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Charge Density Wave Properties of Quasi Low-Dimensional Transition Metal Oxide Bronzes

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Abstract. — Several families of transition metal oxide bronzes including the quasi one-dimensional molybdenum blue bronzes Am3MoO3, the quasi two-dimensional (2D) Mo purple bronzes AMo6O17 and the quasi 2D monophosphate tungsten bronzes (PO)4(WO3)2m show Peierls transitions leading to commensurate or incommensurate charge density wave (CDW) states. The properties of the monophosphate tungsten bronzes (PO)4(WO3)2m are reviewed. These series of compounds provide a model system where both the low-dimensional character and the average electron concentration are function of the m parameter. The low m compounds (m = 4, 6) show conventional CDW instabilities as well as giant positive magnetotransport and quantum oscillations at low temperature. Detailed information on the Fermi surface in the CDW state is obtained from transport data, the size of the pockets left by the CDW gap openings being found of the order of 1% of the high temperature two-dimensional Brillouin zone. The m = 5 compound, which may be considered as an intergrowth of m = 4 and 6, shows also instabilities with slightly different properties. The absence of CDW long range order affects the properties of the m = 8 member which shows low temperature properties possibly due to weak localisation effects. Finally, studies on the 4 ≤ m ≤ 14 compounds show that the Peierls temperatures are increasing with m, reaching high values, up to 550 K, for m = 13. This is attributed to a 2D character increasing with m. The increase of the room temperature resistivity with m is discussed in terms of enhanced electron-phonon or electron-electron interactions.

1. Introduction

The transition metal oxide bronzes are “old” materials which have been studied since the nineteenth century after the discovery of Na2WO3. They were called bronzes because of their metallic luster [1]. Physicists have rediscovered them more recently, especially when the molybdenum bronzes were shown to be quasi low-dimensional metals [2-4]. The general formula of these compounds is A2M2pO5, where A is a cation or any group of elements inducing a partial filling of the conduction band which would otherwise be empty in the transition metal oxide. The families of bronzes of interest for this review are the metallic molybdenum and monophosphate tungsten bronzes [5]. They have layered type crystal structures. The Mo

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bronzes include two types of materials, the so-called blue bronzes $A_0.30MoO_3$ ($A = Li, K, Rb, Tl$) and the so-called purple bronzes $AMo_6O_{17}$ ($A = K, Na, Tl$) [4]. The Mo red bronzes $A_{0.33}MoO_3$ are semiconductors and are not considered in this review. The monophosphate tungsten bronzes have the general formula $(PO_2)_4(WO_3)_{2m}$ where $m$ can be varied from 4 to 14 [6]. In all cases, the layered type crystal structure leads to quasi low-dimensional electronic properties, either one-dimensional (1D) or two-dimensional (2D), depending on the details of the transition metal oxygen polyhedra arrangement.

It is now well known that quasi low-dimensional metals show two types of electronic instabilities, either a Peierls type transition towards a charge density wave (CDW) state or a superconducting instability. Many examples can be found among the organic low-dimensional conductors [6, 7]. The high $T_c$ copper-based oxides provide an inorganic family of materials where superconductivity is stabilized at comparatively high temperatures. In the transition metal bronzes, for reasons not clarified at the moment, the CDW instability seems to be the dominant mechanism. Only one compound is known to show superconductivity at low temperature (1.9 K): the lithium purple bronze, $LiMo_6O_{17}$ [4]. In all other cases, the existence of Peierls transitions is associated to Fermi surfaces (FS) showing so-called nesting properties in the normal high temperature state. These instabilities give rise either to metal-semiconductor transitions, as in the quasi 1D blue bronze, if the Fermi surface is completely destroyed by the gap openings, or to metal-metal transitions if electron and hole pockets are left on the Fermi surface. This is the case of the Mo purple bronzes and of the monophosphate tungsten bronzes. In all cases, the low temperature state is a CDW state, with a modulation of the electronic density and a related periodic lattice distortion of wavevector $2k_F$, $k_F$ being the Fermi wave vector of the high temperature “normal” metal [8]. The CDW wavelength may be, depending on the filling of the high temperature conduction band, either commensurate with the average lattice, as in $KMo_6O_{17}$, or incommensurate as in the blue bronze and in the monophosphate tungsten bronzes.

