Polymorphism and Superconductivity in bilayer molecular metals (CNB-EDT-TTF)₄I₃.

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ABSTRACT.

The electrocrystallization from solutions of the dissymmetrical ET derivative cyanobenzene-ethylenedithio-tetrathiafulvalene (CNB-EDT-TTF) in the presence of triiodide I_3^- , affords to two different polymorphs (β'' - and κ -) with composition $(CNB-EDT-TTF)_4I_3$, both with a bilayer structure of the donors. These polymorphs differ on the packing pattern (β'' - and κ -type) of the donor molecules in each layer, in both cases with bifurcated C-N $\cdots$ H interactions effectively coupling head to head donor molecules between layer pairs. Two β'' - polymorphs can be obtained with different degrees of anionic ordering. In one disordered phase, β''_d - , with a smaller unit cell, the triiodide anions are disordered over two possible positions in a channel between the donor bilayers, while in the ordered phase, β''_o -, the triiodide anions occupy only one of those positions in this channel, leading to the doubling of the unit cell in the layer plane. These results for β'' -phases contrast with the κ -polymorph previously reported, where a weaker disorder of the triiodide anions, over two possible orientations with 94% and 6% occupation factors was observed. While the β'' - polymorphs remains metallic down to 1.5 K with a resistivity ratio $\rho_{300K}/\rho_{4K} = 250$, the κ -polymorph presents a much smaller resistivity ratio in the range 4-10 and superconductivity with an on-set temperature of 3.5 K.

1. Introduction

The field of two dimensional molecular systems has been largely dominated by charge transfer salts of sulphur rich derivatives of the electron donor TTF. In these salts the partially oxidized donor molecules are arranged in compact layers with their long axis parallel to each other, which alternate with anionic layers. BEDT-TTF (or ET= bis-ethylenedithio tetrathiafulvalene) is probably the most prolific of such donor molecules but many other similar TTF derivatives have been used to prepare two-dimensional (2-D) molecular systems. In all these donors the presence of several sulfur atoms in the molecular periphery ensures significant electronic exchange interactions between neighboring molecules in the compact donor layers, while the interaction between layers are much weaker due to their separation by anions. This type of salts have been at the center of many studies due to a wealth of different possible ground states and phase transitions that have been observed including, antiferromagnetism, Mott Insulators, charge ordering, 2-D metallic and even superconducting properties.¹⁻⁵ The physical properties of these two-dimensional systems are critically dependent on the way the flat donor molecules are packed in a layer, which can be quite diverse and have been classified with many different Greek letters.⁶⁻⁸

Weak interactions such as halogen and hydrogen bonds have been extensively explored to control the donor packing pattern of charge transfer salts⁹ with large but not always well predicted consequences in the electrical and magnetic properties of the salts. Recently we have demonstrated that the dissymmetrical TTF derivative, cyanobenzene-ethylenedithio-tetrathiafulvalene (CNB-EDT-TTF)¹⁰ when electrocrystallised in the presence of small anions A, such as I_3^- , ClO_4^- or PF_6^- , leads to a series of salts with an unusual donor to anion stoichiometry 4:1, with general formula $(CNB-EDT-TTF)_4A$.¹¹ These salts are characterized by a bilayer

structure of the donors, arranged head to head between paired layers due to a specific combination of C-N $\cdots$ H-C interactions involving the cyano groups. In the bilayer salts of this donor with different anions, β'' - and κ -type packing patterns of the CNB-EDT-TTF donors have been already observed.

