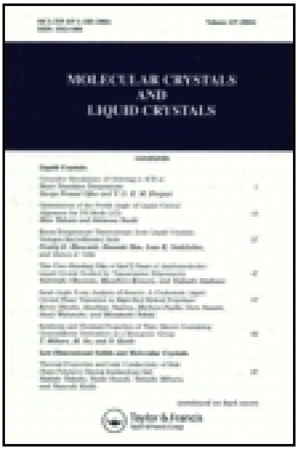

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Physics of Conducting Platinum Chain Compounds

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PHYSICS OF CONDUCTING PLATINUM CHAIN COMPOUNDS

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Partially oxidized tetracyanoplatinate compounds generally behave as excellent model compounds for the Peierls instability. By varying the chemical constituents, the physical parameters are changed systematically. These are the interchain Pt-separation $d_{||}$, the fermivector k_F, the electron-phonon coupling constant λ and the interchain coupling constant η. The variations of λ are quantitatively described from first principles, whereas k_F and η are explained by simple models. Results derived from conductivity and diffuse X-rays are independently confirmed by neutron scattering.

INTRODUCTION

Although conducting platinum chain compounds have been known for about 150 years, it was not until the early seventies that they were widely recognized as interesting examples of one dimensional conductors[1]. The prototype is the well studied compound $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$, abbreviated KCP or KCP(Br). It is a partially oxidized tetracyanoplatinate which may be thought of as derived from the divalent unoxidized salt $K_2[Pt(CN)]_4 \cdot 3H_2O$ by inclusion of Br^- ions in the lattice. The degree of partial oxidation DPO is 0.3 as the nominal valence of the Pt-ion in KCP(Br) is 2.30. Upon oxidation the room temperature conductivity is raised from $5 \cdot 10^{-6}$ $(\Omega \cdot cm)^{-1}$ to 200 $(\Omega\, cm)^{-1}$.

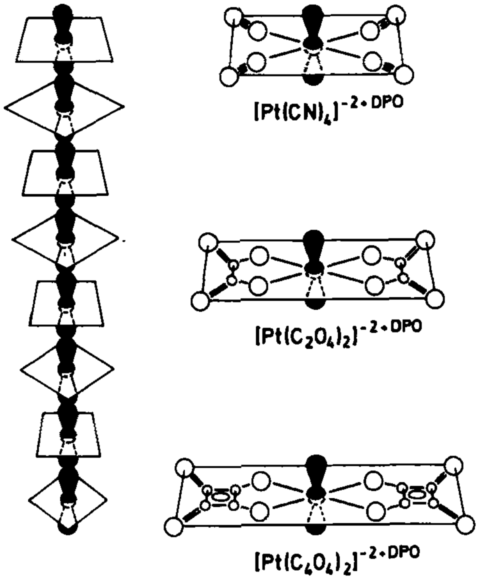

FIGURE 1 Perspective view of the partially oxidized platinum chain. Ligands are:
a) tetracyano- (20 compounds prepared)
b) bisoxalato- (40 compounds prepared)
c) bissquarato-(1 compound prepared)

The columnar structure formed by the square-planar $[Pt(CN)]^{-2+DPO}$ species is displayed in Figure 1. Most often the squares are turned 45° as indicated, but compounds have been prepared with eclipsed ligands. Figure 1 also shows the two other types of ligands which may be partially oxidized namely the bisoxalatoplatinate $[Pt(C_2O_4)_2]^{-2+DPO}$ and the bissquaratoplatinate $[Pt(C_4O_4)_2]^{-2+DPO}$.

In this paper we describe the physical behaviour of 13 partially oxidized tetra-cyano-platinate salts listed in Table I. It will be shown that they behave as excellent model compounds for theories of the Peierls instability in quasi-one-dimensional conductors.

It is an astonishing fact that the physical behaviour of 10 of the compounds is entirely determined by one parameter: The intrachain Pt-Pt separation $d_{\parallel}$. *A priori* one might not at all expect this to be the case since chemically and structurally the compounds are quite different. However the roles of commensurability, crystal symmetry, disorder etc. appear only to be of minor importance

Table 1 Partially Oxidized Tetracyanoplatinates[a]

