ESRF	**Experiment title: Temperature-dependant (4.2 K ≤ T ≤ 300 K) powder diffraction study of α_t-$(ET)_2I_3$ - an organic superconductor with a $T_c \approx 7.5$ K.**	**Experiment number:** CH 341
Beamline: BM 16	**Date of experiment:** from: 1.9.98 to: 3.9.98	**Date of report:** 1.02.98
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Report:

Thermal conversion of electrochemically grown single crystals of the organic metal α-$(ET)_2I_3$ yields a superconducting product of unknown structure (T, ≅ 7 - 8 K), generally referred to as α_t-$(ET)_2I_3$ which is of considerable interest for the manufacturing of composite materials with superconducting properties.

The experimental objective was to determine for the first time the structure and composition of α_t-$(ET)_2I_3$ at ambient temperature and possibly at around or below the superconducting transition, using high resolution powder diffraction and the Rietveld method.

A powder sample of α_t-$(ET)_2I_3$, sealed in a borosilicate capillary (0 0.7 mm) was mounted on the high resolution powder diffractometer equipped with a liquid-helium-cooled flow-cryostat. The capillary was spun on the axis of the cryostat mounted on the axis of the diffractrometer. Three data sets were collected at 4.2 K, 12 K and finally at ambient temperature temperature (in this order) at a wavelength of λ = 0.7742 A. After rapid cooling to 4.2 K, the sample was kept at around 120 K to heal out any frozen in structural disorder. Data refinement was performed using the Rietveld method with PC-GSAS. As structural

model, the atomic coordinates of β_{CO}-$(ET)_2I_3$ were employed. A refinement of the cell parameters at ambient temperature gave values virtually identical to that of the model compound. The presence of several peaks not assignable to a P-type structure made probable the presence of a second phase which could be identified as the polymorphic superconducting phase κ-$(ET)_2I_3$ (T_c = 3.5 K). A quantitative analysis showed that the transformation product contains β_{CO}-$(ET)_2I_3$ (92 weight %) and κ-$(ET)_2I_3$ (8 weight %). The formation of a two superconducting product phases could further be confirmed by AC susceptibility and DC magnetization experiments which showed two separate superconducting transitions at 7.5 K and 3.4 K, respectively. The atomic positions and isotropic thermal parameters of the major product phase could be refined to convergence at ambient temperature and are virtually identical to those determined previously for the organic superconductor β_{CO}-$(ET)_2I_3$. For the data collected at 12 K, very similar results were obtained; the analysis of the 4.2 K data set has not yet been completed.

In conclusion, the composition of the superconducting product α_t-$(ET)_2I_3$ obtained by heat transformation of α-$(ET)_2I_3$ could be identified as a mixture of the organic superconductors β_{CO}-$(ET)_2I_3$ and κ-$(ET)_2I_3$. Cell parameters and physical properties of both phases are summarized in the Table.

Table 1: Crystal data (293 K), ESR line widths [ΔH_{pp}], and transition temperatures T_c of ET phases with the triiodide anion. The figures in parentheses give the experimental standard deviations.

	α-$(ET)_2I_3$ [a]	β_{CO}-$(ET)_2I_3$ [b]	β_{CO}-$(ET)_2I_3$ [c]	κ-$(ET)_2I_3$ [d]	κ-$(ET)_2I_3$ [e]
a [Å]	9.1822(4)	**6.6071(2)**	6.6081(2)	16.4332(9)	**16.433(2)**
b [Å]	10.8013(5)	**9.0953(2)**	9.0878(2)	8.5000(3)	**8.494(1)**
c [Å]	17.4118(8)	**15.272(4)**	15.2683(3)	12.871(3)	**12.877(2)**
α [°]	96.968(4)	**94.351(2)**	94.410(1)	90	**90**
β [°]	97.938(6)	**95.578(2)**	95.575(1)	108.505(9)	**108.55(1)**
γ [°]	90.767(4)	**109.786(1)**	109.761(1)	90	**90**
V [Å^3]	1696.9(2)	**853.68(4)**	852.92(4)	1704.99(4)	**1704.0(4)**
Space group	P -1	**P -1**	P -1	P21/c	**P21/c**
Z [K]	4	**2**	2	2	**2**
T_c [K]	/	**7**	7.2-7.5	3.6 - 4	**≈ 3.4**
ΔH_{pp} [G]	60-70 [f]	**23 [j]**	23 [f]	/	/

[a] Powder diffraction data on microcrystalline α-$(ET)_2I_3$ measured at BM 16. **[b] Powder diffraction data on heat-transformed, microcrystalline α-$(ET)_2I_3$ from this proposal measured at BM 16.** [c] Powder diffraction data on authentic β_{CO}-$(ET)_2I_3$ measured at BM 16 [d] Literature data obtained on a single crystals **[e] Powder diffraction data on heat-transformed, microcrystalline α-$(ET)_2I_3$ from this proposal measured at BM 16.** [f] Unoriented samples at ambient temperature.