In this paper we report for (CNB-EDT-TTF) $_4$ I $_3$ two β'' -type polymorphs, with a donor packing pattern similar to that observed in β'' -ClO $_4$ and PF $_6$ salts but different degrees of anion order, in addition to the previously reported κ -type structure. κ -(CNB-EDT-TTF) $_4$ I $_3$ displays superconductivity below 3 K, while the β'' - polymorphs are regular 2-D metals.¹¹

2. Experimental Section

Sample preparation: The electron donor CNB-EDT-TTF was prepared as previously described.¹⁰ Crystals of β'' -(CNB-EDT-TTF) $_4$ I $_3$ were obtained by electrocrystallization, at room temperature, with platinum electrodes. A dichloromethane solution of the donor CNB-EDT-TTF (2×10^{-3} M) and TBAI $_3$ (6×10^{-3} M) was added to an H-shaped cell. The system was sealed under nitrogen and the current was gradually increased from 0.2 μ A cm $^{-2}$ to 0.5 μ A cm $^{-2}$ on the first three days of the electrocrystallization. After approximately 18 days of applying a constant current density of 0.5 μ A cm $^{-2}$, black elongated platelet shaped crystals grown on the anode, with approximate dimensions $5\times 0.2\times 0.05$ mm 3 , were collected and washed with dichloromethane.

X-ray Crystallography: Selected single crystals were mounted on a loop with protective oil and X-ray data was collected on a Bruker APEX II CCD detector diffractometer using graphite monochromated MoK $_{\alpha}$ radiation ($\lambda = 0.71073$ Å) and operating in a ϕ and ω scans mode. A semi empirical absorption correction was carried out using SADABS.¹² Data collection, cell refinement and data reduction were done with the SMART and SAINT programs.¹³ The

structures were solved by direct methods using SIR97¹⁴ and refined by full-matrix least-squares methods using the program SHELXL97¹⁵ using the winGX software package.¹⁶ Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP 3.¹⁷

[CCDC 1488030, CCDC 1488031 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Electrical transport measurements: Electrical resistivity was measured in the range 1.5 to 300 K in a helium cryostat with an 18 T superconducting magnet (Oxford Instruments). Selected single crystals as elongated platelets were attached to 25 μm diameter Au wires with Pt paint (Demetron 308A), in a 4 in line configuration of the contacts placed along the long axis of the samples which correspond to the donor stacking axis. The AC (77Hz) current was kept in the range 1-10 μA and the sample voltage drop was measured by a lock-in amplifier (Stanford Research Systems Model SR830).

Thermoelectric power measurements in single crystals were performed also along the long axis of the samples in the temperature range 20–300 K in a closed-cycle helium refrigerator using a slow alternating-current (ca. 10^{-2}Hz) technique¹⁸ by attaching two 25 μm diameter 99.99 % pure Au wires (Goodfellow metals) thermally anchored to two quartz reservoirs with Pt paint (Demetron 308A) to the extremities of an elongated sample, as in a previously described apparatus,¹⁹ controlled by a computer.²⁰ The oscillating thermal gradient was kept below 1 K and was measured with a differential Au (0.05 atom-% Fe) vs. chromel thermocouple. The absolute

thermoelectric power of the sample was obtained after correction for the absolute thermopower of the Au leads by using the data of Huebner.²¹

Computational details: The tight-binding band structure calculations²² were of the extended Hückel type and a modified Wolfsberg-Helmholtz formula was used to calculate the non-diagonal $H_{\mu\nu}$ values.²³ All valence electrons were taken into account in the calculations and the basis set consisted of Slater-type orbitals of double- ζ quality for C and N 2s and 2p, S 3s and 3p and of single- ζ quality for H 1s. The ionization potentials, contraction coefficients and exponents were taken from previous work.^{24, 25}

3. Results and discussion

3.1 Crystal structure. X-ray diffraction of selected (CNB-EDT-TTF)₄I₃ single crystals obtained by electrocrystallization revealed two new crystal structures, both with the same bilayer β'' -type arrangement of the donors, but with different degrees of disorder in the positions of the triiodide anions (Table 1). No crystals with the previously reported κ -type structure were obtained and it was not clear which specific electrocrystallization conditions favour the crystallization of the different phases. In one structure called β''_d -(CNB-EDT-TTF)₄I₃ the unit cell is triclinic, P-1, with cell parameters $a=4.8597(9)$ Å, $b=5.7697(11)$ Å, $c=27.733(5)$ Å, $\alpha=89.033(6)^\circ$; $\beta=87.007(6)^\circ$; $\gamma=84.443(7)^\circ$ and $V=772.841$ Å³. The asymmetric unit is composed of one donor molecule and two iodine atoms on special positions with occupation factors of 0.694 and 0.831 for I1 and I2 respectively.

