

TRANSIENT SPECTROSCOPY OF 80 K SECOND ORDER PHASE TRANSITION IN κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X= Cl, I, and Br)

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Abstract

Second order phase transition, observed previously in the title salts in thermal expansion studies close to 80 K, was studied in insulating X= Cl and I salts by a transient spectroscopy of structural relaxation and by controlled annealing. A notable difference in the activation energy of transformation and in annealing behavior compared to the metallic X= Br salt was found, showing transformation towards different structural states at low temperature.

Introduction

Salts of κ -(BEDT-TTF)₂Cu[N(CN)₂]X [BEDT-TTF or ET is bis(ethylenedithio)tetrathiafulvalene, X= Cl, Br and I, we abbreviate the salts by their X in the following] form a family of the highest T_c organic superconductors, T_c=11.6 K in Br and 12.8 K in Cl salts at ambient and 0.3 kbar pressure, respectively [1]. The salts are isostructural and, according to the band structure calculation, should be metals [2]. Br salt really shows metallic resistance temperature dependence R(T) below 90 K [1]. In contrast, Cl and I salts are insulators at ambient pressure. Cl salt can be transformed into a metallic state by application of hydrostatic pressure above 0.3 kbar [3], while I salt remains insulating due to frozen disorder in conformations of terminal ethylene groups of ET molecule [2].

Ethylene ordering is important for the other two salts as well. In all the three salts conformational disorder is observed at room temperature, while the state at low temperatures seems to be different [2]. Random distribution of eclipsed (E) and staggered (S) conformations of ET was found in I salt at 127 K with average population of approximately 0.67 and 0.33, respectively [2]. In Cl and Br salts the situation is more controversial. Initially, it was concluded that ethylene groups are ordered in E-conformation already at 127 K [2]. However, recently the superstructure character of ordering below ca 160 K in Br [4,5] and Cl [6] salts was discovered, unresolved in large thermal factors of carbon atoms in X-ray data [2]. In Br salt further ethylene ordering [7,8] proceeds between the 60 and 90 K sub-branches of phase transition at 80 K [9]. The transformation promotes the formation of a metallic state in Br salt with both usual ET molecule and with the molecule, in which eight hydrogen atoms are completely or partially substituted by deuterium (D-Br salt in the following) [10-15]. Since the difference in R(T) between Cl and Br salts, as well as between Cl salt in metallic and insulating states, appears close to this temperature [16], it can be thought that namely the lack of ordering is responsible for the difference between the metallic and insulating states. Contrary to this intuitive assumption, however, thermal expansion studies have found apparently the same second order phase transition [17,18] in all three compounds, at 73 K (Cl salt), 80 K (Br salt) and 84 K (I salt) (we refer to this feature as '80 K transition' in the

article). In view of recent results for Br salt, it was of interest to study the relation between the 80 K transition in metallic and insulating (Cl and I) members of the family.

We addressed this question by studying (1) the effect of annealing in the vicinity of the 80 K transition on Cl and I compounds, similar to Br and D-Br salts [9-15], and (2) the temperature dependence of the structural relaxation time, similar to our study of Br and D-Br salts [9]. The study is based on a characterization of the isothermal resistance transient $R(t)$ induced by thermal cycling and controlling $R(T)$ as a result of annealing. Large hysteresis of $R(T)$ in Br and Cl salts [17] gave a large magnitude of the transient at a fixed temperature. No hysteresis was noticed in I salt in previous measurements [19]. Contrary to this observation, special isothermal studies in this work revealed resistance relaxation in I salt in 100 to 60 K range, but a small magnitude of the transient (relative resistance change in 10^{-3} to 10^{-4} range, approximately two orders of magnitude smaller than in Br and Cl salts) precluded from its detailed characterization. Hence, in the discussion of relaxation data we focus only on Cl salt in comparison with Br and D-Br salts [9].

As a result of this study we show that annealing of Cl and I salts in the vicinity of the second order 80 K transition does not lead to a gradual transformation towards any new state. We relate this difference in annealing effect compared to the Br and D-Br salts with a profound difference in the temperature dependence of structural relaxation time between Cl and Br salts. This structural difference is interpreted as due to transformation towards different states of ethylene ordering in Cl and Br salts in the ground state. We discuss a pressure-temperature phase diagram of the 80 K transition in the vicinity of metal - insulator boundary in pressure in the framework of competition between superstructure sub-phase and ordering transformations.

