ESRF	Experiment title: **Diffraction Studies of Crystalline Fibers of $(BPhDT\text{-}TTF)_2AsF_6$: A Novel Organic Conductor**	Experiment number: CH-127
Beamline: ID13	Date of experiment: from: 20.1.96 to: 27.1.96	Date of report: 28.8.96
Shifts:	Local contact(s): S. Fiedler	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

H. Muller, ESRF*
C.Riekel, ESRF*
M. Saad, ESRF*

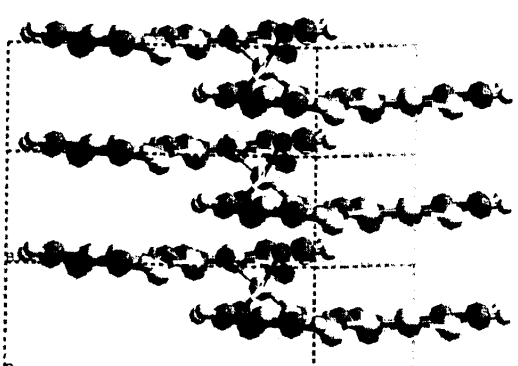
Report:

Background

Synthetic Metals, i.e. organic compounds which exhibit properties typical of metals, such as high electrical conductivity or even superconductivity, have attracted considerable attention during the past decade. Many efforts have been devoted to a better physical understanding and a rational design of new compounds with tailored properties whereas there has been little work on application-oriented research into these materials despite numerous potential applications (e.g. building-blocks for microelectronics, sensors etc.). In this context the successful synthesis of the title compound is of special importance, since $(BPhDT\text{-}TTF)_2AsF_6$, where BPhDT-TTF is bis(phenylenedithio)tetrathiafulvalene ($C_{18}H_8S_8$), is the first organic radical cation salt which combines high electrical conductivity and a relatively high mechanical stability. The material is obtained as greenish fibers (average dimensions 1000OX40X10 μm) with a ribbon-like shape and a rectangular cross section. The microscopic size of the specimen has precluded diffraction studies on single fibers with classical X-ray sources. Synchrotrons powder diffraction data recorded with a bunch of randomly oriented fibres proved inconclusive due to low scattering power and strongly overlapping peaks.

Microdiffraction experiments

Therefore we performed microdiffraction experiments at the microfocus beamline of the ESRF (E = 13.078 KeV, beam size 02, 7, 30 mm) on single, free standing fibers to probe the crystallinity of the specimen and to possibly solve the structure.
Scans along and perpendicular to the fiber axis proved the homogeneous, *crystalline* character of the samples. Oscillation images, however, showed a pronounced mosaic spread of up to 15 deg and diffuse scattering, thus indicating heavy disorder orthogonal to the fiber axis. The poor crystal quality frustrated an attempted structure elucidation. The lattice parameters of $(BPhDT\text{-}TTF)_2AsF_6$ at room temperature, however, could be determined for a primitive monoclinic cell: a = 15.87 Å, b = 3.86 Å, c = 12.67 Å, b = 108.40. The crystallographic b-axis coincides with the fiber axis, thus suggesting a columnar arrangement of the planar donor molecules along *b*. The high electrical conductivity observed in that direction could thus originate in strong overlap of sulfur molecular orbitals of ionized BPhDT-TTF, oriented perpendicular to the molecular plane. This view is further supported by the results of diffraction experiments at 200 K which showed an expansion of the b-parameter of about 490 that correlates well with the temperature dependence of the electrical conductivity. The observed increase of the band gap from 26 meV (280 K -200 K) to 240 meV at around 200 K is suggestive of a structural phase transition which reduces intermolecular interactions along *b* and consequently results in an increase of gap and b-parameter and a decrease of the electrical conductivity.
The figure below shows first results of molecular modelling simulations which match with the obtained data.



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