LETTER TO THE EDITOR

Pressure dependence of the metal–insulator transitions in (TMTTF)$_2$SCN

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Abstract. The pressure-temperature phase diagram (for pressures up to 23 kbar) of bis-tetramethyltetraphthalocyanine thiocyanide, (TMTTF)$_2$SCN, has been determined through needle axis resistivity measurements. We find two distinct metal–insulator (MI) transitions. At low pressures there is an MT transition at high temperature $T_i(P)$ (near 160 K at 1 bar); $T_i$ falls with increasing pressure (d$T_i$/dP $-$2 K kbar$^{-1}$) and is abruptly suppressed for pressures above 15 kbar where a low-temperature ($T_{I1}$ $<$ 15 K) MI transition is stabilised. In a narrow pressure domain just below 15 kbar pronounced hysteretic behaviour is observed near $T_i$ and effects associated with both of these MI transitions are seen. By comparison with the behaviour of other members of the isostructural families (TMTTF)$_2$X and (TMTSeF)$_2$X we associate $T_i$ with an anion–disorder transition and $T_{I1}$ with a lattice distortion or spin density wave instability on the TMTTF stack.

These results confirm a strong correspondence between the properties of the (TMTTF)$_2$X and (TMTSeF)$_2$X families, in particular with respect to the behaviour of those materials containing non-centrosymmetric anions.

Interest has focused recently on the family of organic conductors (TMTSeF)$_2$X (where TMTSeF is the tetramethyltetraselenafullvalene molecule and X is some anion: for example ClO$_4$, PF$_6$ etc), several members of which have been shown to become superconducting above some critical pressure $P_c$ (Jerome et al 1980, Parkin et al 1981a, b: for other references see, in particular, Epstein and Conwell 1982).

At lower pressures metal–insulator transitions are found associated either with anion ordering (restricted to those compounds containing low-symmetry anions) (Pouget et al 1982, Parkin et al 1982d) or with the formation of a spin density wave (SDW) state (Mortensen et al 1981; for other references see Epstein and Conwell 1982). Replacement of the selenium atoms in TMTSeF with sulphur atoms gives the tetramethyltetrathiofulvalene (TMTTF) molecule, with which a second family of materials, (TMTTF)$_2$X, can be formed (Delhaes et al 1979, Coulon et al 1982a, b). Although the (TMTTF)$_2$X materials are isostructural with the (TMTSeF)$_2$X compounds, at ambient pressure the electrical properties of the two families are very different above their respective MI transition temperatures, with an ill-defined minimum in resistivity typically near 100–200 K for the (TMTTF)$_2$X family in contrast with the (TMTSeF)$_2$X compounds which show metallic behaviour. Recently however it has been shown that by applying pressure

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the electrical properties of the former compounds can be made to resemble those of the TMTSeF materials at ambient pressure; in particular at 25 kbar a highly conducting metallic state can be stabilised down to helium temperatures in (TMTTF)$_2$Br (Parkin et al 1982c). At ambient pressure MI transitions have been identified in several (TMTTF)$_2$X compounds through measurements other than electrical conductivity for temperatures where these materials are poor conductors (Delhaes et al 1979, Coulon et al 1982a). X-ray measurements by Pouget et al (1982) have shown an anion order–disorder transition in (TMTTF)$_2$ClO$_4$ near 75 K and a lattice distortion in (TMTTF)$_2$PF$_6$ below 10 K. AFMR (Parkin et al 1982f) and NMR (Creuzet et al 1982) experiments have recently identified a magnetic transition in (TMTTF)$_2$Br at 13.5 K.

Electrical conductivity measurements have unambiguously detected a particularly high-temperature metal–insulator phase transition near 160 K in (TMTTF)$_2$SCN at 1 bar (Coulon et al 1982a); very recently a transition into an antiferromagnetic state below ~7 K has been observed in the insulating phase of this material through EPR measurements (Coulon et al 1982b). In this Letter we present conductivity measurements as a function of pressure for this compound to establish its phase diagram.

