

# Determining ethylene group disorder levels in $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br

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We present a detailed structural investigation of the organic superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br at temperatures  $T$  from 9 to 300 K. Anomalies in the  $T$  dependence of the lattice parameters are associated with a glass-like transition previously reported at  $T_g = 77$  K. From structure refinements at 9, 100 and 300 K, the orthorhombic crystalline symmetry, space group  $Pnma$ , is established at all temperatures. Further, we extract the  $T$  dependence of the occupation factor of the eclipsed conformation of the terminal ethylene groups of the BEDT-TTF molecule. At 300 K, we find 67(2) %, with an increase to 97(3) % at 9 K. We conclude that the glass-like transition is not primarily caused by configurational freezing-out of the ethylene groups.

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Due to their exotic superconducting- and normal-state properties, which resemble those of the high- $T_c$  cuprates, the organic charge-transfer salts  $\kappa$ -(BEDT-TTF)<sub>2</sub>X, X = Cu(NCS)<sub>2</sub>, Cu[N(CN)<sub>2</sub>]Br and Cu[N(CN)<sub>2</sub>]Cl have been intensively studied in recent years<sup>1–6</sup>. Resulting from their layered crystal structure, the electronic properties of these materials are quasi-two-dimensional. This leads to electronic ground state properties for the series of materials which are commonly summarized within a conceptual phase diagram, with the antiferromagnetic insulator X = Cu[N(CN)<sub>2</sub>]Cl and the correlated metals X = Cu[N(CN)<sub>2</sub>]Br, Cu(NCS)<sub>2</sub> on opposite sites of a bandwidth-controlled Mott transition<sup>7</sup>.

In recent thermal expansion measurements on  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br (abbreviated  $\kappa$ -Br hereafter) three kinds of anomalies have been identified<sup>5</sup>: one associated to the superconducting transition at  $T_c = 11.6$  K, a phase-transition-like anomaly at  $T^* \approx 45$  K, and a kinetic glass-like transition at  $T_g = 77$  K. The origin of the  $T^*$  anomaly, coinciding with distinct features in bulk properties, is still unclear<sup>1</sup>. Likewise, the nature of the transition at  $T_g$  remains enigmatic. The lattice response reveals the characteristics of a glass-like transition<sup>5</sup>, where below  $T_g$  some short-range order is frozen in. From the various hypotheses<sup>5,8–10</sup>, the idea of a configurational freezing-out of the terminal ethylene groups of the BEDT-TTF molecule at  $T_g$  received most support.

Fig. 1 displays the orthorhombic crystal structure of  $\kappa$ -Br, space group  $Pnma$  with  $Z = 4$ . It contains alternating layers of a conducting BEDT-TTF cation network (S<sub>8</sub>C<sub>10</sub>H<sub>8</sub>)<sub>2</sub><sup>+</sup> (Fig. 1(b)) and insulating polymeric anion chains Cu[N(CN)<sub>2</sub>]Br<sup>−</sup> (Fig. 1(c)) along the  $a$  direction and shifted by one quarter of a unit cell along  $b$ . The BEDT-TTF molecule network contains centrosymmetric face-to-face dimers in a typical  $\kappa$ -type packing motif, *i.e.*, adjacent dimers are almost perpendicular to each other. Here, the  $\pi$ -framework of each BEDT-TTF donor molecule is inclined to the anion layer, so the ethylene groups (CH<sub>2</sub>)<sub>2</sub> of the donor molecules realize short C–H ··· anion contacts. The polymeric anion, which resides on a mirror plane, contains infinite zig-zag chains of [Cu–dicyanamide–Cu] units, and the copper atoms complete their coordination spheres with the Br atom.

