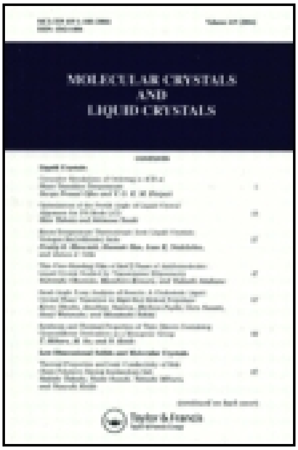

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Superconductivity in the Organic Charge Transfer Salts: $(TMTSF)_2X$ and $(TMTTF)_2X$

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SUPERCONDUCTIVITY IN THE ORGANIC CHARGE TRANSFER SALTS: $(TMTSF)_2X$ and $(TMTTF)_2X$

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We report pressure dependent studies of the a-axis resistivity as a function of temperature for several members of the isostructural families of organic charge transfer salts, $(TMTSF)_2X$ and $(TMTTF)_2X$. For a typical $(TMTSF)_2X$ material the low temperature metal-insulator transition seen at 1 bar is suppressed above some critical pressure, P_c, where a superconducting transition is observed near 1 K. We find a correlation between P_c and the ambient pressure c lattice parameter which reflects the anion size. The $(TMTTF)_2X$ salts exhibit very different ambient pressure behaviour but we find that with the application of sufficiently high pressures (∿30 kbar) their behaviour resembles that seen in the $(TMTSF)_2X$ family but at lower pressures. In particular we find evidence of a possible superconducting transition near 4 K in $(TMTTF)_2Br$ at 25 kbar. At this pressure the conductivity near 4 K is extremely high with a value approaching 10^6 $(\Omega cm)^{-1}$ and the resistivity ratio is about 400.

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INTRODUCTION

Recently there has been much interest in the family of organic charge transfer salts $(TMTSF)_2X$ which become superconducting under pressure[1-5]. However there exists a second family of organic salts of the form, $(TMTTF)_2X$, which are isostructural with the $(TMTSF)_2X$ materials[6,7]. The only chemical difference between these families lies in the organic molecular building block: TMTSF contains selenium atoms which in TMTTF are replaced by sulphur atoms but otherwise these molecules are identical. Moreover the charge transfer in these salts is determined by the valence state of the anion, X, and the ratio of two organic molecules per anion, so that, assuming perfect stoichiometry and for singly charged anions (which are the only ones of interest here) the conduction band is half-filled in both groups of materials.

The similar chemical and crystallographic structure of the TMTSF and TMTTF families would suggest similar electrical properties. However at ambient pressure the electrical behaviour of these families are very different[6-8]. In particular the $(TMTSF)_2X$ salts have higher room temperature conductivities ($\sigma(300\text{ K}) \sim 500\ (\Omega\text{cm})^{-1}$ as compared with $\sigma(300\text{ K}) \sim 50\text{-}300\ (\Omega\text{cm})^{-1}$ for the $(TMTTF)_2X$ salts), much larger resistivity ratios ($\sim 10^2 - 10^3$ as compared with ~ 1) and typically much lower metal-insulator transition temperatures in those materials in which no anion ordering takes place (< 20 K as against $\sim 100\text{-}200$ K).

We have carried out a pressure-dependent study of the temperature dependence of the resistivity for various members of the $(TMTSF)_2X$ and $(TMTTF)_2X$ families for pressures up to 30 kbar. The measurements on the $(TMTTF)_2X$ salts were made so as to attempt to rationalise the apparently inconsistent ambient pressure behaviour of these isostructural families. We find that the electrical properties of the $(TMTTF)_2X$ salts are very sensitive to pressure and that at sufficiently high pressures the salts show similar behaviour to that shown by the $(TMTSF)_2X$ salts at much lower pressures.

