



STRUCTURE DETERMINATION OF AN ORGANIC SUPERCONDUCTOR BY HIGH-RESOLUTION POWDER DIFFRACTION



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The high resolution powder diffraction beamline BM16 has been operating for users since May 1996. The beamline is optimised for carrying out powder crystallography - solving and refining of crystal structures from powder specimens - but also has a wide range of materials science applications, such as anomalous scattering studies, measurement of stress and strain (e.g. in alloys used in aerospace), characterisation of microstructure, studies of glasses and amorphous materials, and dynamic in situ measurements of systems undergoing structural evolution with time (e.g. following the structural changes in batteries during the electrochemical charge and discharge cycles).

Structural characterisation from powders is necessary when single crystals of a material are not available, or for carrying out studies under conditions where single crystals fragment, such as after passing through a destructive phase transition. To understand the physical and chemical properties of crystalline solids, knowledge of the crystal structure is indispensable. Many modern materials do not readily form good quality crystals so that the crystal structure may only be determined by powder methods. Furthermore, a single crystal by its very nature may not be truly representative of a bulk specimen, and it is often the powdered form of a material that may be of use and hence of interest, e.g. zeolite catalysts used in the petrochemical industry are always in the form of powders (tonnes of them) and

pharmaceutical products frequently come in the form of tablets, which are compressed powders.

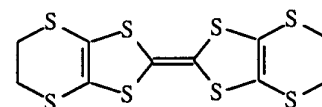
Advantages of the BM16 diffractometer include its operating energy range (5 - 40 keV) and its high angular resolution, so that narrow diffraction peaks can be measured using short-wavelength X-rays. The short wavelengths mean that the sample can be contained in a thin-walled glass capillary without problems of absorption. Spinning the capillary greatly reduces (or eliminates) problems of preferred orientation of needle-like or plate-like crystallites, leading to accurate diffraction intensities. Another advantage is the use of a crystal analyser stage before the detector. Coupled with the high collimation of the incident radiation this leads to the narrow peak widths, but also means that the peak positions are immune to the aberrations present with conventional diffractometers that lead to significant shifts in the measured positions of the diffraction peaks. Hence the positions of the diffraction peaks measured on BM16 are also very accurate. With narrow diffraction peaks whose positions and intensities are accurately known, the diffraction pattern that arises from a complex powder sample can be unravelled to yield an accurate and reliable crystal structure. A recent and interesting example which emphasises some of the features outlined above is the study of the technologically promising, advanced material $\alpha_-(\text{ET})_2\text{I}_3$ [1].

The compound is a superconducting radical cation salt derived from the sulphur heterocycle bis (ethylenedithio) tetrathiafulvalene (BEDT-TTF or ET for short), whose important characteristics are similar to those of commercially used superconducting metal alloys such as NbTi (e.g. superconducting transition temperature T_c , upper critical field H_{c2} and critical current density j_c).

The organic superconductor $\alpha_-(\text{ET})_2\text{I}_3$ ($T_c \approx 8$ K) has been used in the manufacture of prototypic devices, such as superconducting films [5-7].

Recent attempts to employ the compound for the fabrication of superconducting composites are undoubtedly a field of enormous commercial potential, since they could make available polymers which retain their specific material properties, but are electrically conducting at ambient temperature and superconducting at the temperature of liquid helium [8].

A polycrystalline, superconducting product, generally referred to as $\alpha_-(\text{ET})_2\text{I}_3$, [2,3] is obtained by thermal conversion of the organic metal $\alpha_-(\text{ET})_2\text{I}_3$ [4]. All attempts to determine the structure of $\alpha_-(\text{ET})_2\text{I}_3$ proved futile, a consequence of the poor crystal quality resulting after heat treatment [3,5].



BEDT-TTF OR ET



Recently, we succeeded in performing the first structural characterisation of the superconducting radical cation salt $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$. The compound was synthesised in a phase-pure, microcrystalline form by a newly developed redox process suitable for a large-scale preparation [9]. An SEM-image of the microcrystalline product is displayed in Figure 1.

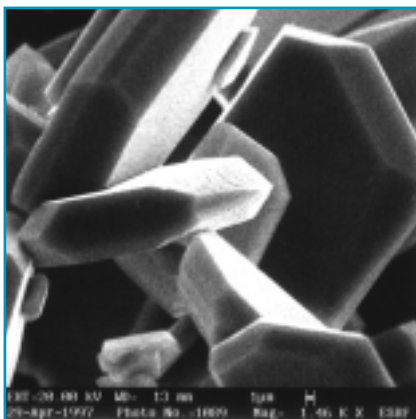


Fig. 1: Microcrystals of $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$.