The theoretical description of the CDW instabilities has been developed mostly for quasi one-dimensional (1D) conductors, using mean field theory of the Peierls transition [8]. Comparatively few results are available for 2D systems. The mechanism of the Peierls instability in quasi 2D conductors is in fact not straightforward, since it is directly related to the nesting properties of the FS. In an ideal 1D metal, the FS being composed of two parallel planes separated by the vector $2k_F$ is perfectly nested and the Peierls instability completely destroys this FS, thus inducing a metal-insulator transition. This is not the case in a 2D metal where the FS is quasi-cylindrical and normally shows perfect nesting for a given wavevector only along a line parallel to the cylinder axis. There is however a special case, for a perfect square lattice with one conduction electron per site, where the FS is perfectly nested for the two wavevectors [110] and [1 1 0] [9]. Real materials usually do not fit into this case. However the concept of hidden nesting (or hidden one-dimensional), which has been primarily developed to account for the properties of the 2D Mo bronzes $AMo_6O_{17}$ ($A = K, Na$), and oxides ($\eta$-Mo$_4$O$_{11}$ and $\gamma$-Mo$_4$O$_{11}$), applies to other families such as the monophosphate tungsten bronzes [10].

The properties of the low-dimensional Mo bronzes and oxides have been reviewed recently [6, 11, 12]. The Mo blue bronze has been and still is the object of intensive studies since non linear transport properties due to the depinning of the CDW had been established [13]. Recent reviews can be found in references [5, 14]. This article will therefore be focused on the series of the quasi-2D monophosphate tungsten bronzes, $(PO_2)_4(WO_3)_{2m}$. These are of special interest since they show high Peierls temperatures, above room temperature for large values of $m$. Also both the low-dimensional character and the average conduction electron density can be varied with the $m$ parameter.
In next section, the properties of these series will be reviewed for the low m values (m = 4 and 6). They can be accounted for by a conventional CDW model. Magnetotransport and quantum transport provide in these cases detailed information on the CDW states. New results obtained on the m = 5 compound are reported in Section 3. They may not fit perfectly in the usual CDW framework, possibly due to a somewhat different crystal structure. Section 4 will be devoted to the description of the transport properties of the m = 8 compound. In this case, X-ray diffuse scattering studies show that CDW are established below the Peierls temperatures with only short range order [15]. Our recent results may indicate the presence at low temperature of weak localization effects related to the CDW disorder. Finally, in Section 5, some properties for large m compounds will be reported, including the increase of the instability transition temperatures and resistivity with m.

2. Quasi Two-Dimensional Monophosphate Tungsten Bronzes: Basic Properties and Conventional Charge Density Wave Regime (m = 4, 6)

2.1. Basic Properties and Hidden Fermi Surface Nesting. — The monophosphate tungsten bronzes, of general formula (PO$_2$)$_4$(WO$_3$)$_{2m}$ have been synthesized and their crystal structure studied more than ten years ago [16, 17]. Their lattice is orthorhombic and built with perovskite ReO$_3$-type infinite layers of WO$_6$ octahedra parallel to the ab plane, separated by PO$_4$ tetrahedra, as shown in Figure 1. Since the 5d conduction electrons are located in the WO$_6$ layers, the electronic properties are quasi 2D. The thickness of the ReO$_3$ blocks and therefore the c parameter, are increasing with m, while a and b are only weakly dependent on it. The number of conduction electrons per primitive cell is always 4, independent of m. On the other hand, the low-dimensional character is expected to change with the thickness of the WO$_6$ layers. Also, the average number of conduction electrons per W is 2/m, therefore decreasing with increasing m. The lower carrier density may lead, for large m values, to weaker screening effects and therefore to increased electron-electron interactions.

The electrical resistivity of the m = 4 and m = 6 members, obtained with current in the ab plane, have been reported in references [19, 20]. Two anomalies in the electrical resistivity,
Fig. 2. — Resistivity of $P_4W_{12}O_{44}$ ($m = 6$) as a function of temperature for magnetic field $B$ of 0 and 6 Teslas. The current is parallel to the $a$ crystallographic axis and the field $B$ is along $c$.

