ESRF	Experiment title: Structural investigation of the charge density wave-driven metal-insulator transition in $(BEDT\text{-}TTF)_3Cl_2.2H_2O$	Experiment number: CH-44
Beamline: **BL 2. ID 1l**	Date of experiment: from: 7/4/1 995 to: 10/4/1995	Date of report: August 8, 1996
Shifts: 12	**Local** contact(s): Åke Kvick, Anette Frost-Jensen, Harald Müller	*Received at ESRF:*

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Background

$(BEDT\text{-}TTF)_3Cl_2.2H_2O$ is a unique member of the extensive family of low-dimensional charge-transfer salts of the BEDT-TTF (bis(ethylenedithio) tetrathiafulvalene) donor molecule. Of the 50 or so superconducting salts known, it is the only one with a 3:2 stoichiometry. Perhaps more importantly, it is one of very few to contain inequivalent BEDT-TTF molecules, and is the only salt where conversion to a semiconducting band structure may potentially occur with no change to the translational symmetry. Recent high precision electrical transport measurements have suggested the presence of a current-carrying charge density wave at low pressure and temperature 11. A low temperature diffraction experiment on BL 2 (ID 11) was proposed with the aim of characterizing the ambient pressure 100K metal-insulator transition in this salt.

Results

The experiment was successful in detecting the existence of a structural modulation in $(BEDT\text{-}TTF)_3Cl_2.2H_20$. Extremely weak, sharp a*/2 satellite reflections were seen at 15K, with intensities three to four orders of magnitude smaller than those of neighboring Bragg peaks. Despite the careful scrutiny of images during data collection, the modulation was unfortunately not detected until after the completion of the

experiment. As a result, only a limited number of satellite reflections were observed, and the temperature-dependence of the modulation was not studied.

A degree of uncertainty remains concerning the cause of the a*/2 modulation. The unexpected periodicity provides compelling evidence that the material may be misformulated, with the correct stoichiometry $(BEDT\text{-}TTF)_3Cl_2.(H_20)_{1.5}(OH)_{0.5}$. The alternative formulation is in agreement with charge analysis by consideration of the intramolecular BEDT-TTF bond lengths. Such a possibility has fundamental importance to the understanding of the electronic properties and band structure, since it would alter the classification of this salt from being a semimetal to being a true metal. The modulation may alternatively reflect a partial separation of charge at low temperature, driven by the narrowing of bands. Steric considerations, such as the opposing alignment of terminal ethylene groups of the BEDT-TTF molecules may also drive the modulation.

Further experimentation is required to resolve the uncertainty of the stoichiometry and ground state of $(BEDT\text{-}TTF)_3C1_2.2H_20$. In particular, the collection of low temperature intensity data is required for structural analysis, in addition to a variable-temperature study to ascertain the temperature-dependence of the modulation.

The remaining beam time was used in the preliminary study of three other phases:

- α'-$(BEDT\text{-}TTF)_2AuBr_2$ undergoes structural transitions at $T_{spin\text{-}Peierls}=5K$ and $T_{localisation}=250K$[2]. At 15K no pre-transitional spin-Peierls fluctuations were detected, although the experiment confirmed the dynamics of the 250K transition.
- $ET_4CuCl_2Br_2$ undergoes an abrupt electronic transition at 55K[3]. The low temperature space group is Pc, with no change to the translational symmetry. Analysis of low temperature structural data and variable-temperature data is on-going.
- $ET_4[Mo_6Cl_8]Cl_6.2CH_2Cl_2$ undergoes a metal-insulator transition at 25K, and shows an anomalous y large negative magnetoresistance[4]. No structural modulation was observed below the transition temperature.

References

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Supplement to CH-44 Experimental Report

Since the Materials Science Beam Line (BL 2, ID 11) was at an early stage of development at the time of the experiment, the author hopes it may be constructive to append to the report the experimental procedure followed, and a list of problems encountered. These have already been communicated to the beam line scientists of BL 2.

