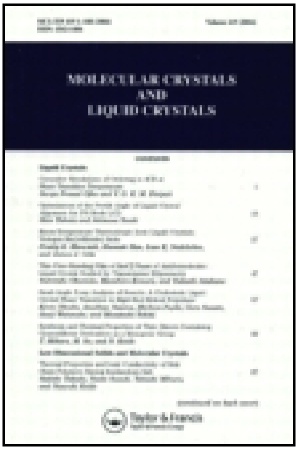

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Peierls Transitions in the Molecular Conductors

Kim Carneiro [a]

[a] Physics Laboratory I, University of Copenhagen Universitetsparken 5, DK-2100, CopenhagenØ, Denmark

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PEIERLS TRANSITIONS IN THE MOLECULAR CONDUCTORS $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$ and $Li_x[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$

KIM CARNEIRO
Physics Laboratory I, University of Copenhagen
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Abstract The Peierls instability originally proposed by R.E. Peierls as an argument against the existence of one-dimensional conductors, has played a paramount role in our understanding of low dimensional solids. Nevertheless very few compounds exhibit a simple Peierls transition from a metal at high temperatures to a charge density wave semiconductor at low temperatures. Two complementary examples are KCP and $Li_xPt(mnt)$. KCP is a wide band ($W_{||} \approx 5eV$) very one dimensional conductor, whereas $Li_xPt(mnt)$ is a narrow band ($W_{||} \simeq 0.4eV$) rather two dimensional conductor. Their physical behaviour is presented and discussed.

INTRODUCTION

Molecular electrical conductors have widened the horizons of solid state and condensed matter physics in several ways. Firstly they tend to form low dimensional strucrures, often one-dimensional, where planar molecules stack on top of each other so that high conductivity is achieved in the stacking direction. In consequence they exhibit properties that reflect the particular physical behaviour of one-dimensional systems which on the one hand is governed by simplicity compared to three dimensional systems, and on the other hand is influenced by a complex richness of phenomena existing only in one dimension. Secondly, because of the flexibility in synthetic chemistry, molecular conductors may be manufactured with a great variation in physical parameters, e.g. their electric band width, hence providing more extreme test-cases to our concepts of solids than do their naturally occurring

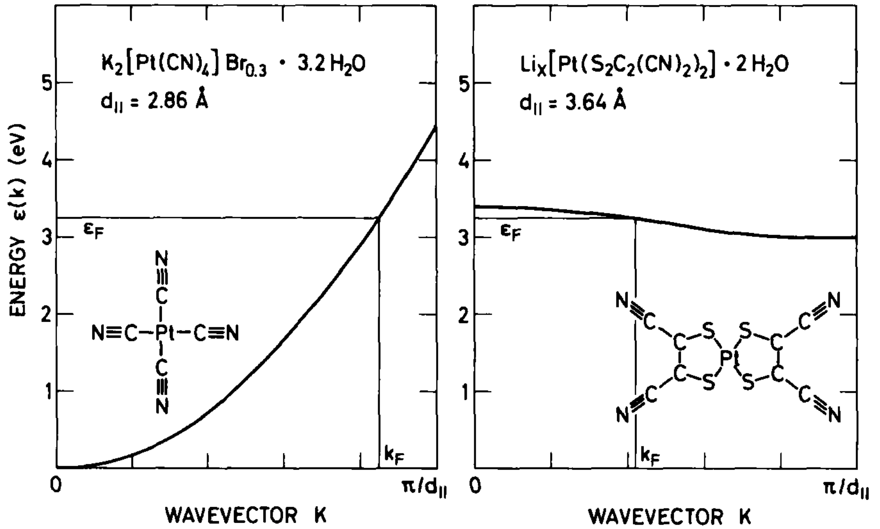

FIGURE 1 Conduction bands of KCP and $Li_xPt(mnt)$ represented by the allowed energy-states $\varepsilon(k)$, and the fermilevels (k_F, ε_F). The "conducting molecules" are also shown.

counterparts, the elemental metals. And last not least, molecular one dimensional metals were synthesized by the chemist J.W. Döbereiner[1] 121 years before the physicist R.E. Peierls[2] predicted that they could not exist!