The powder diffractometer on BM16 (cf. Figure 2) was used to record a high angular resolution X-ray powder diffraction pattern of $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$ at a wavelength of 0.94468(1) Å. The structural model of $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$ was refined with the Rietveld method using the program PC-GSAS [10]. The excellent fit of the peak profiles was obtained using only four peak shape parameters thanks to a special peak shape function [11], although the peaks at low angle are asymmetrical.

Fig. 2:

Powder diffractometer on BM16.



A comparison of observed and calculated diffraction patterns is shown in Figure 3. The excellent agreement of observed and calculated profiles clearly demonstrates the presence of a uniform product. Earlier work, based on spectroscopic evidence and Weissenberg photographs, claimed a close structural similarity of $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$ and the related organic superconductors $\beta(\text{ET})_2\text{I}_3$ ($T_{\text{c}} = 1.5$ K) [3,5]. The lattice parameters and unit cell volumes of $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$ differ marginally but significantly from those of

$\beta(\text{ET})_2\text{I}_3$ [12,13], which thus could represent a crystallographically distinct phase. The cell volume of fully deuterated $\alpha_{\text{T}}(\text{ET})_2\text{I}_3$ is slightly smaller than that of its protonated counterpart. A reduction of the cell volume as a consequence of hydrogen/deuterium exchange has been observed earlier for ET-based superconductors. [14] It is worth noticing that replacement of hydrogen by deuterium in the ET-molecules enhanced T_{c} by 0.3 - 0.4 K. The corresponding crystal data are summarised in Table 1.

Table 1: Crystal data (293 K), ESR line widths and transition temperatures T_{c} of ET phases with the triiodide anion. **a** Powder diffraction data from this work.

The prefix h_8 or d_8 refers to protonated and deuterated ET (donor) molecules, respectively. The figures in parentheses give the standard deviations. **b** Literature data [11]. **c** Unoriented powder samples at ambient temperature. **d** Orientation dependent single crystal data [12].

	$\alpha_{\text{T}}(\text{h}_8\text{-ET})_2\text{I}_3^{\text{a}}$	$\alpha_{\text{T}}(\text{d}_8\text{-ET})_2\text{I}_3^{\text{a}}$	$\beta(\text{ET})_2\text{I}_3^{\text{b}}$
a [Å]	6.6081(2)	6.6093(2)	6.615(1)
b [Å]	9.0878(2)	9.0856(2)	9.100(1)
c [Å]	15.2683(3)	15.2632(3)	15.286(2)
α [°]	94.410(1)	94.452(1)	94.38(1)
β [°]	95.575(1)	95.563(1)	94.41(1)
γ [°]	109.761(1)	109.756(1)	109.78(1)
V [cm ³]	852.92(4)	852.55(4)	855.9(2)
Space group	P-1	P-1	P-1
Z	1	1	1
T_c [K]	7.2 - 7.5	7.8 - 7.9	1.4
ΔH_{pp} [G]	23 ^c	23 ^c	17.6 - 23.35 ^d