Transient spectroscopy

During structural relaxation the system moves from an excited state, created artificially or naturally, towards a stable state. This change has its own activation energy E and is exponential in time, with a relaxation time τ following Arrhenius law, provided that the system can be treated as having two discrete energy levels [20],

$$\tau = \tau_0 \exp(E/kT) \quad (1)$$

τ_0 can vary in a broad range, depending on the physical origin of the process. Structural relaxation can be studied by measuring change in time of any of the physical properties $\alpha(t, T)$ of compound, which in case of exponential relaxation follows the law

$$\alpha(t) - \alpha(\infty) = [\alpha(0) - \alpha(\infty)] \exp(-t/\tau) \quad (2)$$

here $\alpha(0)$ and $\alpha(\infty)$ correspond to the initial and stable values, so the relaxation can be represented by a dimensionless quantity as

$$A(t, T) = [\alpha(t) - \alpha(\infty)] / [\alpha(0) - \alpha(\infty)] = \exp(-t/\tau) \quad (3)$$

An excited state can be created by polarization with an electric field [21], by magnetic field cycling [22] or by thermal cycling [23,9]. In each of these cases the response of the system probes its different properties. By studying the temperature dependence of τ , we can extract from Eq. (1) energy characteristic of the transformation, thus enabling transient spectroscopy of the respective phase transitions.

Experimental

Single crystals of Cl and I salts were obtained as described elsewhere [24]. Sample size was typically $1 \times 1 \times 0.1 \text{ mm}^3$ for Cl salt and $0.6 \times 0.6 \times 0.05 \text{ mm}^3$ for I salt. Standard DC 4-probe technique with current within conducting plane was used for resistance measurements. Detailed $\tau(T)$ dependence was measured on two crystals of Cl salt. Annealing effect data was obtained on two samples of I salt and 2 samples of Cl salt. Except for differences within uncertainty in the relaxation time (see below), qualitative correspondence was observed.

Structural relaxation studies were made by measuring $R(t)$ transient induced by the thermal cycle shown in Fig. 1(a).

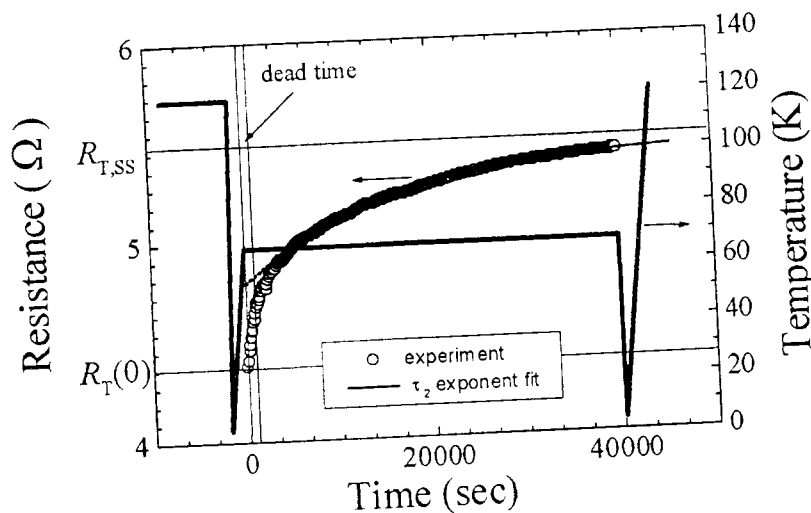


Fig.1. (a) Resistance transient in Cl salt at 68 K and a fit of its tail part with a slow exponent. Two vertical lines show the dead time interval, in which temperature instability is larger than $\pm 0.01 \text{ K}$. Time diagram of the thermal cycle used in the resistance relaxation study corresponds to the right scale. (b) Normalized resistance transients $A_T(t) = [R_T(t) - R_{T,SS}] / [R_T(0) - R_{T,SS}]$ at several representative temperatures.