To exemplify these points it is illuminating to look into the behaviour of the conducting salts $K_2[Pt(CN)_4]Br_{0.3} \cdot 3.2H_2O$, KCP, and $LiHx[Pt(S_2C_2(CN)_2)_2] \cdot 2H_2O$, $LiHxPt(mnt)_2$.

THE LOW DIMENSIONAL METALS KCP AND $Li_xPt(mnt)_2$

The linear Pt-chain conductor $K_2[Pt(CN)_4]Br_{0.3} \cdot 3.2H_2O$ was first prepared in 1842 in an attempt to explore the capabilities of Pt-ions to exist in a multiplicity of valence states.[3] As a result "mixed valence" salts occurred. These are probably more appropriately thought of as non-integral valence or partially oxidized Pt-salts, which within nowadays band theory of solids explains their metallic behaviour. The empirical conduction-band structure $\varepsilon(k)$ of KCP is shown in figure 1. It originates from overlap between d_z2-wave functions of neighboring Pt-atoms within a chain and is remarkably close to a free electron band i.e. well described by $\varepsilon(k) = \hbar^2 k^2/(2m)$ where m is the electron mass. The fermi-

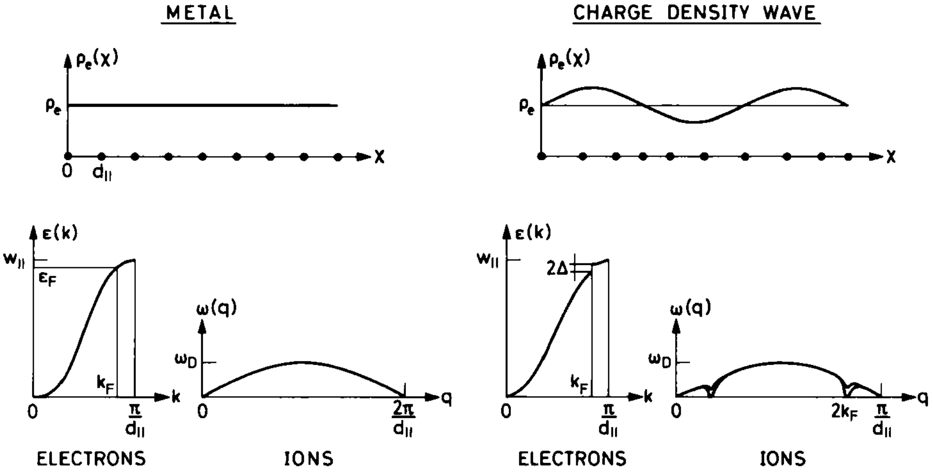

FIGURE 2 Comparison between the one-dimensional metallic state (left) and the charge density wave state (right). The upper part shows the real space electronic density ρ_e and the ionic separation; and the lower part shows the band structure $\varepsilon(k)$ together with the phonon dispersion relation $\omega(q)$. Note that $W_{||}$ (of order 1 eV) is typically much greater than ω_D (or order 10 meV).

vector k_F is determined by the density of conduction electrons ρ_e which is 2-0.3, so that $k_F=(\rho_e/2)\pi/d_{||}=0.85\ \pi/d_{||}$ where $d_{||}$ is the Pt-Pt separation. In consequence the nominal valence of Pt is 2.3. KCP has room temperature conductivity $\sigma_{||} = 200\ \Omega^{-1}\mathrm{cm}^{-1}$ and exemplifies an almost free electron one-dimensional metal.[4-5]

$Li_xPt(mnt)_2$, mnt = maleonitrildithiolate, was first prepared in 1981 in an attempt to explore the possibility of $Pt(mnt)_2$-ion to form a conducting salt. Prior to this, the ion had been used as a counterion in several charge transfer salts without itself beeing partially oxidized. Although the electronic structure is not known it seems plausible that the overlap occurs between delocalized sulfur-orbitals. The empirical structure of the conduction band of $Li_xPt(mnt)_2$ is also shown in figure 1.[7] In contrast to KCP the bandwidth $W_{||}$ is here as narrow as 0.4 eV, which makes $Li_xPt(mnt)_2$ a marginal metal since one could easily imagine that Coulomb repulsion would be of the same magnitude as $W_{||}$. However, that this is not the case is demonstrated by the fact that the measured magnetic susceptibility does not exceed the so-called Pauli-susceptibility stemming from the electronic density of states at the fermi level.[8] Also the high conductivity $\sigma_{||} = 100\ \Omega^{-1}\mathrm{cm}^{-1}$ is a good indication that $Li_xPt(mnt)_2$ is not heavily influenced by Coulomb repulsion between conduction electrons.

