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Pressure-temperature phase diagrams of several (TMTTF)$_2$X compounds: stabilisation of a highly conducting metallic state under pressure in (TMTTF)$_2$Br

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Résumé. — Nous présentons des mesures de résistivité sous pression jusqu'à 32 kbar de plusieurs sels de TMTTF (tétraméthyltétrafulvalène) de formule (TMTTF)$_2$X avec X = Br, ClO$_4$, PF$_6$. Les diagrammes de phase pression-température de ces trois matériaux sont semblables avec stabilisation sous pression d'un état métallique jusqu'à basse température (≈ 20 K), ou existe une transition métal-isolant (M-I) bien définie. Pour le composé (TMTTF)$_2$Br la transition M-I est complètement supprimée pour des pressions supérieures à une pression critique, $P_c$, d'environ 25 kbar et le composé est alors métallique jusque dans les plus basses températures atteintes dans cette étude (≈ 1 K). Des différences significatives sont obtenues pour des échantillons fabriqués à partir de différents solvants chimiques : dans un cas les échantillons ont des rapports de résistance supérieurs à 400 à 25 kbar avec une conductivité plus grande que $10^6$ $(\Omega cm)^{-1}$ à 4 K, ce qui est la plus grande valeur de conductivité jamais atteinte pour un conducteur organique. Dans un autre cas les échantillons présentent une transition supraconductrice possible aux environs de 3,5 K à 25 kbar, mais avec des rapports de résistance plus petits (< 100). Pour ces derniers échantillons il n'y a pas de saturation de la résistance à basse température, alors que pour les premiers la résistance est saturée en dessous de 10 K. Ces résultats suggèrent des pressions critiques légèrement différentes pour ces sels. Les $P_c$ sont beaucoup plus grandes pour les sels de ClO$_4$ et PF$_6$ (> 35 kbar). Des mesures de magnétorésistance en fonction de la pression ont été effectuées sur les échantillons de (TMTTF)$_2$Br, avec le champ magnétique appliqué suivant l'axe c$. La magnétorésistance augmente progressivement avec la pression, atteignant des valeurs non négligeables ($\sim$ 80 kG) à 25 kbar et $\rho(H = 0)/\rho(H = 0)$ ≈ 2-4 près de $P_c$. Ces résultats montrent que sous pression les propriétés physiques des sels de (TMTTF)$_2$X ressemblent de plus en plus à leurs homologues séléniiés (TMTSeF)$_2$X.

Abstract. — Needle axis resistivity measurements on several TMTTF (tetramethyltetrafulvalene) salts of the form (TMTTF)$_2$X, with X = Br, ClO$_4$, PF$_6$, are presented for pressures up to 32 kbar. The pressure-temperature phase diagrams of all three materials are similar with stabilisation under pressure of a metallic state to low temperatures (~ 20 K), below which there is a well defined metal-insulator transition. For (TMTTF)$_2$Br the M-I transition is completely suppressed for pressures above some critical pressure $P_c$ ~ 25 kbar and the compound is metallic to the lowest temperatures considered in this study, ~ 1 K. Significant differences are found between samples grown from different chemical solvents: in one case the samples have resistance ratios exceeding 400 at 25 kbar with a conductivity greater than $10^6$ $(\Omega cm)^{-1}$ at 4 K, the highest values yet reported for any organic conductor. In the other case the samples show a possible superconducting transition near 3.5 K at 25 kbar, but have smaller resistance ratios (< 100). For the latter samples at 25 kbar there is no saturation of the resistance in the low temperature regime, whereas for the former the resistance saturates below 10 K. These results suggest slightly diffe-
rent critical pressures for these salts. \( P_c \) are much higher for the ClO\(_4\) and PF\(_6\) salts (> 35 kbar). Magnetoresistance measurements have been made on samples of (TMTTF)\(_2\)Br as a function of pressure, for field applied along the \( c^* \) axis. The magnetoresistance progressively increases with increasing pressure obtaining substantial values \((\rho(80 \text{ kG}) - \rho(H = 0))/\rho(H = 0) \approx 2 - 4\) near \( P_c \). These results establish that under pressure the physical properties of the (TMTTF)\(_2\)X salts become increasingly to resemble those of their selenium counterparts, (TMTSeF)\(_2\)X.