Compound	Abbreviation	Space Group
$Rb_2[Pt(CN)_4](FHF)_{0.40}$	$RbCP(FHF)_{0.4}$	$I4/mcm$
$Rb_2[Pt(CN)_4][H(OSO_3)_2]_{0.49} \cdot H_2O$[b]	RbCP(DSH)	$P\bar{1}$
$Cs_2[Pt(CN)_4](FHF)_{0.40}$	$CsCP(FHF)_{0.4}$	$I4/mcm$
$Cs_2[Pt(CN)_4]C\ell_{0.3}$	$CsCP(C\ell)$	$I4/mcm$
$K_2[Pt(CN)_4]C\ell_{0.3} \cdot 3\,H_2O$	$KCP(C\ell)$	$P4mm$
$Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5\,H_2O$	$CsCP(N_3)$	$P\bar{4}b2$
$K_2[Pt(CN)_4]Br_{0.3} \cdot 3\,H_2O$	KCP(Br)	$P4mm$
$Pb_{0.27}K_{1.73}[Pt(CN)_4]C\ell_{0.5} \cdot 3H_2O$[12]	$Pb/KCP(C\ell)$	$P4mm$
$Rb_2[Pt(CN)_4]C\ell_{0.3} \cdot 3\,H_2O$	$RbCP(C\ell)$	$P4mm$
$[C(NH_2)_3]_2[Pt(CN)_4]Br_{0.25} \cdot H_2O$	GCP(Br)	$I4cm$
$(NH_4)_2[Pt(CN)_4]C\ell_{0.42} \cdot 3\,H_2O$[b]	$ACP(C\ell)$	$P4mm$
$Rb_{1.75}[Pt(CN)_4] \cdot 1.5\,H_2O$	Rb(def)TCP	
$K_{1.75}[Pt(CN)_4] \cdot 1.5\,H_2O$	K(def)TCP	$P\bar{1}$

[a] From ref. 1, except when specific references are given.
[b] The incorporated $(H_3O)^+$ is not shown

as long as the basic chemical environment of the Pt-chain is the same, in particular the hydrogen bonding network. In this case, the chain of Figure 1 behaves very much like an accordion[2] that may be pulled and pushed, resulting in interesting changes of the physical parameters. Based on the concept of the Peierls instability of a free electron gas on the ionic chains, assuming hopping between chains, one may give a detailed account of experimental results such as conductivity, diffuse X-ray scattering, infrared reflectivity, Raman- and neutron scattering.

THE SYSTEMATIC BEHAVIOUR

The Degree of Partial Oxidation, DPO.

The first hint that the Pt-chain compounds behave in a systematic way was given by Williams[2] who pointed out that the variation of the Pt-DPO *vs.* $d_{\parallel}$ followed the empirical relation:

$$d_{||}(\mathrm{DPO}) = d_{||}(0) + \delta \cdot \log(\mathrm{DPO}), \tag{1}$$

which was originally derived by Pauling[3-4], based on integral valence states. In Figure 2 the DPO is shown for the compounds in Table 1, together with Pauling's results.

Figure 2 gives a solid indication that the intrachain bondlength $d_{||}$ is dominated by a metallic bond formed by the overlapping d_{z^2} orbitals of the Pt-ions, a fact which is not obvious from the complicated crystallographic structures of the salts. Since the electronic Fermi wavevector is related to the DPO in the following way

$$k_F = \pi/d_{||} \cdot (1 - \tfrac{1}{2}\,\mathrm{DPO}), \tag{2}$$

Figure 2 demonstrates that the bandfilling may be varied, as the accordion of Figure 1 is pushed and pulled. Values of $d_{||}$ and k_F are given in Table 2.

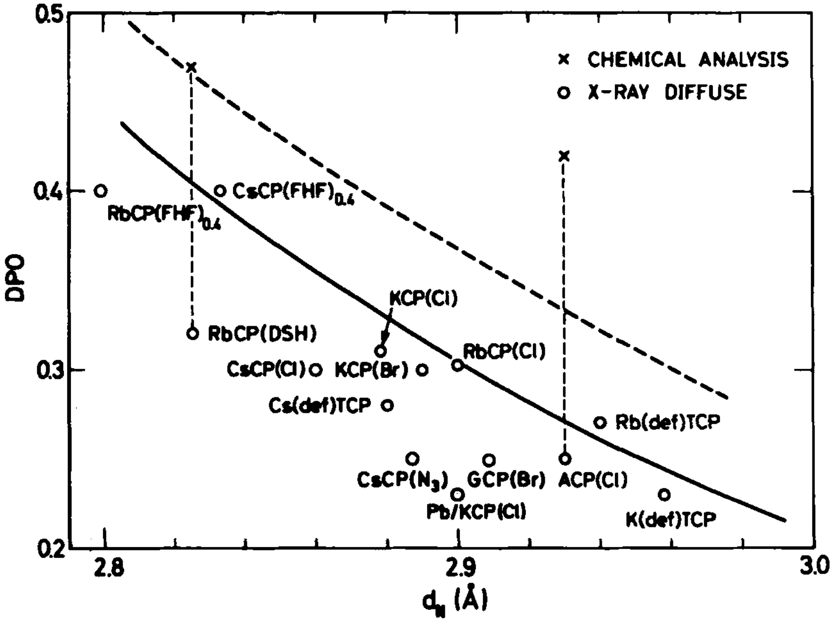

FIGURE 2 Platinum degree of partial oxidation *vs.* average Pt-Pt intrachain separation. Full line: Pauling's theory for "metallic resonance". Dashed line: Pauling's theory for non-metallic resonance.

