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Electronic Supplementary Material for “Evolution of crystal structure of dual layered molecular conductor $(\text{ET})_4\text{ZnBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ with temperature”

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Analysis of field and angle dependencies of interlayer magnetoresistance

Figure S1 shows angular and field dependencies of interlayer magnetoresistance and orientation of the sample during the experiment. Insert (a) shows that Shubnikov – de Haase oscillations appear at magnetic fields $H > 10$ T. Oscillation frequency $F \approx 950$ T, and cyclotron mass $m^* = (1.9 \pm 0.1)m_e$, where m_e is the mass of the free electron.

The angular dependence of magnetoresistance for the crystal of **1** was measured in the polar plane at different azimuthal angles φ (the polar angle between the normal to the conducting plane and the magnetic field direction is denoted by θ , see Insert (b)). Initial angle $\varphi = 0$ was chosen arbitrarily. A comparative analysis of the angular and field dependencies allows us to conclude that magnetoresistance in the field parallel to the conducting plane ($\theta = 90^\circ$) is almost absent and the angular dependency in the polar plane does not depend on azimuthal angle φ and is determined mainly by the projection of the magnetic field on the normal to the conducting layers.

Such behavior of the angular dependence of magnetoresistance is characteristic of both weakly incoherent^{S1} and strongly incoherent interlayer transport^{S2} and is due to the uncertainty of momentum component p_z during the implementation of both modes. However, only for the case of weakly incoherent transport, semi-classical angular magnetoresistance oscillations (AMRO) should exist in the angular dependence of magnetoresistance at sufficiently high magnetic field. The absence of AMRO on the curves of the angular dependencies of magnetoresistance in magnetic fields above 10 T (Fig. S1) allows us to assume that transport below 20 K corresponds to a strongly incoherent mode rather than weakly incoherent one^{S3}. Thus, strongly incoherent interlayer transport in organic metal **1** takes place in the entire temperature range, namely, from room to helium one. Such transport, most likely, occurs simultaneously through two parallel channels, a jump and a resonant one. The jump channel is caused by electron jumps between neighboring layers as a result of their interaction with phonons and lattice imperfections. Resistance associated with this channel increases with a decrease in temperature. The resonant channel corresponds to the transport of charge carriers through resonant impurities having energy levels near the Fermi level of the conducting layer. The resistance caused by transfer of electrons through such impurities is proportional to intralayer resistance^{S5}, has metal type and at low temperatures shunts the resistance of the jump channel.

Changes in the terminal ethylene groups of ET molecules of LT-phase with increasing temperature

When comparing the figures of the independent part of the structure of LT-phase ($T = 130, 180, 240, 280$ and 315 K), where the atoms are shown as ellipsoids of thermal vibrations (Figs S2-S3), it is seen that the amplitudes of thermal vibrations of the terminal ethylene groups of ET molecules increase at temperatures above 260 K. The size and shape of the ellipsoids of thermal vibrations of ethylene groups at 260-315 K indicate their gradual disordering.

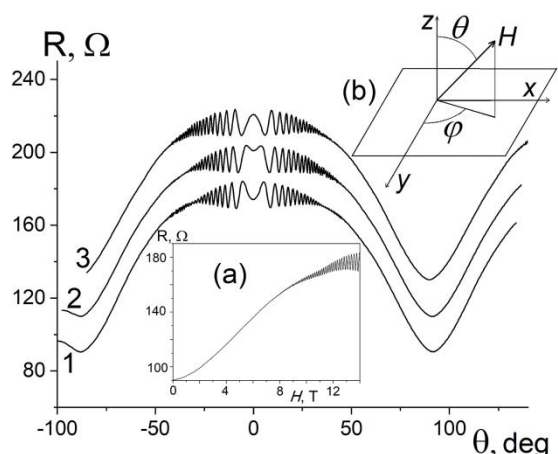


Figure S1. Angular dependencies of interlayer magnetoresistance in the polar plane in the $(\text{ET})_4\text{ZnBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$ crystal for different azimuthal angles φ at $T = 1.5$ K and $H = 14$ T: 1 – $\varphi = 0^\circ$, 2 – $\varphi = 36^\circ$, 3 – $\varphi = 84^\circ$. Curves 2 and 3 are shifted relative to curve 1 by 20 Ohm and 40 Ohm, respectively. Inserts: (a) field dependence of interlayer magnetoresistance, $\theta = 0^\circ$, $T = 1.5$ K; (b) the crystal orientations during the experiment.

