Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

$(BEDTTTF)_2SbF_6$ and $(BEDTTTF)_2AsF_6$: A Metal-Insulator Transition Close to Room Temperature

R. Laversanne [a] , J. Amiell [a] , P. Delhaes [a] , D. Chasseau [b] & C. Hauw [b]
[a] Centre de Recherche Paul Pascal, Domaine Universitaire, 33405, TALENCE cedex, France
[b] Laboratoire de Cristallographie, Universite de BORDEAUX 1, 150 cours de la Libération, 33405, TALENCE cedex, France
Version of record first published: 17 Oct 2011.

To cite this article: R. Laversanne , J. Amiell , P. Delhaes , D. Chasseau & C. Hauw (1985): $(BEDTTTF)_2SbF_6$ and $(BEDTTTF)_2AsF_6$: A Metal-Insulator Transition Close to Room Temperature, Molecular Crystals and Liquid Crystals, 119:1, 405-408

To link to this article: http://dx.doi.org/10.1080/00268948508075191

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 405-408
0026-8941/85/1194-0405/$10.00/0

Printed in the United States of America

$(BEDTTTF)_2SbF_6$ AND $(BEDTTTF)_2AsF_6$: A METAL-INSULATOR TRANSITION CLOSE TO ROOM TEMPERATURE.

R. LAVERSANNE, J. AMIELL, P. DELHAES
Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 TALENCE cedex FRANCE
D. CHASSEAU, C. HAUW
Laboratoire de Cristallographie, Université de BORDEAUX 1, 150 cours de la Libération, 33405 TALENCE cedex FRANCE

ABSTRACT $(BEDTTTF)_2SbF_6$ and $(BEDTTTF)_2AsF_6$ show a metal-insulator transition close to room temperature. We present the D.C. electrical and E.P.R. measurements together with the structural investigations.

The bis-(ethylenedithiolo)tetrathiafulvalene (BEDTTTF) series has revived the studies of the organic conductors, with the discovery of the first superconductor containing only sulfur $(BEDTTTF)_2ReO_4$ [1] and more recently with the $(BEDTTTF)_2I_3$ salts found superconductive above 1.5K [2].

One of the characteristic features of these compounds is their wide range of stoichiometries and structures, contrasting with the 2:1 stoichiometry and triclinic ($P\bar{1}$) arrangement usually found in the TMTTF or TMTSF series [3,4].

In this paper we present the properties of the SbF_6 and AsF_6 salts of BEDTTTF. Both these compounds show a metal-insulator transition close to room temperature, as already found in $\beta(BEDTTTF)_2PF_6$ [5].

STRUCTURE OF $(BEDTTTF)_2SbF_6$

$(BEDTTTF)_2SbF_6$ crystallizes in the monoclinic system with $C_{2/c}$ space group. The unit cell parameters are : a =37.64 Å, b =6.70 Å, c =14.93 Å, β =117.19°. In order to compare this salt with the other BEDTTTF salts and in particular with $\beta(BEDTTTF)_2PF_6$, we described the structure in the unusual space group $I_{2/c}$. In this case the monoclinic unit cell parameters become : a =33.56 Å, b =6.70 Å, c =14.93 Å, β =93.98°.

The shortest S-F distance indicated with the dashed line in figure 1 is shorter than the sum of the Van der Waals radii of the two atoms (3.22 Å). The BEDTTTF molecule is not planar.

The intrastack and interstack overlaps are compared on figure 2. A characteristic feature of this structure is that the shortest S-S contacts are found between neighbouring chains.