The DPO may be determined in 3 ways from experiments. Firstly, platinum oxidation titration yields the nominal oxidation state of the ions directly; but this technique is not always applicable. Secondly, quantitative chemical analysis determines the concentration of oxidizing anions (or the cation-deficiency in the "def" salts). Assuming that only Pt is oxidized DPO follows from this concentration. However, if H_3O^+ is present in the lattice, DPO from chemical analysis gives poor agreement with titration, a problem which first arose in the analysis of ACP(Cℓ).[5] This compound should strictly speaking be written $(NH_4)_2\,(H_3O)_{0.17}\,[Pt(CN)_4]\,C\ell_{0.42}\cdot 2.83\,H_2O$. Similarly RbCP(DSH) incorporates H_3O^+ . The third and most reliable method to determine DPO is diffuse X-ray scattering at room temperature. Owing to the Peierls' instability in one dimensional conductors the lattice distorts along the Pt-chains with the period $2k_F$, giving rise to diffuse scattering lines. DPO's from this technique have always been found to be in accord with titration measurements, when the latter were possible.

The series of compounds in Table 1 allows the study of several effects on the Peierls instability separately. KCP(Br) has an incommensurate band filling as well as anion-disorder, and since both commensurability and disorder have been suggested to be important for the physical behaviour in one-dimension it is of interest that ACP(Cℓ) is commensurate, but with similar disorder. Pb/KCP(Cℓ) has cation disorder, whereas GCP is both ordered and commensurate.

In order to take into account the systematic deviation between our measured DPO's and Pauling's original theory we made a least-squares fit to get better empirical values for $d_{||}(0)$ and δ . They are 2.56 Å and 0.62 Å respectively.

Finally, it should be noted that the relation between the chemistry and $d_{||}$ is well understood for most of the compounds.[6-7] Sizes of cations and anions as well as the amount of H_2O seem to determine the Pt-Pt separations. Exceptions are GCP, Rb(def)TCP and K(def)TCP which have large $d_{||}$ despite the fact that they contain little water. However, structural analysis clearly shows that the H-bonding network in these compounds is different from the others.

The Temperature Dependent Conductivity $\sigma_{||}(T)$

The behaviour of the conductivity in the chain direction $\sigma_{||}$ also exhibits systematic behaviour[8]. At high

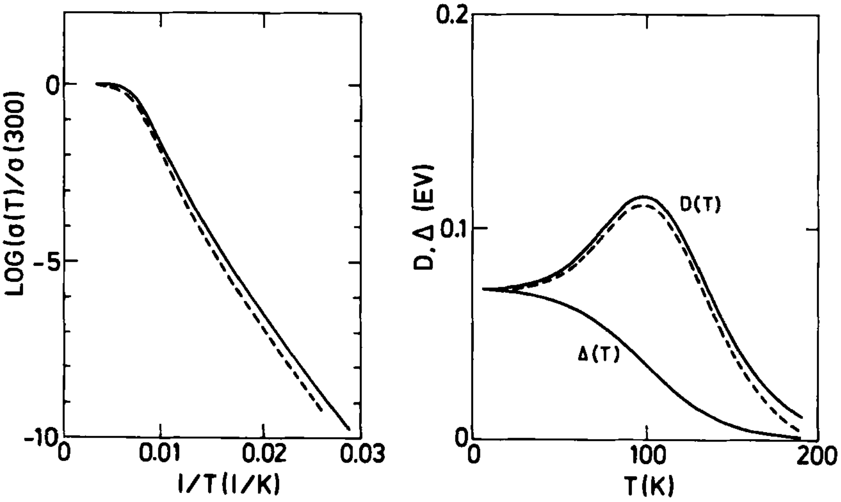

FIGURE 3 Typical conduction characteristics, with parameters chosen to fit KCP(Br). The dashed line shows the effect of including the temperature dependence of the mobility.

temperatures $\sigma_{||}$ is relatively temperature independent, often with a slight maximum at T_m around room temperature. This is associated with metallic conductivity δ_m , given in Table 2. Although σ_m is hard to determine accurately, there is a clear tendency of decreasing conductivity with increasing $d_{||}$, as one would expect.