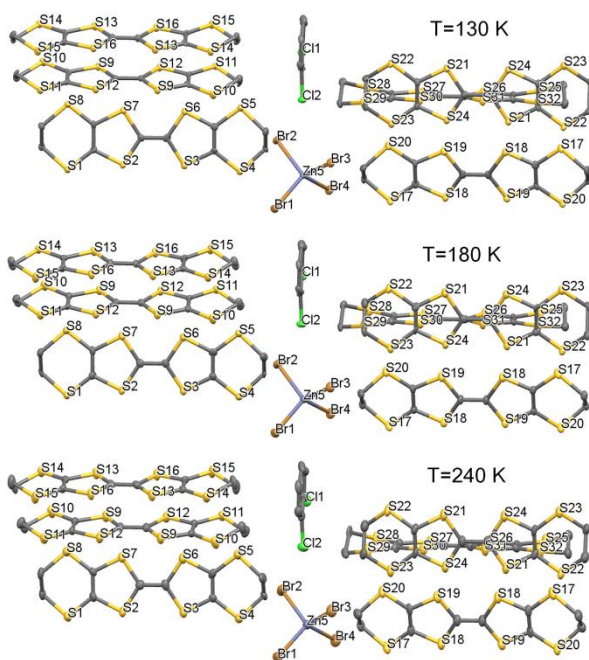


Figure S2. Fragments of the crystal structure of compound **1** below the phase transition at 130 K, 180 K and 240 K. Two independent cationic layers and an anionic layer are presented. The atoms are shown as ellipsoids of thermal vibrations with a 50% probability. Hydrogen atoms are omitted for clarity.

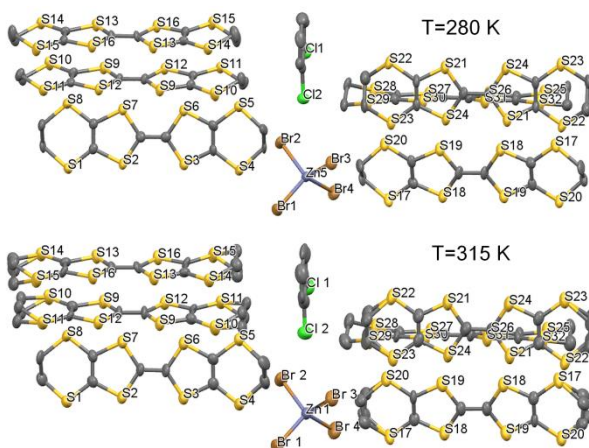


Figure S3. Fragments of the crystal structure of **1** at 280 and 315 K.

Changes in lattice parameters

The temperature dependences of unit cell parameters of **1** in the 100–350 K temperature range are shown in Figure S4. It is seen that parameters a , b , and c change sharply at ~ 320 K, which coincides with T_p found from resistivity measurements. Parameters a and b become equal to each other, and the cell becomes tetragonal. Period c , along which the layers alternate, increases abruptly by $\sim 0.05 \text{ \AA}$. Angles α , β , and γ of the unit cell of the triclinic phase decrease with increasing temperature and at ~ 320 K abruptly become equal to 90° (Table 1). It is noteworthy that in the region of existence of the LT-phase, the rate of changes in parameters a and b (and, consequently, the rate of thermal expansion along the a and b axes) changes

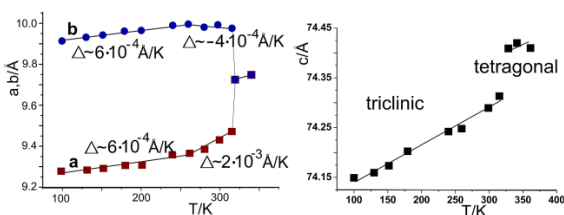


Figure S4. Temperature dependences of the unit cell parameters. The rates of changes in parameters a and b with increasing temperature are designated by Δ .

unevenly. As temperature rises from 100 to 260 K, parameters a and b grow at almost the same rate $\Delta \sim 6 \times 10^{-4} \text{ \AA/K}$. Above 260 K, parameter a grows at a higher rate $\Delta \sim 2 \times 10^{-3} \text{ \AA/K}$ up to 320 K, while parameter b decreases approximately at rate $\Delta \sim -4 \times 10^{-4} \text{ \AA/K}$. Thermal expansion of materials is known to be associated with anharmonic vibrations of atoms and molecules in the structure.⁵⁴ Increasing growth rate for parameter a above 260 K indicates an increase in anharmonic effects in the crystal.