THE $(TMTSF)_2X$ FAMILY

The properties of the $(TMTSF)_2X$ materials can be classified according to the symmetry of the anion as shown in table 1. The octahedral anion salts form an antiferromagnetic insulating state at low temperature at low pressures[9,10]. With increasing pressure the metal-insulator (M-I) transition temperature falls and above a certain critical pressure, P_c, a superconducting state is observed near 1 K[1-5]. Measurements for a typical salt

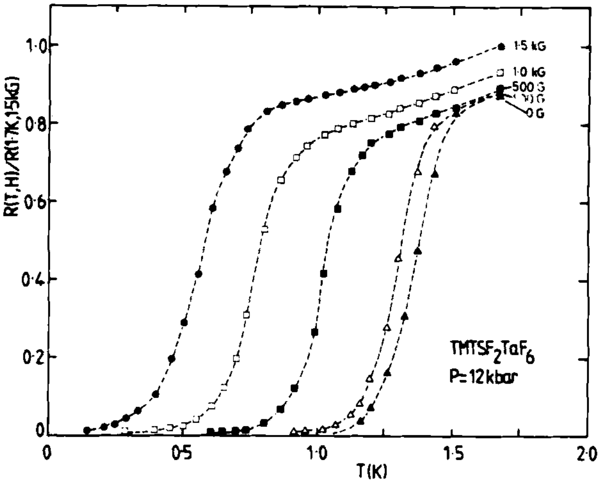

FIGURE 1 Resistivity curves for $(TMTSF)_2TaF_6$ at 12.5 kbar indicating a superconducting transition near 1.3 K where the resistance falls to zero within experimental accuracy. The application of a magnetic field in some arbitrary direction perpendicular to the a axis suppresses the transition.

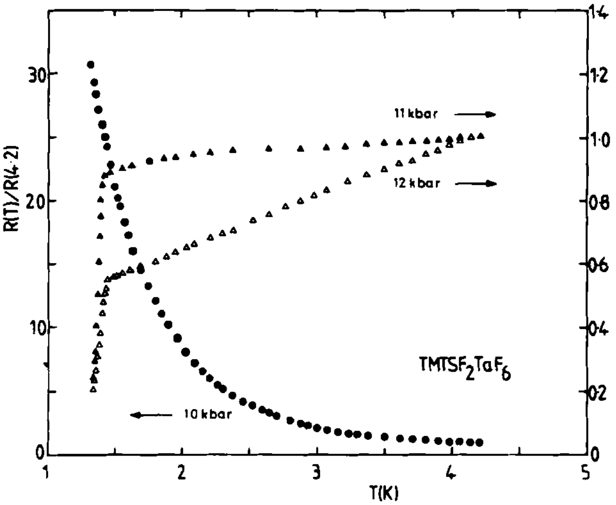

FIGURE 2 Resistivity curves for $(TMTSF)_2TaF_6$ at pressures of 10, 11 and 12 kbar. A M-I transition is seen near 6 K at 10 kbar whereas for the higher pressure runs a SC transition is observed with $T_c \sim 1.35$ K.

TABLE 1 The $(TMTSF)_2X$ Family

<table>
<tr><td rowspan="4">Octahedral</td><td>TaF_6^-</td><td rowspan="5">Anti-[a] Ferromagnetic[9,10]</td><td rowspan="6">Superconducting for $P > P_c$ [1-5]</td></tr>
<tr><td>SbF_6^-</td></tr>
<tr><td>PF_6^-</td></tr>
<tr><td>AsF_6^-</td></tr>
<tr><td rowspan="3">Tetrahedral</td><td>ClO_4^-</td></tr>
<tr><td>ReO_4^-</td><td rowspan="3">Anion[a] Ordering[11-13]</td></tr>
<tr><td>BF_4^-</td><td rowspan="2"></td></tr>
<tr><td>Planar</td><td>NO_3^-</td></tr>
</table>

[a] Low temperature insulating state at 1 bar.

$(TMTSF)_2TaF_6$, are shown in figures 1 and 2. Observation of the superconducting transition from resistivity measurements for a pressure above P_c is shown in figure 1. Resistivity curves for several pressures are shown in figure 2, so defining P_c. We observe similar behaviour in $(TMTSF)_2SbF_6$ with a critical pressure just below that for the TaF_6 salt[3,4] and the phase diagrams of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ have the same form[1,14] but with still lower critical pressures.