At some lower temperature there is a transition into an activated behaviour of $\sigma_{||}(T)$, associated with the low temperature Peierls semiconducting state, characterised by a gap $\Delta(=Eg/2)$, as shown in Figure 3. It is reasonable to assume that the conduction may be described by a temperature dependent gap $\Delta(T)$ together with a power low dependence from the mobility:

$$\sigma_{||}(T) = \delta_m(T/T_m)^{-\alpha} \exp\{-\Delta(T)/k_BT\}.$$

In order to study the temperature variation of $\Delta(T)$ it is often convenient to form the function:

$$D(T) = - \partial \ln \delta_{||}(T)/\partial(1/T)$$
$$= \Delta(T) - \partial\Delta(T)/\partial T - \alpha T,$$

as plotted for $\alpha = 0$ and $\frac{1}{2}$ in Figure 3, with values relevant for KCP(Br). Although in certain organic salts a combination of a large α and a small Δ may have a profound effect on D(T),[9] in our case D(T) is clearly dominated by the variation in $\Delta(T)$.

We identify the maximum of D(T) with the actual transition temperature T_{3D} of this Peierls instability. Since T_{3D} of KCP(Br) can be independently derived from the temperature dependence of diffuse X-ray and neutron scattering, in perfect agreement with the maximum of D(T), this gives confidence to our analysis of D(T). T_{3D} is shown in Table 3.

It is interesting to analyse the shape of D(T) around T_{3D}. Within the framework of critical phenomena, $\Delta(T)$ and D(T) must vanish above the critical temperature, if $\Delta(T)$ were a true representation of the order parameter. Hence, the finite value of $\Delta(T)$ above T_{3D}, e.g. measured by the width of the peak of D(T), must be a measure of the critical fluctuations. These, in turn, are a measure of the "one-dimensionality" of the compound. In fact an inverse correlation does exist between the width of D(T) and the deduced interchain coupling.

A consequence of the fact that $\sigma_{||}(T)$ is dominated by the temperature dependence of the gap is of course that it is difficult to get insight into the electronic transport from an analysis of the conductivity.

The compounds M(def)TCP show evidence of two transitions in log $\sigma_{||}$ *vs.* 1/T plots.[10-11] This anomalous behaviour will be discussed separately.

The Free Electron Band Structure

In order to analyse further the conductivity data in terms of the Peierls instability, knowledge about the electronic band structure is necessary. Although not all of the compounds in Table 1 have been studied, enough is known to make it plausible to assume that along the chains electrons move like free carriers, with an effective mass very close to the bare mass of the electron m. Perpendicular to the chains we assume hopping which leads to a tight binding band; but the details of the perpendicular band do not matter as long as the interchain coupling $\eta = W_{\perp}/W_{||}$ is

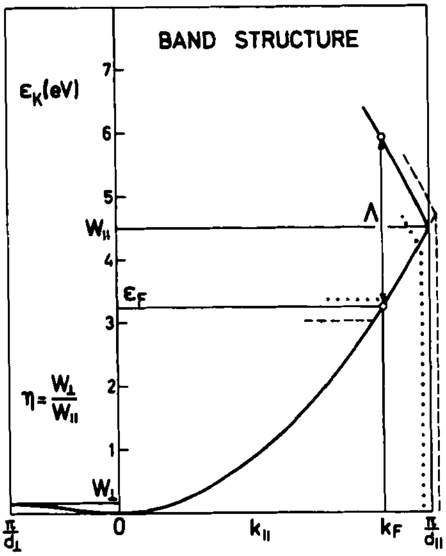

FIGURE 4 Electronic band structure ε_k. Full line is for KCP(Br). Dashed and dotted lines indicate outer extremes for the series.

small. The assumed band structure is shown in Figure 4.

Evidence for the free electron band stems from three entirely different types of evidence. The most direct is probably luminescence[15], which has been seen in both KCP(Br) and K(def)TCP. The luminescence process is sketched in Figure 4. By exciting electrons from the Fermi level into the upper band, they will decay via luminescence and the energy will be

$$\Lambda = (\hbar d_{\parallel}^{*})^{2} / 2m \cdot \{1 - k_F d_{\parallel}/\pi\}, \tag{3}$$

where $d_{\parallel}^{*} = 2\pi/d_{\parallel}$. Calculated and measured values for Λ agree within a few percent.

Independently, Drude fits to the infrared reflectivity of several compounds agree with the free electron picture. Analysis of the plasma edge in the parallel reflectivity yields the plasma frequency ω_p which is related to the effective mass via:

$$\omega_p^{2} = 4\pi\, ne^{2}/m^{*}, \tag{4}$$

where n is the electron density. The derived m^* for KCP(Br) and K(def)TCP is very close to m.[16]

Finally it is worth mentioning that thermopower studies from several salts also indicate the presence of free carriers. Although difficult to interpret rigorously, metallic thermopower gives a measure of the bandwidth since it has the form:

$$S(T) \propto (k_B/e)(k_BT/\varepsilon_F). \tag{5}$$

Hence, the empirical structure of the d_{z^2} band is very close to that of free electrons. It is worth mentioning that this is unexpected from theoretical calculations. The different fermi energies from the relation:

$$\varepsilon_F = \hbar^2 k_F{}^2/2m \tag{6}$$

are given in Table 2.