![Graph showing resistivity as a function of temperature.](image)

Fig. 3. — $P_4W_{12}O_{44}$ ($m = 6$): (a) Band structure (b) Fermi surface (From Ref. [19])

indicating the existence of two electronic instabilities, have been found for $m = 4$ at $T_{P1} = 80$ K and $T_{P2} = 52$ K. X-ray diffuse scattering studies have demonstrated that they correspond to an incommensurate CDW with wavevector components in the $ab$ plane $q_1 = (0.330, 0.295)$ and $q_2 = (0.340, 0)$ [21–23]. In the case of the $m = 6$ phase, these two instabilities are found at $T_{P1} = 120$ K and $T_{P2} = 62$ K ($q_1 = (0.385, 0)$ and $q_2 = (0.310, 0.295)$), therefore at temperatures higher than for $m = 4$. A third instability has also been found at low temperature ($T_{P3} = 30$ K) by structural studies with a wavevector $q_3 = (0.29, 0.11)$. Typical results for the electrical resistivity and magnetoresistivity are shown in Figure 2 for the $m = 6$ compound. One should note that a giant positive magnetoresistance is found at low temperatures for magnetic fields perpendicular to the $ab$-layers.

Band structure calculations using a tight binding extended Hückel method in a 2D approximation have been performed for the $m = 4$ and 6 compounds. Figure 3a shows the results obtained for the $m = 6$ member. Three bands cross the Fermi level. The three corresponding sheets of the FS are shown in Figure 3b [18,19]. Nesting properties appear on the resulting FS obtained from the superposition of these sheets. This has been related to the so-called hidden nesting [10], or hidden one-dimensionality, due to the presence of infinite chains of $WO_6$ octahedra along the $a$ and $(a \pm b)$ axis. In a first approximation, the FS can then be described as
Fig. 4. — Hall coefficient as a function of temperature for $m = 6$. The current is along $a$ and the field along $c$.

being due to the superposition of three quasi-1D FS’s. A similar mechanism has been invoked to account for the existence of Peierls instabilities in the 2D molybdenum bronzes and oxides. This type of mechanism therefore underlies the CDW properties of the quasi-2D transition metal oxide bronzes. Recent results obtained on NaMo$_6$O$_{17}$ by angular resolved photoemission spectroscopy have confirmed this model [23].

In the $m = 4$ and 6 compounds, the nesting properties of the FS combined with electron-phonon coupling induce successive Peierls instabilities which partly destroy the FS. One should note that the Peierls temperatures are higher for $m = 6$ than for $m = 4$, while the normal state resistivity $\rho_{300}$ K is also approximately one order of magnitude larger in $m = 6$. This difference in behaviour cannot be accounted for only by the difference in the calculated carrier concentration which is expected to be much smaller. Therefore, it has to be attributed either to a stronger electron-phonon coupling in $m = 6$ compared to $m = 4$ or to stronger electron-electron interactions due to a weaker screening.

2.2. CHARGE DENSITY WAVE STATE: TRANSPORT, QUANTUM PROPERTIES AND FERMI SURFACE. — Hall effect, magnetoresistance and thermopower have been reported for both compounds [24, 25]. Hall effect data are shown as an example for $m = 6$ in Figure 4. Both Peierls transitions at $T_{P1} = 120$ K and $T_{P2} = 60$ K are clearly seen. In principle, it is possible to analyse the magnetotransport properties by using the so-called two-band model. This analysis is valid for two-band systems if the magnetoresistivity $\Delta \rho / \rho_0$ and the Hall coefficient follow the field dependences given in reference [30]: $\Delta \rho / \rho_0$ should vary as $B^2$ in low fields. It should saturate in high fields, except if the metal is perfectly compensated. $R_H$ should be field independent in the limit of low fields. In our case $\Delta \rho / \rho_0$ does not saturate in high fields [24]. One may therefore assume a full compensation. One can then evaluate the carrier concentrations and mobilities at low temperature, assuming the same electron ($n$) and hole ($p$) concentrations. Figure 5 shows the results obtained in this approximation for the low temperature CDW state. Sharp decreases of the carrier concentrations are found below $T_{P2}$, as expected from the CDW gap opening. $n$ and $p$ are found to be three orders of magnitude smaller in the low temperature CDW state than at room temperature. A similar analysis has been performed for the $m = 4$ compound. Table I shows that $n$ and $p$ are one order of
Fig. 5. — (a) Carrier densities \( n, p \) as a function of temperature obtained with a two-band model assuming perfect compensation \( (n = p) \) for \( \text{P}_4\text{W}_{12}\text{O}_{44} \) \( (m = 6) \). (b) Mobilities \( \mu \) of electrons and \( \nu \) of holes as a function of temperature evaluated with the same model.