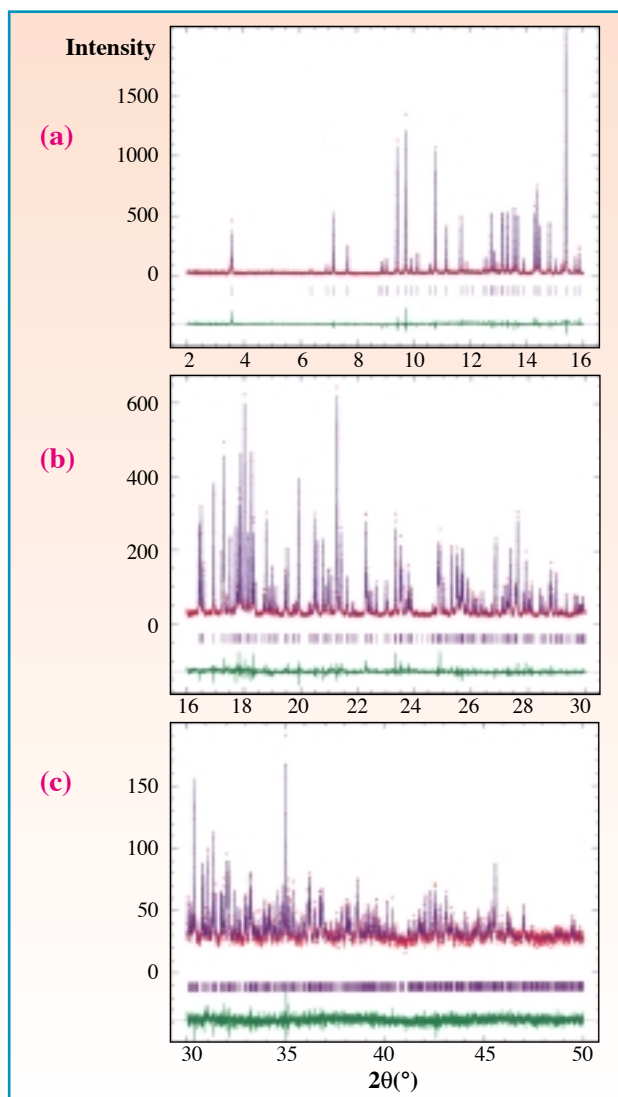


Fig. 3: Diffraction pattern of $\alpha_r\text{-(ET)}_2\text{I}_3$ ((a) $2 \leq 2\theta \leq 16$ deg; (b) $16 \leq 2\theta \leq 30$ deg; (c) $30 \leq 2\theta \leq 50$ deg) showing the observed (red) and calculated (violet) diffraction patterns, and the differences between them (green). The quality of the fit may be judged by eye to be excellent and yields the Rietveld R-factors $R_p = 0.0813$ and $wR_p = 0.0944$ with a reduced $\chi^2 = 2.4$ for 143 variables. The R-factors give a quantitative indication of the quality of the fit (the lower the R, the better the fit).

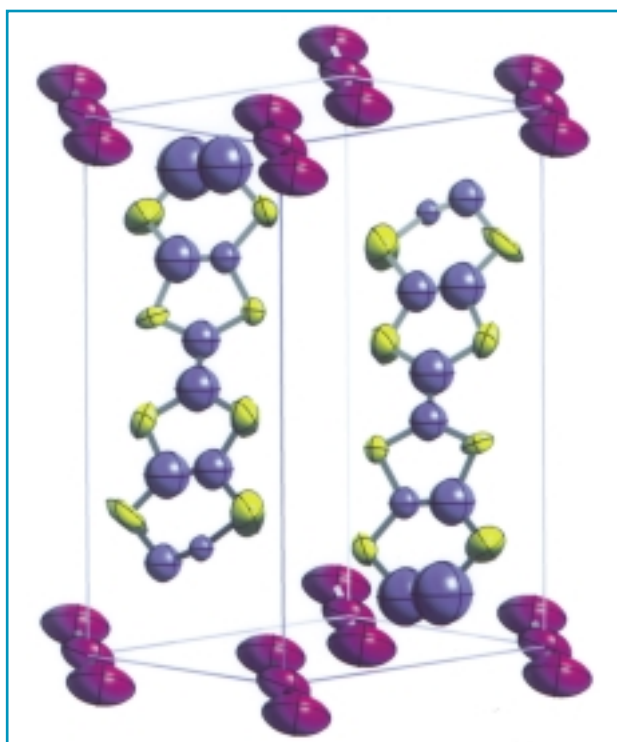


Fig. 4: Crystal structure showing the thermal ellipsoids and unit cell of $\alpha_r\text{-(ET)}_2\text{I}_3$.

The average crystal structure and unit cell of $\alpha_r\text{-(ET)}_2\text{I}_3$ are presented in Figure 4. The ET molecules are non-planar and arranged in dimers which form loosely-connected stacks along the crystallographic [110] axis. The carbon atoms at one edge of each ET-molecule show high thermal parameters, indicating disorder of one ethylene group per donor molecule. In view of the structural similarities it is conceivable that the nearly identical cell parameters and packing motifs of the ET-molecules, but strikingly divergent transition temperatures of $\alpha_r\text{-(ET)}_2\text{I}_3$ (7.1 - 7.9 K) and $\beta\text{-(ET)}_2\text{I}_3$ (1.4 K), are linked to small conformational differences. A pressure-induced disorder-order transition of the ethylene groups of $\beta\text{-(ET)}_2\text{I}_3$ raises T_c from 1.4 K to 8 K [15]. At present, it is not clear whether the disorder of the end groups in $\alpha_r\text{-(ET)}_2\text{I}_3$ at ambient temperature is of statistical nature, as in $\beta\text{-(ET)}_2\text{I}_3$, [12,13] or rather related to the presence of ordered and disordered domains in the same crystallite. The importance of the end group conformation of the donor molecules and their role on lattice softness, electron phonon coupling and hence the superconducting properties are known. [16] It is tempting to speculate on the existence of disorder-order transitions in $\alpha_r\text{-(ET)}_2\text{I}_3$ upon cooling which might account for the peculiar temperature-dependence of the magnetic susceptibility χ of this compound as shown in Figure 5. Low temperature studies well above and below the superconducting transition are planned on BM 16 in the near future to clarify this point. ■

References

- [1] BEDT-TTF and iodine form a plethora of polymorphic phases denoted by small Greek letters, the electrical conductivities of which range from semiconducting to metallic to superconducting (for an excellent review see reference [2]).
- [2] J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M. H. Whangbo, *Organic Superconductors (Including Fullerenes)*; Prentice Hall: Englewood Cliffs, New Jersey, 1992.
- [3] G. O. Baram, L. I. Buvarov, L. S. Degtyarev, M. E. Kozlov, V. N. Laukhin, E. E. Laukhina, V. G. Onishenko, K. I. Pokhodnya, M. K. Sheinkman, R. P. Shibaeva, E. B. Yagubskii, *Pis'ma Zh. Eksp. Teor. Fiz.*, 1986, 44, 293.
- [4] K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, H. J. Keller, *Mol. Cryst. Liq. Cryst.*, 1984, 108, 359.

