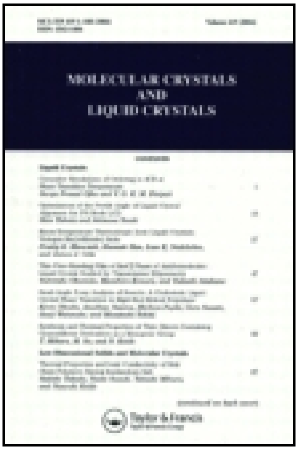

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Regular Properties and Anomalous Behaviour Of Conducting $M_{0.B}$ $[Pt(C_2O_4)_2]$ $6H_2O$, M-OP(M=Ni, Co, Zn, Mg, Mn)

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Version of record first published: 17 Oct 2011.

To cite this article: Kim Carneiro , Lars K. Hansen , Alexander Braude , Kell Mortensen , Claus S. Jacobsen , Derek Turner & Allan E. Underhill (1985): Regular Properties and Anomalous Behaviour Of Conducting $M_{0.B}$ $[Pt(C_2O_4)_2]$ $6H_2O$, M-OP(M=Ni, Co, Zn, Mg, Mn), Molecular Crystals and Liquid Crystals, 120:1, 413-420

To link to this article: http://dx.doi.org/10.1080/00268948508075831

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 413-420
0026-8941/85/1204-0413/$15.00/0

Printed in the United States of America

REGULAR PROPERTIES AND ANOMALOUS BEHAVIOUR OF CONDUCTING $M_{0.8}[Pt(C_2O_4)_2]\cdot 6H_2O$, M-OP(M=Ni,Co,Zn,Mg,Mn)

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Abstract At high temperatures M-OP's are isostructural quasi-one dimensional conductors with conductivities $\sigma = 2\text{-}200(\Omega\text{cm})^{-1}$. At low temperatures σ is activated with $\Delta = 50\text{-}60$ meV suggesting that a simple Peierls transition takes place. However, diffuse X-ray scattering, conductivity and thermopower show unexpected behaviour, which is ascribed to a second competing instability associated with cation ordering. The competition gives rise to the occurrence of metastable states. They relax towards equilibrium in a stepwise fashion reminiscent of the devil's staircase. Our results are discussed within the concepts of the Frenkel-Kontorowa model.

INTRODUCTION

Linear platinum chain conductors have been extensively studied since they were first characterized structurally by Krogman.[1] With few exceptions they are formed by stacking either tetra-cyanoplatinate $[Pt(CN)_4]$-moieties or bis-oxalato-platinate $[Pt(C_2O_4)_2]$ and in both cases the platinum d_{z^2}-orbitals provide the basis for electrical conductivity. Despite their apparent similarity the two kinds of Pt-conductors exhibit some remarkable differences. In the former kind exemplified by $K_2[Pt(CN)]_4Br_{0.3}\cdot 3.2H_2O$, KCP(Br), the Pt-chains behave as an excellent model for the Peierls instability in a quasi-one-dimensional conductor; and different compounds with different in-chain Pt-Pt separation $d_{||}$ exhibit qualitatively similar, but quantitatively different behaviour.[2,3]

In contrast hereto, conducting bis-oxalatoplatinates demonstrate a great diversity in behaviour, most notably revealed by structural investigations.[4-7]

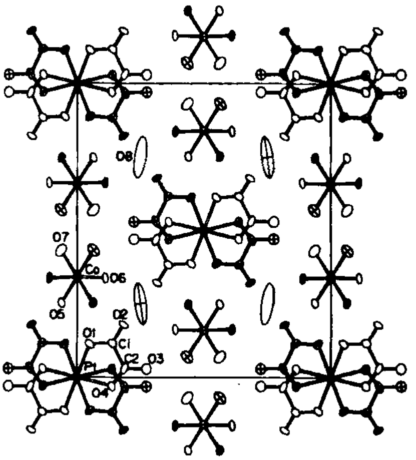

FIGURE 1 Crystallographic structure of Co-OP, viewed along the conducting $\vec{c}$ direction. $[Pt(C_2O_4)_2]$-ions stacks form the linear conductor and the $(M\text{-}6H_2O)^{++}$-cations are situated in columns, two for each Pt-chain.