magnitude smaller for \( m = 6 \) than for \( m = 4 \). This indicates a more complete destruction of the FS for \( m = 6 \) and is probably related to better nesting properties of the FS at high temperature in \( m = 6 \). We believe that this is due to a more pronounced low-dimensional character for larger \( m \) related to an increased thickness of the \( \text{WO}_6 \) layers. Very likely, the conduction electrons are located towards the center of these layers and the transverse coupling is decreasing when \( m \) is increased. This analysis is supported by quantum properties. Figure 6 shows typical results obtained on \( m = 6 \) for the magnetoresistance \( v.s. \) field up to 16 Teslas at 0.3 K. Shubnikov-de Haas oscillations are clearly seen. Table I also shows the areas of the 2D FS pockets evaluated from the periods of the oscillations [26]. They are of the order of 1/100 of the high temperature 2D Brillouin zone area and clearly smaller in \( m = 6 \) than in \( m = 4 \). De Haas van Alphen oscillations have also been observed in \( m = 6 \) through magnetic torque measurements performed down to 0.3 K in fields up to 28 Teslas: they may indicate that magnetic breakdown takes place in high fields, probably between neighbouring carrier pockets [27].
Table I. — Parameters of the \( m = 4 \) and 6 members of the monophosphate tungsten bronzes \((PO_{2})_{4}(WO_{3})_{2m}\). \( T_{P1} \) and \( T_{P2} \) are the Peierls temperatures, \( A \) is the area at 4.2 K of the Fermi surface pocket obtained from the frequency of the Shubnikov de Haas oscillations, \( n \) and \( p \) are the electron and hole concentrations at 4.2 K obtained from the two-band analysis of the transport data.

<table>
<thead>
<tr>
<th>( m )</th>
<th>4</th>
<th>6</th>
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<tr>
<td>( T_{P1} )</td>
<td>80 K</td>
<td>120 K</td>
</tr>
<tr>
<td>( T_{P2} )</td>
<td>50 K</td>
<td>60 K</td>
</tr>
<tr>
<td>( A ) (4.2 K)</td>
<td>( 6.1 \times 10^{18} ) m(^{-2} )</td>
<td>( 1.3 \times 10^{18} ) m(^{-2} )</td>
</tr>
<tr>
<td>( n, p ) (4.2 K)</td>
<td>( 40 \times 10^{18} ) m(^{-3} )</td>
<td>( 6 \times 10^{18} ) m(^{-3} )</td>
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The thermopower (TEP) is shown vs. temperature in Figure 7 for \( m = 6 \). The thermopower is highly anisotropic in the Peierls state. In the high temperature regime, the TEP shows a quasi-linear and isotropic behavior along the \( a \) and \( b \) crystallographic directions. The measurement along \( b \) reveals an anomaly at low temperature, around \( T = 30 \) K, coinciding with the third Peierls transition. Results obtained on \( m = 4 \) are reported in reference [25].

Above the higher Peierls temperature, the monophosphate tungsten bronzes are expected to behave as normal metals below or close to the Debye temperature since this temperature has been found to be approximately 280 K for \( m = 4 \) and 240 K for \( m = 6 \) [28]. However we have found that in both compounds the TEP has a negative slope, while the Hall constant is positive. This indicates that both bronzes are nearly compensated metals. Band structure calculations predict that at room temperature three bands cross the Fermi level [19]. The highest one is electron-like in all directions, the middle one is expected to be electron-like (or flat) along the \( a \)-axis and hole-like along \( b \), while the opposite behavior is expected for the lowest band in both compounds (Fig. 3). The TEP is found to be electron-like in the normal state whatever the direction of the temperature gradient is. This may therefore indicate that the highest band
is associated with the longer relaxation time and primarily determines the transport mass and therefore the sign of the thermopower. On the other hand, the sign of the Hall coefficient is determined by the cyclotron properties and by the electron trajectories along the section of the FS in the ab plane. Our results show that the cyclotron mass is predominantly associated with hole-type carriers. Similar results have been found for the high Tc superconducting oxides and attributed to the complex morphology of the FS [29].