Another structure called β''_o -(CNB-EDT-TTF)₄I₃ is also triclinic P-1 but with cell parameters $a=5.7669(2)$ Å, $b=9.7113(3)$ Å, $c=27.7724(7)$ Å, $\alpha=86.793(2)^\circ$, $\beta=89.079(1)^\circ$, $\gamma=84.558(2)^\circ$, $V=1545.84(5)$ Å³. This unit cell has twice the volume of the previous one, with the cell parameter b corresponding to a doubling of the previous cell parameter a . The

asymmetric unit is composed of two donor molecules and two iodine atoms in fully occupied positions. One of the iodine atoms is located on an inversion center and the other on a general position.

Table 1. Crystal and refinement data for β''_d -(CBN-EDT-TTF)₄I₃ and β''_o -(CBN-EDT-TTF)₄I₃.^a

Compound	β''_d -(CBN-EDT-TTF) ₄ I ₃	β''_o -(CBN-EDT-TTF) ₄ I ₃
Formula	C ₂₆ H ₁₄ I _{1.5} N ₂ S ₁₂	C ₅₂ H ₂₈ I ₃ N ₄ S ₂₄
Molec. mass	929.46	1858.92
T (K)	150(2)	150(2)
Dimensions (mm)	0.40×0.04×0.02	0.60×0.03×0.01
Crystal color	Black	Black
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	4.8597(9)	5.7669(2)
<i>b</i> (Å)	5.7697(11)	9.7113(3)
<i>c</i> (Å)	27.733(5)	27.7724(7)
α (°)	89.033(6)	86.793(2)
β (°)	87.007(6)	89.0790(10)
γ (°)	84.443(7)	84.558(2)
Volume (Å ³)	772.8(2)	1545.84(8)
<i>Z</i>	1	1
ρ_{calc} (g.cm ⁻³)	2.133	1.997
μ (mm ⁻¹)	2.371	2.371
<i>h</i> , <i>k</i> , <i>l</i> range	±5, -6/7, ±33	±6, -11/+10, ±33
θ_{max} (°)	25.87	25.35
Refl. collected	3831	19649
Refl. Unique	2542 [<i>R</i> _{int} = 0.0354]	5303 [<i>R</i> _{int} = 0.0527]
data/ restraints/ parameters	2542/ 0/ 195	5303 /12/ 377
GOF on <i>F</i> ²	1.054	1.065
<i>R</i> ₁ ; ω <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0640; 0.1303	0.0892; 0.2263
Largest diff. peak and hole (e.Å ⁻³)	1.286 and -1.165	4.998 and -2.676
CCDC n°	1488031	1488030

^a Crystallographic data (excluding structure factors) for β''_d -(CBN-EDT-TTF)₄I₃ and β''_o -(CBN-EDT-TTF)₄I₃ were deposited with the Cambridge Crystallographic Data Centre with n^{os}. CCDC 1488031-1488030, respectively.

The donor packing of both β''_d - and β''_o - structures is essentially the same as shown in Figure 1 and it is also identical to that previously described in ClO_4 and PF_6 salts with a bilayer β'' -type packing of the donors.⁴ The CNB-EDT-TTF molecules do not present any disorder in the dithiine ring as previously observed in the PF_6 salt¹¹ and commonly found in many ET salts.^{1, 5} These donors are arranged head to head in bilayers through dipolar and bifurcated $\text{C}-\text{N}\cdots\text{H}$ interactions, which can be described as a combination of dimeric $\text{R}^2_2(10)$ and $\text{R}^2_4(10)$ synthons, in Etter's notation,²⁶⁻²⁸ connecting almost coplanar molecules (Figures 1a).