The "Universal" Phonons

Like the metallic electronic structure is simple, so is the empirical unperturbed lattice dynamics $\omega_0(q_{||})$ of conducting Pt-salts. As the lattice is distorted when $q_{||} = 2k_F$ even at the highest temperatures before crystal disintegration, phonons are influenced by the so-called Kohn anomaly and $\omega_0(2k_F)$ is not directly measurable. However, neutron scattering on both sides of the Kohn anomaly on several compounds[5,17,18] suggest expression for the universal phonons for the whole series of compounds:

$$\omega_0(q_{||}) = \omega_D \sin(\tfrac{1}{2} q_{||} d_{||}), \tag{7}$$

which by interpolation may be used to deduce $\omega_0(2k_F)$. The Debye frequency $\hbar\omega_D = 18$ meV, so that the phonon structure looks as displayed in Figure 5. Note that although k_F does not vary much in Table 2, $\omega_0(2k_F)$ spans an appreciable region, which to a large degree explains the variation in physical parameters.

Another important result from neutron scattering is that the whole $[Pt(CN)_4]$-moiety takes part in the Peierls distortion.[17] Hence the effective ionic mass in these compounds should be taken as $M = 299$ elementary masses.

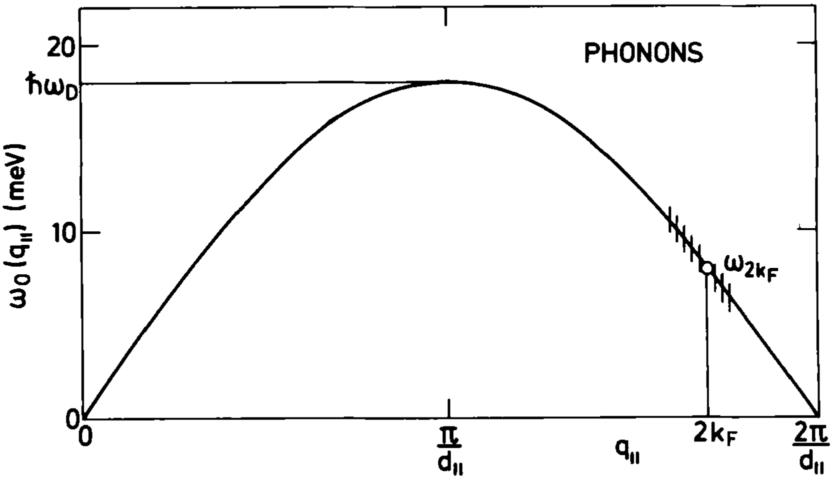

FIGURE 5 Universal phonons $\omega_0(q_{||})$. Hatched region indicates the region relevant for the series.

THE PEIERLS INSTABILITY

Based on the knowledge of the parameters k_F , Δ and T_{3D} as well as ε_F , derived as described above, one may give a detailed account of how the Peierls instability manifests itself in the platinum chain conductors.

The Electron-Phonon Coupling Constant, λ

Our picture of the Peierls instability in quasi-one-dimensional conductors is shown in Figure 6. The scale temperature T_P is set by the mean field theory[19]:

$$T_P = 4.52 \frac{1 - k_F d_{||}/\pi}{1 + k_F d_{||}/\pi} \varepsilon_F e^{-1/\lambda} , \qquad (8)$$

where λ is the dimensionless electron-phonon coupling constant. However, as no phase transition can take place when $T > 0$ in one dimension, it is via a finite interchain coupling that a transition takes place at finite

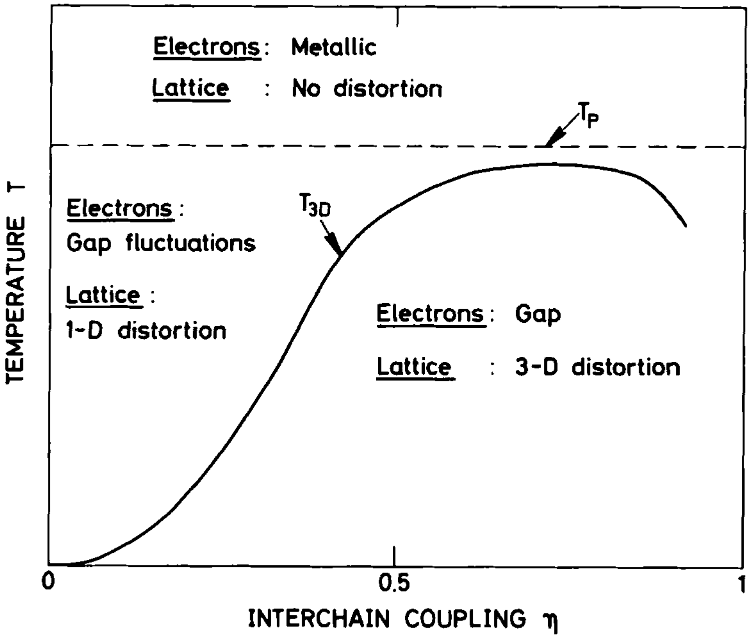

FIGURE 6 Phase diagram for the Peierls instability.

temperatures. When this coupling is small nothing drastic happens at T_P, and this temperature is therefore impossible to derive directly from experiments. However, since T_P and Δ are related via the BCS-relation (i.e. $\Delta = 1.76 \cdot k_B T_P$) knowledge about Δ yields T_P, as shown in Table 2.

