ESRF

Experiment title:

In-situ study of the metal-superconductor phase transition of α-$(ET)_2I_3$

Experiment number:

CH 78

Beamline:

BL2 / ID11

Date of experiment:

from: 041196 to: 101196

Date of report:

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15

Local contact(s):

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Received at ESRF:

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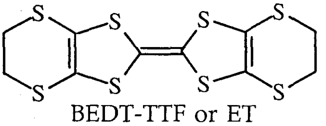
Report:

The synthetic metal α-$(ET)_2I_3$ exhibits a very unusual temperature dependence of the

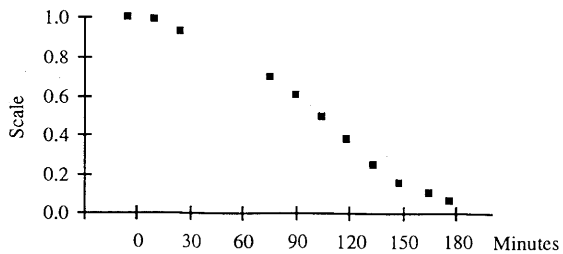


BEDT-TTF or ET

electrical conductivity in that it is characterised by two phase transitions. The Low Temperature (LT) phase transition at T_c = 135 K is a reversible metal-insulator transition. The High Temperature (HT) transition is an irreversible single crystal to single crystal transition, where the metallic conductor α-$(ET)_2I_3$ transforms into the organic superconductor α_T-$(ET)_2I_3$ (T, = 7.5-8.0 K). The reaction velocity is strongly temperature dependent, at T = 430 K it has been reported to take about 5 hours.

The goal of the experiment was to examine kinetics and structural aspect of these two transitions, in particular the HT phase transition, using time-resolved monochromatic single crystal diffraction. Kinetics and origin of both phase transitions are unknown, and up to date no successful attempt to elucidate the structure of α_T-$(ET)_2I_3$ has been performed.

Large single crystals of α-$(ET)_2I_3$ (a=9.183Å, b=10.804Å, c=17.442Å, α=96.95°, β=97.93°, γ=90.75°, Pi) were grown at the ESRF chemistry laboratory. Crystals with a size of about 200 μm were mounted on a Enraf-Nonius crystal heater goniometer head. A monochromatic beam of 38.0 keV and a Be-windowed X-ray Image Intensifier optically coupled to a CCD were used to collect the data. For each image the sample was oscillated 6" with 5 s exposure time. A total of 50 images (1" overlap, total oscillation 200") were collected in each data set, taking about one hour. In order to speed up data collection, we binned the pixels two by two on the CCD, thus reducing the readout time a factor of 4. With binned pixels a full data set was collected in 14 minutes.
For each sample we collected one Room Temperature (RT) data set (not binned). The temperature of the sample was then increased, and two binned data sets were collected. If the transition had not started, the procedure was repeated until the transition was started. Data sets were then collected at constant temperature until the whole sample was transformed into α_T-$(ET)_2I_3$.
The diffraction images were corrected for distortions using the programme FIT2D. DENZO was used for integration the diffraction peaks from α-$(ET)_2I_3$. From each image the intensity of about 300 reflections were integrated up to 0.8 Å resolution. Around 6000 unique reflections were obtained from each data set after scaling and merging (Rsym about 6%). The structure was finally refined using SHELXL 93 (R = 6% for 3000 reflections > 4 sigma, R = 10 % and wR = 14 % for all reflections).
Room-temperature data and LT data for α-$(ET)_2I_3$ are in excellent agreement with previous studies. The HT transition could be monitored over the entire conversion range. The corresponding conversion versus time curve is displayed in the Figure. Each data point corresponds to a complete data set.



Conversion versus time for α-$(ET)_2I_3$

At the time of submission it had become clear that a full structure determination of α_T-$(ET)_2I_3$ will be a real challenge, since the mosaic spread of the α_T-$(ET)_2I_3$-reflections is several degrees.