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Charge density wave phenomena in the family of two dimensional monophosphate tungsten bronzes: $(\text{PO}_2)_4(\text{WO}_3)_{2m}$

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Abstract :

The monophosphate tungsten bronzes with pentagonal tunnels $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ form a family of 2D conductors composed of ReO_3 -type layers of m oxygen sharing WO_6 octahedra belonging to infinite chains running along the non equivalent $\mathbf{a}$ and $\mathbf{a} \pm \mathbf{b}$ directions. X-ray diffuse scattering experiments show that these chains are subject to charge density wave (CDW) instabilities. It is found that the leading CDW instability changes from chains along $\mathbf{a}$ in the $m = 4$ member to chains along $\mathbf{a} \pm \mathbf{b}$ for larger values of m . In the $m = 4$ and $m = 6$ bronzes the CDW wave vector, stabilized below each Peierls like transition, leads to a common nesting between differently oriented 1D Fermi surfaces (FS) associated with these chains. Two and three successive CDW transitions, corresponding to a hierarchy of FS nestings, are observed in these members. The CDW modulation observed in the $m = 7, 9, 10$ and 11 bronzes presents a large number of harmonics, and in $m=7$ its amplitude shows unexpected hysteresis phenomena. It is suggested that these features could be the structural fingerprint of an electron localization, possibly due to the reduction of screening effects when the average number of electron per tungsten, $2/m$, decreases with increasing m .

Introduction :

Low dimensional conductors have been extensively studied because of their anisotropic electronic properties and their instability towards the formation of charge density wave (CDW), spin density wave or superconducting ground states which can be in competition in very rich phase diagrams. Because of their anisotropic structures, the transition metal oxides and bronzes belong to this class of materials. One dimensional conductors (1D) such as the blue bronzes $\text{AMo}_{0.3}\text{O}_3$ ($\text{A}=\text{K}, \text{Rb}, \text{Tl}$) which present a Peierls transition have been particularly studied because the CDW can collectively slide under the action of an external electric field [1]. Recently, the interest for 2D conductors has been renewed and a large number of works has been devoted to the oxide Mo_4O_{11} and the purple bronzes $\text{A}_x\text{Mo}_6\text{O}_{17}$ ($\text{A}=\text{Na}, \text{K}, \text{Tl}; x \approx 1$) [1]. CDW ground states have been observed and related to the nesting properties of hidden 1D portions of their Fermi Surface (FS) [2]. The purpose of this paper is to present some general structural properties of a new series of 2D tungsten bronzes $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ which possess a layer structure, very similar to that of the purple bronzes and Mo_4O_{11} .

Structural arrangement : Hidden one-dimensionality

$(\text{PO}_2)_4(\text{WO}_3)_{2m}$ crystallizes in the orthorhombic system (for $m \neq 5$). The crystal structure detailed in ref. [3] is built with (a,b) ReO_3 -type slabs of corner sharing WO_6 octahedra terminated by PO_4 tetrahedra. The connection between WO_6 and PO_4 groups creates pentagonal tunnels. The thickness of the slab increases with m . An X-ray diffuse scattering investigation of the bronzes of $m=4, 6$ and 7 already reveals at room temperature (RT), different sets of diffuse segments. One set observed in all the members, corresponds to diffuse segments perpendicular to the $\mathbf{a} \pm \mathbf{b}$ directions (oblique arrows figure 2a). Computer simulations of X-ray patterns demonstrate that these diffusions are due to 1D pretransitional fluctuations along the $\mathbf{a} \pm \mathbf{b}$ directions (see figures 1a and b). The corresponding chains are constituted of clusters of m "basal" oxygen sharing WO_6 octahedra connected in a stair case manner by their axial oxygen. The modulation consists in a rigid displacement of this cluster with a polarisation $\mathbf{u}$ which gradually evolves from the chain direction to the cluster direction when m increases (see table). The other set of diffuse lines, observed for $m=4$ and 6 (horizontal arrows figure 1a) is perpendicular to the $\mathbf{a}$ direction and due to 1D pretransitional fluctuations along the $\mathbf{a}$ direction. The corresponding chains are composed of stripes of m corner sharing WO_6 octahedra.

Fig. 1: X-ray patterns taken at 200K(a) and 20K(c) in $m=6$. (b) is the computer simulation of (a).

In addition, band calculations [4] show that the conducting electrons belong to $5d t_{2g}$ orbitals with preferential overlap along the $\mathbf{a}$ and $\mathbf{a} \pm \mathbf{b}$ chain directions. So, the electronic structure is basically composed of 3 quasi-1D partially filled bands with 2 electrons per half unit formula ($2/m$ electron per tungsten). A schematic representation of the Fermi Surface (FS) is given figure 2.

Fig.2 : Schematic FS of $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ ($m>2$) where the 4 MNWV are indicated.

CDW phase transitions:

For all the members of the series, periodic lattice distortions have been observed but with characteristics depending upon the value of m . Two main behaviors which will be analysed separately in the following have been observed.

