STUDIES ON THE ONE-DIMENSIONAL PLATINUM ATOM CHAIN COMPOUND $Rb_3(H_3O)_{0.2}[Pt(CN)_4](O_3SO \cdot H \cdot OSO_3)_{0.5} \cdot 0.8H_2O$

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Abstract

The variation of conductivity and thermopower with temperature for $Rb_3(H_3O)_{0.2}[Pt(CN)_4](O_3SO \cdot H \cdot OSO_3)_{0.5} \cdot 0.8H_2O$ is reported. The abrupt falls in conductivity at low temperature previously reported have been carefully studied and from the non-reproducible nature of the phenomena, it is deduced that these result from cracks in the sample rather than a phase change in the material.

Introduction

Over the past fifteen years, there have been extensive studies of the structures and solid-state properties of the one-dimensional metals based on the anion-deficient tetracyanoplatinate (tcp) anion [1, 2]. The relationship between the chemically-controlled parameters, such as the platinum–platinum separation and the extent of partial oxidation, and the solid-state properties, such as conductivity and thermopower, is well understood, being based on the Peierls instability [3, 4]. Most of the partially oxidized anion-deficient tcps exhibit metal-like conductivity at room temperature, but at some lower temperature there is a smooth transition, smeared over 50 to 100 degrees, to a low temperature semiconducting state. This is in contrast to the cation-deficient tcp, $K_{1.75}[Pt(CN)_4]1.5H_2O$, and the cation-deficient bis(oxalato)platinates, in which much more abrupt changes in conductivity with temperature are observed at the metal-to-semiconductor transition [5, 6]. The title compound, $Rb_3(H_3O)_{0.2}[Pt(CN)]_4/(O_3SO \cdot H \cdot OSO_3)_{0.5} \cdot 0.8H_2O$ (RbCP(DSH)) is exceptional in that it is one of very few non cation-deficient

compounds that has been reported to show sharp falls in conductivity with temperature [7]. The availability of a computer-controlled apparatus for conductivity studies has allowed a much more detailed examination to be made of the properties of this compound than was possible previously.

The preparation and crystal structure of RbCP(DSH) have been reported previously [7, 8]. The structure (see Fig. 1) consists of square planar $[Pt(CN)_4]$ anions stacked along a. The central portion of the unit cell is occupied by the $(O_3SO.H.OSO_3)^{3-}$ anion. The sulphate ions are linked to each other in the a-axis direction by a hydrogen bonded network of water molecules. The intra-chain Pt–Pt separation is 2.826(1) Å, which is ≈ 0.05 Å shorter than that observed in $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ (KCP(Br)). The inter-chain distance along c (13.761(3) Å) is long for this class of compound, whilst that in the b direction (9.373(2) Å) is somewhat less than that found in KCP(Br).
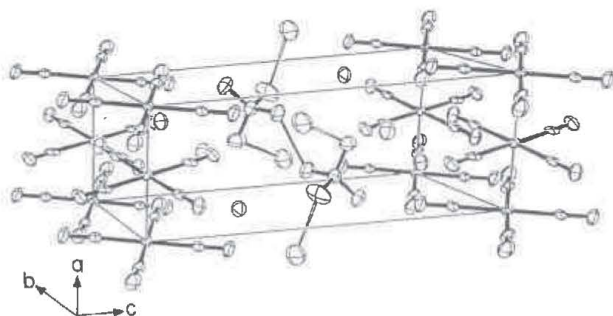

Fig. 1. A view of the triclinic unit cell of $Rb_3(H_3O)_{0.2}[Pt(CN)_4](O_3SO.H.OSO_3)_{0.5} \cdot 0.8H_2O$ with thermal ellipsoids scaled to 50% probability. Hydrogen bonding interactions are indicated by unshaded bonds. The Rb atoms are shown without any bonds drawn to them (reproduced by permission from *Phys. Scr.*, 25 (1982) 873).