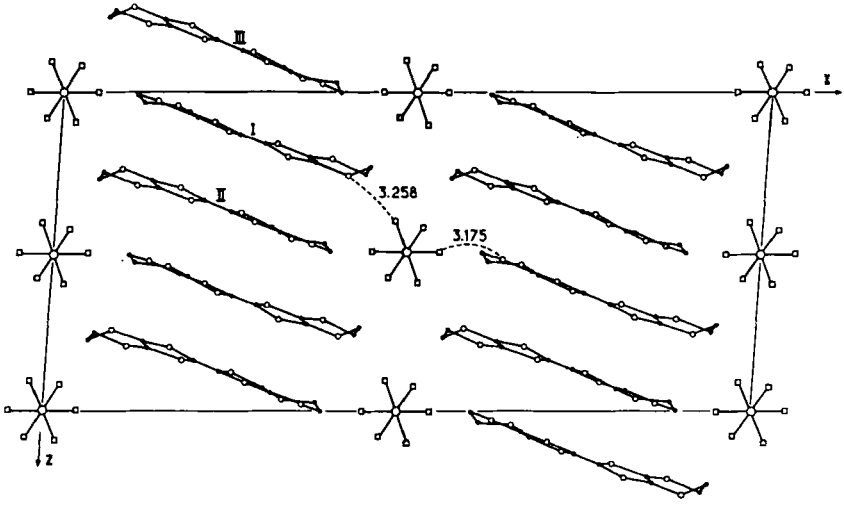

FIGURE 1 Projection of the structure in the ac plane

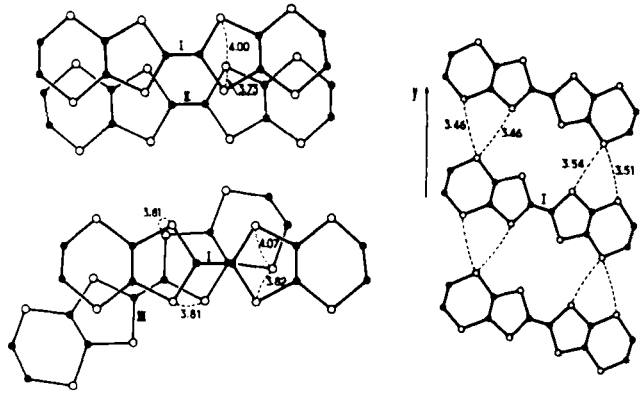

FIGURE 2 Schematic view of the different overlaps (number I,II,III refer to figure 1)

D.C. ELECTRICAL CONDUCTIVITY

The room temperature electrical conductivity is higher along the b axis (side by side axis) than along the stacking axis (c) :

σ_b =4-6, σ_c =0.2 $\Omega^{-1}cm^{-1}$ for the SbF_6 salt and σ_b =2-3, σ_c =0.1-0.2 $\Omega^{-1}cm^{-1}$ for the AsF_6 salt. This is in agreement with the relative strength of the overlap between the neighbouring molecules.

The temperature dependence of the resistivity shows a drastic electronic localization at 273K and 264K for the SbF_6 and AsF_6 salts respectively (fig. 3). This anomaly which may be interpreted as a phase transition is clearly evidenced by the maximum of the logarithm derivative of the resistivity (insert of figure 3)

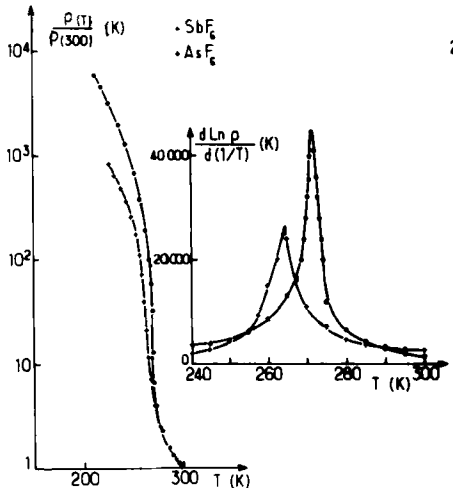

FIGURE 3 Temperature dependence of the normalized resistivity along the b axis (and its derivative in insert)