Although the mean field theory predicts metallic behaviour above T_P, fluctuations which depress the phase transition temperature also show up at temperatures above T_P. This explains why the lattice distortion with period $2k_F$ is always seen by X-rays at room temperature even in compounds with low T_P's as well as the fact that resistive fluctuations show up well above T_P.

When T_P is derived from Δ, an experimental value for the basic physical parameter λ may be obtained from (8). Figure 6 and Table 2 show λ for all the compounds.

Assuming the band structure to be free electron like, we have calculated λ following the same procedure as adopted in the tight binding approximation for TTF-TCNQ.[20] We express λ in terms of the true electron-phonon coupling g, the density of states $N(\varepsilon_F)$, and the bare phonon

Table 2 One Dimensional Parameters[a]

Compound	$d_{\parallel}$[b]	δ_m[b]	k_F[b]	Δ[b]	ε_F[c]	T_P[c]	λ[c]
Units	Å	$(\Omega\mathrm{cm})^{-1}$	$\pi/d_{\parallel}$	meV	eV	K	
Pt	2.775	$9.4 \cdot 10^4$	-	-	-	-	
$\mathrm{RbCP(FHF)_{0.4}}$	2.800	$2 \cdot 10^3$	0.80	~18	3.07	118	0.20
RbCP(DSH)[14]	2.826	$4 \cdot 10^2$	0.85	43	3.40	283	0.25
$\mathrm{CsCP(FHF)_{0.4}}$	2.833	$2 \cdot 10^3$	0.80	27	3.00	178	0.22
CsCP(Cℓ)	2.859	$2 \cdot 10^2$	0.85	30	3.32	198	0.23
KCP(Cℓ)	2.874	$2 \cdot 10^2$	0.84	70	3.21	461	0.29
$\mathrm{CsCP(N_3)}$[13]	2.877	$1.5 \cdot 10^2$	0.875	41	3.48	270	0.26
KCP(Br)	2.888	$2 \cdot 10^2$	0.85	72	3.25	474	0.30
Pb/KCP(Cℓ)[12]	2.899	10^2	0.885	27	3.50	178	0.29
RbCP(Cℓ)	2.900	10	0.845	75	3.20	494	0.30
GCP(Br)	2.910	11	0.875	45	3.40	296	0.27
ACP(Cℓ)	2.920	0.4	0.875	125	3.37	824	0.38
Rb(def)TCP[d]	2.940	0.3	0.875	60	3.33	395	0.27
	("	1	"	?	"	?	?)
K(def)TCP[d]	2.963	0.1	0.875	55	3.09	363	0.29
	("	10^2	0.875	106	"	699	0.36)

[a] Values from ref.1, when no specific references are given.

[b] Measured directly. [d] Deduced from experiments (see text).

[c] Values in parentheses stem from the alternative interpretation (see text).

frequency $\omega_0(2k_F)$, all of which is known from above:

$$\lambda = g^2 \, N(\varepsilon_F)/\omega_0(2k_F)$$

$$= \frac{1}{8} \, \frac{\varepsilon_F}{\hbar\omega_D} \, \frac{\hbar d_{\parallel}^{*\,2}}{2M\omega_D} \, \frac{1}{\sin^2(k_F d_{\parallel})} \, .$$

This <u>theoretical</u> expression for λ is shown in Figure 7 in satisfactory agreement with the experimental values. In

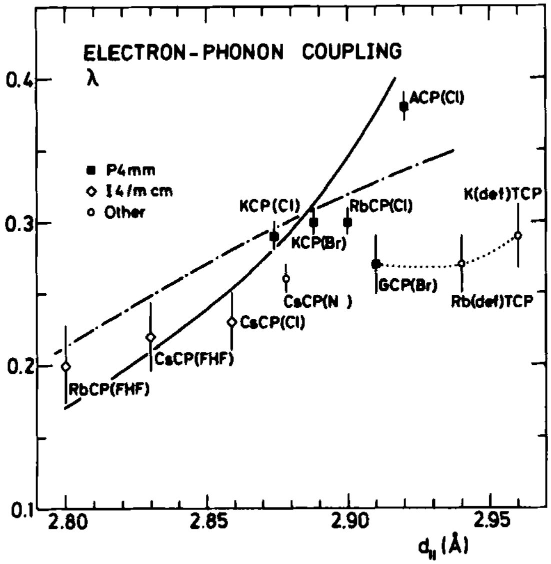

FIGURE 7 Dimensionless electron-phonon coupling constant λ. Full line is the theoretical results, with contribution from $\omega_0(2k_F)$ indicated (dash-dotted). Dotted line combines the three anomalous compounds.

order to demonstrate the two contributions to λ, one from the electronic structure (i.e. $g^2 N(\varepsilon_F)$) and the other from $\omega_0(2k_F)$, the latter is shown separately. In this case λ has been adjusted to the value of KCP(Br).

