Relation between Physical Properties and Chemical Composition of Conducting Pt-Chain Compounds: A New Example, $Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5H_2O$

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The electrical conductivity of the quasi-one-dimensional conductor $Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5H_2O$, $CsCP(N_3)$, has been studied. Values for the intrachain band filling and electron-phonon coupling as well as for the electronic interchain coupling are compared to those of the well studied tetracyanoplatinate complexes. The physical properties of $CsCP(N_3)$ are explained from its structure and characteristic hydrogen bonding.

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Highly anisotropic and quasi one-dimensional conductors have been of great interest to both chemists and physicists in recent years. One major class of these compounds is the anion-deficient partially oxidized tetracyanplatinate (POTCP) complexes[1] as exemplified by the prototype $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$, KCP(Br). In an attempt to understand further some of the extraordinary properties exhibited by these compounds it is essential to synthesize and study new materials in which well defined changes have been made. One such modification is the incorporation of a new anion into the crystal lattice,[1,2] and it is therefore of interest that recently the preparation and crystal structure of a POTCP azide salt, $Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5H_2O$, was reported.[3,4] We here present the electrical conduction properties of this salt and place it in the context of other POTCP salts, which have recently been shown to behave as excellent model systems.[2]

Previously studied anion-deficient POTCP salts have belonged to one of two types of basic structure. One type, of space group *P*4*mm*, is formed by the hydrated anion-deficient POTCP's, e.g., KCP(Br), in which metal cations occupy the upper part of the unit cell and are located in between the planes containing the $Pt(CN)_4$ units. The water molecules are located in the bottom part of the unit cell and form a hydrogen-bonded network cross-linking adjacent $Pt(CN)_4$ chains. The halide anion occupies a position in the center of the unit cell but because of the nonstoichiometry of these compounds this position is only partially occupied by the halide anion and in some cases, at least in the absence of halide, this position is occupied by H_2O. The anhydrous anion-deficient materials, e.g., $Rb_2[Pt(CN)_4]FHF_{0.4}$, RbCP(FHF), crystallize in the space group *I*4/*mcm*, where the cations are located in the planes containing the TCP anions. The small linear FHF anions partially occupy sites, but there is no H_2O available for occupation of the vacant sites.

$Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5H_2O$, $CsCP(N_3)$ hereafter, crystallizes in the tetragonal space group *P*42 with cell dimensions $a = 13.089$ Å and $c = 5.754$ Å.[4] The crystal structure is shown in Fig. 1, and consists of linear chains of platinum atoms with intrachain Pt-Pt separation $d_{\parallel} = c/2 = 2.877$ Å and interchain separation $d_{\perp} = 9.255$ Å.[1] This structure is intermediate between the two types of structures described above. The Cs ions are located in the plane containing the TCP anions and there are no separate H_2O sites to provide a hydrogen-bonded network between the chains. However, water molecules are present in vacant azide sites. With our current understanding of the interplay between the chemistry and physics of the POTCP's we therefore expect $CsCP(N_3)$ to undergo a Peierls transition and to have physical parameters intermediate between the anhydrous and hydrated model compounds.

Separate x-ray experiments have revealed the presence of diffuse scattering arising from a

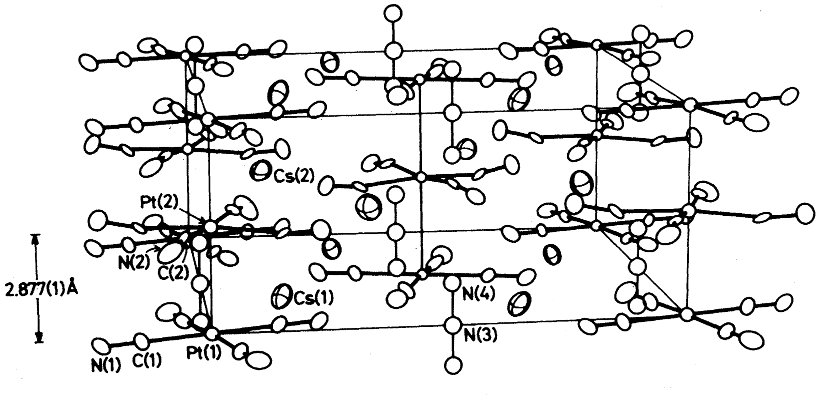

FIG. 1. Perspective view of the unit cell of $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$, $CsCP(N_3)$.