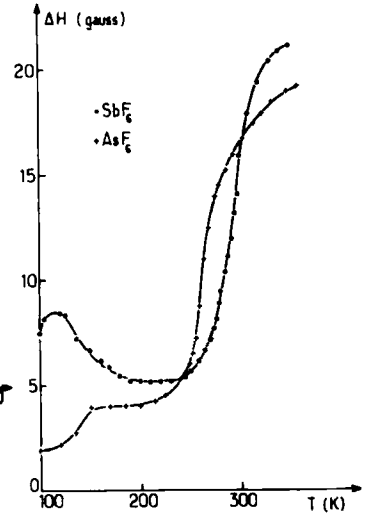

FIGURE 4 Temperature dependence of the E.P.R. linewidth, in the direction of the intermediate value of the g-factor

E.P.R. MEASUREMENTS

The room temperature value of the E.P.R. linewidth is around 20 G for the two salts, in agreement with the results already obtained for $(BEDTTTF)_2ReO_4$[6]. This value significantly larger than the results obtained for the TMTTF salts evidences the enhance of the 2D character of these compounds.

When cooling the linewidth and the intensity of the E.P.R. signal decrease strongly around the temperature of the electrical anomaly (fig. 4). The spin susceptibility χ_p at 100K is less than 1% of the room temperature value. These results indicate that a gap is open in the magnetic excitations at low temperature. In the range 100K-200K, the fit of χ_p to the expression

$\chi_p = (C/T)e^{-\Delta/T}$ gives an estimate of the activation energy : $\Delta \simeq 1000K$.

CONCLUSION

These results show clearly the occurence of a phase transition close to room temperature in both the SbF_6 and AsF_6 BEDTTTF salts. One can remark that such a result has been found on the βPF_6 salt by Kobayashi et al[5], but with a transition temperature (297K) slightly higher than in our salts.

The nature of the transition is not clear. High temperature metal-insulator transitions are often interpreted as order-disorder transitions[7]. However the anions are usually ordered at room temperature in the BEDTTTF series. $(BEDTTTF)_2ReO_4$ which shows at ambient pressure a M-I phase transition presenting striking similarities with that observed in our samples has been extensively studied. The ReO_4 anions are ordered in the metallic phase and the nature of the M-I phase transition is still unknown. Thus the localization occuring for the $(BEDTTTF)_2MF_6$ salts may have a completely new origin. To deepen this point X-ray investigations at low temperature are in progress.

We gratefully acknowledge Dr. C. Coulon for fruitfull discussions

REFERENCES

1. S.S.P. PARKIN, E.M. ENGLER, R.R. SHUMAKER, R. LAGNIER, V.Y. LEE, J.C. SCOTT and RL. GREENE Phys. Rev. Lett. 50,220 (1983)
2. E.B. IAGOUBSKII, I.F. CHEGOLEV, V.H. LAOUKHIN, P.A. KONONOVITCH, M.V. KARTSOVNIK, A.V. ZVAROUIKINA and L.I. BOURAVOV, Pizma V Zh. Eksp. Teor. Fiz. S.S.S.R. 39,12 (1984)
3. K. BECHGAARD, K. CARNEIRO, O. EG, M. OLSEN, F.B. RASMUSSEN, C. JACOBSEN and G. RINDORF, Mol. Cryst. Liq. Cryst. 79,271 (1982)
4. S.S.P. PARKIN, These Proceedings
5. H. KOBAYASHI, T. MORI, R. KATO, A. KOBAYASHI, Y. SASAKI, G. SAITO, and H. INOKUCHI, Chem. Lett. 4,581 (1983)
6. S.S.P PARKIN, E.M. ENGLER, R.R. SHUMAKER, R. LAGIER, V.Y. LEE, J. VOIRON, K. CARNEIRO, J.C. SCOTT and R.L. GREENE, J. Physique C3,791 (1983)
7. For a recent review on the O-D transition see : Colloque International du CNRS sur la Physique et la Chimie des Métaux Synthétiques et Organiques Les Arcs J. Physique C3 (1983)