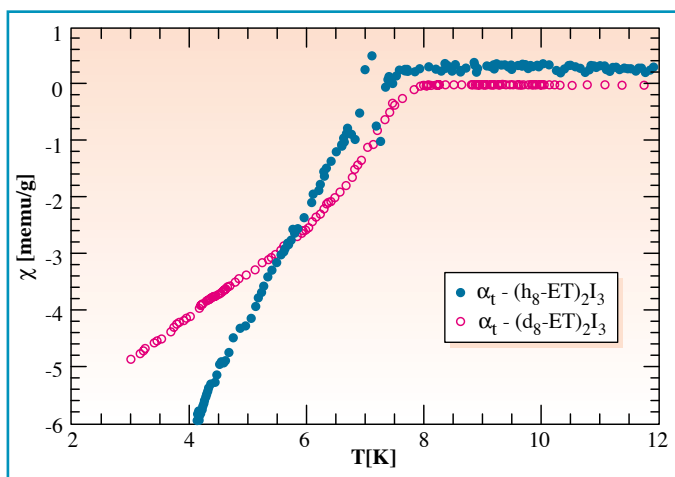


Fig. 5: Superconducting transition curves of protonated and fully deuterated α_T -(ET) $_2$ I $_3$ as determined by AC-susceptibility.

[5] J. Moldenhauer, H. Wachtel, D. Schweitzer, B. Gompf, W. Eisenmenger, P. Bele, H. Brunner, H.J. Keller; *Synth. Met.*, 1995, 70, 791.

[6] Y. Ueba, T. Mishima, H. Kusunoha, *Eur. Pat.* 0407807 A2, 1990.

[7] K. Kawabata, K. Tanaka, M. Mizutani, *Adv. Mat.*, 1991, 3, 157.

[8] a) E. E. Laukhina, V. A. Merzanow, S.I. Pesotski, A.G. Khomenko, E. B. Yagubskii,

J. Ulanski, M. Kryszewski, J. K. Jeszka, *Synth. Met.*, 1995, 797. b) J. Ulanski, A. Tracz, J. K. Jeszka, E.E. Laukhina, A. Khomenko, P. Polanowski, D. Staerk, H. Helberg in *Electrical and Related Properties of the Organic Solid State*, R. W. Munn, A. Miniewicz, and B. Kuchta (Eds.), Kluwer Academic Publishers, Dordrecht, 1997, pp. 241 - 257.

[9] a) H. Müller, Y. Ueba, *Bull. Chem. Soc. Jpn.*,

1993, 66, 32. b) H. Müller, D. G. Xenikos, *Synth. Met.*, 1997, 85, 1461. c) H. Müller, S. O. Svensson, A. N. Fitch, M. Lorenzen, D. G. Xenikos, *Adv. Mat.*, 1997, accepted for publication.

[10] A. C. Larson, R. B. von Dreele, *Los Alamos Laboratory Rep.*, 1987, LA-UR-86-784R.

[11] L. W. Finger, D. E. Cox, A. P. Jephcoat, *J. Appl. Cryst.*, 1994, 27, 892.

[12] J. M. Williams, T. J. Emge, H. H. Wang, M. A. Beno, P. T. Copps, L. N. Hall, K. D. Carlson, G. W. Crabtree, *Inorg. Chem.*, 1984, 23, 2558.

[13] V. F. Kaminskii, T. G. Prokhorova, R. P. Shibaeva, E. B. Yagubskii, *Zh. Eksp. Teor. Fiz., Pis'ma Red.*, 1984, 39, 12.

[14] C. W. Mayer, J. S. Zambounis, B. Hilti, E. Minder, J. Pfeiffer, G. Rihs, *Synth. Met.*, 1991, 41, 2251.

[15] A. J. Schultz, H. H. Wang, J. M. Williams, A. Filhol, *J. Am. Chem. Soc.*, 1986, 108, 7853.

[16] H. H. Wang, J. R. Ferraro, K. D. Carlson, L. K. Montgomery, U. Geiser, J. M. Williams, J. R. Whitworth, J. A. Schlueter, S. Hill, M. H. Whangbo, M. Evain, J. J. Novoa, *Inorg. Chem.*, 1989, 28, 2267.

ACKNOWLEDGEMENT

The authors wish to thank Irina Snigireva from the micromanipulation and microimaging laboratory for providing the SEM image.