sinusoidal modulation of the platinum-atom chains due to the Peierls distortion.[5] The associated superlattice is commensurate with the c axis and has a repeat distance of $7.9(3)d_{\parallel}$. This corresponds to a Fermi vector $k_F = 0.875\times\pi/d_{\parallel}$ implying that the Fermi energy is $\epsilon_F = 3.36$ eV on the assumption of the usual free-electron behavior,[2] and to a platinum degree of partial oxidation DPO $=2(1-k_F d_{\parallel}/\pi)=0.25$ which agrees with the chemical stoichiometry. Four-probe dc variable-temperature conductivity measurements were carried out on ten crystals of $CsCP(N_3)$ as previously described.[6] The crystals exhibited a room-temperature conductivity in the platinum-atom chain direction, $\sigma_{\parallel}$, under ambient humidity (40%–60%), in the range 40–270 $\Omega^{-1}\,cm^{-1}$ with an average value of $\sim 150\ \Omega^{-1}\,cm^{-1}$. Higher values were observed in the presence of mother liquor from the preparation of the complex. It is thought that in these cases the high humidity may produce proton charge carriers on the surface of the crystal by the reaction $[Pt(CN)_4]+2H_2O \rightleftharpoons [Pt(CN)_4(OH)_2]^{2-}+2H^+$ and that these additional charge carriers may lead to an enhanced conductivity. Alternatively these conditions of high humidity may change the degree of hydration of the crystals. In the case of KCP(Br) it has been shown that $\sigma_{\parallel}$ is strongly dependent on the degree of hydration.[7]

The variation of $\sigma_{\parallel}$ with temperature for $CsCP(N_3)$ is shown in Fig. 2. Above 200 K the conductivity is almost independent of temperature with a maximum at ~ 305 K. Below 200 K the conductivity falls rapidly if the temperature is lowered and by 30 K it is about 10^{-6} of the value observed at room temperature. Indeed both the room-temperature conductivity of $CsCP(N_3)$ and its temperature variation are intermediate between those of the hydrated POTCP's, as shown in Fig. 2 by $\sigma_{\parallel}(T)$ for KCP(Br), $(NH_4)_2(H_3O)_{0.17}$-$[Pt(CN)_4]Cl_{0.42}\cdot 3H_2O$ or ACP(Cl), and anhydrous RbCP(FHF).[8,9]

In order to analyze $\sigma_{\parallel}(T)$ of $CsCP(N_3)$ in terms of the physical parameters relevant for the Peierls transition, we show in Fig. 2 the function

$$D(T) = -\partial\{\ln\sigma_{\parallel}(T)\}/\partial\{1/T\} = \Delta(T) - T\partial\Delta(T)/\partial T, \qquad (1)$$

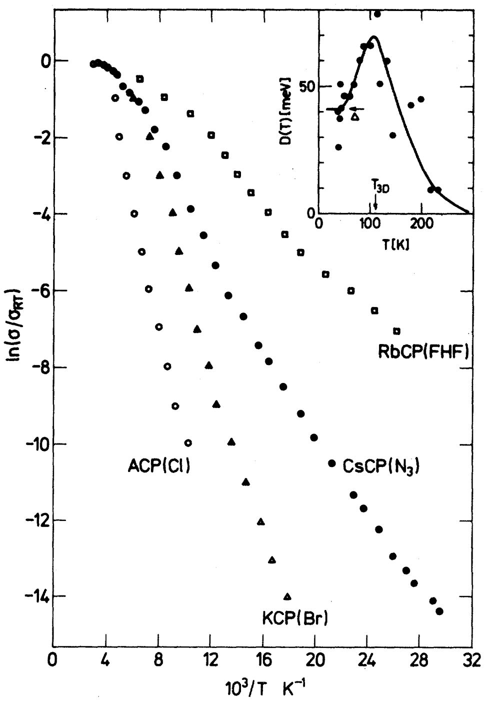

FIG. 2. Variation of $\ln(\sigma/\sigma_{RT})$ vs $1/T$ for ACP(Cl) (open circles) KCP(Br) (triangles), $CsCP(N_3)$ (closed circles), and RbCP(FHF) (open squares). Inset shows the function $D(T)$ vs T for $CsCP(N_3)$.

