation of the reported optical absorption and Raman spectra suggest that CuWO_4 volume contraction induces a dynamics in the CuO_6 octahedra which is firstly associated with a strong linear decrease of the JT energy, and thus to a JT distortion (low-pressure phase). Above this pressure (high-pressure phase) the JT energy of CuO_6 cannot be longer reduced and the structure transforms keeping the JT distortion through CuO_6 rotations. This transformation leads to some CuO_6 complexes to keep their JT distortion but other CuO_6 adopt a nearly octahedron symmetry, the spectrum of which mainly consists of a single band associated with $t_{2g} \rightarrow e_g$ transition (Δ). Additional XRD studies on the structural variation of CuWO_4 at high pressure are currently in progress.

4. Acknowledgments

Financial support from the Spanish Ministerio de Ciencia e Innovación (Projects No. MAT2008-06873-C02-01, MAT2008-06873-C02-02 and MAT2007-65990-C03-01) and the MALTA-Consolider Ingenio 2010 Programme (Ref. CSD2007-00045) are acknowledged. MNSO thanks the MEC for a FPU research grant (Ref. AP-2004-5954). JRF thanks the MEC for a FPI research grant (Ref. BES-2008-002043).

5. References

- [1] Pandey P K, Bhawe N S, and Kharat R B 2005 *Matt. Lett.* **56** 3149
- [2] Butler M 1997 *J. Appl. Phys.* **48** 1914
- [3] Errandonea D and Manjón FJ 2008 *Prog. Mater. Sci.* **53** 711
- [4] Ruiz-Fuertes J, *et al.* 2008 *High Pressure Research* **28** 565
- [5] Aguado F, *et al.* 2004 *J. Phys.: Condens. Matter* **16** 1927
- [6] Valiente R and Rodriguez F 1999 *Phys. Rev. B* **60** 9423
- [7] Aguado F, Rodríguez F and Núñez P 2003 *Phys. Rev. B* **67** 205101
- [8] Rodríguez F and Aguado F 2003 *J. Chem. Phys.* **118** 10867
- [9] Schofield P F, Knight K S, Redfern S A T, Cressey G 1997 *Acta Cryst. B* **53** 102
- [10] Hernandez I, Rodriguez F and Tressaud A 2008 *Inorg. Chem.* **47** 102882008
- [11] Hitchman M A 1994 *Comments Inorg. Chem.* **15** 197
- [12] Valiente R, deLucas MCM and Rodriguez F 1994 *J. Phys. Condens. Matter* **6** 4527.
- [13] Oelkrug D 1971 Absorption Spectra and Ligand Field Parameters of Tetragonal 3d-Transition Metal Fluorides, *Structure and Bonding* **9** 1
- [14] Hidaka M, Inoue K, Yamada I, and Walker PJ 1983 X-ray diffraction study of the crystal structures of K_2CuF_4 and $\text{K}_2\text{Cu}_x\text{Zn}_{1-x}\text{F}_4$ *Physica B and C* **121** 343
- [15] Sanz-Ortiz M N, Rodríguez F, Baranov A and Demazeau G 2008 *J. Phys. Conf. Ser.* **121** 092003
- [16] Sanz-Ortiz M N, Rodríguez F and Demazeau G 2008 *High Pressure Research* **28** 571