The samples used in this study were prepared by the Montpellier group, and their synthesis and structure are described elsewhere (Delhaes et al 1979, Coulon et al 1982a, Galigne et al 1979). A low-frequency lock-in technique was used to measure the needle-axis conductivity of these samples: contacts were made with gold paint in the

![Figure 1. Pressure dependence of the a axis room temperature conductivity normalised with respect to the ambient pressure conductivity $\sigma(0)$.](image-url)
standard four-in-line configuration. Isopentane was used as the pressure transmitting fluid at all pressures in a two-stage Be–Cu pressure bomb.

Figure 1 gives the pressure dependence of the room temperature conductivity normalised to its ambient pressure value \(\sigma(P = 1 \text{ bar}) \sim 30 \Omega^{-1} \text{ cm}^{-1}\) as \(\sigma(dp)/(P = 1 \text{ bar}) \sim 45\% \text{ kbar}^{-1}\), a comparable value to that found in \((\text{TMTTF})_2\text{Br}\) at 1 bar, but considerably higher than rates of increase of \(\sigma\) found in the \(\text{TMTSeF}\) compounds which lie in the range 15–25\% \text{ kbar}^{-1} (Jerome et al 1980, Parkin et al 1982b).

At 1 bar there is a broad maximum in \(\sigma\) near 250 K with a well defined high-temperature MI transition at \(T_1 \sim 160\) K. Figures 2 and 3 give resistivity versus temperature curves for several pressures. At 12 kbar \(T_1\) is lowered to \(\sim 130\) K: a small hysteresis is observed at this transition. At 15 kbar a more complicated behaviour is found with a weak anomaly around 125 K and a transition to an insulating state at some lower temperature (near 20 K). There is considerable hysteresis in the resistivity with the weak anomaly being most pronounced on warming, and a strong dependence of the form of the resistivity curves on the rate of cooling through a temperature region between \(\sim 130\) K and \(\sim 100\) K. As shown in figure 2, by stabilising the temperature within this region, the resistivity slowly increases with time, thus giving rise to various cooling (and warming) curves for which no hysteresis is observed below this temperature region. Finally at higher pressures the anomalous high-temperature behaviour has completely disappeared and we observe only a sharp MI transition at around 15 K at 19 and 23 kbar. At these pressures the material is metallic with a conductivity maximum at low temperatures, in contrast with the ambient pressure result above \(T_1\) mentioned above. These

![Figure 2. Resistivity versus temperature curves at 12 and 15 kbar.](image-url)

- Cooling curve, 12 kbar;
- warming curve, 12 kbar;
- cooling curve, 15 kbar;
- warming curve, 15 kbar. The full lines correspond to cooling very slowly through the transition region near 100 K at 15 kbar (the arrow describes the evolution of the resistivity at a fixed temperature).
results are summarised in the phase diagram given in figure 4. The shaded region corresponds to the pressure region described above in which pronounced hysteresis in the resistivity is found.

Similar hysteretic behaviour to that seen near 15 kbar in \((\text{TMTTF})_2\text{SCN}\) has previously been observed in the TMTSeF family in the compounds \((\text{TMTSeF})_2\text{ReO}_4\) and \((\text{TMTSeF})_2\text{BF}_4\) at pressures of \(-10\) and \(-4\) kbar respectively and temperatures near 90 and 20 K (Parkin et al 1982a, d). In \((\text{TMTSeF})_2\text{ReO}_4\) a structural phase transition involving a doubling of the unit cell along three crystallographic axes has been observed by Pouget et al (1982) at 1 bar near 180 K, which they have suggested is associated with an ordering of the \(\text{ReO}_4\) anions, corresponding to the metal–insulator transition seen at this temperature. The hysteretic behaviour seen in the TMTSeF compounds under pressure has been interpreted as being associated with the formation of a metastable state at low temperatures in which the \(\text{ReO}_4\) and \(\text{BF}_4\) anions are frozen in some partially ordered state (Parkin et al 1982a, d). At higher pressures it is supposed that these anions are frozen in a completely disordered state at low temperature. The results presented here on \((\text{TMTTF})_2\text{SCN}\) clearly suggest, by analogy with \((\text{TMTSeF})_2\text{ReO}_4\), that the high-temperature MI transition seen below 15 kbar is associated with the \(\text{SCN}^-\) anions. (The prerequisite for such a transition is that the anion must at high temperatures
possess some positional disorder, and x-ray measurements show that this is the case (Galigne et al 1979): the linear SCN\(^-\) anions can each take up one of two orientations related by a centre of symmetry, in which the anion axis lies in a plane perpendicular to the conducting needle axis.) This hypothesis has subsequently been confirmed by a recent x-ray determination of a superlattice below \(T_{MI}\) (Coulon et al 1982a, b), although surprisingly these results show there is no doubling of the unit cell along the stacking axis. At first sight it would appear that an alternating arrangement of the SCN\(^-\) anions along the stacking axis (corresponding to a doubling of the cell along \(a\)) would minimise the Madelung energy of the anion array. However, this is clearly a complicated problem with other interactions, in particular the interaction of the anions with the organic stacks, playing a non-negligible role. More detailed measurements of the low-temperature structure might allow a quantitative understanding of the transition for this particularly simple anion.