The density of conduction electrons ρ_e of $Li_x(Pt(mnt)_2$ has been rather difficult to derive. This is in part because the Li concentration x is hard to determine, and in part because of the presence of $(H_3O)^+$. The composite evidence is that $k_F = 0.41\ \pi/d_{||}$ as shown in figure 1 so that the correct formula should be $Li_x^+(H_3O)^+_{0.82-x}[Pt(S_2C_2(CN)_2)_2]^{-0.82}\cdot(1.12+x)H_2O$, leaving the nominal oxidation state of Pt to be 2.88.[9]

THE PEIERLS INSTABILITY

The chain structures of the two molecular metals KCP and $Li_xPt(mnt)_2$ make them susceptible to the so-called Peierls instability.[2] The arguments leading to this instability is indicated in figure 2. The metal is characterized by a uniform density of electrons and a lattice of equidistant ions - or by the electronic states $\varepsilon(k)$ and the lattice vibrations of energy $\hbar\omega(q)$. The alternative phase the charge density wave state or the Peierls semiconductor has a lattice distortion of period $2k_F$ and a concomittant electronic charge density wave. This distortion creates a gap 2Δ in the electronic spectrum at the fermi level, and this lowers the energy of the highest occupied electronic states at the expense of the elastic energy necessary to create the ionic distortion. What Peierls showed was that the charge density wave state has a total energy which is lower than that of the metal and therefore concluded that one-dimensional metals were unlikely to exist. However, given a one-dimensional metal at room temperature his arguments suggest a metal-semiconductor phase transformation at some lower temperature with an associated lattice distortion of period $2k_F$.

Only in one dimension does the above argument work, because only here will all electrons profit from the distortion of the lattice which of course must have a particular direction, namely along the chains. Similarly other instabilities may arise from considering other interactions that the electron-phonon coupling, leading to a wealth of one-dimensional ground states such as the spin density wave, the spin-Peierls

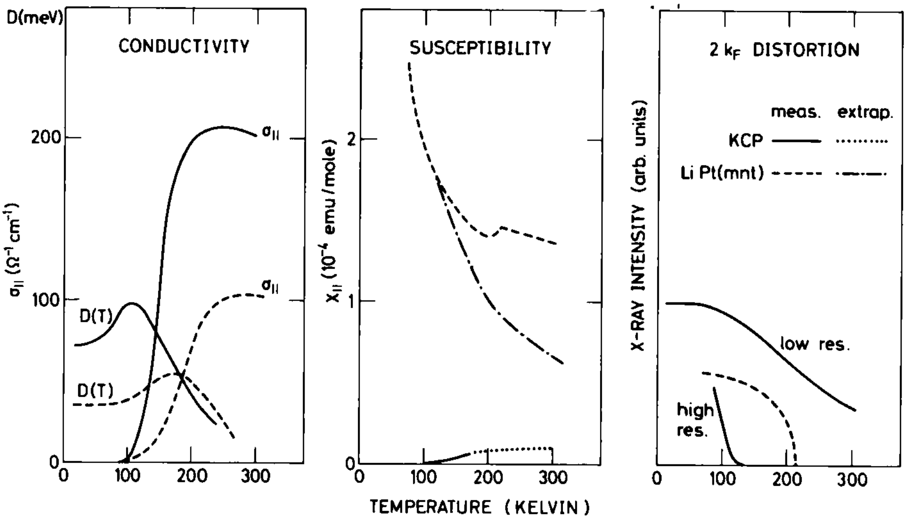

FIGURE 3 Electrical conductivity $\sigma_{||}$, magnetic susceptibility $\chi_{||}$ and measured x-ray intensities from the $2k_F$ lattice distortion as measured in KCP and $Li_xPt(mnt)_2$. The function D(T) is defined in the text.

state as well as - yet hypothetical - novel kinds of superconductivity.