We have studied the isostructural series of cation deficient bis-oxalatoplatinates of the type $M_{0.8}[Pt(C_2O_4)_2]\cdot 6H_2O$, M-OP, where the divalent cation is M = Ni,Co,Zn,Mg or Mn. Their common structure, stable at high temperatures, is shown in Figure 1.[4] Compared to KCP(Br) the following crystallographic features should be noted: Firstly, the variation in $d_{||}$ is very small suggesting that the Peierls instability should give rise to quantitatively similar behaviour amongst M-OP's. Secondly, the cations present as $(M\cdot 6H_2O)^{++}$ are situated in columns. They may therefore order as the temperature is lowered. At high temperatures they are in disorder with a site occupancy of approximately 0.41 corresponding to half the M^{++}-concentration per formula unit. The complex nature of the ordering of cations within the incommensurate crystallographic lattice of Pt-atoms appears to be the major reason for the observed diversity in behaviour of M-OP's.

The electronic band filling is determined by the stoichiometry of the cations which partially oxidise the platinum. However, it is most accurately determined by diffuse X-ray scattering which reflects the $2k_F$-Peierls distortion of the Pt-atoms. Such investigations give band fillings in the range $0.83 \le k_F d_{||}/\pi \le 0.85$.[4]

Optical reflectance studies show a Drude like behaviour[8,9] and suggest that the d_{z^2}-orbital overlap gives rise to a conduction band of a wide band width similar to that observed in KCP(Br).[2,10]

TRANSPORT PROPERTIES

Earlier comparative studies of Co-OP and Mg-OP showed that they have very different transport properties both regarding their conductivity[4] and thermopower[11] a fact which was related to the different symmetries of their superlattice X-ray reflections.[7] We have extended these studies with measurements on Ni-OP, ZnOP and

Mn-OP and they behave either like Co-OP or like Mg-OP.[9] Hence M-OP's may be divided into two classes according to their distinctly different transport properties: Class A consisting of Ni-OP, Co-OP and Zn-OP and Class B consisting of Mg-OP and Mn-OP.

Conductivity

The temperature dependent conductivity $\sigma(T)$ for the M-OP's is shown in figure 2. At room temperature σ varies from an average value of 2 $\Omega^{-1}cm^{-1}$ for Mg-OP to 200 $\Omega^{-1}cm^{-1}$ for Ni-OP and show little temperature dependence. This suggests metallic conductivity which may be analyzed in terms of a Drude model:

$$\sigma = ne^2\tau/|m^*| \qquad (1)$$
$$= \varepsilon_0\omega_p^2\tau$$

In (1) n and m^* are the carrier density and mass respectively and τ the scattering time. ω_p is the plasma frequency which from the abovementioned reflectance studies is $3.7\cdot10^{15}$ s^{-1} corresponding to $\omega_p/(2\pi c) = 19.600$ cm^{-1} in all the M-OP's, and very similar to that of KCP. The low and cation dependent conductivity in M-OP's suggest that the cations play an important role in determining the scattering time τ.

At low temperatures all M-OP's show activated conductivity with an activation energy Δ between 50 and 60 meV. The small variation amongst the compounds is understandable from the Peierls instability as mentioned above.

What separates the two classes of M-OP's in their conductivity $\sigma(T)$ is the way in which they transform from the high temperature metal to the low temperature semiconductor. Ni-OP, Co-OP and Zn-OP (class A) show a dramatic decrease in σ indicative of a very well defined Peierls transition, whereas Mg-OP and Mn-OP (class B) show a minute increase in σ which cannot be interpreted as a Peierls transition. The transition temperatures are typically close to room temperature.

Thermopower

The temperature dependent thermopower S(T) for the M-OP's is shown in figure 3. In the metallic region S falls between 5 and 8 μV/K with a slope $dS/dT \approx 40$ nV/K^2. This shows that hole-like carriers dominate the metallic transport as opposed to electron-like in KCP(Br) and their effective mass is determined both from ω_p and $S(T)$ to be $m^*/m \approx -0.2$.

In the semiconducting region the thermopower approximately follows a linear variation vs. 1/T according to the relation:[12]

$$S(T) = -\frac{B}{e}\,\mu^*[\Delta/(k_BT) + (\tau'(\varepsilon)\varepsilon/\tau(\varepsilon) + 3/2)] \quad , \qquad (2)$$

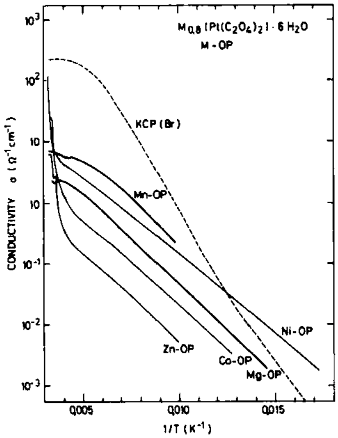

FIGURE 2 Electrical conductivity of M-OP's compared to KCP(Br).

where μ^* is determined by the relative mobilities (or masses) of electrons and holes. A common feature is the change in sign of S which cannot be understood from the simple Peierls instability. There is a significant difference between the A and B classes both regarding μ^* which is smaller for class B as well as the term with $\tau'(\varepsilon)$ which is due to the energy dependence of the scattering time. However, the significant curvature in S(T) vs. 1/T makes it difficult to analyse the thermopower quantitatively.