1. Introduction

The group of isostructural charge transfer salts, (TMTSeF)\(_2\)X (where TMTSeF is the tetramethyltetraselenafulvalene molecule), has stimulated renewed interest in organic linear chain conductors since the discovery of superconductivity in several members of this family (for example, \( X = \text{PF}_6, \text{AsF}_6, \text{TaF}_6, \text{ClO}_4, \text{ReO}_4 \)) for pressures above some critical pressure, \( P_c \) [1-4]. However it is not understood what particular features distinguish these materials from the large number of other known organic quasi-one dimensional materials, in which superconductivity is not found; indeed there are very few such materials in which even a metallic state is observed at low temperatures: in general metal-insulator (M-I) transitions are observed at temperatures typically below 100 K often associated with charge density wave (CDW) formation (for a review, see for example, [5]).

The (TMTSeF)\(_2\)X compounds do however possess several atypical characteristics including a structure incorporating a single organic molecule, and a band filling taken to be independent of temperature and pressure and determined by the stoichiometry and charge state of the anion, \( X \) [6]. It is clearly important to find other organic systems showing superconducting or low temperature metallic behaviour.

Such considerations motivated the studies presented here on the family of organic linear chain compounds, (TMTTF)\(_2\)X, which are isostructural with the (TMTSeF)\(_2\)X materials, but based on the TMTTF (tetramethyltetrafulvalene) molecule. The TMTTF molecule differs from the TMTSeF molecule only by the replacement of the selenium atoms in the latter with sulphur atoms. Both families possess the same triclinic crystal structure with similar lattice parameters [7]. Note, however, that there are subtle differences between the structures of the two families, in for example the disposition of the anions with respect to the organic stacks. Since the crystal structure and chemical composition of the (TMTTF)\(_2\)X and (TMTSeF)\(_2\)X are similar, it might be expected that these materials would also exhibit the same kind of electrical behaviour. However the electronic properties of the (TMTTF)\(_2\)X materials are somewhat different from those of their TMTSeF counterparts at 1 bar [8, 9]. In particular the TMTTF salts exhibit lower conductivities \((\sigma \sim 50-300 \, \text{Gcm}^{-1})\) as compared with \( \sigma \sim 500 \, \text{Gcm}^{-1} \) for the (TMTSeF)\(_2\)X salts), and lower resistance ratios \((\sim 1\) as compared with \( \sim 10^3 \)) with resistance minima typically near 100-250 K and weakly activated behaviour at lower temperatures with in some cases well defined metal-insulator transitions at even lower temperatures (below \( \sim 20 \, \text{K} \)) which have been shown for the PF\(_6\) and Br salts to be associated with a lattice distortion [10] and formation of an antiferromagnetic phase respectively [11, 12]. In contrast for pressures below \( P_c \) the (TMTSeF)\(_2\)X compounds show metallic behaviour to temperatures near 20 K below which there are magnetic transitions [13-15]. Note that in both families of compounds, members containing non-centrosymmetric anions can exhibit metal-insulator transitions at much higher temperatures associated with anion ordering [10, 16].

2. Experimental

Resistivity versus temperature measurements were made, for current along the chain axis, and for several pressures, on the compounds (TMTTF)\(_2\)X, \( X = \text{PF}_6, \text{ClO}_4, \text{Br} \). (Later measurements on the SCN salt are described in a separate article [22]). Resistance was measured using a low frequency \((80 \, \text{Hz})\) lock-in technique: contacts were arranged in the standard 4-in-line array and made with gold or silver paint. The current contacts covered completely the ends of the samples and the voltage contacts were applied so as to make complete loops around the body of the samples. Results were not dependent on sample geometry: checks were made for « unnested voltages » [36] and only samples with nested to unnested voltage ratios greater than 100 were used. Typically this ratio was 1 000. For the magnetoresistance studies, the crystals were oriented with the field along a particular crystallographic axis by indexing the crystal faces (the largest face of a sample can be any of 001, 010 or 011) from a straightforward optical examination of the morphology of the crystal. This procedure only works for well-formed crystals. Various pressure bombs were used, all designed to give hydrostatic pressure transmitted through a fluid, contained within a teflon cell. For these experiments isopentane was used for pressures up to 25 kbar and a 50/50 mixture of isoamyl-alcohol and isopentane was used for higher pressures and in some cases for pressures as low as 22 kbar. Crystals of (TMTTF)\(_2\)Br and (TMTTF)\(_2\)ClO\(_4\) were grown in Montpellier. Two types of (TMTTF)\(_2\)Br crystals were used, synthesized in Montpellier and Copenhagen (identified by F and B respectively in the figures). These crystals were both grown by an electrochemical method but different solvents were used in their preparation: methylene...
chloride and 1,2 dichloroethane were used respectively for the B and F samples. Chemical analysis of the B samples showed the ratio of TMTTF to Br was to within 0.5 % of 2 : 1. A similar analysis was not possible for the F samples because of the more limited quantity of sample. We found that crystals of all three compounds were extremely fragile, much more so than their TMTSeF counterparts; moreover for (TMTTF)$_2$Br we observed very large reversible increases in resistance for samples immersed in isopentane (by up to several orders of magnitude). Contacts made originally with gold or silver paint were considerably improved by a method of gold evaporation. On pressurization crystals often broke and often there were abrupt increases in resistance. For these reasons a large number of crystals were used in this study; in the case of (TMTTF)$_2$Br more than 100 crystals were examined under pressure.

