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Electronic instabilities in the quasi-two-dimensional metallic oxide $K_xP_4W_8O_{32}$

P Roussel[†], D Groult^{†§}, C Hess[‡], Ph Labbé[†] and C Schlenker[‡]

[†] Laboratoire CRISMAT, CNRS UMR 6508, ISMRA, Université de Caen, 14050 Caen Cédex, France

[‡] Laboratoire d'Etudes des Propriétés Electroniques des Solides, CNRS, BP 166, 38042 Grenoble Cédex 9, France

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Abstract. Large single crystals of $K_xP_4W_8O_{32}$ with $x = 1.00(5)$, $x = 1.05(5)$ and $x = 1.30(9)$ were prepared by the chemical vapour transport technique and electron transport properties were investigated.

Thermal variation of the resistivity between 300 K and 4.2 K shows metallic behaviour with anomalies whose onset temperature T_p depends on the potassium content x : $T_p = 135$ K for $x = 1.00$, $T_p = 150$ K for $x = 1.05$ and $T_p = 170$ K for $x = 1.30$. Anomalies can also be observed in the thermal dependence of the thermopower. A conventional metal behaviour is thus observed above T_p while a strong deviation from linearity is observed below T_p with a change of sign from negative to positive which depends on the x value. The magnetic field dependence of the resistivity has been studied in the low-temperature state for $x = 1.30$ and shown to be strongly correlated with the orientation of the magnetic field with respect to the conducting plane.

The results are explained on the basis of Peierls instabilities and charge density waves (CDW) gap openings with electron and hole pockets which compete on the Fermi surface.

1. Introduction

Low-dimensional metallic oxides have been the subject of extensive studies because of peculiar transport properties associated with two kinds of electronic instability. The first type involves a phase transition to a superconducting state, as in the high- T_c superconducting copper oxides. The second, in which a density wave is established, leads to an insulating or a semi-metallic state. In the presence of important electron–electron interactions, the ground state is of a spin density wave (SDW) type with a spatial magnetic modulation.

In the presence of sizeable electron–phonon coupling, the ground state is of the charge density wave (CDW) type with a spatial modulation of the electronic density, as in molybdenum bronzes A_xMoO_3 ($A = K, Rb, Tl$), AMo_6O_{17} ($A = Na, K, Tl$) [1, 2] and in the monophosphate tungsten bronzes $(PO_2)_4(WO_3)_{2m}$ which have been studied more recently [1, 3–7]. In this latter case, it has been shown that the CDW instabilities and Peierls temperatures are strongly dependent upon the parameter m which is related to the thickness of the perovskite $[WO_3]$ -type slabs.

The early members with $m < 7$ ($m = 4–6$) undergo a Peierls transition towards a CDW state characterized by a sinusoidal modulation, as demonstrated by x-ray diffuse scattering

§ E-mail address: groult@crismat.ismra.fr

[4]. Quantum oscillations observed in magnetoresistivity and magnetic torque measurements have given information on the size of the pockets left on the Fermi surface by the CDW gap openings [5].

For large values of m ($8 \leq m \leq 14$), weak localization phenomena take place as well as high Peierls temperatures. The mechanism underlying this peculiar behaviour is not well understood at present and may involve either enhanced electron–electron interactions which would induce strong electron–phonon coupling [6] or a competition between the CDW instability and the antiferroelectric instability of pure WO_3 (i.e. limit $m \rightarrow \infty$) [7].

Progress in the understanding of CDW phenomena could be made by considering other materials with a low-dimensional character together with the possibility of changing the conduction band filling.

In the present paper, we report that CDW instabilities have been observed for the first time on the monophosphate tungsten bronze $\text{K}_x\text{P}_4\text{W}_8\text{O}_{32}$, where the potassium content can be varied.