With the exception of $(TMTSF)_2ClO_4$ the salts of TMTSF containing lower symmetry anions show at ambient pressure phase transitions at much higher temperatures than those seen in the octahedral anion complexes. A metal-insulator transition is observed in the BF_4 and ReO_4 salts at ∿40 K and ∿180 K respectively[5] and a weak anomaly in the resistivity of $(TMTSF)_2NO_3$ at ∿40 K signatures a phase transition[8]. These transitions are associated with ordering of the anions[11]. Under pressure the M-I transitions in $(TMTSF)_2ReO_4$ and $(TMTSF)_2BF_4$ are suppressed above critical pressures of ∿ 9.5 kbar and ∿ 4.5 kbar respectively but whereas in the former a superconducting transition is seen near 1.2 K[12] for pressures just above P_c no such transition is found in $(TMTSF)_2BF_4$ for temperatures down to 1.2 K[13]. Both materials show large hysteretic anomalies in resistivity for a narrow pressure range just above P_c, with the possibility of increasing the resistivity of the low temperature state by several orders of magnitude through temperature cycling[12,13]. This behaviour has been interpreted as indicating a freezing of the anions as temperature is decreased in a metastable state at high pressures[12]. The anomalous behaviour of $(TMTSF)_2ClO_4$ with respect to the other tetrahedral anion complexes in that it is superconducting at ambient pressure with no anion ordering can be rationalised in the above model as discussed in reference 12. One supposes that the intrinsic ordering temperature for the ClO_4^- anion array which will be determined by the effective interaction between the anions is less than E_b/k_B where E_b is the energy barrier between the two possible symmetry related orientations of the non-centrosymmetric ClO_4 anion within its centrosymmetric cage. Then at ambient pressure the ClO_4 anions may be frozen in a disordered state at low temperatures even though the ordered state may be favoured energetically but which is inaccessible. It is interesting to compare this behaviour with that of the isostructural salt, $(TMTTF)_2ClO_4$, in which an ordering of the anions is observed at ambient pressure below 75 K[11,7]. We find that this transition is rapidly suppressed under pressure giving way to a low-temperature insulating state not associated with anion ordering[15] and it is clear that the absence of superconductivity in $(TMTTF)_2ClO_4$ at ambient pressure has nothing to do with the order-disorder transition of the ClO_4 anions, as will be discussed further below.

For the $(TMTSF)_2X$ salts which are superconducting (see table 1) we find an empirical correlation between the critical pressure above which the materials are superconducting and the ambient pressure c lattice parameter[4], as shown in figure 3. c characterises the separation of the two-dimensional sheets of TMTSF stacks[16] and is determined by the anion size. Without detailed structural measurements on each compound it is not possible to be sure that the correlation of P_c with this particular parameter is the most significant. It might, for example, reflect more subtle changes in the crystal structure. However we find no systematic variation in the a or b lattice parameters as the anion is varied[4].

Such a correlation might suggest a critical interstack coupling strength above which the superconducting state is stabilised with respect to the antiferromagnetic instability. We would then postulate a universal P-T phase diagram for all these materials with pressure replaced by some parameter describing the interstack coupling. The various $(TMTSF)_2X$ salts would then lie at various points along this axis and the application of pressure would through changes in the interstack coupling make the different compounds look alike. Such a description is not inconsistent with theoretical models in which the interchain overlap integral plays an important role in determining the stability of the various instabilities of the electron gas[17-19]. The"coexistence"of the SDW and SC

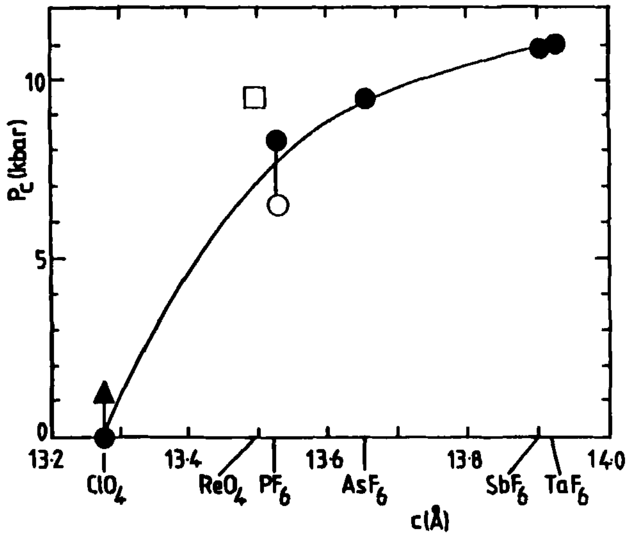

FIGURE 3 Variation of P_c with the ambient pressure room temperature c lattice parameter for the superconducting members of the $(TMTSF)_2X$ family. (ClO_4[3-5]: the arrow indicates the region in which a resistivity upturn above T_c is seen. PF_6: solid circle[1], open circle[20,21]. AsF_6: P_c[14], c[22]. SbF_6 and TaF_6[3,4]. ReO_4[12])

phases for pressures near P_c is theoretically possible[23] and there is some indirect experimental evidence with, for example the observation of an upturn in resistivity above T_c in $(TMTSF)_2PF_6$[20] at 6.5 kbar and in $(TMTSF)_2ClO_4$[3,4]at ^{c}1.5 kbar.

