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Substitution of TMTSeF with TMTTF in (TMTSeF)$_2$ClO$_4$: high pressure studies

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Résumé. — On étudie la résistivité électrique des alliages [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$ à pression élevée (jusqu'à 18 kbar). En substituant TMTSeF par TMTTF, on supprime l'état supraconducteur de (TMTSeF)$_2$ClO$_4$ et on observe, à pression ambiante, une transition métal-isolant (M-I) à basse température. Celle-ci est supprimée au-delà d'une pression critique $P_c$ et un état métallique est stabilisé jusqu'aux plus basses températures atteintes lors de notre étude. Les diagrammes de phase des différents alliages sont similaires; cependant $P_c$ augmente avec la concentration en TMTTF. Enfin, nous n'avons pas observé l'apparition d'un état supraconducteur dans le régime métallique ($P > P_c$).

Abstract. — [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$ alloys have been studied under pressure for pressures up to 18 kbar through resistivity measurements. On substitution of TMTSeF in the superconducting compound (TMTSeF)$_2$ClO$_4$ with TMTTF a low temperature metal-insulator (M-I) transition is found at ambient pressure; above some critical pressure, $P_c$, the M-I transition is suppressed giving rise to a metallic state to the lowest temperatures considered in this study. The phase diagrams of the various alloys are of the same form although $P_c$ increases with increasing TMTTF concentration. Superconductivity was not observed in any of these materials in the metallic high pressure regime.

1. Introduction. — The discovery of superconductivity [1-3] and antiferromagnetism [4-6] in the (TMTSeF)$_2$X compounds caused extensive studies to be made on these materials. The isostructural sulphur compounds (TMTTF)$_2$X were already known, although poorly characterized [7]. Improved understanding of their properties has been gained in subsequent work at ambient pressure [8-9] and through measurements of their pressure-temperature phase diagrams [10-12]. These latter studies have shown that at sufficiently high pressures the (TMTTF)$_2$X compounds behave like the (TMTSeF)$_2$X materials even though their ambient pressure electrical properties are somewhat different and that the pressure-temperature phase diagrams of these families are of the same form [11]. In particular a highly conducting metallic phase is stabilized in (TMTTF)$_2$Br at 25 kbar with the possibility of a superconducting transition near 3.5 K [10]. Recently it has been shown that at ambient pressure (TMTTF)$_2$Br [13-14] and (TMTTF)$_2$SCN [15] have antiferromagnetic ground states; in contrast a structural distortion has been observed in the PF$_6$ salt [9].

The interplay between magnetism and superconductivity in the (TMTSeF)$_2$X salts has long been an important question particularly at pressures close to the critical pressure, $P_c$, above which these materials become superconducting. Early measurements showed for pressures near $P_c$ resistance upturns with decreasing temperature just above the superconducting transition temperature, $T_c$, in several salts [2, 16] perhaps of magnetic character. The most extensive studies have been made on the ClO$_4$ salt for which $P_c$ is close to 1 bar [2, 3]. A magnetic state has clearly been observed in this compound above $T_c$ with the observation of antiferromagnetic resonances and resurrection of the ESR signal at high microwave power [17],
although more recent studies show the presence of this state to be dependent on the rate of cooling at low temperatures [18]. A useful method for further examining the competition between superconductivity, magnetism, and other lattice instabilities is through substitution of TMTSeF with TMTTF in (TMTSeF)$_2$ClO$_4$ to form alloys of chemical formula [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$. Note that (TMTTF)$_2$ClO$_4$ undergoes an anion ordering transition near 70 K at 1 bar [8, 9] which is suppressed under moderate pressure (~ 10 kbar) giving way to a low temperature M-I transition (below ~ 20 K) presumed to be associated with some stack instability [10, 12].

The ambient pressure behaviour of the alloys considered here has been described in a previous paper (paper I) [19]. These results are briefly summarized in the following section. In section 3 we present resistance measurements on the same alloys as a function of pressure, for pressures up to 18 kbar. Some discussion of these results is given at the end of the paper.

2. Summary of ambient pressure results. — Characterization of the alloys used in this study is described in I. The chemical composition of the alloys is of the form [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$ consistent with the 2 : 1 stoichiometry of the pure TMTSeF and TMTTF salts suggesting the alloys follow the same crystal structure, although no detailed X-ray measurements have been made. Preliminary X-ray data show that the lattice parameters of the alloys are intermediate between those of the undoped TMTSeF and TMTTF salts, suggesting that the doped samples are true homogeneous alloys without significant domain structure (D. Chasseau, C. Hauw and J. Gaultier, private communication). The composition of the various alloys is given in table I together with a summary of their behaviour at 1 bar.

For the alloys weakly doped with TMTTF, with $x = 0.2\%$ and $0.5\%$, broad ill-defined drops in resistance of approximately $60\%$ and $15\%$ are observed near 800 mK and 200 mK respectively, suggestive of partial superconducting phase transitions, perhaps related to inhomogeneities in these systems.