3. Results.

3.1 (TMTTF)$_2$PF$_6$. — Ambient pressure measurements on (TMTTF)$_2$PF$_6$ show a maximum in conductivity near 230 K and a phase transition (observed via magnetic susceptibility studies) at about 14 K, at which temperature the material is highly resistive and conductivity measurements difficult to carry out [8, 9]. Previous resistance measurements for temperatures down to 100 K showed no significant change in electrical behaviour for pressures up to 10 kbar [17].

In figure 1 we show data for pressures between 15 and 28 kbar; lower pressures were not considered in this study. For these pressures the high temperature resistance minimum found at 1 bar [9] is not observed. As the temperature is decreased the resistance falls, increasingly rapidly as the pressure is raised, but with a maximum resistance ratio, $R(300 \text{ K})/R_{\text{min.}}$, of only 5 at the highest pressure considered.

Note also that there is a change in slope of the resistance curve near 120 K which somewhat resembles that seen in some samples of (TMTSeF)$_2$PF$_6$. In (TMTSeF)$_2$PF$_6$ such behaviour has been interpreted as being associated with the formation of one-dimensional superconducting fluctuations as the temperature is decreased [18].

Defining the phase transition temperature, $T_{\text{M-1}}$, as that temperature where $-d/dT(\ln \rho)$ has a maximum value, the phase diagram shown in figure 2 can be constructed. Measurements have been made for pressures up to 28 kbar, where $T_{\text{M-1}}$ has fallen to about half its ambient pressure value. Below $T_{\text{M-1}}$ an energy gap, $\Delta$, can be found from the relation $\Delta = kT(\ln(\rho_0/\rho))$ where $\rho_0$ is the minimum resistivity just above $T_{\text{M-1}}$. Figure 2 shows data at 15 and 28 kbar : $\Delta$ decreases more rapidly with pressure than $T_{\text{M-1}}$ such that $2\Delta/kT_{\text{M-1}}$ decreases from $\sim 7.6$ at 15 kbar to $\sim 4.6$ at 28 kbar. The latter value is close to the mean field value (3.5) [19], expected for either CDW or SDW phase transitions. At the lower pressure the higher magnitude of $2\Delta/kT_{\text{M-1}}$ may be indicative of one dimensional fluctuations, so reducing the measured transition temperature. The decrease in $2\Delta/kT_{\text{M-1}}$ would then suggest increasing three-dimensional character under pressure.

3.2 (TMTTF)$_2$ClO$_4$. — A maximum in $\sigma$ is found near 230 K at 1 bar in (TMTTF)$_2$ClO$_4$ with a lower temperature phase transition near $\sim 70$ K, seen as a weak hysteretic anomaly in resistivity [9]. The ClO$_4^-$ anions order on a $2 \times 2 \times 2$ superlattice at this temperature [10]. AT 22 K a second phase transition has been identified via EPR measurements [9], whose character is unknown.