Experimental

Single crystals were mounted with epoxy resin on the tip of the cold finger of a displex continuous-flow helium cryostat. The 15 cm diameter cryostat chamber had mylar windows supported by five aluminium struts, allowing data collection at angles of sphi (horizontal axis of rotation perpendicular to the X-ray beam) in the ranges 10-30°, 45-66°, 82-102°, and 117-135°. Further data could be collected in the ranges 0-10° and 67-81°, with the complication of the exiting beam hitting the aluminium struts and giving intense, diffuse diffraction rings. A beam-stop of diameter 3.2 mm was placed 95 mm behind the crystal. Crystal centring was performed optically with the cryostat oriented vertically. The absence of an adjustable thread mount meant that alignment involved the loosening of bolts and manual translation. The inability to rotate the crystal through more than 135°, and the sensitivity of the alignment to bolt tightening made crystal centring extremely difficult. The focused monochromatic beam had a wavelength of 0.7 Å, and was collimated using horizontal and vertical slits to fully expose one vertical section of each needle-shaped crystal. X-ray beam damage was minimised by periodical y translating the crystal in the horizontal direction to subject unexposed areas of crystal to the beam. Image plate detectors (of EuBa-type, with size 34x42 cm^2 and dynamic range O to 65000) were employed in the vertical orientation at a distance of 470 mm from the crystal, as determined by diffraction from a polycristalline silicon sample. The plates were positioned horizontally central with l/6th of the area lying below the level of the X-ray beam, thereby allowing collection out to 40° in 2θ. Scanning was performed three minutes after the completion of data collection to ensure uniform image plate decay. Data were collected using oscillations in sphi ranging in angle from 0.5 to 10°, and exposure times ranging from 1 second to 3 hours. For scan times longer than 10 seconds several oscillations in sphi were performed to ensure uniform image plate decay.

Grid and decay corrections were performed using the program FIT2D[33]. Indexing of the image plate data sets by refinement of the crystal unit cell, orientation matrix, beam position, crystal-to-detector distance, beam crossfire and cassette corrections, and crystal mosaicity were performed with the program DENZO[34]. The maximum scanned area able to be treated by this program is 35.2x35.2 cm (a 2000x2000 grid of 176 μm pixels), and so a small number of high angle reflections were lost in the analysis. Due to the non-standard coordinates of the cryostat-mounting goniometer (which was used for the first time in this experiment), it was discovered that the rotx component of the orientation matrix required correction according to the expression:

$$rotx(sphi) = rotx(sphi_0) - 2(sphi - sphi_0)$$

The high degree of correlation between many of the experimental parameters and the relatively small number of peaks in each scan (maximum of 150) made over-paramaterisation a problem, and prevented a meaningful refinement of all parameters. It is believed that the close alignment of the rotation axis with one of the crystal axes compounded this problem, since many of the parameters become poorly defined for this geometry. It was necessary to fix the crystal-to-detector distance at 470 mm, and the beam crossfire and cassette corrections to zero for all data. Attempts at fixing the cell dimensions at those given in the literature (or other values) for all the image plate data of any one material proved unsuccessful, even when modifying all other parameters. A similar result was found for the orientation matrix and the beam position. The latter of these varies between plates due to the scanning procedure. The large degree of correlation between the unit cell dimensions, orientation matrix and beam position was treated by refining at most three parameters at a time whilst fixing all others to be constant. The crystal mosaicity was incremented in steps of 0.10 from zero, until all observed diffraction peaks were indexed. Integration and profile-fitting of the diffraction peaks were performed with the DENZO program, which automatically determines which reflections are observed fully.

Technical problems

- The absence of a screw-thread adjustment stage for the cryostat, making crystal alignment time-consuming and very difficult.
- A large amount of diffuse scattering was produced by the mylar and aluminium cryostat housing.
- The construction of the cryostat and diffraction cradle severely limits the scanning range, allowing the collection of only approximately 25 observations per independent non-hydrogen atom for a low-symmetry structure. Collection of a complete hemisphere of structural data requires the warming, reorientation and cooling of the crystal.
- Bottlenecks in data transfer made close examination of image plate data during the experiment time-consuming and difficult.
- The significant variation in the beam position between image plates complicates the indexing of images.
- The indexing software DENZO is designed for biological crystals with large unit cells.
- The indexing procedure is highly over-parameterised for images with fewer than ~100 reflections, and, as a result of the high degree of correlation, only approximate values for the unit cell parameters may be obtained.
- Attempts at performing block refinements for the image plate indexing were unsuccessful due to the high degree of correlation between indexing parameters.

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