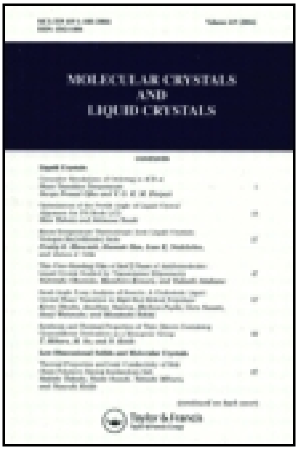

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The Role of TMTSF Synthesis on the Superconducting Properties of $(TMTSF)_2.ClO_4$

A. Moradpour [a], K. Bechgaard [a], M. Barrie [a], C. Lenoir [a], K. Murata [a], R. C. Lacoe [a], M. Ribault [a] & D. Jerome [a]

[a] Laboratoire de Physique des Solides (associé C.N.P.S) Universite Paris-Sud, F-91405, Orsay, France

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THE ROLE OF TMTSF SYNTHESIS ON THE SUPERCONDUCTING PROPERTIES OF $(TMTSF)_2ClO_4$

A. MORADPOUR, K. BECHGAARD, M. BARRIE, C. LENOIR, K. MURATA, R. C. LACOE, M. RIBAULT, D. JEROME.
Laboratoire de Physique des Solides (associé C.N.R.S) Universite Paris-Sud, F-91405 Orsay, France

Abstract The superconducting properties of $(TMTSF)_2ClO_4$ were found to be highly dependent on the origin of the TMTSF obtained by different synthetic procedures. These differences were assigned to the presence of low amounts of sulfur (up to 0.3%), introduced , in place of selenium, in the course of the synthesis avoiding the use of CSe_2. The latter method was improved so the superconducting transition of $(TMTSF)_2ClO_4$ therefrom was found to be the same as for samples prepared with TMTSF synthesized from CSe_2.

INTRODUCTION

Since the first synthesis of tetramethyl tetraselenafulvalene (TMTSF) from CSe_2[1], various preparations of this compound have been reported[2]. Although the latter procedures offer the advantage of avoiding the use of such tediously obtainable (CSe_2) or highly expensive or toxic intermediates (H_2Se), the ultimate interest of these synthesis lies, beside an easier access to TMTSF, on the solid-state properties of the material derived therefrom. We wish to report here that significant differences are found in the superconducting properties of $(TMTSF)_2ClO_4$ which depend on the method and/or origin of the TMTSF. We have also improved the procedure based on the use of N,N-dimethylphosgenimminium chloride[2] and report that TMTSF, prepared this way, when converted to the perchlorate salt recovers the usual superconducting behaviour of samples coming from the CSe_2 preparations.

RESULTS AND DISCUSSION

All of the $(TMTSF)_2ClO_4$ crystals here were obtained by constant current electrocrystallizations in THF with $nBu_4N^+ClO_4^-$ as electrolyte, after various TMTSF have been recrystallized twice and gradient sublimed before use. The conductivity was measured using a dilution refrigerator by the usual a-c four probe method. The sample resistance was measured simultaneously for samples a and c during the first run, c and d during the second (see table 1)

TABLE 1 Origin and purity of $(TMTSF)_2ClO_4$ samples

Sample	Origin	Sulfur content as determined by microanalysis(%)
a	CSe_2 (standard sample for this work)	not detected
b	prepared as described in ref 2	0.3
c	prepared from purified N,N-dimethylphosgenimminium chloride (new synthetic procedure)	not detected
d	commercial TMTSF (Strem Co.)	0.1

The time of cooling from 30 K to 4.2 K was controlled to be 2 h., which corresponds to the relaxed-state[3] and which was sufficient for verifying the superconducting properties. The resistance upturn at liquid helium temperature and a broad superconducting transition below 0.9 K were observed (figure 1) in sample b (prepared from N,N-dimethylphosgenimminium chloride[2] as received