In (TMTSeF\(_2\))\(_2\)ReO\(_4\) the driving mechanism of the anion order–disorder transition is not well understood. Whereas Parkin et al (1982d) have suggested that the order–disorder transition temperature is determined predominantly by the anion array, Jacobsen et al (1982) have proposed that for this compound the energy of the anion array is actually increased at the phase transition. The latter base their arguments on a transition involving only a simple reorientation of the anions at the MI transition, but Parkin et al have pointed out the possibility of a partial displacive character to the transition, which
would weaken the assumptions on which Jacobsen et al's model is based and which has since been observed at a similar anion ordering transition recently found in the isostructural compound (TMTTF)$_2$ReO$_4$ (Parkin et al 1982e).

Above 15 kbar, a low-temperature MI transition is seen near 15–20 K. As mentioned above, phase transitions are found in this temperature range in other (TMTTF)$_2$X compounds associated with a lattice distortion in the PF$_6$ salt (Pouget et al 1982) and a spin density wave transition in (TMTTF)$_2$Br (Creuzet et al 1982, Parkin et al 1982f). It seems clear by comparison with these and other (TMTTF)$_2$X materials that the low-temperature MI transition observed in (TMTTF)$_2$SCN at high pressures is associated with the intrinsic behaviour of the TMTTF stack. It is interesting to speculate on the nature of this transition as a function of pressure, both in this compound and in particular in (TMTTF)$_2$PF$_6$. As mentioned above, (TMTTF)$_2$Br has a magnetic transition at 1 bar which is suppressed with pressure and above 25 kbar no MI transition is observed: a similar phase diagram is found in the (TMTSeF)$_2$X compounds, in none of which has evidence of CDW distortions been found (Pouget et al 1982). The phase diagram of (TMTTF)$_2$PF$_6$ has been measured for pressures up to 32 kbar and by extrapolation a critical pressure of about 40 kbar is required to suppress completely the MI transition (Parkin et al 1982b), yet in this material the MI transition at 1 bar corresponds to a lattice distortion. Perhaps the nature of this transition changes with pressure and becomes magnetic at the phase boundary near $P_c$. It may be that in some (TMTTF)$_2$X compound pressure might cause a change in the low-temperature state from an anion ordered state at low pressure through a lattice stack instability, a magnetic stack instability and finally a superconducting state above some $P_c$. There thus exists the possibility of a more complicated phase diagram for the (TMTTF)$_2$X family. Finally note that, as mentioned above, Coulon et al (1982b) have recently identified an antiferromagnetic phase near ~7 K at ambient pressure in (TMTTF)$_2$SCN, well below the high-temperature metal–insulator transition, $T_1$, which further complicates the phase diagram.

We have shown that the high-temperature metal–insulator transition in (TMTTF)$_2$SCN at 1 bar is suppressed by the application of a moderate pressure giving rise to a low-temperature MI transition at pressures above 15 kbar. Large hysteretic anomalies are observed in the resistivity in a narrow intermediate pressure range, similar to those seen in (TMTSeF)$_2$ReO$_4$. We propose that there is a crossover from an anion order–disorder transition at low pressures to an instability of the TMTTF stack itself at higher pressures. The simple linear shape of the SCN anion makes this an ideal material for further detailed studies of the anion ordering at low pressures.

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