Figure 1. β''_d -(CNB-EDT-TTF)₄ I₃ structure; a) viewed along a ; b) Partial view of one donor layer along the molecule long axis showing a β'' -type molecular packing pattern.

Similar synthons are quite common in molecules with nitrile groups²⁹ and it is worth referring that a dimeric $\text{R}^2_2(10)$ synthon has been previously observed in a 1:1 salt of the cyano substituted TTF 3-cyano-3',4'-ethylenedithiotetrathiafulvalene (EDT-TTF-CN), (EDT-TTF-CN)I₃. However without the $\text{R}^2_4(10)$ synthons which in the CNB-EDT-TTF salts ensure the bilayer structure.

In $\beta''_d\text{-(CNB-EDT-TTF)}_4\text{I}_3$ the iodine atoms appear in two positions I1 and I2, located in channels between the donor bilayers (Figure 2) with anomalously large displacement parameters along the channels (cell axis b) and occupation factors 0.694 and 0.831 respectively. These occupation factors, corresponding to 1.525 iodine atoms for 2 donors, are very close to the expected for a 4:1 (Donor: I_3^-) stoichiometry in these compounds. The distance between these iodine positions 2.429 Å is slightly shorter than typical I-I distance in triiodide (2.92 Å) which cannot be precisely accommodated in these positions and the elongated displacement parameters ellipsoids denote position disorder of triiodide anions. Therefore this structure with a small unit cell parameter a should be regarded as an average structure involving disorder of triiodide anions. The repeat length of the anions in this chain of iodine positions cannot be smaller than the triiodide length (~ 9 Å), and in other channel structures it is observed to occur typically with repeats in the range 9.4-9.9 Å,³⁰⁻³² close to the doubling of the unit cell parameter a . In fact the occupation factors of these two iodine positions in the $\beta''_d\text{-(CNB-EDT-TTF)}_4\text{I}_3$ structure can be seen as resulting from a superposition of a random occupation of these sites by triiodide anions, 60% in positions close to I2-I1-I2 and 40% in positions close to I1-I2-I1 as schematically depicted in blue and green in Figure 2. It should be also noted that iodine atoms in positions I1 and I2 present slightly different environments in the channel between donors; I1 has two short contacts with sulfur atoms S6 at 3.649 Å while the closest contacts of I2 are with H13 at 3.094 Å.

Figure 2. ORTEP diagram for iodine atom positions (violet) in the a,c anionic layer of β''_d -(CNB-EDT-TTF) $_4$ I $_3$ drawn at 50 % probability level. In blue and green are schematically depicted two possible locations for the triiodide anions along the chains of iodine atom positions, which with occupations factors of ~60% and 40% account for the observed occupation factors of 0.694 and 0.831 for I1 and I2 respectively.

The asymmetric unit of β''_o -(CNB-EDT-TTF) $_4$ I $_3$ contains two donor molecules and half a triiodide anion with the central iodine atom at an inversion centre. The β''_o -(CNB-EDT-TTF) $_4$ I $_3$ structure presents the same packing pattern of the donors as the disordered β''_d -phase, however with a doubling of the cell parameter along the channel of the iodine positions and with the iodine atoms in ordered positions, very close to the preferred I2-I1-I2 positions of the disordered β''_d -phase. As a consequence of this anion ordering and cell doubling, the donor units become inequivalent with one molecule A (blue) in closer contact with anions than the other unit B (red) (Figure 3). Donor molecule A bearing closer anionic contacts S5-I1 at 3.669 Å and H13A-I2 at 3.071 Å is expected to present larger positive charge. The analysis of donor bond lengths in molecules A and B show small differences consistent with such possibility. However these differences are within the experimental uncertainties precluding at this point a more positive conclusion about donor charge distribution.