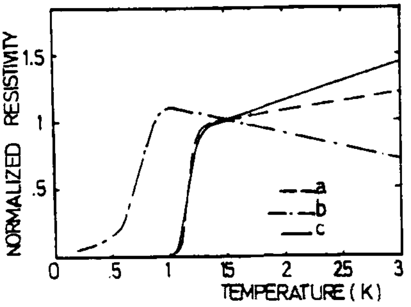

FIGURE 1 Normalized resistivity vs. temperature for samples a-c (table 1)

from Fluka.),which is in contrast to that of the standard sample a from CSe_2. The results with sample b are similar to the alloys works on $((TMTSF)_{1-x}(TMTTF)_x)_2ClO_4$[4] in which the broad superconducting transition appeared below SDW (spin density wave) temperature in the concentrations $x < 0.5\%$. Similar properties have been seen in other alloys systems, for example $(TMTSF)_2(ClO_4)_{1-x}(ReO_4)_x$[5] with low concentration of x . The importance of the impurity in the crystal prompted us to examine the purity of the corresponding samples. In fact sample b contains low amounts of sulfur, easily detected by mass spectrometry and determined by microanalysis to be 0.3% . Almost the same amount is found in the starting phosgenimminium salt,while no sulfur was detected by either method in sample a . These low amounts of sulfur, in place of selenium can be rationnalized assuming the presence of traces of N,N dimethylcarbamoylchloride, an intermediate in the preparation of phosgenimminium chloride[6] . In fact, the former compound — presently an impurity — has been considered[7] and used[8] for the synthesis of mixed thiaselenafulvalene . Removal of the sulfur was then required . This is possible by repeatedly subliming the starting N,N-di methylphosgenimminium chloride (6 successive runs at 100°C, 0.1 torr) . Sample c with no residual sulfur is obtained and the expected superconducting transition (figure 1, curve c vs. a) is recovered this way. By the time this study was made, TMTSF became commercially available (Strem Co.), so we have also examined the perchlorate salt from this origin (table 1,sample d and figure 2). A small but significant difference is observed

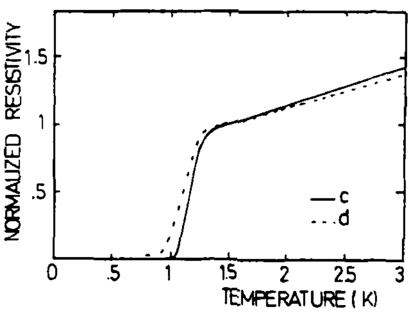

FIGURE 2 Normalized resistivity vs. temperature for samples c,d (table1)

between the latter and the sulfurless sample c (figure 2 , curve c and d). This difference is certainly related to 0.1% sulfur we have found in sample d .

In summary , these results show that it is possible to synthesize TMTSF by the phosgenimminium route with a purity comparable to samples obtained by the more tedious CSe_2 synthesis. These results obviously also illustrate the already well established high sensitivity of the organic superconductivity to any defect or disorder in these solids.

REFERENCES

1. I. Johannsen, K. Lerstrup, L. Henriksen, K. Bechgaard, J. Chem. Soc., Chem. Commun. (1984),89.
2. A. Moradpour, V. Peyrussan, I. Johannsen, K. Bechgaard, J. Org. Chem.,48, 388, (1983) and references cited therein .
3. T. Takahashi, D. Jerome, K. Bechgaard, J. Phys. Lett., 43, L-565 (1982) .
4. C. Coulon, P. Delhaes, J. Amiell, J. P. Manceau, J. M. Fabre, L. Giral , J. Phys. 43, 1721, (1982) .
5. S. Tomic, D. Jerome, D. Mailly, M. Ribault, K. Bechgaard J. Phys. C3 , C 3-1075, (1983).
6. H. G. Viehe, Z. Janousek, Angew. Chem. Inter. Ed. 12, 806, (1973) .
7. F. Wudl, K. Andres, D. B. Mc Whan, G. A. Thomas, D. Nalewajek, W. H. Walsh Jr., L. W. Rupp Jr., F. J. Di Salvo, J. U. Waszczak, A. L. Stevens, Chem. Script. 17, 19, (1981)
8. F. Wudl, W. M. Walsh Jr., J. J. Hauser, J. Di Salvo , D. Nalewajek, L. W. Rupp, J. U. Waszczak, R. J. Felder, T. O. Poehler, P. M. Chaikin, R. C. Lacoe, J. Chem. Phys. 79, 1004, (1983).