The previous study of the electrical conduction properties indicated that the conductivity varied a great deal from crystal to crystal, with values as high as 2000 S cm^{-1} [7]. At some temperature below 200 K the conductivity was reported to become time dependent and fell sharply with both time and decreasing temperature. This appeared to be similar to that recently observed in $Mg_{0.82}[Pt(C_2O_4)_2] \cdot 6H_2O$ and discussed in terms of competing forces leading to chaos [9].

Experimental

Crystals of RbCP(DSH) were prepared by the published method [7]. Electrical conduction measurements were made by the four-probe d.c. technique using colloidal graphite as the contact between the crystal and the gold wire leads. The apparatus was controlled by a microcomputer as described previously [10]. Thermopower measurements were made using a conventional apparatus involving a slow alternating temperature difference of 0.2 K. The crystals were mounted on 35 μm gold wires and contacts were made using aquadag.

Results and discussion

In the present study, values of room-temperature conductivity ranging from 20 to 4800 S cm^{-1} were measured, with most values being around 100 S cm^{-1}. The value of 4800 S cm^{-1} is the largest so far reported for a compound of this type, and is a reflection of the short intra-chain platinum–platinum separation in this compound. The very wide variation from crystal to crystal observed in both this and the previous study is much greater than that found for other compounds.

Figure 2 shows the variation of conductivity with temperature for a crystal slowly cooled from room temperature down to 20 K and then slowly warmed back up to room temperature. As can be seen from the Figure, the conductivity is almost independent of temperature above 180 K. The conductivity slowly falls with decreasing temperature below 180 K and a rapid decrease in conductivity is observed below 140 K.
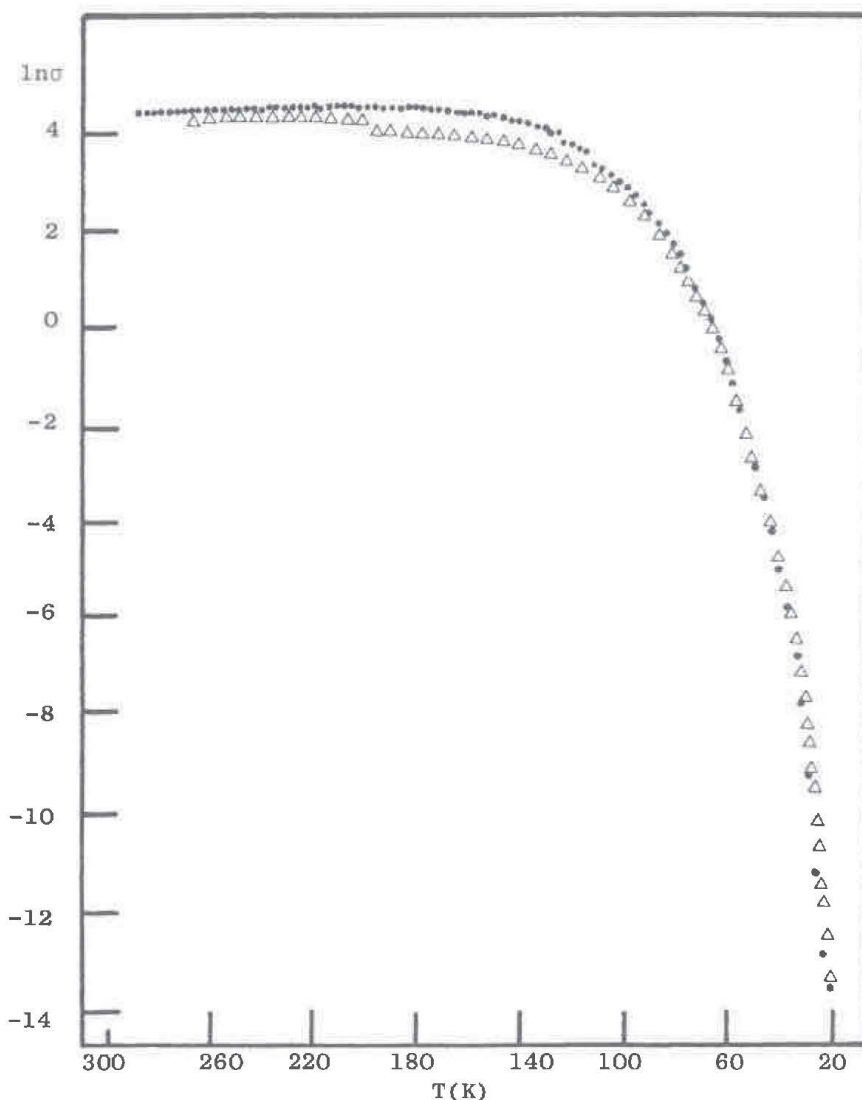

