

# Effect of pressure on a Charge Density Wave transition in the $m=10$ member of the MonoPhosphate Tungsten Bronze Family

E. Duverger-Nédellec<sup>1,2\*</sup>, A. Pautrat<sup>2</sup>, O. Pérez<sup>2</sup>, B. Vignolle<sup>3</sup> and P. Rosa<sup>3</sup>

<sup>1</sup>Charles University, Matematicko-fyzikální fakulta, Condensed Matter Department, Ke Karlovu 3  
121 16 Praha 2, Czech Republic

<sup>2</sup>CRISMAT - UMR6508, 6 Boulevard du Maréchal Juin - F-14050 CAEN cedex 4, France

<sup>3</sup>ICMCB - UMR5026, 87 Avenue du Docteur Schweitzer 33608 PESSAC cedex, France

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\*e-mail: elenduvergernedellec@gmail.com

Low-dimensional conductors have been studied for several decades due to their remarkable properties such as thermoelectricity, high electronic mobility or superconductivity. This low electronic dimensionality makes the appearance of another phenomenon favorable: the Charge Density Wave (CDW) instability. The transition toward this electronic instability was described by Peierls [1] as a gap opening at the Fermi surface, caused by a Fermi surface nesting, leading to a modulation of the electronic density accompanied by a periodic distortion of the atomic lattice. This phenomenon, usually studied because of its presence in superconducting compounds, is ruled by the Chan-Heine instability condition [2] given by:

$$\frac{4g_q^2}{\hbar\omega_q} - 2U_q + V_q \geq \frac{1}{\chi_0(\mathbf{q})} \quad (1)$$

with  $g_q$  representing the electron-phonon coupling constant,  $\omega_q$  the frequency of the phonon mode involved in the lattice deformation,  $U_q$  the Coulomb interaction,  $V_q$  the exchange interaction in the mean-field approximation and  $\chi_0(\mathbf{q})$  the electronic susceptibility. The transition temperature, in the 1D case, can be expressed as:

$$k_B T_0 \sim E_F \exp\left[\frac{-\hbar\omega_{\mathbf{q}_0}}{g_{\mathbf{q}_0}^2 N(E_F)}\right] \quad (2)$$

with  $T_0$  the transition temperature,  $E_F$  the energy of the Fermi level,  $N(E_F)$  the density of states at the Fermi level and  $\mathbf{q}_0$  being the wave vector characteristics of the CDW.

Consequently, the appearance of the CDW state is influenced by several properties of the material. We choose here to study the effect of the electronic dimensionality on the CDW transition within the MonoPhosphate Tungsten Bronzes family (MPTB).

Monophosphate tungsten bronzes, of general formula  $(\text{PO}_2)_4(\text{WO}_3)_{2m}$  (with  $4 \leq m \leq 14$ ), are low-dimensionnal oxides exhibiting successive transitions toward charge density wave (CDW), spin density wave (SDW) and/or superconducting states [3]. These compounds can be described as the regular stacking of  $\text{WO}_3$  slabs of  $\text{ReO}_3$ -type structure and slices of  $\text{PO}_4$  groups [4]. Conduction electrons provided by the

phosphate groups are localized in the  $\text{WO}_3$  slabs, leading to  $4/2m$  electrons per tungsten atom. The variation of the value of the parameter  $m$  enables the modification of the density of carriers in the  $\text{WO}_3$  slabs and the electronic anisotropy of the system. Therefore, this family of compounds is perfect to study the effect of variations of the electronic dimensionality on the CDW transition.

Observations by X rays diffraction [5] and transport [3,6] measurements of the CDW transitions of the MPTB members have evidenced an increase of the transition temperatures with the value of  $m$  increasing and a change of the CDW characteristics between the  $m < 7$  and  $m > 7$  members, called respectively low and high members. Consequently, these observations lead to a questioning about the origin of this change and regarding the driving forces of the CDW formation in this family of compounds. With the aim of obtaining precious information for the understanding of the driving forces of the CDW instabilities in these low-dimensional conductors, pressure studies were performed on several members of the MPTB family.

Resistivity experiments under pressure are reported for the low members of the family  $m=4$  ( $\text{P}_4\text{W}_8\text{O}_{32}$ ) and  $m=6$  ( $\text{P}_4\text{W}_{12}\text{O}_{44}$ ) [7]. Upon applying pressure, a destabilization of the first CDW state is observed for the  $m=4$  member and for both of the two first CDW states for the  $m=6$  member, with a  $dT_0/dP$  rate ranging from  $-0.9$  to  $-5$  K.kbar<sup>-1</sup>. However, the second CDW state of the  $m=4$  member is stabilized up to 5 kbar, with a  $dT_0/dP$  rate of  $+0.9$  K.kbar<sup>-1</sup>, and then destabilized under higher pressure. In order to compare low and high members we selected the  $m=10$  member ( $\text{P}_4\text{W}_{20}\text{O}_{68}$ ), for room temperature X-rays diffraction measurements under pressure. This compound can be considered as the perfect candidate for such a study as it is in a CDW state at room temperature (CDW1) and is bounded by another CDW phase (CDW2) that sets in below 210 K and an unmodulated phase above 475 K [5]. The room temperature CDW1 phase is characterized by the modulation vector  $\mathbf{q}_1=3/7\mathbf{a}^*$ [5] while the low temperature CDW2 phase is characterized by the modulation vectors  $\mathbf{q}_{21}=1/2\mathbf{a}^*$  and  $\mathbf{q}_{22}=2/5\mathbf{a}^*$ [8]. The occurrence of a transition between those states at room temperature with applied pressure can be directly probed by X-rays diffraction.