Results we have obtained as a function of pressure are summarised in figure 3. For pressures below 22 kbar the resistance increases as temperature is decreased, with no sign of the resistance minimum seen by Coulon et al. at ambient pressure [9]. The data we present in figure 3 may not correspond to the intrinsic behaviour of the material; as mentioned earlier some deterioration of the samples does occur on pressurization. Poor quality samples, as evidenced by high room temperature resistivity values, show low resistance ratios ($R(300 \text{ K})/R_{\text{min.}}$) with the functional form of the resistance curve increasingly dominated by an activated component. It is interesting to compare the extreme sensitivity of these (TMTTF)$_2$X
compounds to pressure with the behaviour of the (TMTSeF)$_2$X materials which are much less sensitive: in previous studies on the latter compounds we have found that even though the absolute resistance of particular samples may increase substantially on pressurization or cooling, through irreversible jumps in resistance, the functional dependence of resistance on temperature is little affected except in extreme cases, suggesting that simply the effective area of cross-section of the samples is reduced. One possible interpretation of such different behaviour is that the (TMTTF)$_2$X compounds are more one-dimensional than their selenium counterparts so that defects such as chain breaks may result in some kind of electron localisation. Recent theoretical modelling of the effect of radiation damage on TMTSeF-DMTCNQ suggests that a primary effect of such damage is the localization of electrons on portions of the organic organic chains segmented as a consequence of irradiation [20]. Coulon et al. have suggested that the ambient pressure resistance behaviour of the (TMTTF)$_2$X materials is determined by possible electron localization effects and have argued on the basis of structural data that the family of (TMTTF)$_2$X compounds are indeed more one-dimensional than those of the (TMTSeF)$_2$X family: however such arguments which assumed the most important interchain interactions were nearest S-S or Se-Se contacts must be treated with great caution since recent band structure calculations show that these contacts are not necessarily those which determine the band anisotropy [21].

At 22 kbar $\rho$ is almost independent of temperature for a temperature range extending to below 100 K. At higher pressures a metallic regime is found for temperature above $\sim$ 50 K, with well defined metal-insulator transitions at still lower temperatures. The phase diagram, determined from these data is shown in figure 3. (Note that we include only a portion of the phase diagram for temperatures below 30 K). The ambient pressure data point is inferred from an anomaly that is clearly visible near 22 K in the data presented in figure 4 of [9], concerning the temperature dependence of the linewidth of the $g = 2$ ESR signal, although the authors of [9] do not refer to this anomaly in their discussion. They do however consider that a similar anomaly for the Br salt of TMTTF near 16 K is the signature of a phase transition, as confirmed by NMR and AFMR studies [11, 12]. $T_{M-I}$ falls with increasing pressure and by extrapolation will go to zero for some critical pressure, $P_c$, in excess of 35 kbar. An energy gap was determined from the resistivity data as described earlier for the PF$_6$ salt. At 17 kbar $2/kT_{M-I}$ for (TMTTF)$_2$ClO$_4$ is $\sim$ 3.6, a much lower value than that measured for
Fig. 4. — (a) Resistance versus temperature curves for F samples of (TMTTF)\textsubscript{2}Br. The insert shows results in a magnetic field applied perpendicular to the needle axis. Values of field are given in kG. (b) Log (\rho) versus log (T) for (TMTTF)\textsubscript{2}Br (F samples) at 22 and 26 kbar.

(TMTTF)\textsubscript{2}PF\textsubscript{6} at a comparable pressure (∼ 7.6 at 15 kbar). Such a result is consistent with a fall in 2 Δ/kT_{M-I} with increasing pressure as found above for (TMTTF)\textsubscript{2}PF\textsubscript{6}, but with pressure scaled to the critical pressure above which the low temperature insulating phase is suppressed i.e. both P_{c} and 2 Δ/kT_{M-I} (P) are smaller for the ClO\textsubscript{4} salt than for the PF\textsubscript{6} salt. A shoulder can be seen on the resistance curve at 6 kbar near 50 K, which may correspond to the anion order-disorder transition observed near 70 K at 1 bar: no effect is seen at higher pressures. Such a disappearance of the effect of the anion ordering transition on the electrical conductivity with increasing pressure has been found in (TMTTF)\textsubscript{2}SCN [22] and several TMTSeF\textsubscript{2} compounds [16, 23]. For (TMTTF)\textsubscript{2}SCN an anion-ordering M-I transition near 160 K at 1 bar gives way above 15 kbar to a M-I transition below 20 K. It thus appears that the phase diagrams of (TMTTF)\textsubscript{2}SCN and (TMTTF)\textsubscript{2}ClO\textsubscript{4} are similar with anion-ordering transitions suppressed under moderate pressure and at higher pressures lower temperature metal-insulator transitions presumably associated with instabilities derived from the organic stacks themselves, since these transitions occur at similar temperatures to the ambient pressure CDW and SDW transitions in the PF\textsubscript{6} and Br salts.