Fig. 2. Variation of ln σ with temperature cooling cycle (△); warming cycle (●).

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The previous study revealed that at some temperature below 200 K, which varied from crystal to crystal, the conductivity became time dependent and fell sharply with both time and decreasing temperature. We therefore made a special study of the region from 250 to 130 K, investigating some 20 crystals.

Figure 3 shows crystals exhibiting two types of behaviour in this region. In all these experiments, the conductivity was measured at fixed time intervals of approximately nine minutes at constant temperature. After observing the conductivity at a fixed temperature for 90 min, the temperature was lowered by 1 - 2 K and the conductivity again monitored at the new temperature for 90 min. It can be seen that two very different types of behaviour are observed. In Fig. 3(b), the crystals show the same smeared out metal-to-semiconductor transition shown in Fig. 2 and found for many anion-deficient tcps. However, the crystals in Fig. 3(a) show abrupt falls in conductivity with decreasing temperature. It can be seen that the fall in conductivity does not occur at a given temperature, but varies from crystal to
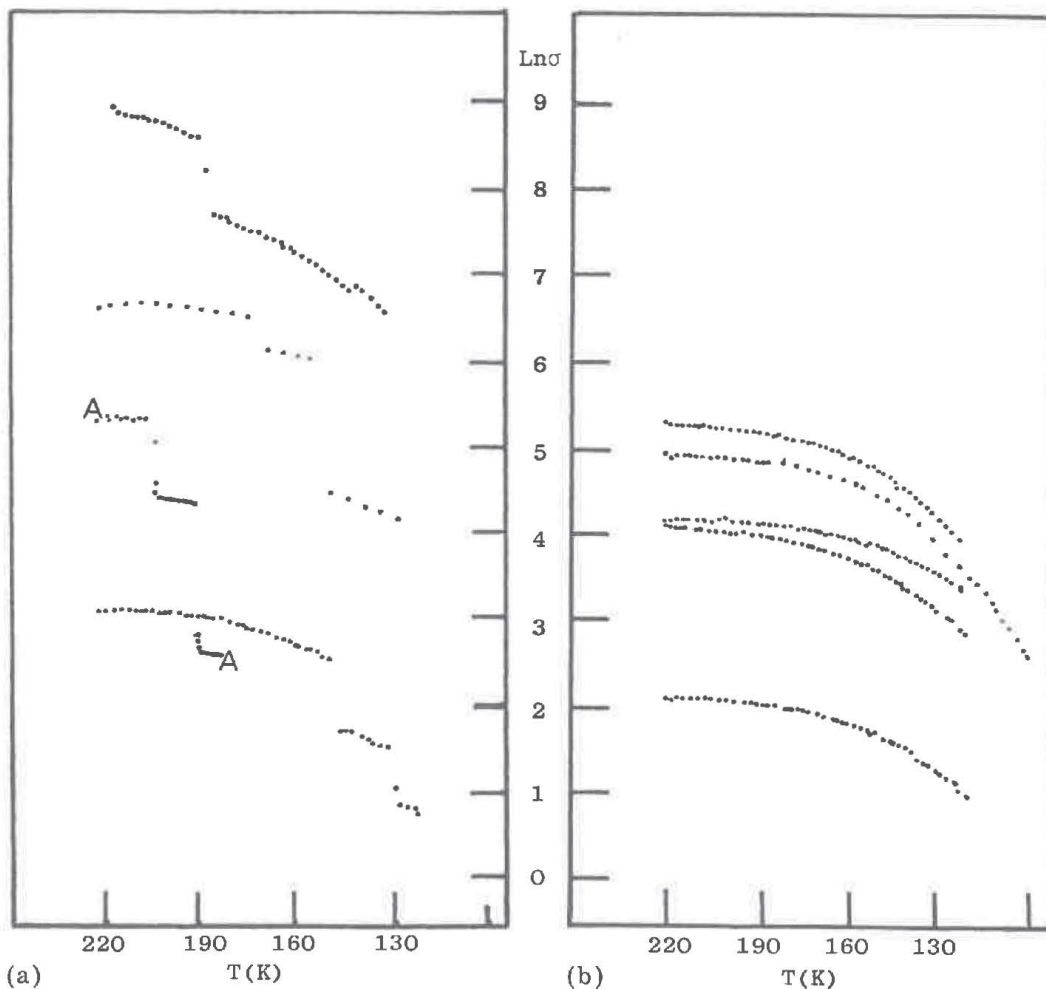