Like the conductivity, the thermopower varies much more dramatically around the transition temperatures for class A compounds than for class B. The peculiar features of S(T) in Mg-OP and Mn-OP probably reflects a complicated way of reaching a semiconducting state with an apparent gap Δ without passing through a regular Peierls transition.

STRUCTURAL PROPERTIES

In order to explain the two kinds of transport behaviour in M-OP's we have investigated in detail the structural evolution with temperature in the M-OP's by means of X-ray diffraction.[9] From this we are able to characterize the two classes A and B as follows: A common high temperature metallic phase I. A phase II in which cations are ordered, but differently in A and B compounds. A phase III which may be conceived as the charge density ground state according to the Peierls instability; only A-compounds are found in phase III.

Phase I: The One-Dimensional Metal

At high temperatures all M-OP's are found in the crystal structure shown in figure 1. Diffuse scattering at wavevectors with components $2k_F$ along $\vec{c}$ show the existence of a Peierls instability in the one-dimensional metal formed by the Pt-chains. In contrast to KCP(Br) the electronic structure deviates significantly from free

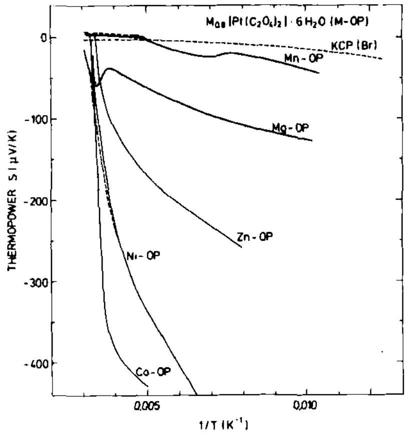

FIGURE 3 Thermopower of M-OP's compared to KCP(Br)

electron-like, since $S > 0$. This indicates a stronger electron-lattice potential as one might expect from the more bulky ligands in M-OP.

Phase II: Cation Ordering

At a temperature T_1 cations order along the columns in M-OP's ($T_1 = 315$ K in NiOP and $T_1 = 284$ K in Mg-OP).[13] This ordering distorts the regular $[Pt(C_2O_4)_2]$-lattice into a complicated super structure which reflects the incommensurability between the cations and the lattice.[6] In the class A compounds the cation sublattice is commensurate with $2k_F$ along $\vec{c}$ and therefore an external field is felt by the electrons in phase AII, giving rise to semiconducting behaviour. In the BII phase the cations order incommensurately with $2k_F$ along $\vec{c}$ and therefore has little influence on transport properties.

Phase AIII: The Charge Density Wave

The lattice distortion in phase AII acts as a natural precursor for the Peierls transition which occurs at a temperature $T_2 = 301$ K in in NiOP. Both the characteristics of transition and the low temperature properties of Ni-OP, Co-OP and Zn-OP may be understood on the basis of a Peierls instability on the Pt-chains in the presence of the $2k_F$-potential from the cation-sublattice.[14] On the other hand the BII phase has a symmetry which prevents a simple Peierls transition. In consequence no second structural transition occurs in Mg-OP and Mn-OP although they gradually develop semiconducting conductivity at low temperatures.

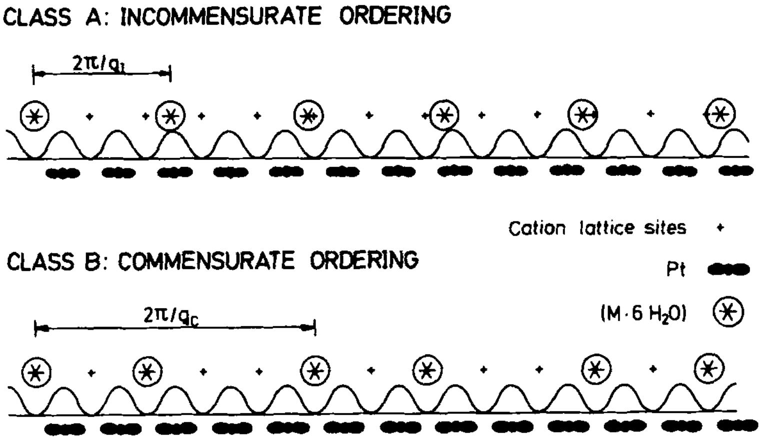

FIGURE 4 The Frenkel-Kontorowa model for the cation ordering in M.OP's. Class A behaviour corresponds to a weak potential from the Pt-lattice, class B to a strong potential.