The above correlation between P_c and c suggests that the superconducting properties of these materials are associated primarily with the TMTSF stack and that the anions play a subsidiary role once any possible ordering is frozen out. In particular note that for the compounds $(TMTSF)_2NO_3$ and $(TMTSF)_2BF_4$, for which the c lattice parameter is smaller than that for the ClO_4 salt, negative critical pressures are implied by this empirical relationship; since there is evidence in the PF_6 and ClO_4 salts that T_c falls rapidly with increasing pressure above P_c[20,21,4] and assuming similar behaviour in the other TMTSF salts the absence of superconductivty in the BF_4 salt for pressures above P_c (for temperatures down to 1.2 K)[13] and in $(TMTSF)_2NO_3$ at 12 kbar (for temperatures down to 100mK) would be consistent with such "negative" P_c.

THE $(TMTTF)_2X$ FAMILY

At ambient pressure the conductivity of all the $(TMTTF)_2X$ salts exhibits a broad maximum near 100-250 K[6,7], together with additional features in for example $(TMTTF)_2ClO_4$ (a weak hysteretic anomaly near 75 K, associated with anion ordering[11]) $(TMTTF)_2SCN$ (a sharp metal-insulator transition at 160 K, whose behaviour under pressure indicates it is related to an anion ordering[24]) and $(TMTTF)_2Br$ (a M-I transition near 19 K). Anomalies in other physical properties, for example susceptibility and EPR measurements indicate well-defined phase transitions at lower temperatures (∿10-20 K)[6] and it has been postulated that the broad conductivity maximum may be associated with electron localisation[7], suggesting these compounds are more one-dimensional in their electronic properties than the $(TMTSF)_2X$ materials. The low temperature state in the $(TMTTF)_2X$ salts may have a complex character. X-ray measurements indicate the low temperature state at 1 bar in $(TMTTF)_2PF_6$ is a lattice distorsion[11]. However measurements on the system $((TMTSF)_{1-x}(TMTTF)_x)_2ClO_4$ show that, for small x (>1%), an insulating state is seen at low temperatures, whose character changes from being magnetic (SDW) at low x to non-magnetic at high x (CDW) with at intermediate values a more complex nature[25]. Recent NMR measurements on $(TMTTF)_2Br$ at 1 bar suggest the character of the low-temperature state corresponds to that seen in the ClO_4 alloy system at intermediate x values[26].

For $(TMTTF)_2PF_6$ and $(TMTTF)_2ClO_4$ we find that under pressure the conductivity maxima seen near 230 K at 1 bar[7] are quickly suppressed and at 30 kbar we find M-I transitions near 10 K and 30 K respectively with metallic behaviour above these temperatures. Note that as mentioned above the order-disorder transition in $(TMTTF)_2ClO_4$ at 75 K at 1 bar is quickly frozen out under pressure. The effect of pressure on $(TMTTF)_2Br$ for which at 1 bar the conductivity maximum is at only 100 K, a relatively low temperature with respect to other members of this family[7], is more dramatic. At 22 kbar a metallic state is stabilised to ∿10 K with for the sample shown in figure 4 a resistance ratio of 16. Figure 5 shows results on the same sample at 25 kbar , indicating a possible superconducting transition near 4 K, a transition which is suppressed with a transverse magnetic field. The sample has clearly deteriorated between the consecutive pressure runs at 22 and 25 kbar, as indicated by the lower resistance ratio at the higher pressure. We have however observed similar falls in resistivity near 4K in several other samples, some of which had higher resistance ratios.