3.3 (TMTTF)\textsubscript{2}Br. — The data above on (TMTTF)\textsubscript{2}ClO\textsubscript{4} and (TMTTF)\textsubscript{2}PF\textsubscript{6} near 30 kbar are similar to that seen in the (TMTSeF)\textsubscript{2}X materials at pressures close to P_{c} (P_{c} is in the range 1 bar to 12 kbar for the (TMTSeF)\textsubscript{2}X compounds [1-4]) and as mentioned above, by extrapolation, P_{c} near 35-45 kbar are suggested for the TMTTF materials. Previous experiments on (TMTSeF)\textsubscript{2}X compounds have shown a correlation between the critical pressure, P_{c}, required for superconductivity and the anion size (through the c lattice parameter) in those cases where anion ordering does not play a role at P_{c} [2, 3] (note that one can define a second critical pressure P_{c}^A for suppression of anion ordering which is unrelated to P_{c}) [16, 23, 22]. This result caused us to consider (TMTTF)\textsubscript{2}Br which, of all the known (TMTTF)\textsubscript{2}X materials, has the smallest anion and c lattice parameter. Consequently P_{c} is expected, if the above relation also holds in the (TMTTF)\textsubscript{2}X compounds, to be low relative to other (TMTTF)\textsubscript{2}X salts in (TMTTF)\textsubscript{2}Br. We find this is the case: P_{c} is near 25 kbar for (TMTTF)\textsubscript{2}Br. Data at 25 kbar for a Montpellier sample are shown in figure 4a. The sample remains metallic to 4 K where a possible superconducting transition is observed with a transition temperature near 3.5 K. The insert in the figure shows the effect of a transverse applied magnetic field. The drop in resistance near 3.5 K is suppressed but a large transverse critical field is suggested. The same sample in an earlier experiment at a slightly lower pressure of 22 kbar shows metallic behaviour to ∼ 10 K where there is a metal-insulator transition. The resistance ratio for this sample at 22 kbar was 16 but as shown in figure 4a is only ∼ 2 at 25 kbar: the lower resistance ratio at the higher pressure clearly shows the sample has deteriorated between the two consecutive runs. The large residual resistance may be associated with breaks in the crystal chains induced through strains during pressurization. Such breaks may change the current path through the sample such that the measured resistance probes not only the longitudinal resistance but also the transverse resist-
tance; it is then conceivable that this effect may explain the observed drop in resistance since the transverse resistance drops relatively rapidly below the one to three-dimensional cross-over temperature which may itself be low if these materials are highly one-dimensional at these pressures. Alternatively, a similar argument involving superconducting fluctuations may be possible since the transverse paraconductivity will grow more rapidly than the longitudinal component in this temperature region [18].

The Fabre (F) samples are of poor crystal morphology. Following these studies, we carried out a series of measurements on the Bechgaard (B) samples; these crystals had very good morphology with well-defined faces. These differences may be associated with the solvents from which the samples were grown: the preparation methods were otherwise the same. Both the F and B samples show similar phase diagrams, in that at 25 kbar a metallic state is found to the lowest temperatures obtained in these experiments, with at a slightly lower pressure a weak resistivity upturn near 8 K (compare data shown in figure 5 for B samples with similar data for the F samples given in figure 4b). The phase diagram derived from data on B samples is shown in figure 6a and various resistance curves are shown in figure 6b. The insert to figure 6b shows the variation of conductivity with pressure measured on two B samples to 15 kbar, above which there was some crystal deterioration. No high temperature minimum in resistance was found for all pressure considered. In particular, as shown in figure 6b, $\rho$ decreases smoothly at 4.5 kbar with decreasing temperature to just above the metal-insulator transition near 16 K. As mentioned above, however, at 1 bar a minimum in resistance has been reported for (TMTTF)$_2$Br near 100 K [9]. In this work well-defined resistance minima were observed on several samples at pressures of up to 25 kbar at temperatures of up to 100 K but with no correlation between the temperature of the minimum and pressure (for these samples unnested voltages were low and otherwise the measurements appeared good in particular no hysteresis was observed in the measurements). These samples however were clearly degraded on pressurization or cooling through resistance jumps which substantially increased their resistance. Our studies on large numbers of samples show unam-

Fig. 5. — Log ($\rho$) versus log (temperature) for B samples of (TMTTF)$_2$Br.