ANOMALOUS BEHAVIOUR

The ordering of the cations in the presence of the potential from the crystallographic lattice is conveniently discussed in terms of the Frenkel-Kontorowa model,[15,16] where the energy of the $(M{\cdot}6H_2O)$-cations is expressed in terms of the Hamiltonian:

$$H = \sum_n \frac{1}{2}F(x_{n+1}-x_n-2\pi/q_I)^2 + V(1-\cos x_n \cdot 2\pi/d_{||}) \quad . \qquad (3)$$

In (3) x_n is the position of the n'th cation, the force constant F describes the coulomb repulsion between cations and V the cation-lattice interaction. q_I denotes the average period of the cations and since there are two sites for the divalent cations for each Pt-atom we get $q_I = k_F$. The situation is shown schematically in figure 4. In the case where V is weak the cations order in a sublattice which is incommensurate with the crystallographic lattice but commensurate with $2k_F$. From the structural observations this is the case in the AII phase, and the fact that we observe semiconducting behaviour in this phase is understood because of the $2k_F$ potential from the ordered cations which opens a gap in the electronic spectrum at the fermi level.

If the potential V is strong the cations will order in a sublattice, commensurate with the crystallographic lattice but incommensurate with the $2k_F$ electrons. This corresponds to the situation in class B, and consequently the BII phase does not show evidence of a gap at the fermi level at the I-BII transition. In fact the con-

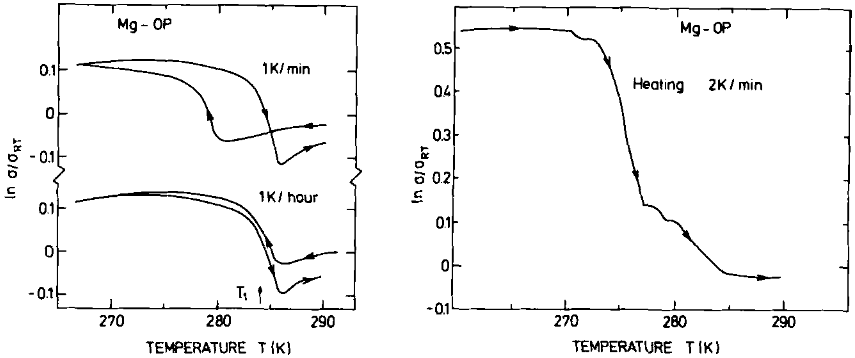

FIGURE 5 Anomalous behaviour in Mg-OP. Stepwise behaviour of the time dependent conductivity is shown to the left. Hysteresis loops and metastable (chaotic) behaviour is shown to the right, as discussed in the text.

ductivity of Mg-OP increase by up to a factor of 2.

Both theoretically studies[16] of the Frenkel-Kontorowa model and earlier experimental results[17,18] on Mg-OP and Zn-OP suggest the existence of anomalous behaviour around the phase transition at T_1. We have investigated the cation ordering transition in some detail and found evidence for both a devil's staircase and chaotic behaviour.

Stepwise Behaviour

When heated through the transition certain crystals show a stepwise behaviour of the conductivity in Mg-OP. This is shown in figure 6. We interpret this as stemming from the fact that as the commensurate cation—sublattice ground state melts into the incommensurate "subliquid" it goes through a series of transitions through different commensurate phases, which have different influences on the conduction electrons. Unfortunately, the time scale of this stepwise behaviour reminiscent of a devil's staircase is too fast for X-ray structural studies to be feasible.

Metastable States

When cycled through the transition the conductivity in Mg-OP exhibits hysteresis of a width which increases with the rate of change in temperature. An example is shown in figure 6. However, an interesting feature prevails independent of cooling rate namely the significant undershoot of the conductivity when crystals are heated through T_1 . This means that as the crystal warms up it goes through less conducting states compared to cooling, although the conductivity eventually recuperates. These metastable states together with observation of coexistence of different superstructures at low temperatures underlines the chaotic nature of the B-class of M-OP's.

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