2. Experimental techniques

2.1. Crystal growth

A stoichiometric mixture of K_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$ and WO_3 in accordance with the formula $\text{K}_x\text{P}_4\text{W}_8\text{O}_{32}$ ($1 \leq x \leq 2$) was first heated in air at 600°C for 12 hours to decompose the phosphate and the carbonate. An appropriate amount of powder metallic tungsten used as a reducing agent and corresponding to $((4+x)/6)$ mole per formula unit, was added to the decomposed initial mixture before grinding intimately; samples were then heated in evacuated silica ampoules at 1000°C for 2 days. This procedure allows well crystallized powder $\text{K}_x\text{P}_4\text{W}_8\text{O}_{32}$ samples to be obtained, which are subsequently used for crystal growth.

A charge of about 2 g of the powder is then weighed and put into a quartz tube (≈ 20 cm long and 1.8 cm internal diameter) which is sealed under vacuum. After placing the tube in a horizontal furnace, a temperature gradient of $\approx 10^\circ\text{cm}^{-1}$ is applied along its length i.e. the hot zone = 1200°C and the cold zone = 1000°C . The samples were held under these conditions for 2 weeks in order to grow single crystals by chemical vapour transport at the cold zone.

2.2. Characterization of the crystals

X-ray powder diffraction patterns of the products were recorded using a Philips diffractometer with monochromatized $\text{Cu K}\alpha$ radiation. The quality and cell parameters of the single crystals were checked with Weissenberg photographs.

Electron probe micro-analysis of the crystals was performed with a Philips FEG-XL30 scanning electron microscope equipped with an EDS-LINK analysis system.

Conventional four-probe DC resistivity measurements were carried out on oriented single crystals. Electrical contacts were made by ultrasonic soldering of indium on the surface of the crystal. Resistivity was measured along the b axis.

The thermopower was measured by applying a temperature gradient along the (a, b) plane of the crystals.

Magnetic field dependence of the resistivity was studied at 4.2 K with a magnetic field perpendicular or parallel to the (a, b) plane.

3. Results

3.1. Synthesis

Copper-coloured needles and platelike crystals of $K_xP_4W_8O_{32}$ were obtained in the cold zone. The largest crystals have dimensions $10 \times 2 \times 0.4 \text{ mm}^3$.

Powder XRD patterns and Weissenberg photographs confirm the monoclinic cell parameters of the crystals which depend upon the x content of potassium: $a \approx 6.70 \text{ \AA}$, $b \approx 5.30 \text{ \AA}$, $c \approx 8.90 \text{ \AA}$, $\beta \approx 100.5^\circ$. Eighteen crystals grown from three different preparations were selected and analysed. A P:W ratio of 0.52 ± 0.06 close to the theoretical value 0.50 was obtained for all the samples. The K:W ratio was found to change from one preparation to the other; it corresponds to the values $x = 1.30 \pm 0.09$, $x = 1.05 \pm 0.05$ and $x = 1.00 \pm 0.05$ respectively.

The structure determination of $K_xP_4W_8O_{32}$ has previously been performed on a crystal with $x = 0.84 \pm 0.08$ [8]. A schematic drawing of the structure is shown in figure 1(a). Like that of $P_4W_8O_{32}$ (figure 1(b)), the structure of $K_xP_4W_8O_{32}$ is built up of parallel perovskite ReO_3 -type layers of corner sharing WO_6 octahedra, which are infinite in two directions; these two-dimensional slabs are linked to one another through PO_4 tetrahedra. The two structures differ only in the orientation of two successive $[WO_3]$ slabs: for $K_xP_4W_8O_{32}$, the WO_6 octahedra strings in successive slabs are all oriented parallel to the same direction, whereas for $P_4W_8O_{32}$, subsequent strings are staggered. As a result, the tunnels delimited at the borders of $[WO_3]$ slabs and PO_4 tetrahedra are hexagonal and partly filled by K^+ cations for $K_xP_4W_8O_{32}$ whereas they are pentagonal and empty for $P_4W_8O_{32}$.

3.2. Transport properties

The thermal dependence of the resistivity is shown in figure 2 for three crystals of $K_xP_4W_8O_{32}$ selected from the three preparations mentioned earlier. An anomaly in the resistivity is clearly seen as T decreases for all compositions, but the transition temperature depends on the potassium content, x : $T_p = 170 \text{ K}$ for $x = 1.30$, $T_p = 150 \text{ K}$ for $x = 1.05$ and $T_p = 135 \text{ K}$ for $x = 1.00$.