Note that the present analysis allows derivation of the one dimensional parameters without making use of any specific assumptions about interchain coupling.

The Interchain Coupling Constant, η

Assuming that the three dimensional nature of both phonons and electrons in real quasi-one-dimensional conductors may be parameterised into a transverse electronic bandwidth $W_\perp = \eta W_{\parallel}$, Horowitz et al. have given an expression for the actual transition temperature T_{3D}:[21]

$$T_{3D}/T_P = \exp\{-2.5/\eta \cdot (k_B T_P/\varepsilon_F)\}. \qquad (9)$$

Since T_{3D} is found as the peak in D(T), η may be derived

Table 3 Three Dimensional Parameters[a]

Compound	T_{3D}(K)	η^b	$d_\perp/d_{\|\|}$	$\sigma_{\|\|}/\sigma_\perp$	η^c
RbCP(FHF)$_{0.4}$	80	0.021	3.20		
RbCP(DSH)[14]	$\lesssim$80	0.014	3.18		
CsCP(FHF)$_{0.4}$	80	0.016	3.26		
CsCP(Cℓ)	90	0.016	3.26		
KCP(Cℓ)	95	0.020			
CsCP(N_3)[13]	110	0.019	3.22		
KCP(Br)	100	0.020	3.43	10^4	0.003
Pb/KCP(Cℓ)[12]	~85	0.015			
RbCP(Cℓ)	110	0.022	3.50		
GCP(Br)	100	0.015	3.80		
ACP(Cℓ)	195	0.036	3.43	$1.5\cdot10^2$	0.008
Rb(def)TCP[d]	50	0.012			
	(?	?			)
K(def)TCP[d]	50	0.012	3.20	>60	<0.04
	(308	0.059		"	")

[a] From ref.1, when no specific references are given.
[b] Based on (9). [c] Based on (10).
[d] Values in parentheses stem from the alternative interpretation (see text).

from $\sigma_{||}(T)$, once the one-dimensional parameters of Table 2 are given. This experimental value for η is shown in Table 3 and in Figure 8. Strictly, (9) is here used outside its range of validity, for some of the compounds, but this is not believed to be serious.

As no theory has produced a theoretical η, its variation from compound to compound can only be said to be reasonable. *A priori* one would expect the transverse transfer integral $\frac{1}{4}W_\perp$ to decrease with increasing interchain distance $d_\perp$, and therefore with $d_{||}$ since $d_\perp/d_{||}$ does not vary much over the series. This trend is demonstrated for short $d_{||}$'s, but at larger $d_{||}$'s the inclusion of larger ions, and in particular hydrogen bonds perpendicular to the chains, have the effect of increasing η.

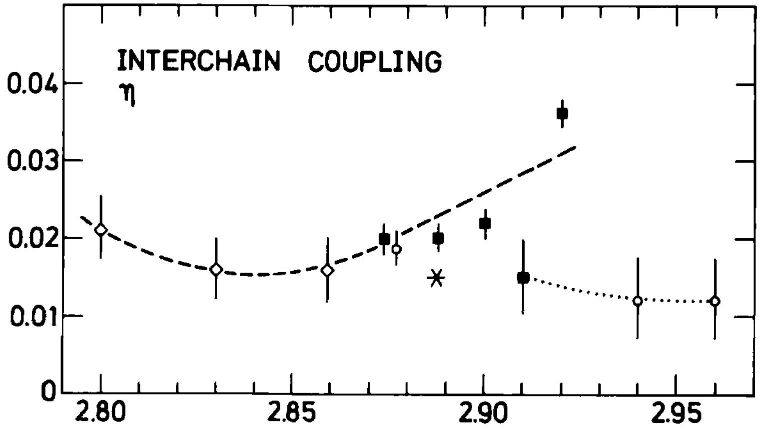

FIGURE 8 Electronic interchain coupling η. Dashed line indicates expected behaviour, and dotted line shows atypical behaviour. * shows the independent result of neutron scattering for KCP(Br).

