	Experiment title: *Charge Ordering in 1D Conductors*	**Experiment number**: CH-1426
Beamline: BM 1	**Date of experiment**: from: 12 Nov. 2003 to: 18 Nov. 2003	**Date of report**:
Shifts: 15	**Local contact(s)**: Jon Are Beukes	*Received at ESRF:*

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Report:

We have used the 15 shifts attributed for this experiment to measure Bragg diffraction at low temperature on two compounds of the $(TMTTF)_2X$ series to perform accurate charge density analysis in this family of 1D organic conductors. Recently, it has been demonstrated that many members of the $(TMTTF)_2X$ family with centrosymmetric anions undergo a new phase transition (at $T_{CO} = 70$ K in $(TMTTF)_2PF_6$ and 100 K in $(TMTTF)_2AsF_6$). This new phase transition has been interpreted as a charge-ordering transition due to electron-electron Coulomb correlated interactions. Below T_{CO}, the TMTTF molecules would be inequivalent with unequal electron densities with possible uniform shift of the anions with respect to the oppositely charged organic chains. This would break the centre of symmetry between adjacent molecules and induces the ferroelectric character of the transition.

We used the 4 circles diffractometer KM6 equiped with a 2D CCD detector at a wavelength of 0.7 Å to study the electron density redistribution at the transition.

During the first shift, we have carefully selected the best crystals for the charge density analysis among the 7 crystals of $(TMTTF)_2PF_6$ and 5 crystals of $(TMTTF)_2AsF_6$ preselected for this study (from a quick X-ray laboratory analysis). 2 and 1 crystals were selected for the PF_6 and AsF_6 compound respectiveley.

The crystal have platelike shape of typical dimension of 0.7x0.25x0.08 mm³ for the PF_6 compounds and 0.55x0.10x0.07 mm³ for the AsF_6 compounds. These are not ideal shapes when using the Oxford Helijet helium blower since the helium flux is non laminar (depending on the orientation of the sample) and induced icing at the surface of the sample. Furthermore, these compounds are particularly sensitive to the cooling rate: a quench has a dramatic effect on the "mosaicity" of the sample.

Two data sets have been collected above and below the "charge ordering" transition temperature T_{CO} for the PF_6 crystal: at T = 110 K (using the Oxford liquid nitrogen blower Cryojet system) and at 15K (using the Oxford Helium blower Helijet system). Unfortunately for practical reasons (cooling rate problems), the same crystal could not be used in the two data collections.

Only one data has been collected for the AsF_6 crystal. During the data collection at 15 K, the "icing" of the sample became too sizeable. An attempt to remove it damaged the sample. The data collection at 15 K has however been completed but the data collection above T_{CO} could not be considered. We have used approximately 30h for each data collection at each temperature.

The data reduction is still underwork. The intensity integration prossess is indeed complicated by the two following effects: i) the sample quality is not ideal and the Bragg spots have an elongated shape. Unfortunately, the integration software used (Oxford CrysAlis) can't take into account this elongated shape but rather assume circular spots. This bias the calculated integrated intensity. An other software is at the moment tested that can adequately calculated the integrated intensity for non disk-like Bragg spots. ii) all the samples were twinned. The contribution of the second crystal has not yet been described in a satisfactory way.

The overall completeness of the data collection is about 82% up to 1.24 $Å^{-1}$ (d_{min} ~0.4 Å) and up to 92% up to 0.67 $Å^{-1}$ (d_{min} ~ 0.76 Å) which means that charge density analysis are in principle possible.

Primary intensity integration results are summed up in the following table:

	Internal consistency R_{int} (%)	$(\sin(\theta)/\lambda)_{max}$ ($Å^{-1}$) / d_{min} (Å)	N* measured / N unique
PF_6 110 K (sample 1)	7.2	1.25 / 0.40	61668 / 20555
filtered incident beam (150 μm Cu)	5.9	0.80 / 0.62	8697 / 4822
PF_6 15 K (sample 2)	12.6	1.25 / 0.40	53765 / 16698
filtered incident beam (150 μm Cu)	18	0.80 / 0.62	7453 / 4106
AsF_6 15 K	20	1.25 / 0.40	30103 / 14257
filtered incident beam (100 μm Cu)	to be integrated		

*were N is the number of reflexions.

The last 12h of the allocated beam time was use to test the feasability of a single crystal diffraction analysis of $BaVS_3$. $BaVS_3$ is a metallic one-dimensional (1D) compound formed of V^{4+} chains, exhibiting a succession of phases whose nature is still not understood. In particular, the accurate determination of the low temperature structures is particularly difficult due to the presence of 6 equivalent crystallographic domains below the hexagonal to orthorhombic transition (at 70 K) and the low intensity of the superstructure peaks observed below 70 K. Recently, we have performed a high resolution X-ray powder diffraction study on the ID31 beam line (ESRF/HS-2280), which has shown for the first time that below T_{MI}, the orthorhombic symmetry is broken and the V zig-zag chains are slightly dimerized. However, this experiment failed to give reliable information concerning the superstructure stabilized below 70K (only few weak peaks of superstructure were detected). The results of our test of feasibility of this challenging experiment are very promising: Firstly, numerous superstructure peaks have been observed below 70K. Secondly, thanks to the high resolution of the beam, the twin reflections have been separated (which is not possible in lab. experiments), leading to determination of the twinning rule.