Figure 3. Partial view along the molecule long axis of one donor layer in β'' -(CNB-EDT-TTF)₄ I₃ showing two inequivalent donor units depicted in blue (molecule A) and red (molecule B)

3.2. Electronic Structure. The structure with disordered anions β''_d -(CNB-EDT-TTF)₄ I₃ contains one bilayer with only one donor molecule as the repeat unit for every single layer. As shown in Figure 4, in this average structure there are three different types of intermolecular interactions among molecules in the same layer: those along the π -stacks in the a -direction (I), the lateral contacts along the $(a+b)$ -direction (II), and those along the step-chains in the b -direction (III). As shown in Table 2, the stronger HOMO $\cdots$ HOMO intermolecular interactions³³ are those along the step-chains whereas those along the π -stacks are approximately half strong. Note that the lateral interactions despite being associated with the shorter S $\cdots$ S contacts are the weakest because they are associated with usually weak π -type interactions whereas those along the step-chains or the π -stacks are of the stronger σ -type. The interaction between donors in different layers of the bilayer (IV) is very weak (0.6 meV). These values are very similar to those previously reported for the isostructural (CNB-EDT-TTF)₄X salts with X= PF₆ and ClO₄.⁵ Note

that the relative strength of the interactions along the π -stacks and the lateral interactions is reversed with respect to most β'' salts.³⁴

Figure 4. Donor layer in bilayers of $\beta''_d-(\text{CNB-EDT-TTF})_4 \text{I}_3$ (left) and in $\beta''_o-(\text{CNB-EDT-TTF})_4 \text{I}_3$ (right), where the different interactions are labeled.

Table 2. Calculated values of the $|\beta_{\text{HOMO-HOMO}}|$ [eV] for the different donor...donor interactions in $\beta''_d-(\text{CNB-EDT-TTF})_4 \text{I}_3$ and $\beta''_o-(\text{CNB-EDT-TTF})_4 \text{I}_3$.

Interaction type	$ \beta_{\text{HOMO-HOMO}} $ (meV)	
	$\beta''_d-(\text{CNB-EDT-TTF})_4 \text{I}_3$	$\beta''_o-(\text{CNB-EDT-TTF})_4 \text{I}_3$
I	125.0	90.9
		162.3
II	51.2	50.6
		50.4
III	219.6	218.0
		207.7
IV	0.6	0.6

The calculated band structure and Fermi surface assuming a +1/4 charge for the donor molecules are shown in Figure 5. As usual for β'' salts³⁴ the Fermi surface has a closed ellipse-like shape centered at the border of the Brillouin zone along the a^* -direction (a being the direction of the π -stacks) for every layer. The orientation and shape of this ellipse depends on the relative strength of the three different interactions.³⁴ Since the interaction of the layers is very small, the area of each ellipse is practically 1/8 of the cross-section of the Brillouin zone. Thus, if the average structure provides a good description of the system it is predicted that magnetoresistance measurements should exhibit Shubnikov-de Haas oscillations with frequencies of 1/8 of the cross-section of the Brillouin zone.

Figure 5. Calculated electronic band structure (left) and Fermi surface (right) for the donor bilayer of the anion disordered structure β''_d -(CNB-EDT-TTF)₄I₃, assuming a +1/4 charge per donor. The dashed line in the band structure refers to the Fermi level and $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$ and $M = (a^*/2, b^*/2)$.

The structure with ordered anions β''_o -(CNB-EDT-TTF)₄I₃ contains one bilayer with two donor molecules as the repeat unit for every single layer. As shown in Figure 4, in this structure there are six different types of intermolecular interactions, two of each type previously described.

Note that the direction of the π -stacks is now b whereas the direction of the step-layers is a . As shown in Table 2, it is only for the interactions along the π -stacks (I and I') that the cell doubling has an important effect; those along the other directions are practically not affected.