The anomalies found at the Peierls temperatures in the curves of the TEP vs. T (Fig. 7) are due to the gap openings which modify the density of states at the Fermi level and the carrier mobilities. Below T_{P2}, the Seebeck coefficient S is clearly p-type when the temperature gradient is along the a-axis and n-type along b. This indicates that the CDW pockets induced by the T_{P1} transition are predominantly electrons along b and holes along a. These results should be related to the geometry of the gap openings and therefore to the position of the CDW satellites which are close to (a^* + b^*)/3 [15, 21, 22]. The hole-type behaviour along a indicates that the TEP is dominated by carriers left from the Fermi sheet corresponding to the lower band (first Brillouin zone), which have a p-type behaviour due to the negative curvature along this direction (Fig. 3b). Below T_{P2}, the TEP indicates that hole-type pockets are induced by this second gap.

The above results show that transport and magnetotransport properties provide detailed information on the FS both in the normal and CDW state. In the CDW state, the size of at least part of the 2D FS is known thanks to quantum transport.

3. Transport Properties and Instabilities in P_4 W_{10} O_{38} (m = 5)

The m = 5 compound is different from the other members of the series since the crystal structure is built with alternate layers of WO_6 octahedra of different thickness: it can be viewed as resulting from an intergrowth of the compounds m = 4 and 6 [31]. The band structure and the FS have been calculated with the same tight-binding 2D approximations as for the m = 4 and 6 members and FS nesting had been predicted [18]. It is therefore interesting to study its physical properties in order to compare them with those of the more “conventional” members m = 4 and 6 which have neighbouring crystal structures and conduction electron densities.
Fig. 8. — Resistivity of $P_4W_{10}O_{38}$ ($m = 5$) as a function of temperature. The current is along the $a + b$ crystallographic axis.

Fig. 9. — Low temperature resistivity of $P_4W_{10}O_{38}$ ($m = 5$) as a function of temperature for different magnetic fields $B$. The current is parallel to the $a + b$ crystallographic axis and the field $B$ is along $c$.

Figure 8 shows the resistivity $\rho$ vs. temperature measured with the dc current parallel to the $ab$ plane: $\rho$ is characteristic of a metal, with a room temperature value higher than that of the compound $m = 6$. Two anomalies can be seen. The first one is in the vicinity of $T_1 = 100$ K and corresponds mainly to an increase of slope at low temperature announced by a slight minimum around 180 K. The second one is seen as a weak kink around $T_2 = 30$ K and is better seen in Figure 9 (curve $B = 0$). Figure 9 shows the resistivity vs. temperature under magnetic field perpendicular to the plane of the layers in fields up to 6 Teslas in the low temperature regime. Huge magnetoresistance clearly appears below $T_2$. No X-ray diffuse scattering data are presently available on this compound. However, it is very likely that the two anomalies observed in the transport properties are due to CDW gap openings. The high temperature anomaly is puzzling since it does not appear as a clear bump on the resistivity curve: this could indicate that the onset of CDW gap or pseudo-gap opening takes place around 180 K,
with a small decrease of the carrier concentrations and a large increase of the mobilities. This could be due to the presence of CDW fluctuations above $T_1$ which would anomalously decrease the collision time and therefore increase the resistivity. The freezing of these fluctuations when the long range CDW order is established could explain the strong decrease of the resistivity below $T_1$, which appears as a change of slope. Similar properties have been observed in the past in some layered dichalcogenides showing CDW instabilities [32]. Structural studies could corroborate this model.