P₄W₈O₃₂ and P₄W₁₂O₄₄ :

Upon cooling, the diffuse lines quoted above condense into satellite reflections at the reduced wave vector q_{im} (i for the i^{th} transition of the m^{th} member) from the main Bragg reflections (see table). For these two compounds, 2 and 3 successive second order structural transitions with incommensurate modulation are respectively observed. Each kind of satellite reflections appear at the intersections of different sets of diffuse lines (see figure 1c in the case of $m=6$). These structural transitions give rise to conductivity and magnetic susceptibility anomalies [5,6]. They correspond to successive CDW instabilities of the FS. The CDW stabilized at the upper transition corresponds to a maximum nesting of the FS. There are 4 Maximum Nesting Wave Vectors (MNWV) defined figure 2. For $m=6$, q_{16} corresponds to q_H while for $m=4$, b^*-q_{14} to q_O ". This difference between the wave vectors is probably due to the fact that the leading CDW instability changes from chain **a** in the $m=4$ member to chains **a** $\pm$ **b** for $m\geq 6$. If the high temperature (HT) description of the FS is kept, the mechanism of stabilisation for the second and third transition is similar : for $m=6$ q_{26} and q_{36} correspond to q_O " and q_O' while for $m=4$ q_{24} corresponds to $q_H \equiv q_O'$ because of the special value $1/3$ of $2k_F$ for the chains **a** and **a** $\pm$ **b**. The modulation wave vector of each transition corresponds to one MNWV defined figure 2. No structural modulation with the wave vector q_v is observed probably because there is no chain running along **b**.

$(\text{PO}_2)_4(\text{WO}_3)_{2m}$	$T_c(\text{K})$	q_c	α_{chain}	α_{segment}
$m = 4$	80 (± 1) 52 (± 1)	$q_{14} = (0.330(5), 0.295(5), ?)$ $q_{24} = (0.340(5), 0, ?)$	16° ($\pm 10^\circ$)	35 ($\pm 10^\circ$)
$m = 6$	120 (± 1) 62 (± 1) ≈ 30	$q_{16} = (0.385(5), 0, 0)$ $q_{26} = (0.310(5), 0.295(5), ?)$ $q_{36} = (0.29(1), 0.12(1), ?)$	25° ($\pm 10^\circ$)	30° ($\pm 10^\circ$)
$m = 7$	188 (± 1) 60 (± 2)	$pq_{17} \quad p = 1, 2, 3, 4, 5, 6, 7, \dots$ $q_{17} = [0.260(3), 0.073(3), 0.27(5)]$ $rq_{27} \quad r = 1, 3, 5, \dots$ $q_{27} = [0.12(1), 0.03(1), 0.15(5)]$	35° ($\pm 10^\circ$)	15° ($\pm 10^\circ$)
$m = 9$	above RT	$pq_{19} \quad p = 1, 2, 3, \dots$ $q_{19} = (1/6, 0, 0)$	?	?
$m = 10$ and 11	above RT	$pq_{110} \quad p = 1, 2, 3, 4, \dots$ $q_{110} = (1/7, 0, 0)$	?	?

Table : Critical temperatures and modulation wave vectors for each member of the series $(\text{PO}_2)_4(\text{WO}_3)_{2m}$. α_{chain} and α_{segment} are the angle of **u** with respect to the chain and segment directions respectively.

(PO₂)₄(WO₃)_{2m} with m≥7:

In P₄W₁₄O₅₀ (m=7), two structural transitions are also observed upon cooling. However in contrast to the m=4 and 6 members, the satellite reflections of the upper transition exhibit very unusual behaviors. Firstly, the modulation is triply incommensurate and shows a large number of harmonics. Secondly, the thermal dependence of the satellite intensities present anomalies and giant hysteresis (also observed in resistivity measurements [7]). The lower transition corresponds to dimerization of the q₁₇ modulated structure (q₂₇=q₁₇/2). The m=8 member also develops CDW instabilities below RT. (PO₂)₄(WO₃)_{2m} with m≥9 exhibits already at RT a superstructure which can be described as a commensurate modulation q_{1m} with multiple harmonics pq_{1m}. From m=9 to m=10, the wave vector q₁ change from 1/6 a* to 1/7 a*, a value which is also observed for m=11 and thus seems to have a special stability. The common feature of the modulations observed in the tungsten bronzes with high m is the presence of a large number of harmonics. The harmonics correspond to a structural distortion with a rapidly changing amplitude in direct space. This could be the structural fingerprint of an electron localization phenomena achieved either by strong electron-phonon or/and by strong electron-electron interactions. The effect of Coulomb interactions could be particularly relevant in the tungsten bronzes, because a decrease of the screening effects is expected when the number of electron per tungsten (2/m) decreases with increasing m (in addition the m=2 bronze PWO₅ is localized and exhibits an antiferromagnetic ground state [8]).

Concluding remarks :

The monophosphate tungsten bronzes show very rich physical phenomena related to the hidden one dimensionality of their electronic structure. The most intriguing feature is the observation of a hierarchy of CDW ground states whose characteristics evolve with the thickness of the slab (i.e. with m). The CDW instabilities observed in m bronzes with m=4 and m=6, have some resemblance with those previously reported in Mo₄O₁₁ and the purple bronzes A_xMo₆O₁₇. Instabilities observed in the high m bronzes are more unusual and require further studies. A full account of this structural work can be found in ref. [9].

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