In addition, Fig. 1(b) schematically depicts the two possible relative orientations of the terminal ethylene groups (CH<sub>2</sub>)<sub>2</sub> of the BEDT-TTF molecule. While the outer C–C bonds are parallel in the *eclipsed* configuration, they are canted against each other in the *staggered* one. At high temperatures the terminal groups are thermally excited and fluctuate between the two states, but upon lowering the temperature a preferential orientation in the eclipsed configuration occurs. It has been sug-

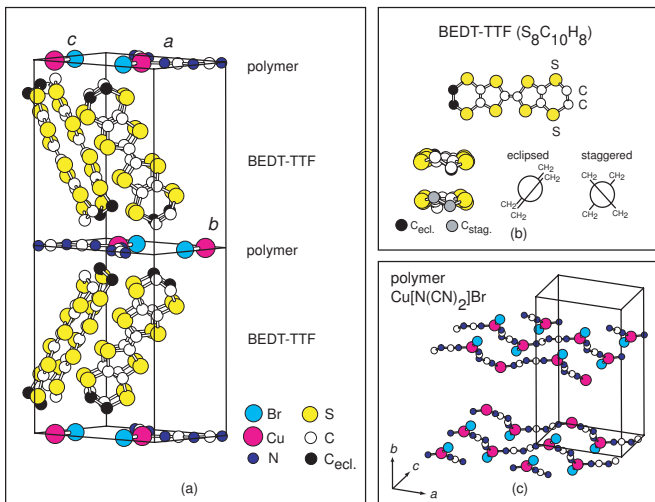


FIG. 1: (Color online) (a) The crystallographic structure of  $\kappa$ -Br. (b) The *eclipsed* and *staggered* configurations of the ethylene groups (CH<sub>2</sub>)<sub>2</sub> of the BEDT-TTF molecule. Lower part shows the view along the long axis of the molecule. (c) View of the packing of the polymeric anion chains in  $\kappa$ -Br. Protons on the BEDT-TTF molecule are omitted for clarity.

gested that at  $T_g$  these excitations freeze out, giving rise to the glass-like phenomena<sup>5</sup>. Then, the "glassy" state below  $T_g$  would be characterized by the level of frozen-in disorder, which will strongly depend on the cooling rate employed experimentally.

Such residual disorder might also account for the pronounced cooling-rate dependence of various normal state properties such as the resistivity<sup>9,11</sup>, as well as it might be the cause for controversial experimental findings concerning the symmetry of the superconducting order parameter of these materials<sup>12,13</sup>. Here, via high-sensitivity ac-susceptibility measurements it was shown that the level of residual disorder and the electronic properties at low temperatures are critically determined by the cooling procedures in the region of the glass-like transition. Indeed, those experiments demonstrate that in the ground state with lowest residual (ethylene) disorder, the behavior is consistent with an unconventional  $d$ -wave order parameter, whereas it might be reasonably well described by the  $s$ -wave model for all states achieved by rapid cooling rates. Further, Sasaki et al.<sup>10,14</sup> revealed a cooling-rate dependent electronic phase separation into metallic and insulating domains in the band-width-controlled Mott system  $\kappa$ -[(h-ET)<sub>1-x</sub>(d-ET)<sub>x</sub>]<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br, and which was associated with the "bad metal" state of these organic superconductors. This state has been linked to a spatial variation in the free energy<sup>10,14</sup> possibly due to progressive freezing-in of disorder associated with the terminal ethylene groups of the BEDT-TTF molecule. Moreover, this kind of disorder has also been considered to have impact on the pinning effect of vortices<sup>15</sup> and on the quasiparticle scattering rate of  $\kappa$ -Br<sup>16</sup>. Hence, for a full understanding of these materials, including their electronic properties, a detailed knowledge of the structural properties is essential.

Despite extensive experimental efforts to unravel the nature of the anomalous glass-like transition at  $T_g$ , a direct proof for a relation between a configurational freezing-out of the ethylene groups, with associated residual ethylene group disorder, and the glass-like transition is lacking, although the accompanied activation energy<sup>5,17</sup> and the observed isotope effect<sup>5</sup> indicate that the terminal ethylenes are involved. While Refs.<sup>5,18</sup> present ample evidence for the existence of a glass-like structural anomaly, the crystallographic structure at low temperatures  $T$  has never been determined with very high resolution. In fact, x-ray diffraction studies<sup>19,20</sup> carried out at 127 and 20 K claimed the observation of a fully ordered structure at these temperatures, with the ethylene groups exclusively adopting the eclipsed configuration (within an experimental uncertainty<sup>5</sup> of  $\sim 10$  %). These studies imply that a disorder-order transition of the terminal (CH<sub>2</sub>)<sub>2</sub> groups should occur above 127 K. Structural investigations by Watanabe et al.<sup>21</sup> identified an irregular  $T$  dependence of the structural parameters near  $T_g$ , but were unable to associate this to a disorder-order transition of the terminal ethylene groups.

