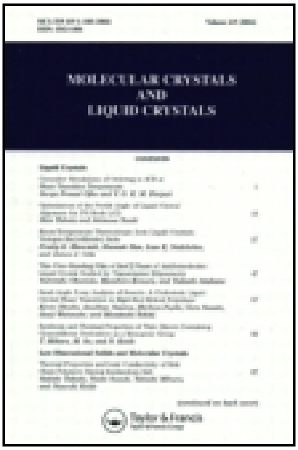

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Synthesis and Properties of Trimethyl-TSF Containing Alloys of the $TMTSF_2$, Family

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SYNTHESIS AND PROPERTIES OF TRIMETHYL-TSF CONTAINING ALLOYS OF THE $TMTSF_2$ FAMILY

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Abstract Cation-radical salts of the general formula $(TriMTSF_zTMTSF_{1-z})_2$ (X = PF_6, ClO_4, z ranging from 0 to 0.3) were isostructural. The incorporation of TriMTSF resulted only in minor changes in the transport properties, but the superconducting ground state was completely suppressed.

INTRODUCTION

The discovery of a superconducting ground state in the $TMTSF_2X$ compounds has generated extensive interest in this class of materials. Along with a vast number of investigations on the pristine materials a few studies of alloys have been undertaken. These alloys were made admixing either sulfur containing analogues of TMTSF or different monovalent anions.[1-6]

In order to study the effect of a very weak perturbation in the donor stack we have prepared alloys containing the new donor trimethyltetraselenafulvalene (TriMTSF). This compound only differs from TMTSF by having a hydrogen atom in place of one of the (four) methyl groups. In contrast to the various sulfur containing dopants the ionisation potential of TriMTSF is expected to be very close to that of TMTSF.

In this work TriMTSF doped cation-radical salts of both the PF_6 and ClO_4 series have been studied.

SYNTHESIS AND CRYSTAL GROWTH

TriMTSF was synthesized by mixed triethylphosphite coupling of mono- and dimethyl-2-selenoxo-1,3-diselenole[7] in refluxing benzene. The resulting mixture of di-, tri-, and tetramethyl TSF was fractionated by means of repeated recrystallization and gradient sublimation onto teflon (2 times, 0.1 torr He, 120°C).[8] The TMTSF used was gradient sublimed twice.

The cation-radical salts were grown from THF solutions of TriMTSF and TMTSF in the desired molar ratios. The counter ions (ClO_4^- and PF_6^-) were added as their tetrahexyl ammonium salts (0.1 M).

RESULTS AND DISCUSSION

The electrochemical oxidation potentials and visible absorption spectra of the neutral donors were measured. As expected there was no significant difference between the first oxidation potentials of TriMTSF and TMTSF. In the absorption spectra there is a lone blue shift going from TMTSF to TriMTSF. This is in accordance with the removal of one electron donating methyl group.

The electrochemically prepared alloy crystals containing TriMTSF concentrations up to 30% had the same morphology as the pristine crystals although there was an increased tendency to twinning in the samples with the highest TriMTSF content.

Single crystal X-ray diffraction clearly demonstrated that the alloy samples were isostructural with the corresponding pure TMTSF compounds.

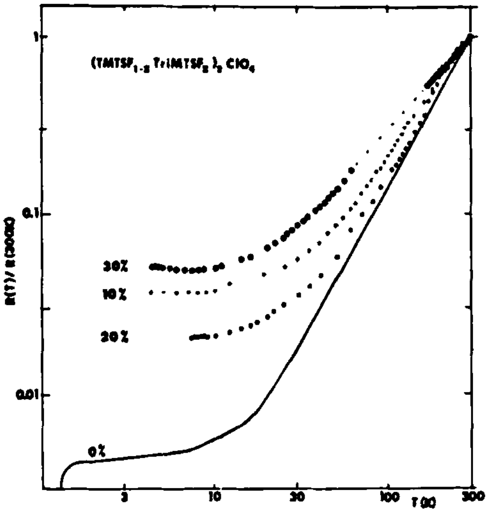

FIGURE 1 DC-conductivity of $(TMTSF_{1-z}TriMTSF_z)_2ClO_4$

The ClO_4-series was studied in more detail. The unit cell volumes were determined with high accuracy as a function of molar ratio. A small but significant contraction of the unit cell was observed upon doping.

Transport Properties

DC-conductivities were measured using the conventional 4-probe technique. In the samples of high TriMTSF concentrations resistivity jumps occured frequently on cooling due to microcracking. The effects arising from these microcracks were substracted in the data given in figs 1 and 2.

ClO_4-series

The DC-conductivity of the alloy samples of $(TriMTSF_x-TMTSF_{1-x})_2ClO_4$ exhibits strong deviation from T^{-2} dependency at higher temperatures than the pristine material does. The conductivity enhancements from RT to low temperature are thus lower. The 30% doped sample exhibits a shallow conductivity maximum around 10K. However, the overall picture is not dramatically different from that of the pure material, and it is quite different from the behaviour of $TMTSF_2ClO_4$ doped with TMTTF. In the latter case TMTTF concentrations as low as 0.5% give a substantial rise in resistivity at temperatures below 40K.[3]

In order to see if the superconducting ground state could survive doping a single crystal containing 10% TriMTSF was subjected to DC-Meissner effect measurements. No Meissner effect was observed, and thus no bulk superconducting state appeared. (T > 0.1K, P 0-5 kbar).

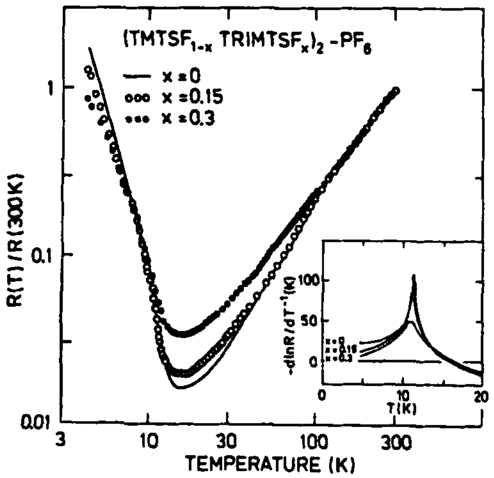

FIGURE 2 DC-conductivity of $(TMTSF_{1-z}TriMTSF_z)_2PF_6$

PF_6-Series

The DC-conductivity data are given in fig. 2. As in the

ClO_4 series no dramatic effects were observed upon doping. Most remarkable is that even in the samples with high TriMTSF concentrations the metal-insulator transition temperature is virtually unchanged. The transition in $(TriMTSF_{0.3}TMTSF_{0.7})_2PF_6$ is broadened to some extent (see inserted fig.) indicating the presence of some disorder.

In conclusion the conductivity data for the alloyed samples in both the PF_6 and ClO_4 series agree with the expected behaviour, namely that the doping with TriMTSF gives rise to very little perturbation of the periodic potential since the SDW state is only sligthly affected. On the other hand the Meissner effect measurements again emphasize the sensitivity of the superconducting state to non magnetic defects.

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