After establishing a standard initial state by annealing at 120 K for 2 hrs, resulting in the stable and reproducible resistance $R(120\text{K})$ in each cycle, the sample was quenched into liquid helium. Thus a strongly non-equilibrium initial state was created, and its relaxation was studied below 120 K, in the range of 80 K phase transition. The sample was brought to the target temperature by rapid warming (2 K/min) from 4.2 K. This procedure enabled rapid bypassing of the high-temperature range, characterized by exponentially decreased τ according to Eq.(1). It gives the technical advantage of using controlled heating, resulting in a shorter dead time, in which initial temperature instability after reaching the target temperature exceeds $\pm 0.01\text{K}$. The determination of τ in this case encounters some problems, since the most characteristic initial part of the transient is not precise. Keeping this in mind, we adopted the following scheme of transient characterization. (1) We used the value of R_T after first reaching the target temperature T during the initial sweep as $R_T(0)$. (2) The transient was represented in accordance with Eq.(3) as $A_T(t) = [R_T(t) - R_T(\infty)] / [R_T(0) - R_T(\infty)]$. The steady

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state value $R_T(\infty) \equiv R_{T,ss}$ was used as a fitting parameter to obtain an exponential description of the transient tail. This was done by appropriate choice of $R_{T,ss}$ giving a linear $\log A$ Vs. t plot (Fig. 1(b)). The minimum possible $R_{T,ss}$ value was chosen. (3) From the slope of the plot the relaxation time in the tail part of the transient τ_2 was deduced, while the amplitude A_2 of the component was determined from extrapolation of the linear part of the plot till crossing the A axis at $t=0$. Then the transient was fitted beyond the dead time interval by a two-exponential decay function, $A_T(t) = A_1(T) \exp(-t/\tau_1) + A_2(T) \exp(-t/\tau_2)$, $\tau_1 < \tau_2$. This procedure allowed us to obtain a satisfactory fit at all T , though there is an uncertainty of τ_2 within a factor of two and related smaller uncertainties in the values of other parameters due to ambiguity of the precise $R_{T,ss}$ choice in step (2).

Results

An Arrhenius plot of resistance temperature dependence in Cl salt, measured on warming and cooling at a rate of 1 K/min, is shown in Fig. 2.

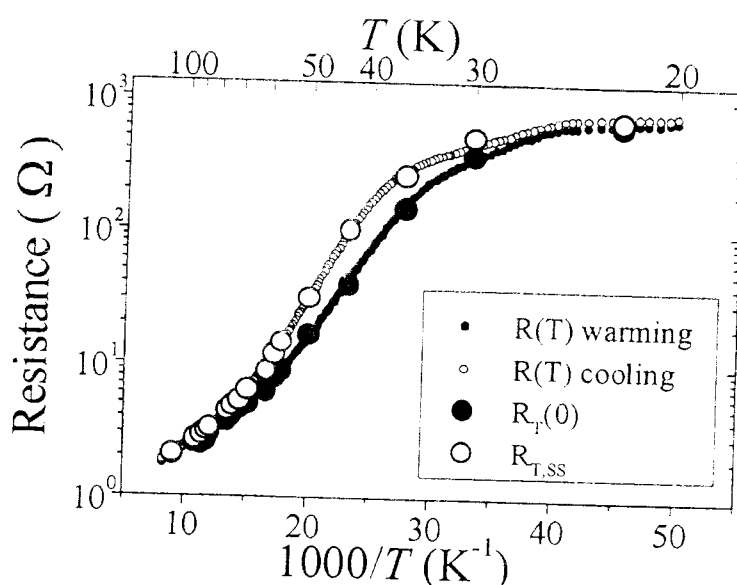


Fig.2. Temperature dependence of the resistance of Cl salt measured on warming and cooling (small circles). Temperature dependence of the initial $R_T(0)$ and steady state $R_{T,ss}$ values, used in transient fit (large circles).