In this contribution we present a single crystal struc-

tural investigation of the organic superconductor  $\kappa$ -Br at temperatures  $9 \text{ K} \leq T \leq 300 \text{ K}$  combining laboratory structure refinements and high-resolution synchrotron x-ray diffraction experiments. Distinct anomalies are identified in the  $T$  dependence of all three lattice parameters. Structure refinements between 9 and 300 K reveal that the crystalline symmetry remains orthorhombic, space group  $Pnma$  ( $Z = 4$ ). We determine the residual level of orientational disorder of ethylene configurations to  $3 \pm 3$  % at lowest temperatures.

The single crystal studied here was grown by an electrochemical technique using different solvents with respect to the standard procedure<sup>6</sup>: 60 mg BEDT-TTF, 80 mg tetraphenylphosphoniumdicyanamid and 20 mg CuBr were solved in a mixture of 80 ml tetrahydrofuran (THF) and 20 ml ethylenglycol. Such differences may cause variations in the purity of the material and the structural perfection. The crystal has been characterized in full detail including resistivity experiments<sup>6</sup> (sample #3 with a residual resistivity ratio of 84). Following this non-standard synthesis route the crystal shows a lower residual resistivity  $\rho_0$  and a higher residual resistivity ratio  $\rho(300\text{K})/\rho_0$ , clearly indicating its superior quality. Further, a less pronounced resistivity maximum around 90 K has been observed, which contrasts with "high resistive" behavior observed for materials prepared along the standard route (see *e.g.* Fig. 1 in Ref.<sup>6</sup> for a detailed discussion). Apart from this sample-dependent, extrinsic scattering contribution, however, the different variants behave almost identically with regard to the glass-like transition at  $T_g$ , abrupt changes in the resistivity data at  $T^*$  and the superconducting transition at  $T_c \approx 12 \text{ K}$ .

Synchrotron x-ray diffraction experiments were performed on the 7 T multipole wiggler beamline MAGS,<sup>22</sup> operated by the HMI at the synchrotron source BESSY in Berlin. The measurements were carried out in vertical scattering four-circle geometry at a photon energy of 12.398 keV. All  $T$  dependencies were measured on heating in order to avoid hysteresis effects, with cooling and subsequent heating rates of  $\sim 2 \text{ K/min}$  for these investigations. To avoid sample heating as well as irradiation damages<sup>23</sup> the power of the beam (full beam intensity  $10^{12}$  photons/s at 10 keV) was reduced by four orders of magnitude using absorber foils.

For the structure refinement the crystal was mounted to a displax cryostat on a four-circle Huber goniostat using Mo  $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a scintillation counter. Details of the refinement procedure are given below. For these x-ray diffraction investigations a high cooling rate of  $\sim 4 \text{ K/min}$  was used. According to Ref.<sup>5</sup> this may influence the glass-like transition by shifting the value of  $T_g$  by about 2 K to higher temperatures. As well, if the scenario of a configurational freezing-out is correct, a high cooling rate should lead to a comparatively high level of residual ethylene group disorder.

The  $T$  dependence of the lattice parameters  $a$ ,  $b$ ,  $c$  and the unit cell volume  $V$  were investigated between 10 and 200 K using high-resolution synchrotron x-ray diffraction.