Table I. — Summary of ambient pressure data on various [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$ alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$ (%)</th>
<th>$\sigma_{RT}$ (Ω cm)$^{-1}$</th>
<th>$g(RT)$</th>
<th>$T_M$ (mK)</th>
<th>$T_{M-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2 ± 0.1</td>
<td>550</td>
<td>1.990</td>
<td>800</td>
<td>8$^M$</td>
</tr>
<tr>
<td>2</td>
<td>0.5 ± 0.1</td>
<td>500</td>
<td>1.990</td>
<td>200</td>
<td>8$^M$</td>
</tr>
<tr>
<td>3</td>
<td>2.0 ± 0.3</td>
<td>450</td>
<td>1.990</td>
<td>—</td>
<td>11$^M$</td>
</tr>
<tr>
<td>4</td>
<td>4.0 ± 0.7</td>
<td>340</td>
<td>2.002</td>
<td>—</td>
<td>8$^M$</td>
</tr>
<tr>
<td>5</td>
<td>6.5 ± 0.5</td>
<td>300</td>
<td>2.002</td>
<td>—</td>
<td>13$^M$</td>
</tr>
<tr>
<td>6</td>
<td>30.0 ± 0.5</td>
<td>40</td>
<td>2.002</td>
<td>—</td>
<td>13$^M$</td>
</tr>
</tbody>
</table>

M = magnetic phase transition; N = Non-magnetic (see text); RT = room temperature; $T_{M-1}$ = metal-insulator transition temperature; $g(RT)$ = corresponds to room temperature $g$ value for applied magnetic field along stacking axis. Data from paper I [19].

3. Experimental. — The experimental arrangements are the same as those described in [2]. Needle axis resistivity measurements were made with gold paint contacts using the standard 4-probe method. The crystals were fragile with poor morphology. No absolute measurements of resistivity were attempted, so only normalized resistivities are given.
Figure 1 gives resistivity versus temperature curves at different pressures for the $x = 2\%$ alloy (sample 3). With increasing pressure the M-I transition seen clearly at 4 kbar (and at 1 bar, as shown in 1) is gradually weakened and finally suppressed above 10 kbar. In figure 2a the low temperature portion of these curves is shown on a $\ln(\rho)$ versus $1/T$ plot. The inflexion points for the various curves give an estimate of the M-I transition temperatures, so that the phase diagram can be drawn as shown in figure 2b. $P_c$ is thus about 10 kbar. Note that above 10 kbar the resistance saturates at low temperatures: at 10 kbar saturation of the resistance was found to 200 mK with no sign of superconductivity (M. Ribault, private communication).

Similar phase diagrams were found for the alloys with $x \sim 6.5\%$ and 30\%. Results for the latter are shown in figure 3. The curve at 12 kbar is similar to that at 1 bar with a broad minimum in $\rho$ at high temperature. Metallic behaviour is found at 18 kbar indicating a $P_c$ of about 17 kbar. Figure 4 shows $P_c$ for several alloys plotted as a function of $x$. Also included in the figure is $P_c$ for pure (TMTTF)$_2$ClO$_4$ obtained in previous measurements by Parkin et al. [10, 12].

4. Discussion. — Stack instabilities (SDW or CDW), which must be distinguished from anion order-disorder transitions which occur at much higher temperatures) are found at similar temperatures ($\sim 20$ K) in both the (TMTSeF)$_2X$ and (TMTTF)$_2X$ salts, even though the electrical conductivities of these materials are very different [21, 8]. In the same way the $\left[(\text{TMTSeF})_{1-x} (\text{TMTTF})_x\right]_2$ClO$_4$ alloys which display a wide range of conductivities exhibit M-I transitions at 1 bar at very similar temperatures (see table 1; $T_{M-I} \sim 10$ K). In this point is discussed in more detail, where it is suggested that the dispersion in $\sigma$ values and the weak metallic behaviour found in the more heavily doped TMTTF alloys may be associated with electron localization through the growth of a 4 $k_F$ CDW on the organic stacks as described in a recent theory of Emery et al. [22].

As mentioned above in addition to stack instabilities, for salts of TMTTF and TMTSeF containing non-centrosymmetric anions there is the possibility of anion ordering transitions which can give rise to either metal-insulator transitions or weak resistivity anomalies. There is an anion order-disorder transition in (TMTTF)$_2$ClO$_4$ near 70 K [8, 9] where the CI0$_4$ anions order on a 2 x 2 x 2 array. This transition is suppressed with pressure [12] although the possibility of an anion ordering with a different structure under pressure cannot be ruled out, in view of recent studies on (TMTSeF)$_2$ClO$_4$. Careful measurements on this compound have revealed a weak knee in the resistance versus temperature curve near 24 K [23] associated with an anion ordering [24] for which there is no change in the $a$-axis periodicity. NMR studies on (TMTSeF)$_2$ClO$_4$ suggest the anion ordering is absent under pressure [18]. The possibility of anion ordering in the alloys studied here cannot be ruled out by these resistivity measurements, although no indications of anion ordering through anomalies in resistivity were found.

