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### Superconductivity in $(\text{TMTSF})_2\text{ClO}_4$ at Zero Pressure

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SUPERCONDUCTIVITY IN  $(\text{TMTSF})_2\text{ClO}_4$  AT ZERO PRESSURE

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The organic charge transfer salt di-tetramethyl-tetraselenafulvalenium perchlorate becomes superconducting with transition temperatures from 0.9-1.4 kelvin. We compare our results to those of other groups and discuss possible reasons for the observed differences. Preliminary results are given for an alloy with the corresponding perrhenate.

SUPERCONDUCTIVITY IN  $(\text{TMTSF})_2\text{ClO}_4$

The exciting finding that the organic charge transfer salt  $(\text{TMTSF})_2\text{ClO}_4$  becomes superconducting in the absence of applied pressure<sup>1</sup> has opened new possibilities for the study of superconductivity in organic crystals.<sup>2-5</sup>

The structure and typical resistivity curves are shown in figure 1. The structure consists of columnar stacks of densely packed TMTSF-cations with large electronic overlap, whereas the  $\text{ClO}_4$  anions seem to play no role in the conduction. At room temperature the resistivity is  $1.5 \cdot 10^{-5} \Omega\text{m}$  ( $=1.5 \cdot 10^{-3} \Omega\text{cm}$ ). The resistance vs. temperature follows an approximate  $T^2$  down to a sample dependent temperature  $T_1$  between 5 and 15 K. When  $1.5 \text{ K} < T \leq T_1$ ,  $\rho(T) = \rho_0(1 + \alpha T)$  with typical values of  $\rho_0 = 0.7 \cdot 10^{-8} \Omega\text{m}$  and  $\alpha = 1 \text{ K}^{-1}$ . The superconducting transition takes place at  $T_c \approx 1.4 \text{ K}$  in our crystals. Note that the value of  $\rho_0$  is close to the

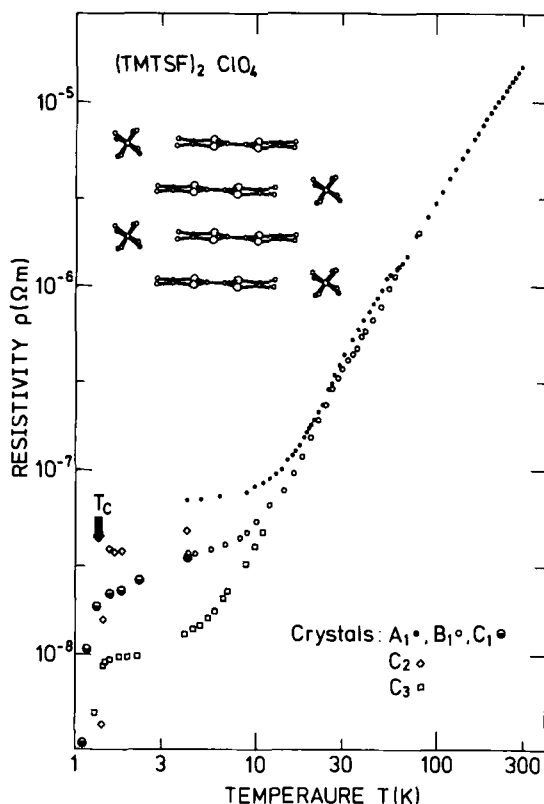


FIGURE 1  
Temperature dependence of the resistivity  $\rho(T)$  of several  $(\text{TMTSF})_2\text{ClO}_4$  crystals from different batches. The inset shows a side view of the conducting stack. The  $\text{ClO}_4$  disorder is indicated by the two orientations of the anions.

resistivity of copper at room temperature.

In figure 2 we compare our results to those obtained by others,<sup>2-5</sup> and indeed notable differences are found which seem to exceed the differences between samples found by each group. It is close at hand to ascribe the relatively large discrepancies in figure 2 to differences in synthesis and crystal growth.

#### CRYSTAL PERFECTION

One of the reasons why the properties near  $T_c$  of  $(\text{TMTSF})_2\text{ClO}_4$  are so sample dependent may stem from the fact that this compound is probably very close to the borderline between superconducting and insulating ground states. Although all investigated crystals have become superconducting some of the results in figure 2 show a definite rise in  $\rho(T)$

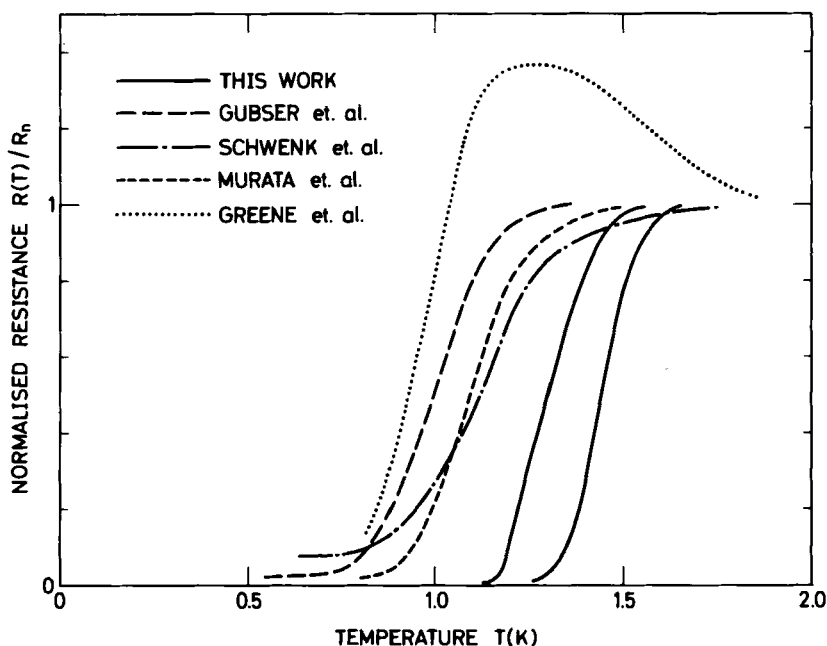


FIGURE 2 Normalized resistivity curves for  $(\text{TMTSF})_2\text{ClO}_4$  from different measurements.

just above  $T_c$ ,<sup>5</sup> reminiscent of  $(\text{TMTSF})_2\text{PF}_6$  at intermediate pressures.<sup>6</sup> At this borderline where the compound presumably exhibit both superconducting and insulating precursors slight amounts of imperfections may well distort the balance between the two instabilities.