Fig. 6. — (a) Phase diagram for (TMTTF)$_2$Br derived from resistance versus temperature curves given in (b). The ambient pressure points are taken from [11, 12] (triangle) (NMR and AFMR studies) and [9] (open circle) (conductivity data). We do not consider the difference between these values is highly significant. The experimental error in the former value is about 0.5 K [11, 12] and the latter is unspecified [9], but probably much larger. Moreover, the transition temperatures are defined using different criteria for the magnetic and conductivity measurements. The insert to (b) gives the normalized room temperature conductivity as a function of pressure; similar results were observed for several crystals.
biguously that there is no intrinsic resistance minimum for pressures of 4.5 kbar and above. Moreover thermoelectric data on (TMTTF)_2Br at 1 bar suggests metallic behaviour to just above \( T_{M-I} \) with no indication of any phase transition near 100 K [24]. The temperature dependence of the thermopower of the various TMTTF salts is interesting with a range of behaviour found in the large number of salts that have been examined [24].

In other respects there are some significant differences between the F and B samples. Firstly the B samples have very high resistance ratios. Sample B30 at 26 kbar, shown in figure 5, has a resistance ratio of 400 with a conductivity at 4 K greater than \( 10^6 \, \text{Qcm}^{-1} \), an extraordinarily high value exceeding that of even the most conducting of the (TMTSeF)_2X salts at ambient pressure, and to our knowledge of all other known organic linear chain conductors. Resistance ratios of ~ 400 are considerably larger than typical values measured in the (TMTSeF)_2X materials under pressure [1-3], and comparable with the best values obtained in the TMTSeF materials at ambient pressure [6]. (Note that resistance ratios as high as 100 were found in some F samples for pressures above 25 kbar).

A second and perhaps more significant difference between the F and B samples is the low temperature behaviour below \( \sim 30 \, \text{K} \), as shown in figure 7. The resistance of the B samples saturates below \( \sim 10 \, \text{K} \), whereas that of the F material continues to drop in this temperature range; for example for sample F29 the resistance falls by a half between 10 and 2 K. This behaviour appears to be insensitive to the resistance ratios of the F and B samples, which might otherwise be expected to reflect crystal quality. In particular note that sample F29 has a fairly high resistance ratio of about 100, comparable to that of the poorest B samples (~ 200) whereas the resistance ratio of sample F28 is much lower, yet the same behaviour is found between 4 and 1 K. In order to discount the possibility that these contrasting behaviours could be attributed to slightly different applied pressures measurements were made simultaneously within the same pressure bomb on a F and a B sample (samples F29 and B30 in Fig. 6). These data therefore show that there is a very important intrinsic difference between the B and F crystals. One possibility is that there is a slightly different critical pressure for the B and F samples with a slightly higher \( P_c \) in the B samples since at some pressure (24 kbar), intermediate between those for which data are presented in figure 4, a weak resistivity upturn (with resistance increasing by only a factor of 2 below \( \sim 8 \, \text{K} \)) was found in sample B19. This sample had an excellent resistance ratio of \( \sim 390 \). (Such a resistivity upturn has been observed in some of the (TMTSeF)_2X salts above superconducting transitions for pressures near their \( P_c \) [25, 2, 3], which has been variously interpreted, but which may simply be associated with inhomogeneous samples perhaps through strains induced on cooling). It would clearly be interesting to examine the transport properties of the B samples for temperatures below \( \sim 10 \, \text{K} \) at slightly higher pressures. That there is such different behaviour in samples prepared in very similar ways has important implications for understanding the low temperature resistance behaviour of both the TMTTF and TMTSeF families.

As mentioned above since the low temperature behaviour of the F samples is independent of resistance ratio even for high \( R \, (300 \, \text{K})/R_{\text{min}} \), and presumably therefore of crystal quality there must be some intrinsic chemical difference between the F and B samples, perhaps through the ratio of TMTTF to Br (as mentioned above, for the B samples chemical analysis shows perfect stoichiometry to within 0.5 %) and so through band filling. The recent discovery of a second TMTTF-Br phase which is insulating at room temperature with a very different structure, crystals of which were grown under the same conditions and in the same batch as (TMTTF)_2Br [24], suggests that (TMTTF)_2Br may not be stable with respect to other TMTTF-Br combinations, complicating its chemistry.

Having established that the phase diagram of (TMTTF)_2Br has many characteristics in common with those of the (TMTSeF)_2X family it is clearly interesting to compare other physical properties. Of particular importance is the magnetoresistance, for which
extraordinarily high values have been reported for various (TMTSeF)$_2$X salts [1-3 and references therein]. Results are shown in figure 8 for (TMTTF)$_2$Br for magnetic field applied along the $c^*$ axis and current along $a$ for a range of applied pressure. The most obvious feature of these results is the progressive increase in magnetoresistance with increasing pressure. For example the quantity, $(\rho(80 \text{ kG}) - \rho(H = 0))/\rho(H = 0)$, evaluated at 15 K, increases from $\sim 0$ at 1 bar, to 0.31 at 16 kbar to 1.22 at 22 kbar.