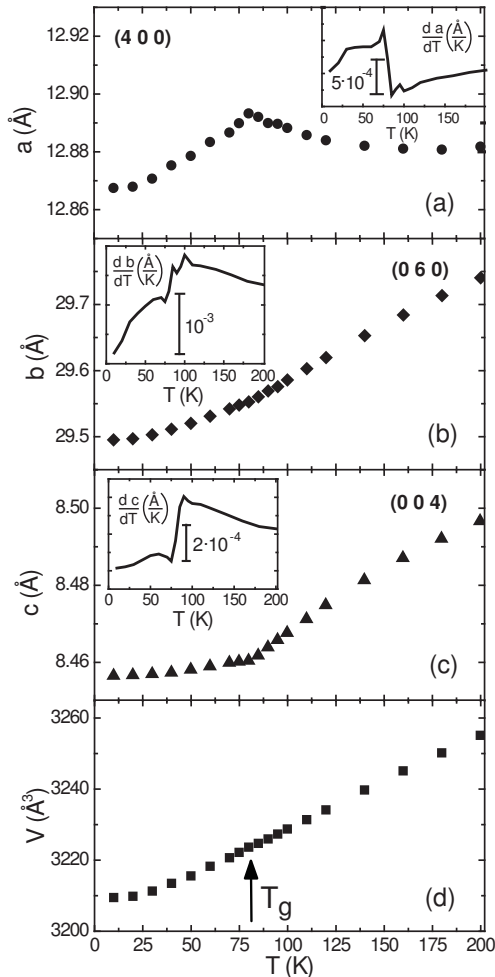


FIG. 2: (a)-(d) The  $T$  dependence of the lattice parameters  $a$ ,  $b$  (out of plane),  $c$  and the unit cell volume  $V$  of  $\kappa$ -Br from synchrotron x-ray diffraction. In the insets the derivatives  $dx/dT$  of the lattice parameters  $x = a, b, c$  are shown.

The results of the (4 0 0), (0 6 0) and (0 0 4) Bragg reflections investigated here for the  $a$ ,  $b$  and  $c$  parameters, respectively, are depicted in Fig. 2. The data for the three principal axes show a highly anisotropic behavior. Upon heating, for the  $a$  axis an upturn is observed. After reaching its maximum at  $T_g$ , the lattice constant abruptly decreases again up to  $\sim 200$  K. In contrast, for the  $b$  and  $c$  directions we find a monotonic increase up to 200 K, with only a small kink at 80 K. Here,  $T_g$  is more accurately determined from the temperature derivatives of the lattice parameters (insets of Fig. 2). However, as result of compensating lattice parameter anomalies, no anomaly in the unit cell volume  $V(T)$  is observed at  $T_g$ . Our data reproduce the findings on the  $T$  dependence of the lattice parameters previously obtained from thermal expansion and x-ray diffraction<sup>5,21,24,25</sup>.

The anomalous behavior of the  $a$  lattice parameter suggests an anomalous change in the bond angle of  $-\text{CN}-\text{Cu}-\text{NC}-$  in the polymeric chain in the temperature range

well above  $T_g$ . This in turn might induce a change in the hydrogen bonding  $-\text{CH}\cdots\text{N}-$  between terminal ethylene groups and nitrogen atoms on the polymer, thus affecting the electronic properties of  $\kappa$ -Br.

It has been proposed that the anomalies in the  $T$  dependence of the lattice parameters are due to a conformational order-disorder transition of the terminal ethylenes<sup>24</sup>. In order to test this hypothesis, we carried out a detailed study of the temperature dependence of the atomic coordinates and the occupation factor, OF, of the eclipsed configuration of the  $(\text{CH}_2)_2$  groups. Intensities of 5398, 7045 and 6986 reflections were measured in the range  $2^\circ \leq 2\theta \leq 34^\circ$  for 300, 100 and 9 K, respectively. The lattice constants were refined by least-square fits to the positions of 72 reflections in the range  $25^\circ \leq 2\theta \leq 30^\circ$ . After absorption corrections the intensity data with  $I/\sigma(I) \geq 10$  were merged to 908, 980 and 965 unique reflections for 300, 100 and 9 K, respectively. The structure has been refined using the program XTAL 3.4<sup>26</sup>, and the atomic coordinates and the anisotropic displacement parameters for non-hydrogen atoms were refined against  $|F|$ . Weights were calculated as  $\sigma^2(F)$ , where  $\sigma(F)$  and  $|F|$  are calculated from  $\sigma(I)$  and  $I$  using non-Bayesian statistics. Weight modification such as  $w = 1/\sigma^2(F)$  has the effect of decreasing the influence on least-squares refinement of reflections affected by larger random or systematic error relative to those less affected.