Gubser et al.<sup>2</sup> have investigated the influence of chemical purification on  $T_c$ , and they do find that purer crystals have higher  $T_c$ 's. From their study Schwenk et al.<sup>3</sup> have argued that  $(\text{TMTSF})_2\text{X}$  crystals have a very high degree of crystal perfection, since it is possible to force domain walls through crystals without breakage.

We, on the other hand, have found evidence of substantial crystal imperfections. Figure 3 shows room temperature electron micrographs of a crystal of  $(\text{TMTSF})_2\text{ClO}_4$  after it had been cooled down below  $T_c$  once. Deep grooves are found to penetrate deeply into the crystal, and it is not astonishing if such crystal imperfections will influence  $T_c$ .

$(\text{TMTSF})_2(\text{ClO}_4)_{1-x}(\text{ReO}_4)_x$  COMPOUNDS

One way of inserting controlled and well characterized imperfections into a metal is by alloying, and indeed  $\text{ReO}_4$  seems to mix with  $\text{ClO}_4$  to give the alloy series  $(\text{TMTSF})_2(\text{ClO}_4)_{1-x}(\text{ReO}_4)_x$ . This series is potentially very interesting, since for  $x=0$  it becomes superconducting as described above, whereas for  $x=1$  it exhibits a sharp metal-insulator transition at 180 K. This latter transition is atypical as a Peierls transition because it seems related to an unusually strong lattice distortion which does not show one-dimensional precursor effects.<sup>7</sup> Below 180 K the anions order in a  $2 \times 2 \times 2$  superlattice i.e. matching the usual superlattice of the Peierls instability. This means that one should really talk about two coupled instabilities, one leading to anion ordering (this instability is three dimensional in nature) and the other leading to the Peierls transition (one-dimensional in nature). Such a coupling has previously been described for conducting Pt-chain salts.<sup>8,9</sup> In  $(\text{TMTSF})_2\text{X}$  compounds the ordering of anions is believed to be crucial to whether or not superconductivity occurs.

Figure 4 shows the resistivity result for  $x = 0.16$ , compared to  $x = 0$  and 1. At least for  $T > 0.5$  K the alloy shows no sign of superconductivity. On the other hand  $\rho(T)$  seems to approach a constant value at low temperatures i.e. no evidence for activated behaviour. Hence the anions do probably not order, but rather the mixed anion stack seems to form a strong disorder potential giving rise to a dirty metal behaviour. Studies of other alloy concentrations are in progress.

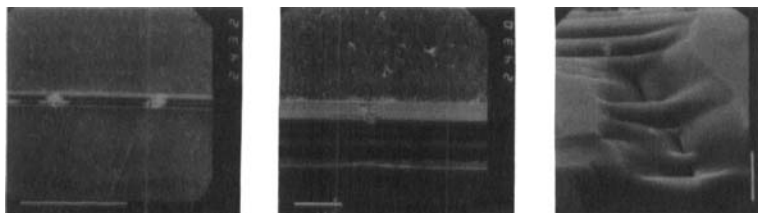


FIGURE 3 Electronmicrographs of a single crystal of  $(\text{TMTSF})_2\text{ClO}_4$  with a large imperfection. To the left is shown the crystal with the two aquadag voltage contacts (one gold lead has fallen off); the groove is barely visible. In the middle the imperfection is clearly seen even at the bottom part of the crystal. To the right a blow-up reveals deep holes in the crystal.

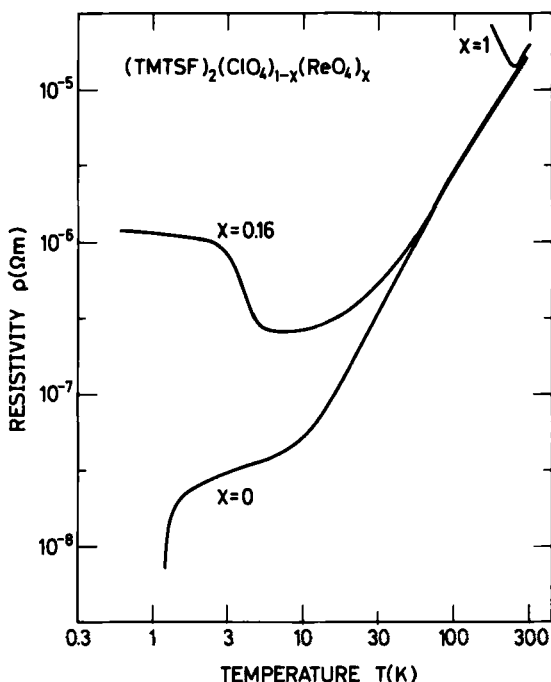


FIGURE 4 Resistivity of  $(\text{TMTSF})_2(\text{ClO}_4)_{1-x}(\text{ReO}_4)_x$  with  $x = 0, 0.16$ , and  $1$ .

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