The doubling along the π -stacks and the induced sizable differentiation of the interactions along such direction leads to a large splitting of the two pairs of bands along all directions of the Brillouin zone (see Figure 6 left) so that one pair of bands is completely filled and the other pair is 1/4 empty, ultimately leading to the warped but open Fermi surface shown in Figure 4 right. This is in stark contrast with the closed Fermi surface calculated for the average structure of the anion disordered structure. However, the shape of this Fermi surface can be easily rationalized noting that the main difference between the ordered and disordered anion structures is a doubling along the direction of the π -stacks. Consequently, as shown in Figure 7, the Fermi surface of the ordered anion phase can be approximated by folding the Fermi surface of the disordered anion structure along a^* (which will become b^* in the ordered phase because of the labeling change). Because of the folding and the variation in the interactions strength along the π -stacks direction, the successive ellipses only slightly touch and this is the reason why a pair of warped open lines is generated. If the area of the ellipses had been larger, their overlap would have been larger and in addition to the warped open lines a new and smaller closed pocket would have been generated in that region.³⁴

Figure 6. Calculated electronic band structure (left) and Fermi surface (right) for the donor bilayer of β''_o -(CNB-EDT-TTF)₄I₃. The dashed line in the band structure refers to the Fermi level and $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$ and $M = (a^*/2, b^*/2)$.

Figure 7. Schematic construction of the open Fermi surface of the anion ordered structure β''_o -(CNB-EDT-TTF)₄I₃, from that of the anion disordered structure by a folding process. Note the different axis labeling in the two structures.

The absence of closed portions of the Fermi surface in the anion ordered structure of the β''_o -(CNB-EDT-TTF)₄I₃ leads to the prediction that no Shubnikov-de Haas oscillations should be observed in the low temperature magnetoresistance measurements. This is in agreement with the experimental magnetoresistance studies. The fact that such oscillations have not been observed

for the (CNB-EDT-TTF)₄X salts with X = PF₆ and ClO₄ also exhibiting a β'' -type structure strongly suggests that the presently known structures for these anions are only average structures as in the present case.

3.3. Electron Transport Properties. The β''_d - and β''_o - structures above described are specific situations of disordered and ordered anions but probably other intermediately disordered situations may exist in the crystals. Real crystals may even present domains with different degrees of anion ordering. The electrical conductivity and thermoelectric power of several crystals coming from different preparations was measured and in 9 samples no significant differences which could be ascribed to different degrees of anions ordering could be observed in the temperature dependence of both electrical conductivity and thermoelectric power. The behavior of the β'' -type crystals are however strikingly different from that of the κ -phase crystals obtained in previous preparations.

Electrical conductivity of β'' -crystals measured along the long dimension of the elongated plate shaped crystals (donor stacking axis) was found in the range 30-110 S/cm at room temperature. This range of values is believed to reflect mainly the difficulty in accurately measuring the thickness of the small platelet shaped crystals, rather than possible variable degrees of anion ordering. In all samples the electrical resistivity, ρ , decreases upon cooling in the same regular metallic fashion with a resistivity ratio between 300 and 4 K (ρ_{300K}/ρ_{4K}) reaching values of about 120 to 250 depending on the sample quality.

The electrical conductivity of κ -crystals at room temperature (24 S/cm) is slightly below that of the β'' -phases and most significantly it presents a different temperature dependence (Figure 8).¹¹ Upon cooling from room temperature there is first a metallic decrease of resistivity, ρ , although not so fast as in the β'' -phases. This initial decrease of resistivity is however followed

by an anomalous increase upon cooling starting around 150 K and reaching a maximum at ~ 100 K, followed by a final decrease upon further cooling. The magnitude of the maximum in this resistivity hump was found to be sample dependent, reaching in some samples values well above the room temperature value. This anomalous hump has been previously speculated as possibly associated with charge ordering,⁵ but its origin remains unclear. It is worth referring that a similar behavior has been observed in other ET-iodine salts such as in γ -(ET)₃(I₃)_{2.5}.³⁵

Figure 8. Temperature dependence of the electrical resistivity of (CNB-EDT-TTF)₄I₃ single crystals.