The disordering of the solvent molecule in the HT-phase and the X-ray method for determining transition temperature T_p

Above the phase transition, in the structure at 340 K, all atoms have higher amplitudes of thermal vibrations than at 315 K, which is seen when comparing Fig. S3 and Fig. 5 since thermal vibrations of atoms usually increase with increasing temperature. The dichlorobenzene solvent molecule in the structure at 340 K is disordered over four positions. This is experimentally confirmed by the transformation of a single-domain crystal into a merohedral twin during the transition from the tetragonal to the triclinic phase. Such a twin consists of blocks, each of which corresponds to one of the positions of the solvent in the initial structure. A similar transformation was described by us for the Co-analog¹⁰. Such a transformation can occur with a high probability when the crystal is kept above T_p for a long time and does not occur at all when it is briefly located above the transition temperature.

Figures S5 and S6 show profiles of Bragg reflection with indices (2, 2, 2) above and below the phase transition for a low-quality crystal, which, after heating above the phase transition, became suitable for X-ray studies. The unit cell of this crystal was determined, and a single (Fig. S5) reflection profile was obtained. Then the crystal remained in the same reflecting position, and with a slow decrease in temperature, the profile of this reflection was periodically recorded. Figure S6 shows a profile of reflection of the crystal with indices (2, 2, 2) below the phase transition. Splitting of the peak indicates occurrence of a phase transition. The technique we used makes it possible to determine the phase transition temperature by the X-ray method. When heating a sample at a low rate and using small crystals, changes in the peak profiles can occur in a narrow (approximately one Kelvin) temperature range, while heating and cooling a large crystal leads to shifts in the phase transition temperature since it is difficult to maintain crystal temperature with high precision when the system is open.

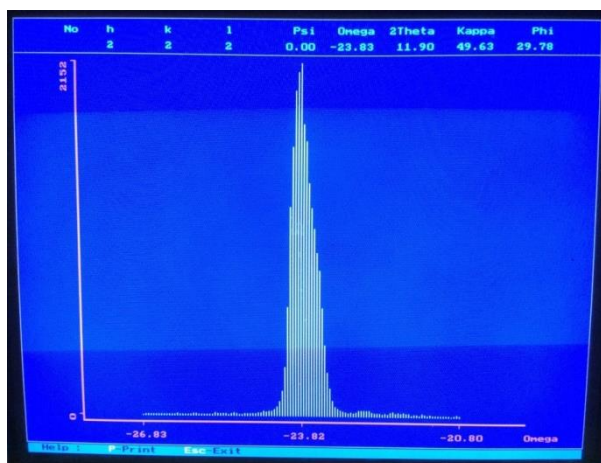


Figure S5. X-ray reflection profile (2, 2, 2) in the HT-phase at 326 K, scanning along the omega axis of a diffractometer with a KM-4 point detector. Tetragonal phase.

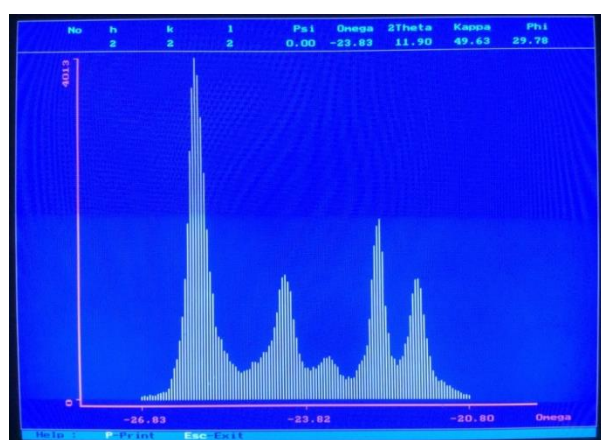


Figure S6. X-ray reflection profile (2, 2, 2) in the LT-phase at 318 K, scanning along the omega axis of a diffractometer with a KM-4 point detector. Triclinic phase.

In accordance with the Curie rule, if any element of symmetry is lost during the phase transition, it is conserved over an ensemble of crystals or within a single crystal breaking it into blocks. Therefore, if crystals are grown at temperature above the phase transition, it is almost impossible to find a single-domain crystal below the transition temperature, and our data confirm this. Growing the $(\text{ET})_4\text{ZnBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$ crystals at temperatures below the phase transition yields single-domain crystals, but sometimes with a small admixture of a twin component.

Notes and references

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