$R(T)$ shows notable hysteresis, similar to previous reports [17,19]. The hysteresis was actually present at all temperatures studied, starting from room temperature, though its magnitude increases notably below 70 K, almost coinciding with the Arrhenius plot slope increase. It is worth noting that warming after quenching gave nearly the same $R(T)$ as obtained on warming after slow cooling, contrary to Br and D-Br salts. Figure 1(b) shows normalized resistance transient in $\log A$ Vs. t plot at several representative temperatures. Below approximately 50 K the plot is linear for almost the full interval studied. At higher temperatures notable non-linearity is observed in the initial part, indicating the essential

contribution of the rapid τ_1 component. The values of $R_T(0)$ and $R_{T,ss}$ used in the transient linearization are shown in Fig.2. They coincide reasonably with R values measured on warming and cooling, indicating a lack of long-term $R(T)$ change towards a new state, contrary to that found in Br and D-Br salts [9-15].

This conclusion was additionally checked by long term annealing (100 hrs) in the vicinity of the second order transition. Annealing was performed at temperatures in the interval 73 ± 10 K for Cl salt and 84 ± 10 K for I salt with a step of 1 K. We have not found any deviation of $R(T)$ beyond the hysteresis curves for both salts, supporting thus the lack of the long-term transformation into any new state.

In order to understand this striking difference between Cl and Br salts we show in Fig.3 the temperature dependence of relaxation time for slow and rapid components, $\tau_1(T)$ and $\tau_2(T)$.

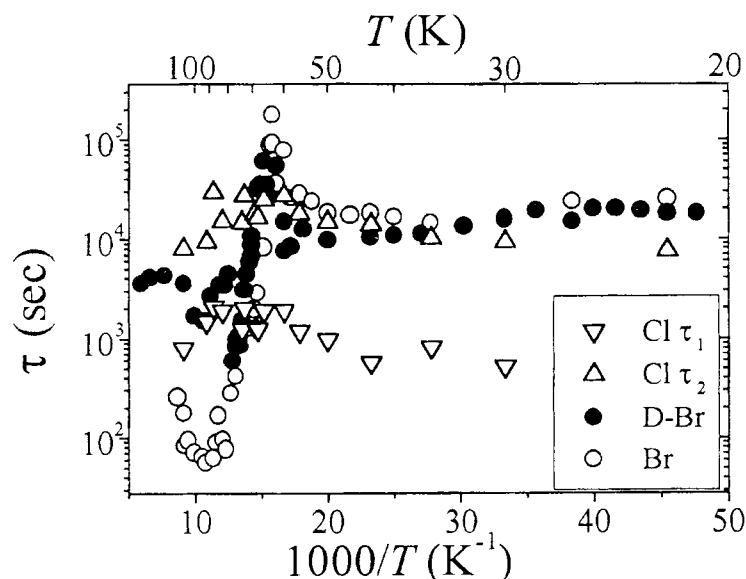


Fig.3. Temperature dependence of the relaxation time for the rapid (τ_1) and slow (τ_2) components of the transient in Cl salt, shown in comparison with τ for Br and D-Br salts [8].

For comparison we show $\tau(T)$ in Br and D-Br salts [9]. As can be seen, neither the rapid nor slow component of the transient in Cl salt show notable deviation beyond an experimental scattering upon passing 73 K second order phase transition. On the other hand, the temperature dependence of the amplitude of the rapid component A_1 (Fig.4) shows notable suppression below approximately 50 K, so that the relaxation becomes nearly exponential below this temperature.

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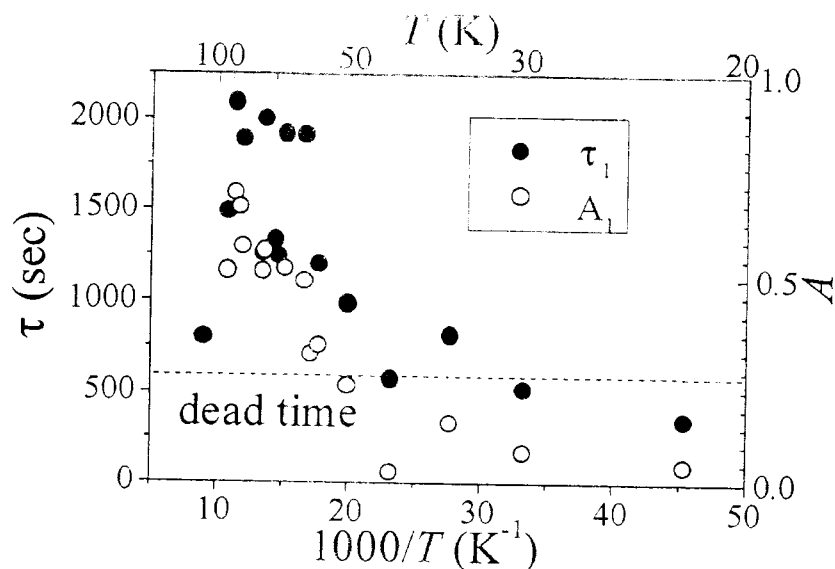


Fig.4. Temperature dependence of the τ_1 and A_1 . Below approximately 50 K the amplitude of the rapid component is zero within experimental scattering.