Figure 10 shows the thermopower $S$ vs. temperature measured with the temperature gradient along the layer plane. The two transitions are clearly seen as extrema in the curve. These extrema correspond to the CDW gap openings and indicate that the sign of the dominant carriers changes at each transition. While $S$ is always negative, the change of slope below $T_1$ indicates that hole pockets become important at this temperature and that electron pockets are again dominant below $T_2$. Further low temperature magnetoresistance data and possible quantum transport should complete this information.

4. Short Range Order and Weak Localisation in the Charge Density Wave State of $P_4W_{16}O_{56}$ ($m = 8$)

Diffuse X-ray scattering studies have been performed on the $m = 8$ member of the series [15]. Diffuse sheets or lines are observed up to room temperature, indicating the presence of CDW fluctuations. These diffuse features condense into broad satellites at $T_{P_1} = 220$ K with wavevector $q_1 = (0.47, 0.02, 0.15)$ and at $T_{P_2} = 200$ K with wavevector $q_2 = (0.19, 0.03, 0.06)$. This corresponds to the establishment below the transition temperatures of short range ordering. This lack of long range ordering persists down to the lowest measurement temperature of 35 K. The $q_2$ short range order modulation is also accompanied by higher harmonics $nq_2$ detectable up to $n = 6$. This might indicate that this modulation is not sinusoidal and does not correspond to a conventional CDW. In this context, it is interesting to study the transport properties in order to find out how they are affected by these anomalous structural properties.

Figure 11a shows the electrical resistivity $\rho$ measured as a function of temperature between 4.2 K and 600 K, for current parallel to the $ab$ plane. Above room temperature, the curve is typical of a metal. Below approximately 300 K, $\rho$ increases down to the lowest temperature.
This behaviour may indicate weak localisation effects [33] due to the disorder induced by the CDW short range ordering. One may therefore plot the conductivity $\sigma$ vs. temperature in the low temperature regime in order to compare it with results obtained on other disordered metals [34]. Figure 11b shows that a linear dependence of $\sigma$ is found up to approximately 60 K. This may be due to quantum interference effects induced by the CDW disorder and giving rise to weak localisation, possibly combined with electron-electron interactions.

Magnetoresistance $\Delta \rho/\rho_0$ has also been measured as a function of magnetic field. Figure 12 shows that it is positive and anisotropic, larger for field applied perpendicular to the layers. It is weak, in the range of the % at 4.2 K in fields of 6 Teslas. Figure 13a shows that $\Delta \rho/\rho_0$ follows a law in $B^2$ in a field interval increasing with increasing temperatures (up to 6 Teslas at 40 K). One could analyse these data either with a two-band model, assuming semi-classical transport, or in relation with a weak localisation model. In the first case, the slope $\alpha$ of the curves of Figure 13a ($\Delta \rho/\rho_0 = \alpha B^2$) would be in a first approximation the square of an effective carrier mobility $\mu_{\text{eff}}$, assuming a perfectly compensated two-band model with equal hole and electron.
Fig. 12. — Magnetoresistance as a function of magnetic field for \( m = 8 \), showing the anisotropy. \( T = 4.2 \) K. Magnetic field perpendicular or parallel to the layers.

mobilities. Figure 13b shows the curve of \( \alpha \) vs. temperature. Values of \( \mu_{\text{eff}} \) decreasing from 900 to 100 cm\(^2\)/Vs between 4.2 and 40 K are found on this basis. While these values are not unreasonable, this model is inconsistent with the low temperature increase of the resistivity. One may then invoke a weak localisation mechanism. In this second model, the slope \( \alpha \) would be related to the inelastic scattering time characteristic of the disorder [35] and therefore of the CDW correlation length. The inset of Figure 13b shows \( \alpha \) as a function of temperature on log-log scales: a temperature power law with an exponent of \(-3/2\) is well obeyed. This behaviour could be the signature of a weak localisation mechanism. Further work is in progress in order to corroborate this analysis.

Thermopower \( S \) has been measured as a function of temperature between 10 K and 300 K. Figure 14a shows that \( S \) is always n-type and that \(|S|\) decreases with decreasing temperature except for an anomaly detected in the vicinity of the \( T_{P1} \) transition. This anomaly is clearly the signature of this transition which was not detected on the \( \rho(T) \) curve. It may indicate that small gaps open on the FS at this temperature.