In the case of KCP(Br) η may be derived independently from the temperature variation of the transverse correlation length $\xi_\perp(T)$, as measured by neutron scattering. The theory leading to (9) also gives the following expression to determine η:[21]

$$\xi_\perp(T) = d_\perp \frac{\eta}{2\pi} \frac{\varepsilon_F}{k_B T} \left(\ln \frac{T}{T_{3D}} \right)^{\frac{1}{2}} . \tag{10}$$

The fit between theory and experiments[22] is shown in Figure 9, with $\eta = 0.15$ in reasonable agreement with our analysis of $\sigma_{||}(T)$.

Having deduced plausible and consistent values for η, it is interesting to look at the results of conductivity anisotropy measurements $\sigma_{||}/\sigma_\perp$. This ratio is related to η as follows if electrons are transported by hopping:[22]

$$\sigma_\perp/\sigma_{||} = \eta^2 (d_\perp/d_{||})^2 . \tag{11}$$

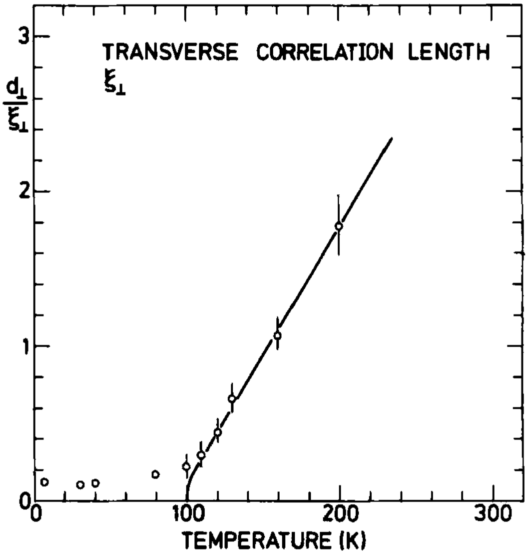

FIGURE 9 Transverse correlation length $\xi_\perp(T)$. Full line represents the theory when $\eta = 0.015$.

The results of such an analysis are shown in Table 2. The poor agreement between the two different ways of obtaining values for the interchain coupling, both regarding the magnitude and trend is probably due to inaccuracies in (11). Not only does the band structure suggest that hopping does not occur along the chains, but also it seems questionable to identify the hopping distances $d_\perp$ and $d_{||}$ with unit cell lengths. Together with the fact that large anisotropies are exceedingly difficult to measure, it is not astonishing that (11) gives rather unreliable results. This should be kept in mind when the more rigourous analysis cannot be performed and only $\sigma_{||}/\sigma_\perp$ is available to get an estimate of η .

Atypical Behaviour

Figures 7 and 8 show that GCP, Rb(def)TCP and K(def)TCP have atypical parameters λ and η , according to our analysis. K(def)TCP is known to obey the systematic behaviour described above, as regards DPO *vs.* $d_{||}$, ε_k and $\omega_0(q_{||})$ and yet the conductivity indicates two transition temperatures. Rb(def)TCP also shows two transitions, but the upper one shows strong hysteresis. The question naturally arises of how to identify appropriately the Peierls transition temperature T_{3D} .

In our analysis[11] we have identified the lower transition as T_{3D}. This makes the two M(def)TCP's look similar with respect to the Peierls instability. As with GCP the two salts have an atypical hydrogen bonding network in which the few H_2O's bind both along and perpendicular to the chains. The low H_2O - content explains the low η , and it is an intriguing possibility that H-bonds along the chain give rise to a low λ , owing to a high $\omega_0(2k_F)$ of the protons. Raman scattering data may be compared between K(def)TCP and KCP with the result that T_{3D} is lower in K(def)TCP. Altogether this compound may be consistently analysed as a Peierls system with low λ and η .

In this case the high temperature transition is identified as a so-called non-Peierls transition, which frequently occurs in the oxalates and possibly also in RbCP(DSH). Non-Peierls instabilities are found both as mean field like as well as first order transitions.

Alternatively, Epstein et al.[10,16] have identified the mean field transition at 308K as T_{3D} . This is a possible interpretation. Carrying our analysis out using $\Delta = 106$ meV and $T_{3D} = 308$ K , we obtain the picture of K(def)TCP as a compound with high values for λ and η , given in Tables 2 and 3. However η is not large enough to be theoretically consistent with the observation of mean field behaviour.

This alternative interpretation places Rb(def)TCP and K(def)TCP as two distinctly different Peierls systems, and it neglects entirely the lower transition.

CONCLUSIONS

Based on a simple description of the Peierls instability in an ionic lattice with free electrons, we are able to account quantitatively for the physical properties of conducting tetracyanoplatinates. The systematic behaviour of the electron-phonon coupling λ and the interchain coupling η is understood from the chemistry of the compounds. The exceptions, GCP and the two M(def)TCP's are also explained consistently, but alternative interpretations are not excluded.

From the consistency of our interpretation it follows that neither disorder nor commensurability seem to have any great effects on the Peierls instability as presented here.

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