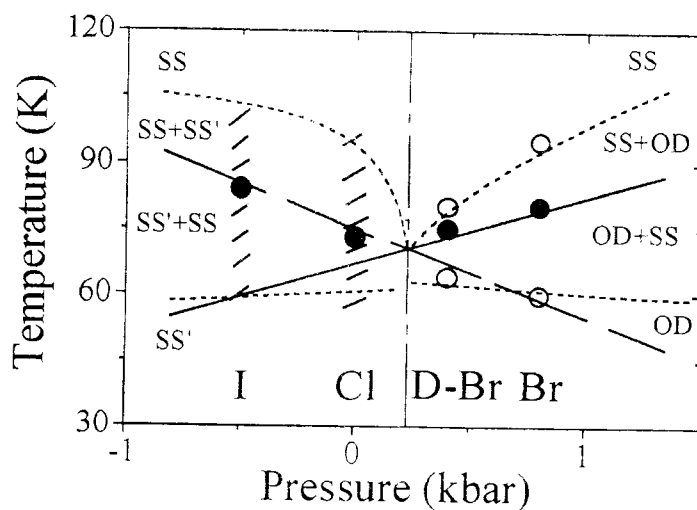


Fig.5. Phase diagram of the 80 K transition. Open circles show location of the hysteresis branches [8], solid circles correspond to the second order phase transition [17-19,9]. Dashed area shows transformation range in Cl and I salts. Cl salt is used as a reference for pressure scale. Positions of D-Br and Br salts on the scale are evaluated from comparison of experimental P-T diagrams [25-27]. position of I salt is arbitrary. Short dashes are guides for eyes for the upper and lower hysteresis branches. Solid line corresponds to the second order superstructure-ordered phase (SS-OD) transition, long dashes correspond to a line of the superstructure sub-phase (SS-SS') second order transition. Metal-insulator pressure boundary is shown with a dashed-dotted vertical line. The sub-phase boundary can be traced into the ordered phase and can be observed experimentally, provided the transformation is incomplete.

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Discussion

We summarized the existing data about 80 K transformation in the pressure-temperature (P-T) phase diagram (Fig. 5). To establish pressure scale we used experimental diagrams for Cl and Br salts [3,5,25-27], showing that the diagrams for Cl, D-Br and Br salts can be matched by a shift in pressure, approximately 0.3-0.4 kbar per salt [25-27]. The position of I salt on this diagram is not clear. Increased stability of the insulating state in the salt to pressure [1,3] can indicate a further shift into the insulating state from the metal-insulator boundary. On the other hand, from consideration of the lattice constants it can be argued that the salt corresponds to higher pressure [4] and may belong to a new insulating domain [28]. We can arrange the salts in the sequence Cl - D-Br - Br, corresponding to increasing pressure, and plot the data from thermal expansion [17-19] and relaxation measurements in the vicinity of the metal-insulator pressure boundary as shown in Fig. 5. The dashed area for Cl salt represents the temperature range in which the amplitude of the rapid component is not equal to zero.

The results of this study show essential difference in the 80 K transformation between the salts. This difference becomes more evident when analyzing the phase diagram. As can be seen from Fig. 3, the width of the interval of the ordering transformation, involving crossing of the 2000 K barrier, sharply decreases from Br to D-Br salt, mainly due to the rapid decrease of the temperature of the upper hysteresis branch. Extrapolation towards the pressure boundary implies crossing of the branches, so the absence of this range in Cl salt seems to be systematic. This conclusion finds support in the existing data for Cl salt under pressure. In the vicinity of pressure boundary at 185 bar resistance relaxation becomes qualitatively similar to Br and D-Br salts [29]. Thus, the same transformation, though taking place both in the metallic and insulating phases, is notably different on both sides of pressure boundary, namely in the lack of 2000 K transformation range.