Fig. 3. Variation of ln σ with temperature for a number of crystals showing the two types of behaviour described in the text.

crystal. Indeed, crystals may show more than one abrupt fall separated by 20 - 30 degrees. As reported previously, crystals do not regain their previous room-temperature conductivity after exhibiting this type of behaviour.

In the previous study of this compound, the conductivity was reported as being time dependent during these abrupt conductivity changes. Figure 4 shows the variation of conductivity with time at the fixed temperatures of 187.9 and 187 K ($\pm$0.05 K) for sample A in Fig. 3. It can be seen that the conductivity is constant for over 60 minutes at 187.9 K and then falls by a factor of four over the next nine minutes, with another small fall over the next nine minutes. At 187 K, there is very little change of conductivity with time. This demonstrates beyond doubt that the sharp fall in conductivity is not due to some form of phase transition, since it occurs after the crystal has been at thermal equilibrium for at least 55 minutes. This is also supported by the non-reproducible nature of these changes. The results also demonstrate that the time dependency of the change is relatively small and occurs at the end of the fall in conductivity. This is quite different from that observed in $Mg_{0.8}[Pt(C_2O_4)_2] \cdot 6H_2O$ and attributed to the presence of competing interactions [9].

The thermopower of RbCP(DHS) is small and positive at room temperature in contrast to that found for KCP(Br), which was small and negative. However, the cation-deficient bis(oxalato)platinates show small positive values of thermopower at room temperature. The positive value of the thermopower suggests transport dominated by hole-like charge carriers. The variation of thermopower with temperature is shown in Fig. 5. It can be seen that the value of the thermopower decreases with decreasing temperature to
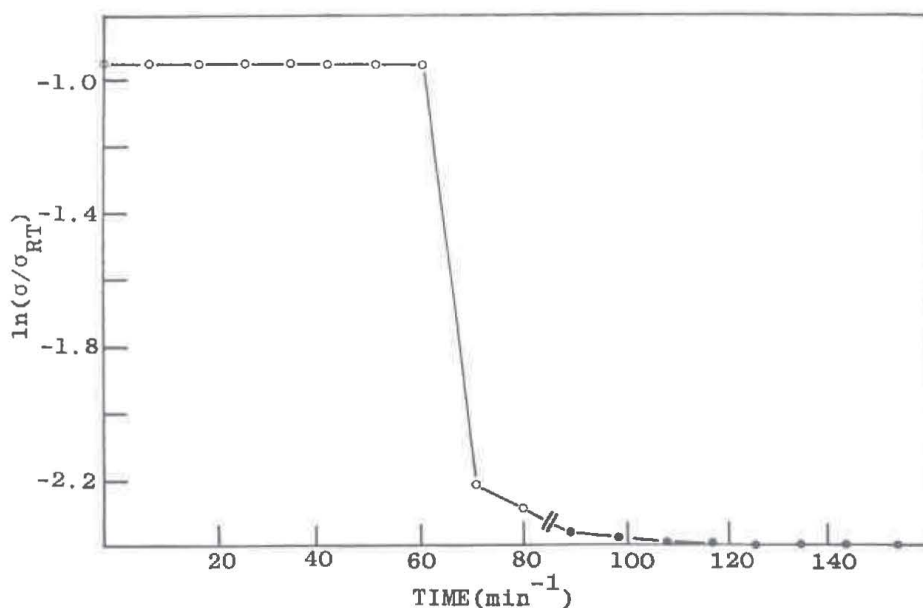