Such a behaviour is different from that observed for the Na-based analogue $Na_{1.6}P_4W_8O_{32}$ which exhibits indeed below 100 K a broad and very weak metal to metal transition as stated by Wang *et al* [9] (see inset of figure 2). On the other hand, the transition appears as strong as that observed for $P_4W_8O_{32}$ which presents two resistivity anomalies at 52 and 80 K [3, 10].

At room temperature, the materials are metallic with conductivities close to that found for other quasi-two-dimensional metallic oxides such as the previously studied Mo bronzes and phosphate tungsten bronzes [2, 3].

The thermopower S has been measured for $K_{1.00}P_4W_8O_{32}$ and $K_{1.30}P_4W_8O_{32}$. Figure 3 shows the temperature variation of S . Above 130 K for $K_{1.00}P_4W_8O_{32}$ and 170 K for $K_{1.30}P_4W_8O_{32}$ the thermopower is negative and linear with T (K). Below 130 K, S increases as T decreases and becomes positive above 108 K for $K_{1.00}P_4W_8O_{32}$; a maximum is found at about 78 K. However, for $K_{1.30}P_4W_8O_{32}$ the thermopower is more negative below 170 K and shows a minimum value at about 120 K.

Magnetoresistance has also been measured at low temperature as a function of magnetic field (up to 7.5 T at 4.2 K), as shown in figure 4 for $K_{1.30}P_4W_8O_{32}$. It depends strongly on the orientation of the magnetic field B with respect to the conductivity plane (a , b). Figure 5