![Graph 1](image1.png)

**Fig. 8.** Normalized resistance versus temperature curves for B samples of (TMTTF)$_2$Br in various magnetic fields along $c^*$ and for a number of applied pressures. Results on more than one crystal.

4. Discussion.

The results presented above show clearly that the phase diagram of the (TMTTF)$_2$X compounds is of the same form as that of the (TMTSeF)$_2$X materials but with considerably higher critical pressures. The character of the low temperature insulating phase for pressures below $P_c$ has not been determined except at ambient pressure in the Br and PF$_6$ salts which are respectively magnetic [11, 12] and non-magnetic. It cannot be ruled out and indeed appears quite likely that the nature of this phase may vary with pressure in the PF$_6$ salt so that at pressures close to $P_c$ this phase is magnetic. By substituting TMTSeF with TMTTF in (TMTSeF)$_2$ClO$_4$ magnetism in the TMTSeF salt is suppressed giving way to a non-magnetic ground state in TMTTF rich alloys [26]. Alloying (TMTTF)$_2$ClO$_4$ with TMTSeF mimics the effect of pressure and thus a similar change in character may be expected with pressure. Clearly it would be very interesting to examine the nature of the insulating phase in the PF$_6$ salt as a function of pressure through EPR, NMR and X-ray scattering experiments.

In addition to low temperature M-I transitions associated with intrinsic stack instabilities there is the possibility of anion order-disorder transitions for non-centrosymmetric anions. These are found in several (TMTTF)$_2$X salt, including the ClO$_4$, SCN and most recently the ReO$_4$ salt. A complete structure determination has only been made below the anion ordering transition on (TMTTF)$_2$ReO$_4$ [27] showing as previously suggested by Parkin et al. [16, 23] for the selenium analogue that the anions are displaced sideways from the centre of the cage in which they sit at high temperatures above the transition and that there are distortions of the organic stack including a tetramerization of the stack below the order-disorder transition. This result may then explain the very large values of activation energies observed below anion order-disorder transitions in both (TMTTF)$_2$X and (TMTSeF)$_2$X salts. The gross features of the anion ordering in (TMTTF)$_2$ReO$_4$ [27] are the same as those found in the selenium analogue including a $2 \times 2 \times 2$ superlattice [10] and a volume conserving shear of the unit cell at the phase transition [28]. Similarities between other TMTTF and TMTSeF salts for low symmetry anions exist and are discussed elsewhere [23]. These results show that the (TMTTF)$_2$X salts not only have similar phase diagrams to those of the TMTSeF salts, with regard to stack instabilities for the centrosymmetric anions, but also with regard to anion ordering transitions for the lower symmetry anions.

There are further similarities between the (TMTTF)$_2$X and (TMTSeF)$_2$X salts which we will briefly discuss. Firstly, as already mentioned, the critical pressure for superconductivity increases with anion size in the (TMTSeF)$_2$X salts [2, 3] and we find evidence for a similar relationship in the more limited number of (TMTTF)$_2$X compounds that we have studied. In particular $P_c$ for the Br salt is much lower than that for the ClO$_4$ and PF$_6$ salts and the Br anion is the smallest anion. Moreover the ClO$_4$ anion is smaller than the PF$_6$ anion and extrapolation of the data presented here suggests a lower $P_c$ for the ClO$_4$ anion. We emphasize again that anion-ordering
transitions must be considered independently of organic molecular stack instabilities, and that the critical pressure we are discussing refers to that pressure required to suppress stack instabilities and not that needed to suppress anion ordering which may be higher or lower than $P_c$ [16, 23]. This point is perhaps more clearly shown by the behaviour of the SCN salt [22].