The experiment was performed using a diamond anvil cell adapted on a Bruker Kappa Apex II single-crystal diffractometer. 16:3:1 methanol-ethanol-water solution was used as a hydrostatic pressure medium [9]. A ruby was placed in the diamond anvil cell with the single-crystal of  $m=10$ . The pressure in the diamond-cell was determined from a pressure-shift in the sharp R-line fluorescence spectrum of ruby [10]. X-rays diffraction measurements were performed using a Molybdenum source under four different pressures up to  $6.8 \pm 0.7$  kbar.

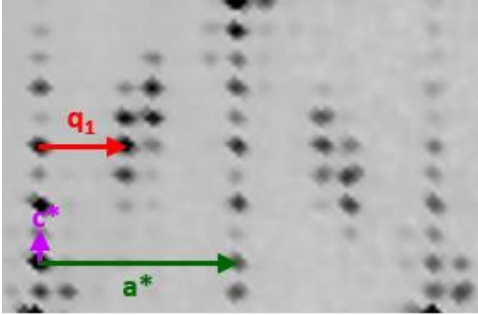


Figure 1: Area of the  $(h0l)^*$  plane reconstructed from X-rays diffraction on a  $m=10$  MPTB single-crystal at ambient pressure. The pattern presents main reflections described by the reciprocal lattice vectors  $\mathbf{a}^*$  and  $\mathbf{c}^*$  and satellite reflections reflecting the modulation of the atomic lattice. The satellite reflections are indexed by the modulation vector  $\mathbf{q}_1=3/7\mathbf{a}^*$ , characteristic of the room temperature CDW state (CDW1).

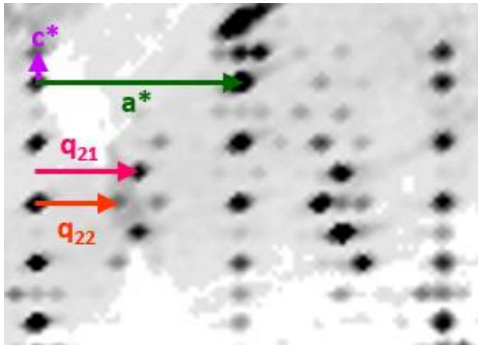


Figure 2: Area of the  $(h0l)^*$  plane reconstructed from X-rays diffraction on a  $m=10$  MPTB single-crystal under 4.8 kbar. The pattern presents main reflections described by the reciprocal lattice vectors  $\mathbf{a}^*$  and  $\mathbf{c}^*$  and satellite reflections reflecting the modulation of the atomic lattice. The satellite reflections are indexed by the modulation vectors  $\mathbf{q}_{21}=1/2\mathbf{a}^*$  and  $\mathbf{q}_{22}=2/5\mathbf{a}^*$ , characteristic of the low temperature CDW state (CDW2).

Figure 1 presents a part of the reconstructed  $(h0l)^*$  plane characteristic of the room temperature CDW1 phase at ambient pressure. The reciprocal lattice vectors  $\mathbf{a}^*$  and  $\mathbf{c}^*$  together with the superstructure vector  $\mathbf{q}_1$  are displayed. Figure 2 presents the same  $(h0l)^*$  part measured at room temperature under an applied pressure of 4.8 kbar. While little change is observed for the reciprocal lattice vectors  $\mathbf{a}^*$  and  $\mathbf{c}^*$ , the superstructure pattern has clearly changed, the modulation vectors being now  $\mathbf{q}_{21}$  and  $\mathbf{q}_{22}$ , which are representative of the low temperature CDW2 phase. The transition toward the low-temperature CDW2 state begins below  $3.2 \pm 0.3$  kbar and

is fully completed under  $4.8k \pm 0.5$  kbar. At  $6.8 \pm 0.7$  kbar, the X-rays diffraction pattern still corresponds to the low-temperature CDW2 state. From these measurements, we can estimate an upper and lower bound for  $dT_0/dP$ , the rate at which the transition temperature of the low temperature CDW2 phase varies with applied pressure. This  $dT_0/dP$  rate of  $17.3 \pm 1.7$  K.kbar<sup>-1</sup> (lower bound) and  $25.9 \pm 2.6$  K.kbar (upper bound) is exceptionally high compared to the rates found in the literature. The maximal rate, reported for  $\text{KM}_6\text{O}_{17}$ , is about 10 K.kbar<sup>-1</sup> [11], making the  $m=10$  member of MPTB the compound with the highest  $dT_0/dP$  rate ever reported for the stabilization of a CDW state under pressure.

From this experiment we can conclude that the application of hydrostatic pressure stabilizes the low-temperature CDW state of the  $m=10$  MPTB, at least up to 6.8 kbar. The  $dT_0/dP$  rate measured for the second transition of the  $m=10$  shows that this high term is much more sensitive to pressure than the low terms  $m=4$  and  $m=6$ . This might be explained by a large change in the strength of the electron-phonon coupling between low and high terms of the MPTB family. It has been demonstrated that the CDW transitions of  $m=4$  and  $m=6$  [3] can be explained by the Peierls model, describing CDW transition in materials with a weak electron-phonon coupling. A high electron-phonon coupling for the  $m=10$  could then explain its high pressure-sensitivity and that a weak pressure is able to decrease enough the thermal fluctuations to stabilize the low-temperature CDW state.

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