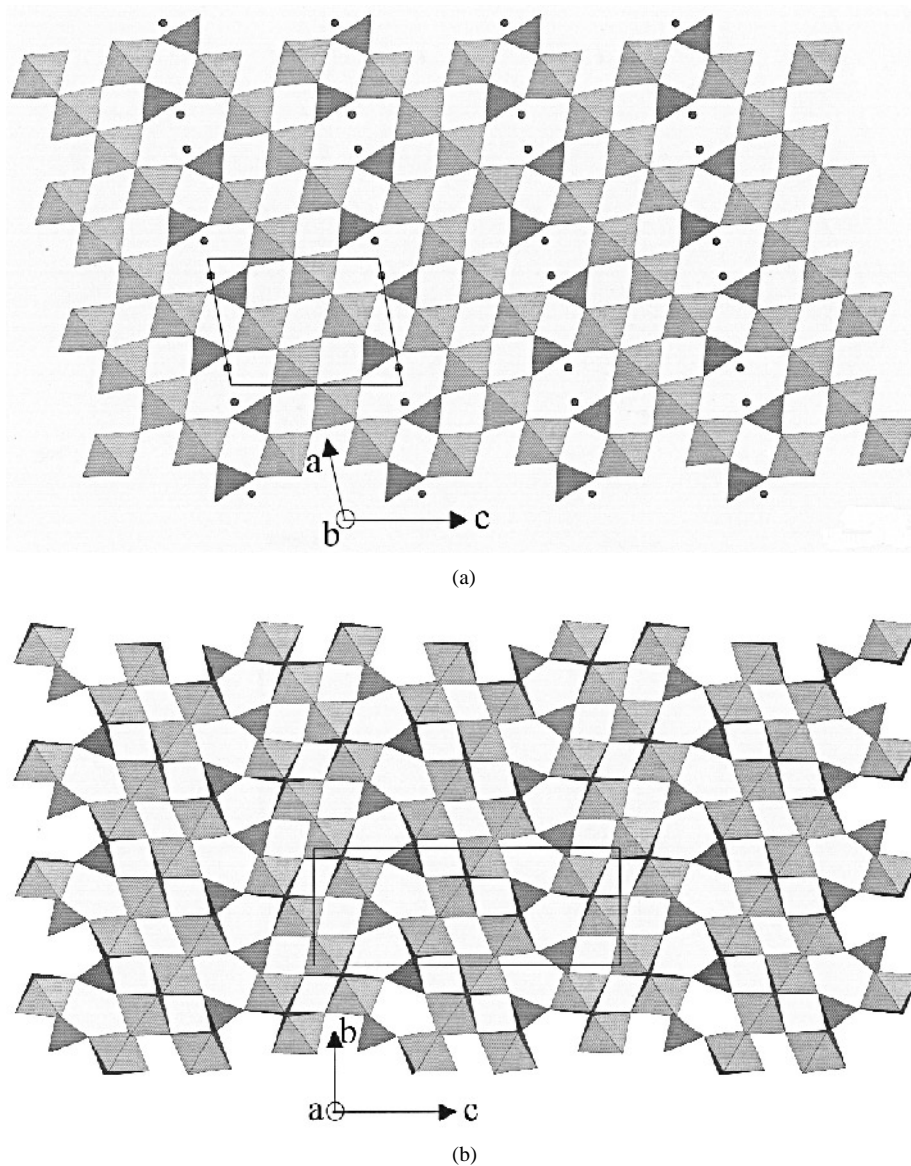


Figure 1. Crystal structure of: (a) $K_xP_4W_8O_{32}$ (black spots are K atoms located in hexagonal tunnels with an occupancy rate of $x/4$); (b) $P_4W_8O_{32}$.

shows that the highest value of magnetoresistivity is obtained when B is perpendicular to this plane.

4. Discussion and conclusion

The transitions found in $K_xP_4W_8O_{32}$ have to be attributed to Peierls instabilities as in the neighbouring compound $P_4W_8O_{32}$. These instabilities are related to the nesting properties of the Fermi surface and therefore to quasi-two-dimensional electronic properties.

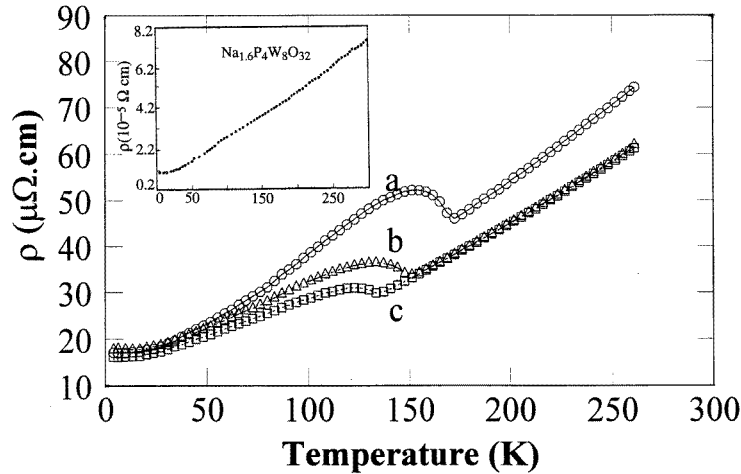


Figure 2. Resistivity as a function of temperature. The current is parallel to the b crystallographic axis. (a) $K_{1.30}P_4W_8O_{32}$; (b) $K_{1.05}P_4W_8O_{32}$; (c) $K_{1.00}P_4W_8O_{32}$. The inset shows the resistivity as a function of temperature for $Na_{1.6}P_4W_8O_{32}$. From [9].

The Peierls temperatures seem to increase with the potassium content, x , and therefore with the filling of the conduction band. This could be due to the variation with x of the density of states at the Fermi level. Previous band structure calculations performed for both Na and K monophosphate tungsten bronzes [11] did predict such electronic instabilities but were not accurate enough to provide reliable values of the density of states at the Fermi level. One may assume that the Peierls temperature increases with the density of states $g(\epsilon_F)$ at the Fermi level, as predicted for the mean field instability temperature T_{MF} in the case of a one-dimensional system [12]:

$$kT_{MF} = 2.28\epsilon_F \exp \left[\frac{-\hbar\omega_0(2k_F)}{\lambda^2 g(\epsilon_F)} \right]$$

where $\omega_0(2k_F)$ is the frequency of the soft phonon at the Fermi wavevector k_F and λ an electron–phonon coupling constant. The increase of T_p would therefore indicate that in our case $g(\epsilon_F)$ is increasing with x in the explored range of x .