The low temperature behaviour of \( S(T) \) is puzzling. Figure 14b shows that the curve of \(|S|/T\) vs. \( T \) shows a peak at low temperature around 30 K. Similar effects found in disordered metals have been in the past attributed to mass enhancement due to electron-phonon coupling [36]. A similar mechanism could take place in our case.

The \( m = 8 \) compound is the only member of the series showing no long range order in the distorted state. This could be due to the competition between the two instabilities at \( T_{P1} \) and \( T_{P2} \) which take place at neighbouring temperatures. Whether the short range order state corresponds to the coexistence of domains associated to one or the other modulation or to a more complicated situation is not known at the moment.

5. Instabilities in the Monophosphate Tungsten Bronzes \((\text{PO}_2)_4(\text{WO}_3)_{2m}\) as a function of \( m \) (4 \( \leq \) \( m \) \( \leq \) 14)

Instabilities have been detected both by transport and structural studies in large \( m \) compounds [15,37]. One should note that high temperature transitions are found: for \( m > 8 \), these temperatures are above room temperature and reach 550 K for \( m = 13 \). While most compounds
show incommensurate modulations, another type of commensurate distortion appears for \( m \geq 9 \): this corresponds to a doubling of the lattice parameter along \( a \), the related satellites are comparatively intense and are not characteristic of CDW. This modulation has been described in terms of an antiferroelectric-type distortion in reference [15]. This is supported by the existence of such distortions in the neighbouring compound WO₃.

Figure 15 shows the critical temperatures obtained from both resistivity measurements and structural studies as a function of \( m \). Four types of transitions can be distinguished. The transition temperatures labelled \( T_{C1} \) and \( T_{C2} \) correspond for small values of \( m \) to \( T_{P1} \) and \( T_{P2} \). The third transition found in \( m = 6 \) at low temperature is labeled \( T_{C3} \) in this graph. Finally, the transition temperature corresponding to the commensurate distortion is labelled \( T_{C0} \). It is clear from these results that the transition temperatures \( T_{C1} \) and \( T_{C2} \) are increasing rapidly with \( m \) up to \( m = 13 \).

The high values of the transition temperatures and their rapid increase with \( m \) are the most remarkable properties of the monophosphate tungsten bronzes. One should note that for
large values of $m$ ($m = 13$), the compounds are close to the oxide WO$_3$, since the thickness of the WO$_6$ layers is large. However, electronic instabilities seen in the transport properties appear at high temperature [37]. The same arguments as those developed for the $m = 4$ and 6 compounds could therefore apply: a more pronounced twodimensional character would be found in the large $m$ compounds, inducing a more cylindrical FS and therefore higher instability temperatures. Detailed structural studies including crystallographic refinements on large $m$ members are presently missing to corroborate this mechanism. One should also note that X-ray diffuse scattering studies show the existence of high order harmonics of the satellites for $m \geq 7$. This shows that the distortion is not sinusoidal for large $m$ and therefore does not correspond to a conventional CDW. This could be attributed to strong electron-phonon coupling inducing a bipolaron-type mechanism, as described in reference [38]. Electron-electron interactions could also possibly be responsible for such distortions.

Other related interesting properties of the monophosphate tungsten bronzes lie in the variation of the resistivity as a function of $m$. Figure 16 shows the room temperature resistivity

Fig. 14. — (a) Thermoelectric power $S$ as a function of temperature for $m = 8$. Temperature gradient along the $a$ crystallographic axis. The inset shows the high temperature data with enlarged scales. (b) $-S/T$ as a function of temperature showing the low temperature peak.
Fig. 15. — Critical temperatures as a function of \( m \) (see text). The crossed data points correspond to results obtained by crystallographic studies only. Other data points correspond to results obtained by transport studies (and often by structural studies). The lines are guides to the eye for the \( T_{C1} \) and \( T_{C2} \) transitions.

Fig. 16. — Left scale and close symbols: room temperature resistivity as a function of \( m \). Right scale and open symbols: reciprocal electron concentration evaluated from the chemical formula (2/\( m \) per W ion).