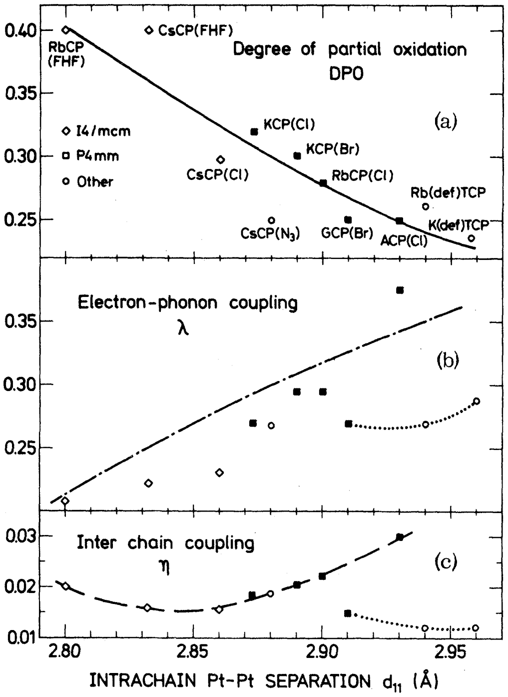

FIG. 3. Relationships between the intrachain platinum separation $d_{\parallel}$ and (a) the degree of partial oxidation DPO. Solid line shows empirical Pauling relationships. (b) The electron phonon-coupling constant λ. The dash-dotted line shows the variation of assuming a universal phonon model and the dotted line shows the anomalous behavior. (c) The interchain coupling constant η for CsCP(N_3) and ten other POTCP compounds. The dashed line shows the regular behavior and the dotted line shows the anomalous behavior.

where we have assumed activated conductivity $\sigma_{\parallel}(T) \propto \exp[\Delta(T)/T]$, with a temperature-dependent gap $\Delta(T)$. From the function $D(T)$ we get the low-temperature activation energy $E_g/2 = D(T \to 0) = \Delta = 41$ meV, which in turn gives the scale temperature $T_p = 270$ K from the relation $k_B T_p = \Delta/1.76$. At the transition temperature T_{3D}, $D(T)$ is maximal since $\Delta(T)$ is rapidly vanishing in the high-temperature metallic phase. For CsCP(N_3) we find $T_{3D} = 110$ K.

The analysis of $\sigma_{\parallel}(T)$ together with the knowledge of k_F and ϵ_F allows us to determine the dimensionless electron-phonon coupling λ from the equation[10]

$$\Delta = \frac{1 - k_F d/\pi}{1 + k_F d/\pi} \times 8\epsilon_F e^{-1/\lambda}, \tag{2}$$

and we find $\lambda = 0.27$ for CsCP(N_3). We can also determine the interchain coupling constant η which is the ratio of the transverse to parallel electronic bandwidth. We get $\eta = 0.019$ from the equation[11]

$$\eta = \frac{2.5(k_B T_p/\epsilon_F)}{\ln(T_p/T_{3D})}. \tag{3}$$

The values for the platinum degree of partial oxidation DPO, the electron-phonon coupling λ, and the interchain coupling η for CsCP(N_3) are shown in Fig. 3 vs $d_{\parallel}$ together with those of ten other well studied POTCP compounds. It is seen that the dependence of $d_{\parallel}$ vs DPO is of the Pauling character[12]:

$$d_{\parallel} = d_0 + \delta \log \text{DPO}, \tag{4}$$

with $d_0 = 2.56$ and $\delta = 0.62$ Å determined from a least-squares fit to the data.

The monotonic increase in λ with increasing $d_{\parallel}$ obtained for the seven "regular" compounds in Fig. 3 is explained as follows. Inelastic neutron-scattering results indicate that the unperturbed phonon spectrum $\omega_0(q)$ in POTCP complexes is universal in the sense that

$$\omega_0(q) = \omega_D \sin(qd_{\parallel}/2), \tag{5}$$

with $\hbar\omega_D \approx 18$ meV for all compounds. Since $\lambda \propto [\omega_0(2k_F)]^{-1}$ the dependence of λ upon $2k_F$ [and from (4) upon $d_{\parallel}$] is easily computed by inserting different k_F values in (5). The result is shown in Fig. 3 in quantitative agreement with the independently deduced λ from (2).

