Superperiodic states in the MonoPhosphate Tungsten Bronze $P_4W_{16}O_{56}$: Evidence for the coexistence of two antagonistic electronic instabilities

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The MonoPhosphate Tungsten Bronzes (MPTB), with the chemical formula $(PO_2)_4(WO_3)_{2m}$ (with ***m*** ranged from 2 to 14), form a large family of quasi 2d-conductors. They are built from a regular intergrowth of (PO_4) tetrahedra layers providing carriers and of slabs of corner-sharing-WO_6 octahedra, with a thickness depending on the ***m*** parameter. The dimensionality, electronic anisotropy and the density of carriers can be directly changed by modifying the thickness ***m*** of the WO_3 slabs to such an extent that the MPTB family is a textbook case to tune the electronic properties.

Temperature-dependent X-ray Diffraction (XRD) [1] and transport measurements reported in the literature, for different terms of the family, reveal drastic changes between members with a low and high ***m*** value. The MPTB with low ***m*** (***m***≤6) values are known to present successive transitions toward classical Charge Density Wave (CDW) states while ferro or anti-ferro electric (AFE) instabilities are expected for members with large ***m*** values (***m***≥10); incommensurate or commensurate structural modulations are associated to these different states [1,2,3].

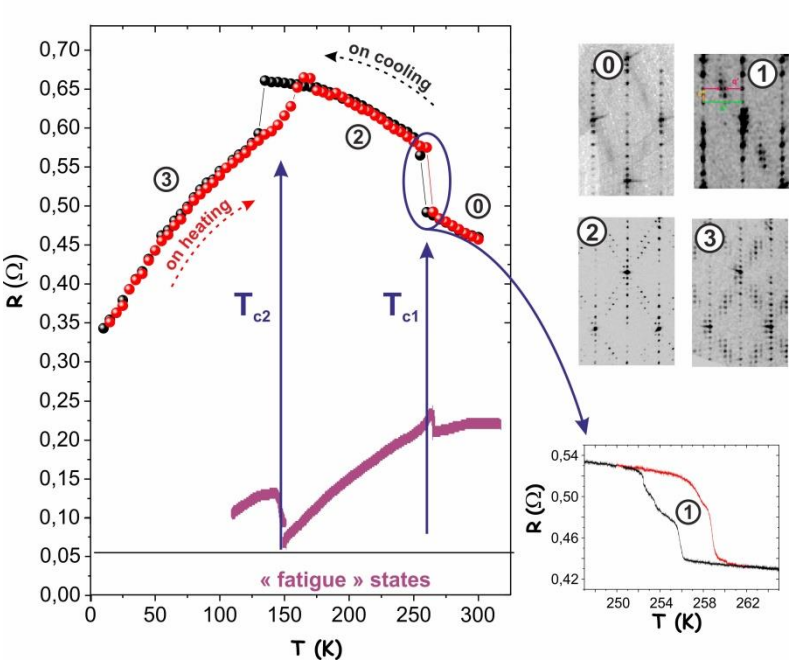

Figure 1: Resistance of $P_4W_{16}O_{56}$ versus T. Part of the (h0l)* X-ray diffraction plane is proposed for the different states showing pre-transitional diffuse scattering in the fundamental state ⓪ and different set of satellite reflection for the ①,②, ③ states. The purple curve shows the response after the "fatigue" phenomenon.

In this context, $P_4W_{16}O_{56}$ (***m*** =8), situated in the border area between the low and the high ***m*** values in the MPTB family, opens an opportunity to discuss the competition regime between CDW and ferroelectric instabilities. Parallel studies of both the transport properties and of the structural modulations have been performed for this member. Resistivity measurements and X-ray diffraction show three sharp first-order transitions associated with large thermal hysteresis (Figure 1). The structural analyses using superspace formalism, evidenced both anti ferro-electric-type atomic displacements for tungsten atoms and the formation of tungsten clusters for the different states. These signatures could be associated with the AFE and CDW states respectively. Transport measurements confirm this assertion *via* the observation of a "fatigue" phenomenon for the compound; in these new “fatigue”-type states sharp and hysteretic transitions disappear to the benefit of transitions, occurring at the same temperatures but characterized by smooth resistivity bumps expected for a classical CDW (Figure 1).

This fascinating coexistence of two antagonistic properties (a metallic state with anti-ferro electric distortion) for $P_4W_{16}O_{56}$ may realize the scenario described by Anderson and Blount [4] predicting the possibility of a ferroelectric metal.

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