Thermal- and Field-induced Anomalies in the One-dimensional Conductor $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$

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Summary The temperature dependence of the electrical conductivity of $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ shows two distinct regions with the possibility of one-dimensional metallic conduction at low temperatures.

SOME recent work has shown considerable interest in the possibility of one-dimensional electrical conduction,[1,2] and several transition metal complexes have been suggested to fit this model. Studies of the temperature variation of the conductivity of $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ were reported[3,4] during the course of our investigation, but these are at variance with some of the results reported here.

The partially oxidised compound $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ belongs to a class of complexes in which $[Pt(CN)_4]^{x-}$ units are stacked above one another in the solid state to produce linear chains of metal atoms throughout the crystal structure.[5] All the Pt atoms are crystallographically identical, indicating that the structure does not contain a distribution of Pt^{2+} and Pt^{4+} ions, but that some delocalisation of the electrons must occur within the metal chains. In the unoxidised complex, $K_2Pt(CN)_43H_2O$, which has a similar structure, the intermetallic distance along these chains is 3·35 Å,[6] whereas in $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ this distance is 2·89 Å showing the presence of a greater interaction in the partly oxidised complex. It has been suggested that in the partly oxidised complex the electrons are removed from a filled band of molecular orbitals formed from overlap of the d_{z^2} orbitals on adjacent platinum atoms, and that therefore these complexes may exhibit metallic conduction in the direction of the metal chains.

The d.c. electrical conduction of small crystals (0·2 × 0·2 × 1 mm) of $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ having an analysis given previously by Gomm and Underhill[7] was measured in the direction of the c-axis by a two-probe technique using both silver paste and colloidal graphite electrodes to establish the absence of electrode effects, while a single experiment using a four-probe technique confirmed these results. Several measurements were made with an earthed guard-ring on the crystal and these indicated that surface conduction effects were negligible. The temperature dependence of the conductivity is shown in the Figure and is representative of all the crystals examined. The initial and final points agree within experimental error. During all the measurements the applied electric field was kept below 120 V cm^{-1} (usually at 10 V cm^{-1}) because above this value decomposition of the crystal could be seen to occur.

The specific conductivity along the c-axis of the crystals was in the range 4×10^{-3} to 4×10^{-4} Ω^{-1} cm^{-1} at 22 °C for some eight crystals examined, in agreement with ref. 5. Difficulties in measuring the electrode areas on such small crystals are reflected in the scatter encountered in the conductivities of different crystals. The conductivity of crystals of $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ is considerably greater than that of the unoxidised complex $K_2Pt(CN)_4xH_2O$ (5×10^{-7} Ω^{-1} cm^{-1}),[2] but the temperature dependence of this conduction shows that it is certainly not metallic in nature at high temperatures.

The Figure shows two distinct regions of conduction in these crystals with a transition between 200 and 220 K.

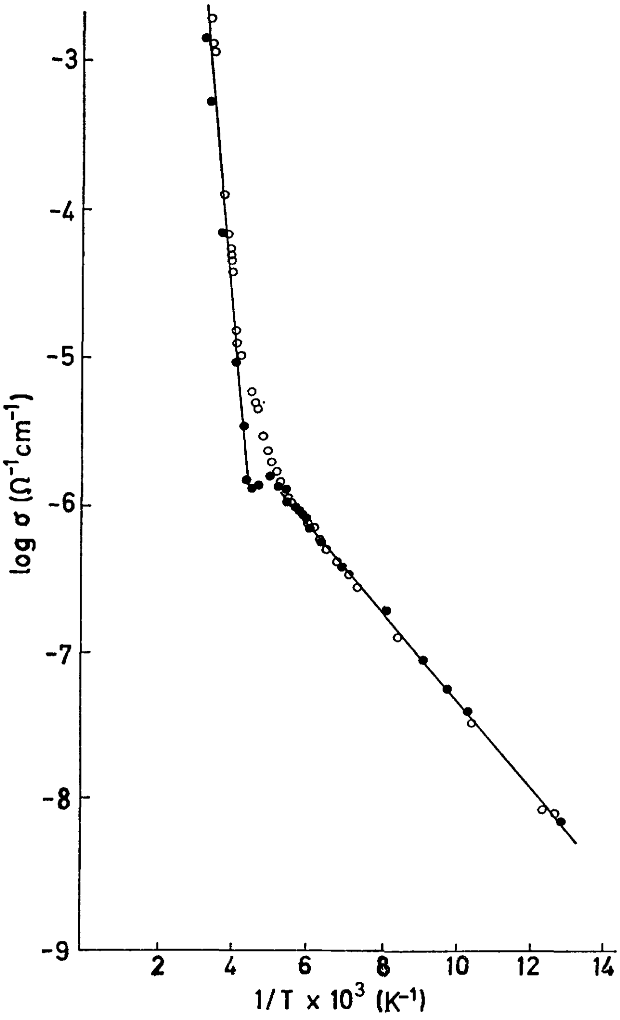

FIGURE. *Variation of conductivity* σ *with temperature for single crystals of* $K_2Pt(CN)_4Br_{0\cdot32}\cdot3H_2O$ (● *:cooling,* ○ *: heating*)

This change in the conductivity could be brought about by a phase change in the crystal, but differential scanning calorimetry showed no evidence of phase change. The Arrhenius plot for the region above 220 K shows that the crystal behaves as a semiconductor with a thermal activation energy for conduction of 1·5 eV, and the conduction appears to decay on initial application of a voltage, a phenomenon described previously by Gomm and Underhill.[7,8] Below 200 K however, the activation energy falls to 0·06 eV, and no decay of the initial current is observed. The linearity of this part of the Arrhenius plot continues down to liquid helium temperatures.

In the low temperature region (<200 K) it is possible that the low thermal activation energy reflects the presence of small dislocations in a one-dimensional metallic conduction pathway within the metal–metal chain. Such dislocations must be expected in a real crystal and will have profound effects on any one-dimensional property.

At higher temperatures it could be that the conduction is enhanced by the presence of ionic conduction, leading to a large activation energy. Experiments leaving the electric field applied for 24 hours produced only a small diminution in the room temperature conductivity, but the discharge of bromine from the lattice at higher electric fields[8] indicates the possibility of such an ionic mechanism at lower fields. The high temperature region of the Arrhenius plot would thus represent the reduction in the ionic mobility with decreasing temperature until, at about 220 K, the ions are "frozen" into the lattice and unable to migrate to the electrode. Such an ionic mechanism would also account for the conduction behaviour on application of a voltage, since the ions, migrating to the electrode, set up a field in opposition to the applied field until a steady state is reached, at which point the ions migrate to the electrode at the same rate as they are discharged.

The high temperature behaviour of the conductivity given here is at variance with that published recently by Kuse and Zeller[4] and by Berenblyum *et al.*,[3] whereas the low temperature region of their studies also indicates the possibility of one-dimensional metallic conduction in this complex. However, since no analysis is given by these other workers it is difficult to assign the differences in the observed conduction behaviour. The characterization of the degree of perfection or imperfection of these crystals from a chemical and physical point of view is necessary for a full understanding of their properties.

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