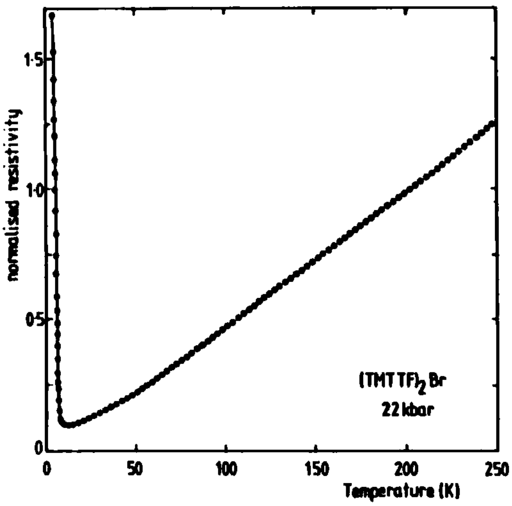

FIGURE 4 Normalised resistance versus temperature for $(TMTTF)_2Br$ at 22 kbar

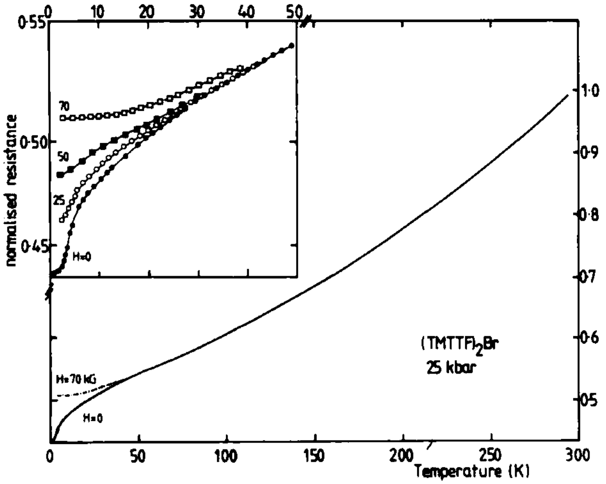

FIGURE 5 Normalised resistance versus temperature for $(TMTTF)_2Br$ at 25 kbar for the same sample shown in figure 4 on a subsequent run. The inset shows the result of the application of a magnetic field (at 25, 50 and 70 kG) along some arbitrary direction perpendicular to the a axis.

The measurements shown in figures 4 and 5 correspond to work on crystals grown by J.M. Fabre. We have also studied crystals grown by K. Bechgaard using a slightly different technique. We have made measurements on more than 50 samples of $(TMTTF)_2Br$ from these two different batches and we find significant differences between these batches although crystals from the same batch show similar behaviour. In particular we have observed results such as those shown in figure 5 only on the samples grown by Fabre. At the same pressure the crystals grown by Bechgaard (KB) exhibit metallic behaviour for temperatures down to 2 K with saturation of the resistivity below $\sim$4 K. At a slightly lower pressure,for these samples,we observe metallic behaviour to low temperatures but with a very weak upturn in resistivity similar to that observed in some of the TMTSF salts near P_c as mentioned above. These results suggest a slightly higher critical pressure for the KB samples as compared with the JMF samples, and perhaps might explain the different behaviour found at 25 kbar. Previously different critical pressures have been reported for $(TMTSF)_2PF_6$ as shown in figure 3.

For the KB samples at 25 kbar we have measured a resistance ratio of up to 400 indicating a conductivity at low temperatures of some $5 \times 10^5 - 10^6$ $(\Omega cm)^{-1}$, an extraordinarily high conductivity, comparable to that measured in the most conducting of the $(TMTSF)_2X$ salts at ambient pressure[5] and much higher than values of conductivity previously reported in the $(TMTSF)_2X$ materials under pressure. Further deatils of these measurements will be published elsewhere[15].

CONCLUSION

Pressure dependent studies of the resistivity of several $(TMTTF)_2X$ salts have shown that this family exhibits similar behaviour at high pressures to that shown by the $(TMTSF)_2X$ family at lower pressures. In particular a metallic state is stabilised in $(TMTTF)_2Br$ to low temperatures with a remarkably high conductivity approaching 10^6 $(\Omega cm)^{-1}$, a value comparable or greater to that seen in the most highly conducting $(TMTSF)_2X$ salts. We find some evidence for a possible superconducting transition near 4 K in $(TMTTF)_2Br$ at 25 kbar.

We find an empirical correlation between P_c and the c lattice parameter for the $(TMTSF)_2X$ salts. The results on the $(TMTTF)_2X$ salts (X= Br, ClO_4, PF_6) suggest a similar behaviour in these materials also,with a lower critical pressure in the Br salt as compared with the ClO_4 and PF_6 salts, and the Br anion is considerably smaller than the latter anions.

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