\( \rho(300 \text{ K}) \) (log scale) vs. \( m \) for \( 4 \leq m \leq 14 \). The reciprocal carrier density evaluated from the chemical formula (2/\( m \) conduction electron on the average per W atom) is also plotted vs. \( m \) for comparison. One notes a steep increase of \( \rho(300 \text{ K}) \) with \( m \) for even \( m \) compounds. The increase is weaker for odd \( m \) members. The larger room temperature resistivity for large \( m \) members of the series is striking: it could be related to slightly different crystal structures since most odd \( m \) compounds show monoclinic distortions [39]. Whether this induces stronger electron-phonon coupling is not clear at the moment. One should also note that the difference in resistivity between odd and even \( m \) seems to vanish for large \( m \), thus when one approaches WO\(_3\).
In order to account for these results, one has also to consider the existence of intergrowths in the large \( m \) compounds (see for example Ref. [39]). These intergrowths may induce inhomogeneities and disorder which could increase the electrical resistivity. However this should not be the case for the low \( m \) compounds: for example the factor of 10 between the room temperature resistivity of the \( m = 4 \) and 6 compounds has been found in crystals from different origins and is very reproducible. This cannot be attributed to intergrowth problems since these phases do not suffer from such defects. Some intrinsic mechanism must then be involved.

The large increase of \( \rho(300 \text{ K}) \) vs. \( m \) for even \( m \) compounds cannot either be attributed to the change in the carrier concentration which in a first approximation should induce a much weaker increase, as shown in Figure 16. Two mechanisms can be invoked to account for these properties, either an increase of the electron-phonon coupling or of the electron-electron interactions. An increase of the resistivity has been observed at low temperatures on most compounds for \( m \geq 7 \). This may suggest that the second mechanism is more likely to be dominant.

6. Conclusion

The monophosphate tungsten bronzes \((\text{PO}_2)_4(\text{WO}_3)_{2m}\) provide a model system for quasi-two dimensional conductors where the Peierls temperatures and the electrical resistivity can be varied as a function of the \( m \) parameter. This parameter is correlated with the thickness of the conducting layers as well as with the average carrier concentration density.

The small \( m \) compounds \((m = 4, 6)\) show conventional CDW properties, with metallic or semi-metallic behaviour over the whole temperature range and a decrease of carrier concentrations below the Peierls temperatures. In the low temperature CDW states, they exhibit giant positive magnetoresistance attributed to the coexistence of high mobility electron and hole pockets left by the CDW gap openings. Quantum transport allows an evaluation of the size of these pockets which are found to be of the order of 1\% of the two-dimensional high temperature Brillouin zone. The \( m = 5 \) compound also shows instabilities, with a behaviour different from what is found in the 4 and 6 compounds. This could be due to the different crystallographic structure since the \( m = 5 \) member can be viewed as an intergrowth of the \( m = 4 \) and 6 ones. Also CDW fluctuations may be important in this compound above the instability temperatures.

For \( m \geq 7 \), different type of transport properties as well as higher order harmonics of the CDW satellites found by X-ray diffuse scattering studies show that the instabilities are not conventional Peierls transitions. For \( m = 8 \), the transport properties are determined by the absence of long range CDW ordering and may be attributed in the low temperature regime to weak localisation related to quantum interference effects induced by the short CDW correlation length.

Systematic studies of these bronzes for \( 4 \leq m \leq 14 \) show that the Peierls or instability temperatures are increasing with \( m \). High transition temperatures, above room temperature and up to 500 K, are found for \( m > 8 \). The increase of \( T_P \) with \( m \) may be attributed to an increase of the low-dimensional character. This may be due to a decrease of the transverse coupling with increasing \( m \), taking place if the conduction electrons are located towards the center of the \( \text{WO}_6 \) layers. The Fermi cylinder would then be less warped for larger \( m \), this favouring the onset of CDW instabilities at higher temperatures.

Finally the room temperature resistivity \( \rho(300 \text{ K}) \) is found to increase with \( m \), rapidly for even \( m \) compounds. The odd \( m \) members show higher values of \( \rho(300 \text{ K}) \). This can be due to a different crystal structure since most odd \( m \) compounds show a monoclinic distortion. The
steep increase of $\rho(300 \text{ K})$ for even $m$ members is discussed in terms of enhanced electron-phonon coupling or electron-electron interactions for larger $m$ values.

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