LOW TEMPERATURE PROPERTIES OF KCP AND $Li_xPt(mnt)_2$

Noting the different electronic structures of KCP and $Li_xPt(mnt)_2$ and presumably also their quite different lattice vibrations, it is interesting to compare their response to the Peierls instability. The temperature dependence of some relevant properties in the two molecular metals are summarized in figure 3.

The conductivity in the chain direction $\sigma_{||}(T)$ shows a broad transition from high temperature metallic to low temperature semiconducting behaviour in both compounds.[10,7] The activation energy Δ and the transition temperature may be derived from the logarithmic derivative $D(T)=\sigma_{||}^{-1}\partial\sigma_{||}/\partial(1/T)$ yielding $\Delta = 0.07$ eV and $\Delta = 0.04$ eV as well as $T_c \simeq 100$ K and $T_c \simeq 180$ K for the two salts respectively.

The magnetic susceptibility $\chi_{||}(T)$ also reflects the Peierls transition, both in KCP[11-13] and in $Li_xPt(mnt)_2$,[8]

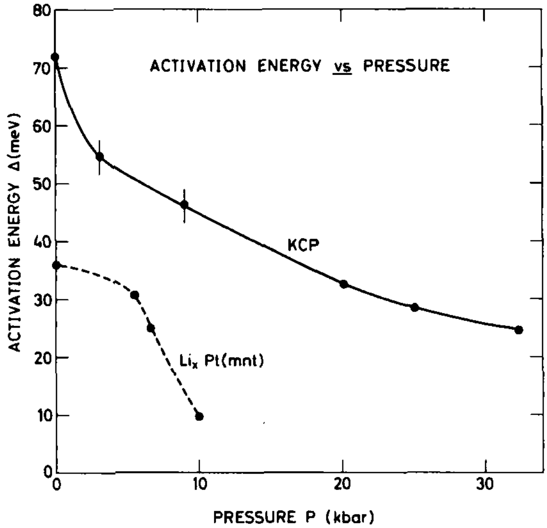

FIGURE 4 Pressure dependence of the low temperature activation energies Δ in KCP and $Li_xPt(mnt)_2$.

although χ has only been crudely estimated at high temperatures in the former case. Below the transition $\chi_{||}(T)$ is activated with the same activation energy as derived from conductivity, provided that one subtracts an apparent Curie-like susceptibility in $Li_xPt(mnt)_2$, corresponding to a few percent $s = \frac{1}{2}$ impurities per molecule. It is also noteworthy that the transition seems well-defined in this compound as judged from the kink in $\chi_{||}(T)$ at $T_c = 213$ K . The fact that the susceptibility goes from Pauli-like at high temperatures to activated at low temperatures with the same activation energies in $\chi_{||}(T)$ and $\sigma_{||}(T)$ is a characteristic feature of the Peierls instability in the absence of significant Coulomb repulsions.

The third fingerprint of the Peierls instability is the occurrance of x-ray or neutron superlattice reflections owing to the $2k_F$-lattice distortion. In the case of $Li_xPt(mnt)_2$ the x-ray intensity vanishes at $T_c = 213$ K with little diffuse scattering above this temperature[14] in nice accordance with the susceptibility results. However, in KCP the situation is more complicated. Figure 3 shows two results, one being a neutron elastic scattering result where the resolution was poorer than what corresponds to the natural width of the diffraction profile along the chain direction,[15] whereas the other, high resolution results, originates from a recent synchrotron experiment where the profile was well resolved.[16]