One should compare this result with the increase of the Peierls temperature with m through the series $(PO_2)_4(WO_3)_{2m}$. First let us point out that the band filling in this latter case is independent of m . The four (PO_2) groups always provide four electrons per unit cell to the conduction band whatever m is. In a first approximation and in a two-dimensional model, the Fermi surface does not depend on m , since the 2D Brillouin zone is approximately the same for all m (the a and b lattice parameters are only weakly dependent on m). However, since the c parameter is increasing with m , the conduction electron density is decreasing with increasing m . At the same time the low-dimensional character is changing, since the thickness of the perovskite $[WO_3]$ -type slabs is increasing with m . We have proposed previously [6] that for the low- m compounds ($m < 7$), the increase of the Peierls temperature with m may be due to an increase of the low-dimensional character. For the high- m compounds, other mechanisms, such as stronger electron–electron interaction and electron–phonon coupling, may be involved.

In the case of $K_xP_4W_8O_{32}$ the mechanisms involved for the series $(PO_2)_4(WO_3)_{2m}$ do not apply. We believe that the change of the Peierls temperature is rather due to changes of

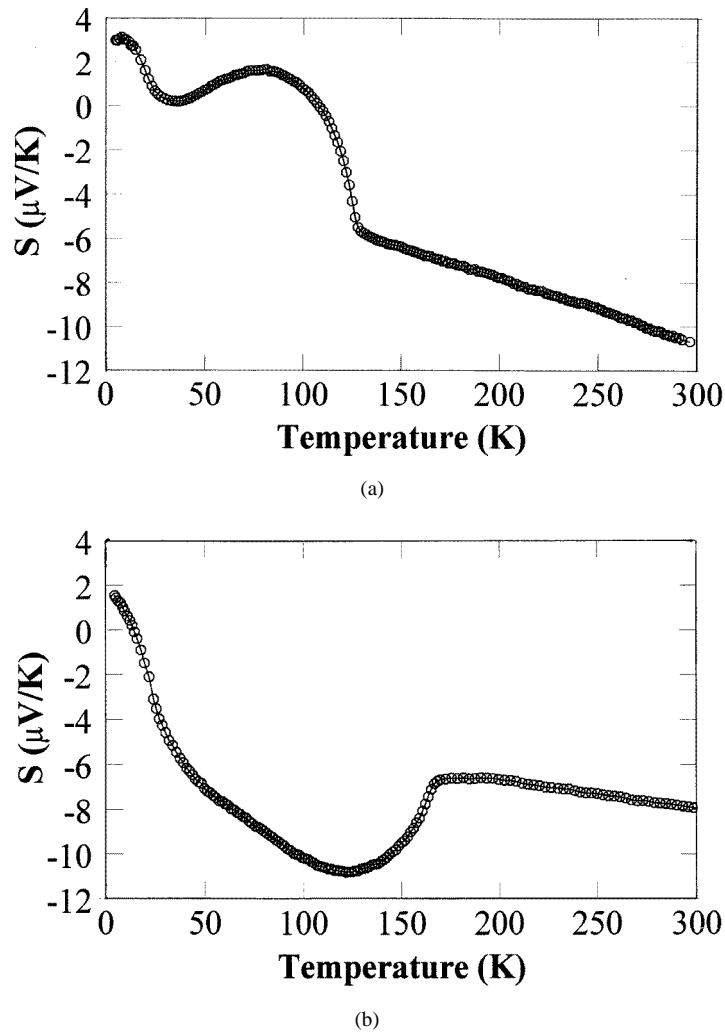


Figure 3. Thermoelectric power as a function of temperature. Temperature gradient parallel to the *(a, b)* plane for (a) $\text{K}_{1.00}\text{P}_4\text{W}_8\text{O}_{32}$ and (b) $\text{K}_{1.30}\text{P}_4\text{W}_8\text{O}_{32}$.

the Fermi surface and of the density of states at the Fermi level as mentioned above. It is likely that the nesting properties of the Fermi surface also depend on x , as shown in [11].

The thermal dependence of the thermopower corroborates the model of the Peierls transitions. In the high-temperature metallic state the negative values of S indicate that the dominant carriers are electrons; above the Peierls temperature T_p the two compounds behave as conventional metals.