A second similarity between the (TMTSeF)$_2$X and (TMTTF)$_2$X salts is in the temperature dependence of the resistance below 300 K. As can be seen from figure 5 the resistivity of (TMTTF)$_2$Br in the high pressure metallic regime follows a simple power law dependence. $\rho$ can be described by $\rho_0 + T^\alpha$ over a wide temperature range. For the B samples $\rho$ follows an almost quadratic dependence on $T$ from 30 to 300 K (a least squares fit gives $\alpha \sim 1.95 \pm 0.05$ for B30 and $1.85 \pm 0.05$ for B29). For the F samples a similar law holds over a more limited range with $\alpha \sim 1.5-1.6$. The exponent appears to decrease as the resistance ratio and consequently crystal quality falls. It was previously noted for the (TMTSeF)$_2$PF$_6$ salts that $\rho$ follows a quadratic temperature dependence over a similarly wide temperature range in high quality samples [29]. For this material such a temperature dependence has been interpreted in terms of either two-phonon (libron) scattering [30] or single phonon scattering [31] as being the dominant scattering mechanism. As was the case for TTF-TCNQ the temperature dependence of $\rho$ must be treated cautiously since it must be corrected to take into account changes in unit cell volume with temperature [32]. For TTF-TCNQ at constant pressure $\alpha \sim 2.3$ whereas $\rho$ varies quasi-linearly at constant volume (for a recent review, see [33]). Such a change in $\alpha$ clearly greatly affects any theoretical interpretation.

A third similarity between these two families lies in the large values of magnetoresistance reported for temperatures below about 40 K, which are not well understood. Various models have been proposed to explain this effect in the (TMTSeF)$_2$X family including the possibility that magnetic field might suppress a contribution to the conductivity, a paraconductivity, derived from superconducting fluctuations [1, 18]. A recent review examines this point in more detail [35]. The results we have presented on (TMTTF)$_2$Br show that large values of magnetoresistance are only observed in this material for pressures close to $P_c$. The model of superconducting fluctuations, if applicable in this case, would then suggest that a paraconductivity contribution increases with increasing pressure and that near $P_c$ there is a competition between the increasingly important fluctuation superconductivity and the magnetic phase.

Finally we mention the very high values of conductivity found in (TMTTF)$_2$Br above $P_c$. As we mentioned earlier these values are the largest yet observed in any organic conductor. Conductivities comparable in magnitude have been found in only a very few organic compounds, including the (TMTSeF)$_2$X salts [37] and TMTSeF-DMTCNQ [38, 39]. The phase diagram of the latter compound is very different from those of both the (TMTSeF)$_2$X and (TMTTF)$_2$X families. TMTSeF-DMTCNQ exhibits a Peierls distortion near 40 K at 1 bar, which abruptly disappears above about 9 kbar where the material is metallic to 100 mK [38, 39]. The origin of such large conductivities in such very different systems is not understood at present. A paraconductivity derived from superconducting fluctuations has been proposed [1, 35, 38] whereas other explanations assume these materials have extremely low defect concentrations as compared to typical organic conductors [40]. The explanation of the high conductivity values in these materials is probably the key to the understanding of many of their highly unusual properties.

5. Conclusion.

At high pressures the (TMTTF)$_2$X family of compounds behaves similarly to its isostructural counterparts based on the selenium analogue of the TMTTF molecule, TMTSeF. This result was perhaps unexpected in view of the very different electrical behaviour of these materials at 1 bar, but is not surprising with regard to their closely related crystal structures and band filling. We have demonstrated that at sufficiently high pressures the (TMTTF)$_2$X materials remain metallic to low temperatures. A metallic state is stabilized in (TMTTF)$_2$Br for pressures above some critical pressure, $P_c$ (analogous to that previously defined for the TMTSeF salts) of 25 kbar. Samples of the Br salt grown from different chemical solvents showed some significant differences in electrical behaviour, suggestive of slightly different critical pressures. In particular whereas indications of superconductivity was found in F samples near 3.5 K with no low temperature saturation of $\rho$, the B samples showed no evidence of superconductivity and $\rho$ becomes saturated below ~ 10 K. Very high resistance ratios (>$400$) and large conductivities (> $10^6$ (Qcm)$^{-1}$) were found in the B samples at high pressure. These values exceed those previously observed in any other organic conductors including the (TMTSeF)$_2$X compounds. The resistivity of the best samples of (TMTTF)$_2$Br can be described by a simple power law over a wide temperature range (30-300 K) with an exponent close to 2. As the resistance ratio, ($RR$) indicative of crystal quality, falls the exponent drops to a value close to 1.5 for an $RR$ of ~ 100 and almost 1 for $RR \sim 10$.

These results suggest that $P_c$ for the sulphur compounds varies in proportion to the anion size as previously found for the selenium materials [2, 3]. Finally anion order-disorder transitions in the ClO$_4$ and SCN salts are quenched under pressure : a similar
result has previously been observed in the ReO₄ and BF₄ salts of TMTSeF [16, 23].

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References