The interchain coupling η increases at both small and large values of $d_{\parallel}$, and has a minimum at $d_{\parallel} \simeq 2.84$ Å. Also here CsCP(N_3) is intermediate with $\eta = 0.019$. *A priori* one would expect the transverse bandwidth to decrease with increasing $d_{\perp}$, and since the ratio $d_{\perp}/d_{\parallel}$ is fairly constant over the series, this is indeed observed in the decreasing η vs $d_{\parallel}$ for small $d_{\parallel}$'s. The increasing η at larger $d_{\parallel}$'s, opposite to the expected trend, reflects (*vide infra*) that bulky ions and in particular hydrogen-bonding species are effective both in expanding the lattice as well as in mediating electron transfer from chain to chain.[2] Hence, CsCP(N_3) shows the characteristics of a quasi-one-dimensional conductor with a Peierls instability, having basic physical parameters λ and η intermediate within the class of POTCP salts analyzed earlier.

The parameters λ and η of GCP(Br) [G = guanidinium = $C(NH_2)_3$] and M(def)TCP (M = K and Rb) fall far off the regular trends in Fig. 3. These compounds are commensurate, but since CsCP(N_3) and ACP(Cl) are also commensurate and yet behave regularly, this atypical behavior does not appear to come from commensurability. Rather it seems to be related to the particular hydrogen-bonding network which is present in the three compounds. Speculatively, one may rationalize their low λ as coming from a high ω_0 in the expression for λ, since high-frequency hydrogen motion may well couple to the electrons along the chains. As there is relatively little hydrogen bonding transverse to the chains, this explains the low η in GCP(Br), K(def)TCP, and Rb(def)TCP.

In conclusion, the new quasi one-dimensional conductor CsCP(N_3) exhibits both structural and physical properties which may be understood in the context of previously described partially oxidized tetracyanoplatinates. It also demonstrates that commensurability does not in itself give rise to unusual features in connection with the Peierls transition.

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[1] For a recent review, see, for instance, J. M. Williams, A. J. Schultz, A. E. Underhill, and K. Carneiro, in "Extended Linear Chain Compounds," edited by J. S. Miller (Plenum, New York, to be published), Vol. 1, pp. 73–118.

[2] A. E. Underhill, D. J. Wood, and K. Carneiro, Synth. Met. 1, 395–405 (1980).

[3] J. M. Williams, in *Molecular Metals*, edited by W. Hatfield (Plenum, New York, 1979), pp. 337–368.

[4] R. K. Brown, D. A. Vidusek, and J. M. Williams, Inorg. Chem. 18, 801 (1979).

[5] A. Braude, A. Lindegaard-Andersen, K. Carneiro, and A. S. Petersen, Solid State Commun. 33, 365 (1980).

[6] A. E. Underhill and D. J. Wood, Ref. 3, pp. 377–383.

[7] S. Drosdziok and M. Engbrodt, Phys. Status Solidi (b) 72, 739 (1975).

[8] K. Carneiro, A. S. Petersen, A. E. Underhill, D. J. Wood, D. M. Watkins, and G. A. Mackenzie, Phys. Rev. B 19, 6279 (1979).

[9] D. J. Wood, A. E. Underhill, A. J. Schultz, and J. M. Williams, Solid State Commun. 30, 501 (1979).

[10] J. B. Nielsen and K. Carneiro, Solid State Commun. 33, 1097–1099 (1980). The results derived in this paper are approximate, but numerical calculations show that they are accurate to a few percent, when applied to the compounds considered here.

[11] B. Horowitz, H. Gutfreund, and M. Weger, Phys. Rev. B 12, 3174 (1975).

[12] L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, 1940).

Observation of a Tamm-Type State on $Cu_{0.9}Al_{0.1}$(100) Surface: Disorder Effects and Bulk Electronic Structure of an Alloy

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The electronic structure of a $CU_{0.9}Al_{0.1}$(100) single crystal has been studied with use of an angle-resolved photoemission technique. An intrinsic Tamm-type surface state is found to exist in the disordered alloy. The linewidth of the surface state is analyzed to deduce the disorder-induced smearing of energy levels. These and other experimental results are discussed in terms of the computed band structure of the alloy on the basis of coherent-potential approximation applied to a realistic muffin-tin Hamiltonian.

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Angle-resolved photoemission spectroscopy (ARPES)[1] has proved in recent years to be an important experimental tool in clarifying the nature of bulk and surface electronic structure of perfect crystals. The application of this technique to disordered alloys has been hampered, in part, by metallurgical difficulties associated with preparing oriented single crystals of alloys with clean surfaces. For example, often during the anneal-sputter cleaning procedure, annealing

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