κ -crystals below liquid helium temperatures present a sharp decrease of the electrical resistivity upon cooling starting at circa 3.5 K, which is completely suppressed by the application of magnetic fields as small as 0.5 T (Figure 9). This decrease of electrical resistivity does not reach-zero values (resistivity at 1.5 K under zero field is still about 35% of the value at 4 K)

indicating an incomplete superconducting transition with an on-set temperature of circa 3.5 K and a critical field of 360 mT at 1.5 K (Fig S1). This behavior of the κ -crystals contrasts with the β'' -crystals which show no indication of superconductivity down to 1.5 K. In both κ - and β'' -phase crystals no signs of any oscillation were found in the magnetoresistance at 1.5 K under fields up to 18 T. The magnetoresistance at 1.4 K just shows a regular behavior with positive values of $\sim 2.5\%$ per Tesla up to 16 Tesla in the case of the β'' - crystals and $\sim 0.8\%$ per Tesla up to 16 T, in the case of the κ -crystals.

Figure 9. Low temperature dependence of the electrical resistivity of κ -(CNB-EDT-TTF) $_4$ I $_3$ single crystals under different magnetic fields indicated.

The thermoelectric power, S , of β'' -crystals, $75 \mu\text{V K}^{-1}$ at room temperature, show a behavior comparable to that previously reported for β'' -(CNB-EDT-TTF) $_4$ ClO $_4$ and β'' -(CNB-EDT-TTF) $_4$ PF $_6$, with large positive values consistent with the large band filling (7/8) of these 4:1 salts and quite different from that of κ -(CNB-EDT-TTF) $_4$ I $_3$ (with half-filled bands) with $30 \mu\text{V K}^{-1}$ at

room temperature.¹¹ The absolute thermoelectric power of β'' -(CNB-EDT-TTF)₄I₃ crystals decreases regularly upon cooling, first almost proportionally to temperature as in a regular metal but below 200 K it starts decreasing faster, crossing zero at 93 K to reach $-5 \mu\text{V K}^{-1}$ at 60 K and then staying almost temperature independent down to 22 K. The larger thermoelectric power of the β'' - crystals at room temperature when compared with κ -crystals reflects the larger band filling of the first phases. A quite similar temperature dependence of thermoelectric power with sign change upon cooling has been reported in β -(BEDT-TTF)₂I₃ although with a smaller values due to the smaller band filling of the 2:1 salt.^{36, 37} This change in sign of thermoelectric power in β -(BEDT-TTF)₂I₃ at low temperatures was interpreted within a simple band model as a consequence of 2D Fermi surface with points very close to the zone boundary³⁸ in a situation close to the predictions for β'' -(CNB-EDT-TTF)₄I₃.

Figure 10. Temperature dependence of the absolute thermoelectric power of (CNB-EDT-TTF)₄I₃ single crystals

4. Conclusions

In conclusion the present results show that the well-known polymorphism associated with donor packing pattern variation in single layer ET salts is also present in bilayer salts of CNB-EDT-TTF. For (CNB-EDT-TTF)₄I₃ at least two type of polymorphs characterized by β'' - and κ -type packing patterns of donors, have been observed with the same triiodide anions. κ -(CNB-EDT-TTF)₄I₃ displays superconductivity below 3 K while β'' -(CNB-EDT-TTF)₄I₃ crystals remain regular metals down to 1.5 K with a large resistivity ratio ($\rho_{300\text{K}}/\rho_{4\text{K}}$). In addition to the donor packing pattern variations, in β'' -(CNB-EDT-TTF)₄I₃ different degrees of anion ordering over two possible positions of the I₃⁻ anions are possible. A unit cell doubling associated with triiodide anion ordering in these positions is observed. In principle the variable anion order/disorder could affect the shape of the Fermi surface. However, no significant variable disorder effects were detected in the electrical transport properties of different single crystals. The experimental conditions favouring the preparation of any of these polymorphs remain undetermined. The present results most probably just anticipate the possibility of a much larger structural diversity and richer polymorphism in bilayer salts of CNB-EDT-TTF.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of Charge on the ACS Publications website at DOI: [/acs.inorgchem....](#)

Crystallographic data (CIF) and Supplementary Material.

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Author Contributions

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Notes

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