In a three-dimensional free-electron model, assuming an energy independent mean free path, one obtains: $S = -2\pi^2 k_B^2 T g_{eff}(\epsilon_F)/9e$. One can then deduce the effective densities of states at the Fermi level: $g_{eff}(\epsilon_F) = 0.76 \text{ eV}^{-1} \text{ mol}^{-1}$ for $\text{K}_{1.30}\text{P}_4\text{W}_8\text{O}_{32}$ and $g_{eff}(\epsilon_F) = 1.78 \text{ eV}^{-1} \text{ mol}^{-1}$ for $\text{K}_{1.00}\text{P}_4\text{W}_8\text{O}_{32}$. These results agree with values reported for other low-dimensional oxides (e.g. $g_{eff}(\epsilon_F) = 1.7 \text{ eV}^{-1} \text{ mol}^{-1}$ for $\text{KMo}_6\text{O}_{17}$). It should be noted that the density of states at the Fermi level evaluated from the thermopower is

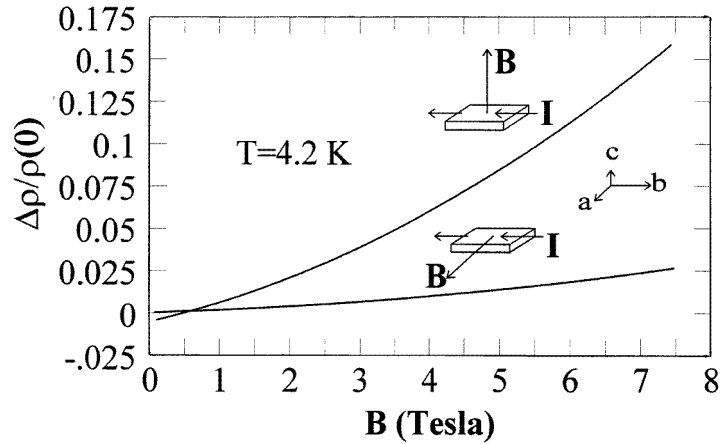


Figure 4. Magnetoresistivity as a function of magnetic field for $K_{1.30}P_4W_8O_{32}$ with $B \parallel (a, b)$ and $B \perp (a, b)$. $T = 4.2$ K.

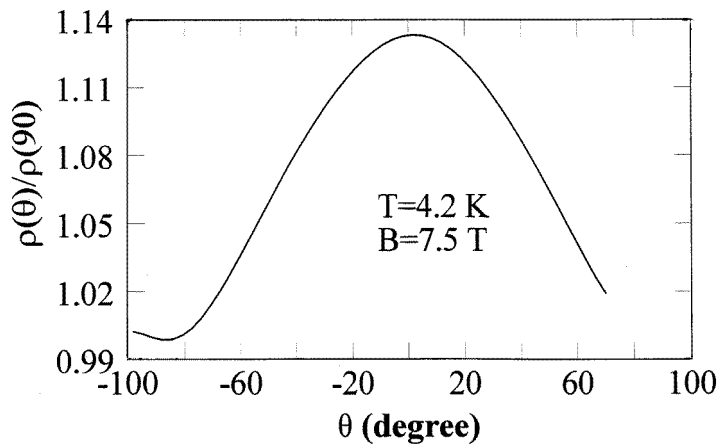


Figure 5. Angular dependence of the magnetoresistivity for $K_{1.30}P_4W_8O_{32}$ with $B = 7.5$ T at $T = 4.2$ K. θ is the angle between the magnetic field and the perpendicular to the (a, b) plane.

an effective density of states $g_{eff}(\epsilon_F)$, since electron and hole bands give contributions to $g_{eff}(\epsilon_F)$ with different signs. One therefore cannot relate simply these values to the Peierls temperature. This is due to the complexity of the Fermi surface which includes both electron and hole-type sheets. The thermopower data show that for $x = 1.00$ and $x = 1.30$, the dominant carriers are electrons. The above values of $g_{eff}(\epsilon_F)$ may indicate that the contribution of holes increases with x . It is difficult to decide whether the available band calculations are consistent with this result. More accurate calculations would be required for that.