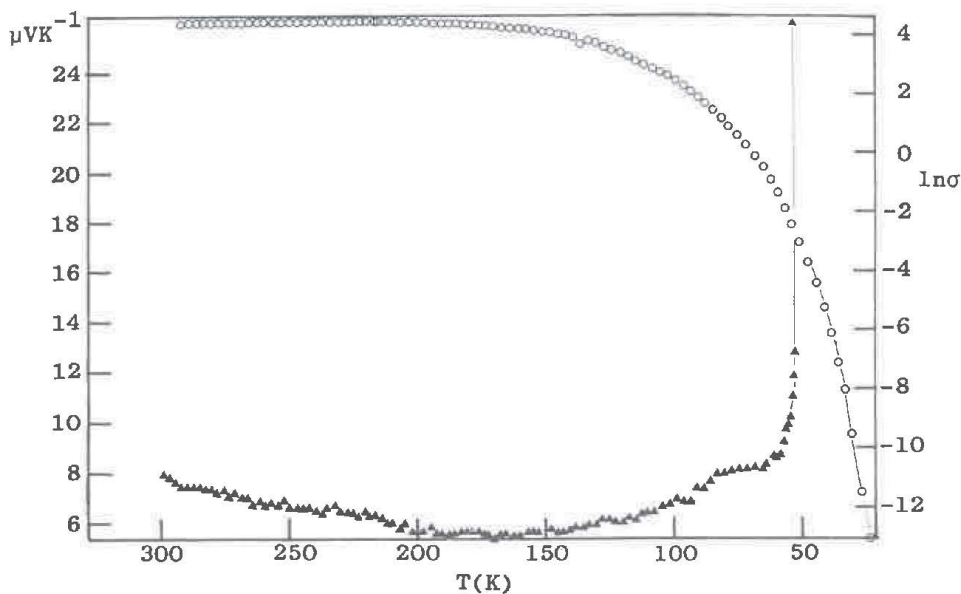Fig. 4. Variation of ln σ with time for crystal A in Fig. 3(a) at 187.9 K ($\bigcirc$) and 187.0 K ($\bullet$).

Fig. 5. Variation of thermopower (▼) with temperature. (The variation of ln σ with temperature (○) is included for comparison.)

a minimum value around 160 K. The thermopower then increases with decreasing temperature down to about 50 K, when a rapid fall is observed at lower temperatures. In many ways this reflects the conductivity results shown in Fig. 2.

Discussion

The conductivity results discussed here confirm RbCP(DSH) as exhibiting the highest conductivity yet observed for tcp salts. This is probably due to a combination of short intra-chain separation and the absence of any random potentials, since all the anion sites are filled.

There appears to be much less inter-chain interaction in RbCP(DSH) than in KCP(Br). In particular, there is only one molecule of water per $[Pt(CN)_4]$ anion, thus reducing the opportunity for intra-chain hydrogen bonding interactions contributing to the coulombic interactions. It is also significant that one of the inter-chain distances is exceptionally large at over 13 Å. The structural features that decrease intra-chain interactions compared with most other tcp compounds will weaken the mechanical properties of the crystals and make them more susceptible to fracture. The abrupt falls in conductivity observed in cooling the crystals most likely arise from the development of cracks within the crystal due to the stress imposed on the crystal from the electrical leads, which will vary with temperature due to thermal contractions. This also probably accounts for the wide variation of room-temperature conductivities observed for RbCP(DSH), since the crystals may have faults present at room temperature for the same reasons.

Acknowledgements

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