One of our central issues was to determine if the crystal symmetry remains the same upon cooling through  $T_g$ . Systematic absences of reflections correspond to space group  $Pnma$  for all three temperatures 300, 100 and 9 K, excluding a change of symmetry. Overall, we conclude that the crystallographic structure of  $\kappa$ -Br remains essentially the same above and below  $T_g$ . The lattice parameters, unit cell volume and fit details of our refinements are summarized in Table I. Within experimental accuracy, a comparison to data taken previously yields good agreement regarding lattice parameters, unit cell volume and atomic positions<sup>6,19,20,27</sup>.

The most noteworthy effect of temperature is the tendency towards ordering of the terminal ethylene groups. The values OF were determined using an iterative refinement procedure. First, a full refinement of 187 variables, *i.e.*, atomic coordinates and anisotropic thermal displacement parameters of all atoms except for terminal ethylene groups, was repeated for different population parameters of the carbon atoms in eclipsed and staggered configuration in the interval [1%,99%]. Then, using the solution with minimal  $R$ -factor, a refinement of all atomic coordinates and thermal parameters<sup>28</sup> was performed, iteratively followed by the refinement of all 187 variables and tuning of the population factor. The results obtained for the last cycle are shown in Fig. 3 for temperatures 300, 100 and 9 K. Fits to the data using a parabolic relation yield an occupation factor at room temperature (100 K) of  $\text{OF} = 67 \pm 2\%$  ( $89 \pm 3\%$ ) of the ethylene groups in the eclipsed configuration, in agreement with Ref.<sup>6</sup>. At 9 K,

	300 K	100 K	9 K
$a$ (Å)	12.942(4)	12.884(5)	12.869(4)
$b$ (Å)	29.986(7)	29.581(8)	29.495(6)
$c$ (Å)	8.542(4)	8.484(4)	8.466(3)
$V$ (Å <sup>3</sup> )	3315(3)	3233(4)	3214(2)
OF eclipsed config.	67±2 %	89±3 %	97±3 %
unique reflections	908	980	965
refined variables	187	187	187
$R$ -factor	0.081	0.109	0.114
$wR$ -factor	0.050	0.029	0.052

TABLE I: Lattice parameters, unit cell volume, occupation factor OF and refinement parameters for  $\kappa$ -Br, crystallizing in space group  $Pnma$ , at 300, 100 and 9 K obtained via laboratory x-ray diffraction experiments.

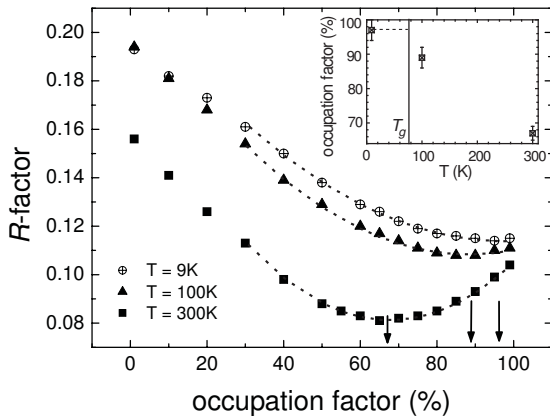


FIG. 3: The refinement parameter  $R$  as function of the occupation factor OF of the  $(\text{CH}_2)_2$  groups in eclipsed configuration at 9, 100 and 300 K. The arrows indicate the positions of minimal  $R$ -values for 300 K, 100 K and 9 K. The inset depicts the  $T$  dependence of OF; for details see text.

the occupation of the eclipsed configuration is clearly favorable with a refined value of OF = 97±3 %.