The nature of the low temperature insulating phases in the $\left[(\text{TMTSeF})_{1-x} (\text{TMTTF})_x\right]_2$ClO$_4$ alloys has been examined in I through EPR studies; it appears that the phase has magnetic character in the alloys lightly doped with TMTTF but is non-magnetic.
in the alloys rich in TMTTF. It is not unlikely that
the non-magnetic M-I transitions in the TMTTF rich
alloys at 1 bar develop some magnetic character
under pressure as has been postulated for the pure
(TMTTF)$_2$X compounds which are non-magnetic
at ambient pressure [11, 12]. The pressure measure-
ments presented above cannot address this question,
since both SDW and CDW transitions affect simi-
larly the resistivity of these materials.

It is interesting to compare the effect of irradiation
damage on the properties of the (TMTSeF)$_2$X salts
with that of TMTTF doping. Bouffard et al. [25]
have shown that the M-I transition in (TMTSeF)$_2$PF$_6$
is smeared out and the temperature depressed on
irradiation. ($T_{M\text{-}1}$ falls by about 40 % for a molecular
defect concentration of about $6 \times 10^{-4}$ at 4 and
6.5 kbar). Similar results have been obtained by
Choi et al. [26]. In contrast doping with TMTTF
causes an increase in $T_{M\text{-}1}$ of about 40 % for a 3 %
dopant concentration with smaller increases in $T_{M\text{-}1}$
observed for dopant concentrations as low as
0.5 % [20]. Mortensen et al. [20] discuss in some
detail possible explanations for the increase in $T_{M\text{-}1}$
and suggest that they arise from a sharp decrease
in bandwidth. The contrasting behaviour observed
on irradiation and alloying clearly suggests that the
disorder introduced by TMTTF doping is of a very
different character from that associated with radiation
damage which introduces breaks in the organic
chains giving rise to magnetic defects [25]. The absence
of a Curie tail in EPR measurements on the
[(TMTSeF)$_{1-x}$(TMTTF)$_x$)$_2$ClO$_4$ alloys considered
here indicates no spin defects are introduced by
TMTTF alloying. A similar result is found for
[(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$PF$_6$ alloys [20]. The different behaviours of irradiated an doped
(TMTSeF)$_2$X salts may therefore be attributed, at
least in part, to the magnetic and non-magnetic cha-
racter of the defects respectively.

Consistent with the above discussion is the mono-
tonic variation of $P_c$ with $x$ (see Fig. 4), indicating
that the alloys become increasingly like the undoped
(TMTTF)$_2$ClO$_4$ compound as the TMTTF concen-
tration is increased. This is also seen, as previously
mentioned through the gradual reduction in $\sigma$ as
$x$ increases to a value corresponding to that of the
undoped TMTTF salt and through changes in $g$
factors. Thus various measurements indicate that the
properties of doped (TMTSeF)$_2$ClO$_4$ are intermediate
between those of the pure TMTSeF and TMTTF
salts suggesting these materials are true alloys.

The data shown in figure 4 suggest that $P_c$ increases
more rapidly at low values of $x$ with perhaps a cross-
over to a slower increase in $P_c$ for $x \geq 2 \%$, although
the data is limited. One might describe this behaviour
as resulting from the competition between two types of
instabilities, affected differently by dopant. One possi-
bility is the competition between superconductivity
at low $x$ to other stack instabilities at higher values
of $x$.

5. Conclusion. — The pressure temperature phase
diagrams of various [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$
alloys have been determined through resistivity
measurements. Pressure suppresses insulating states
observed at 1 bar at low temperatures restoring
metallic states above some critical pressure, $P_c$
which increases monotonically with increasing
TMTTF concentration, to that previously found in
undoped (TMTTF)$_2$ClO$_4$ [12]. The behaviour of
various properties and the very different effects of
radiation damage on other (TMTSeF)$_2$X salts sug-
gests that these materials are true alloys with few
spin defects. The absence of superconductivity in
these compounds may therefore reflect the intrinsic
behaviour of the TMTTF salt, or may simply be
associated with the limited number of defects. A
recent theory suggests that defects by limiting the
possible coherence lengths may more easily suppress
long range order in the superconducting state than
for other electronic instabilities [27].

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Fig. 4. — Variation of the critical pressure, $P_c$
(defined in the text) with TMTTF concentration ($x$)
for [(TMTSeF)$_{1-x}$(TMTTF)$_x$]$_2$ClO$_4$ alloys.
References