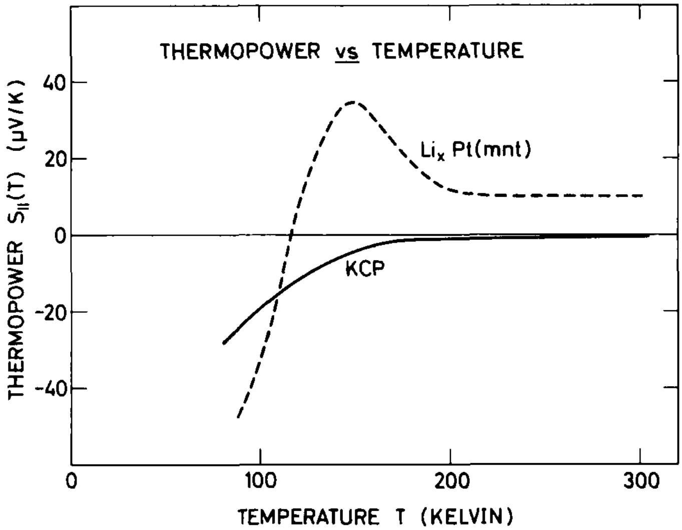

FIGURE 5 Thermoelectric power $S_{||}(T)$ in KCP and $Li_xPt(mnt)_2$.

The latter experiment shows a clear indication of a phase transition in KCP at T_c = 117 K.

Neglecting the resolution effects of the x-ray scattering in KCP and the excess Curie-like magnetic susceptibility in $Li_xPt(mnt)_2$ one may conclude that the two molecular conductors show the Peierls instability in a very similar way despite their very different characteristics regarding $\varepsilon(k)$ and $\omega(q)$. In the case of KCP the results are perhaps not so astonishing since the wide conduction band ensures the simple metallic behaviour which was the starting point for Peierls' argument. But in the case of $Li_xPt(mnt)_2$ it is truly astonishing that correlation effects seem to play such a small role, given the very narrow band width.

DIMENSIONALITY AND PRESSURE EFFECTS

One striking difference between KCP and $Li_xPt(mnt)_2$ is demonstrated by the counter intuitive results: Whereas the gap Δ is higher in the former salt T_c is higher in the latter case. This feature is related to the fact that we are dealing with quasi-one-dimensional compounds of varying anisotropy and is explained as follows. In a strictly one-dimensional system a phase transition cannot take place at finite temperatures, and therefore the charge density wave state would be achieved only at T=0 . Considering weak interactions between chains the transition temperature becomes finite and increases until the system is too three-dimensional for the Peierls instability to lead to a phase transition. Hence the low T_c in KCP suggests that it is a very one-dimensional conductor in agreement with other observations, whereas $Li_xPt(mnt)_2$ is rather three-dimensional.

By applying pressure to anisotropic compounds one in general increase their dimensionality. This is nicely demonstrated in figure 4, where the pressure dependence of the activation energy Δ is shown. Although it decreases with increasing pressure in both cases the effect in KCP[17] is far less pronounced than in $Li_xPt(mnt)_2$.[9] When it is further considered that T_c increases with pressure in KCP one naturally concludes that this salt is so one-dimensional that increasing the interchain coupling has the effect of increasing the critical temperature. On the other hand in $Li_xPt(mnt)_2$ both Δ and T_c vanish in similar ways. This indicates that pressure drives this compound too three-dimensional so that it does not undergo a Peierls transition at high enough pressure.

COMPLICATING FEATURES OR NEW HORIZONS?

Having demonstrated that the two molecular metals KCP and $Li_xPt(mnt)_2$ are good test cases for one of the unique features of low dimensional conductors namely the Peierls instability one may naturally ask whether they are likely to teach us more. In fact they are.

In KCP the new results from synchrotron radiation gives novel insight into an old problem. It has long been known that long range order was not achieved below the transition temperature,[15] at least perpendicular to the chains. We now know that the same is true for the correlation length along the chains, and hence in the literal sense there is no phase transition in KCP. It therefore remains an intriguing task of the future to resolve the detailed behaviour of the Peierls instability in KCP.

Also $Li_xPt(mnt)_2$[2] has its unexplained features. Above the low temperature susceptibility was mentioned, and in figure 5 is shown a similarly astonishing temperature behvaiour of the thermopower $S_{||}(T)$.[7] In KCP, $S_{||}(T)$ varies as expected in a system undergoing a Peierls transition;[18] but the change in sign in $Li_xPt(mnt)_2$ indicates defect states in the semiconducting gap. However, an attempt to characterize these defects from their influence on both $\sigma_{||}$, $\chi_{||}$ and $S_{||}$ leads to the conclusion that the impurity states do not have usual spin-charge relations, suggestive of solitary excitations. So also this compound is likely to open new horizons in the future.

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