Below T_p , one observes a strong deviation of S from linearity which corresponds to the onset of the CDW metallic state. Such a thermal variation of the thermopower is correlated to the thermal evolution of the Fermi surface. In spite of a change of behaviour between $K_{1.00}P_4W_8O_{32}$ and $K_{1.30}P_4W_8O_{32}$, the phase transitions at $T_p = 135$ K and $T_p = 170$ K, respectively, are similar. In both cases the behaviour is consistent with the partial opening

of a gap at the Fermi surface which leads to a change in the concentrations of electrons and holes. The anomalies found in the thermopower are, thus, the result of a temperature dependent competition between both types of carrier. While holes progressively become the dominant carriers below 130 K for $K_{1.00}P_4W_8O_{32}$, electrons are the dominant ones below 170 K for $K_{1.30}P_4W_8O_{32}$.

It should also be recalled that if the CDW instability opens up a Peierls gap at the Fermi surface, partial nesting is responsible for the existence of small pockets of carriers left over by the gap opening below the Peierls temperature. The anomalies in the thermopower are then related to the presence of such pockets.

The magnetoresistance found in the CDW state agrees with such a model. One should note that it depends on the angle between the magnetic field and the (a, b) plane, following roughly a cosine law. This behaviour is consistent with quasi-cylindrical Fermi surface pockets with axes perpendicular to the (a, b) plane. This establishes that the quasi-two-dimensional character is strong also in the CDW state. Similar results have been previously found in the molybdenum bronzes and oxides and in the $(PO_2)_4(WO_3)_{2m}$ series [1, 2].

In summary, all these experimental results establish that $K_xP_4W_8O_{32}$ undergoes a Peierls transition with Peierls temperature depending on the K content, therefore on the conduction band filling.

It is not clear at the moment why the sodium-based analogous compound $Na_xP_4W_8O_{32}$ does not show similar anomalies. Further work is necessary to understand this difference in behaviour. One should note that possible cation ordering in the hexagonal tunnels could play a role for the onset of CDW instabilities.

However, since the conduction band filling can be changed in the series $K_xP_4W_8O_{32}$, we believe that a new route has been found to deepen the understanding of electronic instabilities in low-dimensional conductors.

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References

- [1] Schlenker C, Dumas J, Greenblatt M and Van Smaalen S 1996 *Physics and Chemistry of Low-Dimensional Inorganic Conductors (NATO ASI Series 354)* (New York: Plenum)
- [2] Schlenker C (ed) 1989 *Low-dimensional Electronic Properties of Molybdenum Bronzes and Oxides* vol 11 (Deventer: Kluwer)
- [3] Hess C, Schlenker C, Dumas J, Greenblatt M and Teweldemedhin Z S 1996 *Phys. Rev. B* **54** 4581
- [4] Foury P and Pouget J P 1993 *Int. J. Mod. Phys. B* **7** 3973
- [5] Le Touze C, Bonfait G, Schlenker C, Dumas J, Almeida M, Greenblatt M and Teweldemedhin Z S 1995 *J. Physique I* **5** 437
- [6] Hess C, Le Touze C, Schlenker C, Dumas J, Groult D and Marcus J 1997 *Int. Conf. on Synthetic Metals (Snowbird, 1996) Synth. Met.* **86** 2419
Schlenker C, Hess C, Le Touze C and Dumas J 1996 *J. Physique I* **6** 2061
- [7] Ottolenghi A and Pouget J P 1996 *J. Physique I* **6** 1059
- [8] Girault J P, Goreaud M, Labbé Ph and Raveau B 1982 *J. Solid State Chem.* **44** 407
- [9] Wang E, Greenblatt M, Rachidi I E I, Canadell E and Whangbo M H 1989 *J. Solid State Chem* **81** 173
- [10] Teweldemedhin Z S, Ramanujachary K V and Greenblatt M 1992 *Phys. Rev. B* **46** 7897
- [11] Canadell E and Whangbo M H 1991 *Phys. Rev. B* **43** 1894
- [12] Fröhlich H 1954 *Proc. R. Soc. A* **223** 269