As expected for the excitation from eclipsed to staggered configuration involving an energy barrier, the occupation factor of the eclipsed configuration shows a pronounced  $T$  dependence. However, the number of terminal groups in the staggered configuration turns out to be unexpectedly small with ~11 % at 100 K, and a residual value of only  $3 \pm 3$  % at zero temperature (inset Fig. 3). This value is the more surprising since we had deliberately chosen relatively high cooling rates in our experiment, which should result in larger residual disorder values. For most experiments reported in literature, the residual disorder levels thus ought to be even smaller. It appears highly unlikely that such small residual disorder is responsible for the transition at 77 K. In structural terms, taking into account that there are 8 pairs of ethylene groups per unit cell, our value at 100 K implies

that  $\leq 8$  % ethylene group disorder leads to an average distance between staggered end groups of the order of 10-30 Å close to  $T_g$ , and which increases substantially as temperature is lowered. In view of the sharp anomalies in thermal expansion measurements<sup>5</sup> as well as the steep steplike increase of the specific heat upon heating through  $T_g$ <sup>18</sup>, there seems to be some cooperativity between the ethylene moieties at the transition. For a disorder-order transition or a configurational freezing-out of the ethylene groups to occur under these conditions a structural element providing a coupling between end groups so far apart is required, that is, the transition at 77 K cannot involve only a freezing-out of terminal ethylene groups activation<sup>29</sup>.

In this context, we note that as a result of our refinement we have obtained unusually large thermal displacement parameters  $U_{ij}$  at low temperatures, *i.e.*,  $U_{ij}(300\text{K})/U_{ij}(100\text{K}) \approx U_{ij}(100\text{K})/U_{ij}(9\text{K}) \approx 1.2-1.5$ , and pronounced anisotropic thermal displacement parameters in particular for the C and N atoms on the polymeric chain. In accordance with only small changes in the resistivity<sup>6</sup> at  $T_g$  despite the pronounced  $a$ -axis anomaly, this observation might indicate that the glass-like transition involves reorientational behavior of the insulating polymeric chain rather than the conducting BEDT-TTF molecule. Unfortunately, even with our detailed structural investigation the experimental resolution is not sufficient to clearly resolve this issue. In particular the large unit cell and thus large number of free parameters in the refinement leads to some parameter interdependency of the atomic coordinates and anisotropic thermal displacement parameters prohibiting to extract further details regarding these structural issues. However, our proposal is supported by various studies on the family of  $\kappa$ -(BEDT-TTF)<sub>2</sub>X<sup>30-33</sup> salts. For instance, extended X-ray absorption fine structure investigations<sup>31</sup> on  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -Br clearly revealed an anomaly around 100 K in the temperature dependence of nearest-neighbor distances around the Cu-atom and which has been directly related to the anomalous transport behavior. Furthermore, even in another class of BEDT-TTF salts<sup>34,35</sup>, *i.e.*,  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]Y, where M is a magnetic or nonmagnetic ion and Y is a solvent molecule, the intrinsic tendency to disorder in the anion chain has been discussed for different solvents in the context of a phase separation in the samples into insulating and metallic states.

Taking together the requirement for another structural element involved in the glass-like transition and the anomalous  $T$  dependence of the  $a$ -axis parameter, very likely the orbital overlap within the BEDT-TTF molecules is affected. Here, structural transformations of the polymeric chain will translate into changes of the orbital overlap within the BEDT-TTF layers. This would account for the experimental observation of a pronounced cooling-rate dependence of the resistivity<sup>11</sup>, and which would be difficult to explain with the small residual level

of disorder of terminal ethylene groups in  $\kappa$ -Br determined experimentally.

In conclusion, for the first time we have directly established the level of residual ethylene group disorder in the organic superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br. We conclude that the glass-like transition does not primarily involve a configurational freezing-out of the terminal ethylene groups. In consequence, other structural or electronic degrees of freedom must be considered in order

to resolve the issue of relevance of disorder and intrinsic sample properties as for instance an anomalous change in the bond angle in the polymeric chain.

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- <sup>28</sup> With the small number of carbon atoms in staggered configuration at low  $T$ , we adopted their atomic coordinates and thermal displacement parameters according to results at 127 K reported in Refs.<sup>19,20</sup>.
- <sup>29</sup> Note, that our conclusion, *i.e.*, that the glass-like transition is not primarily caused by configurational freezing-out of the ethylene groups, is at variance with the statement from Ref.<sup>18</sup>. However, in their discussion the authors did not rule out the presence of a phase transition other than the freezing-out of terminal ethylenes as the origin of anomalies in resistivity and thermal expansion.
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