On the other hand, the relaxation phenomena below the low temperature hysteresis branch are similar (Fig. 3), showing certain similarity of the respective states. Similar correspondence exists between relaxation phenomena induced by magnetic field cycling [22] in the both salts.

The line of second order phase transition seems to have a minimum in the vicinity of the boundary pressure [25-27]. This conclusion can be made by tracing associated anomaly in resistance temperature dependence under pressure, used to plot pressure diagrams for Cl and D-Br salts. It can even be considered as two crossing lines coming with different inclination from the insulating (Cl) and metallic (D-Br and Br) domains (in view of this fact and higher temperature of the second order transition, we place tentatively I salt to the left of the Cl salt). However, common to both metallic and insulating domains, besides the transition itself, is observation of a 'halo' of relaxation in its vicinity.

We start the discussion with Br salt, in which the 80 K transformation is described well by a pseudo-spin variable model of ethylene ordering (EO) [30]. Ordering of ethylene groups on cooling proceeds in two stages: (1) freezing of ethylene motion (at 160 to 200 K) leads to an incomplete order (superstructure phase, SS); (2) transformation to the completely ordered phase OD proceeds on further cooling by second order phase transition at 80 K. The transformation (2) actually proceeds in a broad temperature range in the vicinity of SS to OD phase transition (indicated in the experiment by $\tau(T)$ anomalies, Fig. 3). This peculiarity is caused by the presence of two minima of free energy with a small energy difference (of the order of temperature), separated by a high potential barrier; and smooth change of this energy difference on cooling. This leads to large metastability effects [31]. Existence of SS above 80 K was indeed found in several studies [4,5,32] in Br salt. The coexistence of two phases in the transformation range was observed in the ESR spectra of quenched samples [33]. However, complete ordering predicted by the model for the state below 60 K, although corresponding to

the results of structure determination [7], is in conflict with the existence of SS at low temperatures in high resolution X-ray data [5] and the notable anomaly in relaxation time temperature dependence [9]. This discrepancy seems to arise from interaction between conformational ordering and the electronic system [9,33], not considered in EO model [30].

For the application of the EO model to Cl and I salts, we have to assume the lack of complete order upon the freezing of ethylene motion at around 200 K [34] and the formation of a superstructure in a second order transition [30]. In I salt existing experiments support this model. Second order transition is observed at 230 K [18], and large disorder at 127 K [2] can be assigned to the unresolved SS order. More difficulties arise when dealing with Cl salt. Despite of notable anomalies in the thermal expansion, a second order transition was not detected, similar to Br salt [17]. Formation of the SS at around 160 K was reported only in FTIR and Raman studies, directly probing the ethylene fragment of the molecule and the closely related CN bond in the polymeric anion [6]. If this interpretation is correct, along with small thermal factors of carbon atoms at 127 K and the lack of detectable SS reflections in the X-ray [5], it may indicate small amplitude of modulation of the eclipsed conformation in the crystal.

Stabilization of the SS state upon pressure decrease, as predicted by the EO model [30], could explain the difference in the relaxation phenomena between Cl (and I) and Br (and D-Br) salts. However, according to the model, the SS-OD boundary should go to zero temperature on pressure decrease and no second order transition should be observed within the SS phase. At this point it is worthwhile to recall the discrepancy between the experiment and the model for Br salt [9,33] at the low temperature transformation boundary and the similarity of the relaxation for Cl and Br salts below this line (Fig.3). In view of notable change of electronic properties at this boundary it is natural to conclude a contribution of electronic energy into the transformation. All the predicted features of the EO transformation hold if a sub-phase transformation (SS to SS') of the superstructure takes place instead of a transformation into an ordered phase, provided the SS' is more stable than the OD phase by even the smallest electronic energy gain. If the electronic energy effects the process, for its decrease the sub-phase transformation should push the electronic system of the compound towards an insulating state. This is indeed seen in $R(T)$ in Cl salt as an increase of the activation energy in the temperature range of the transformation (Fig.2). An electronic energy gain should become more important upon pressure decrease, since (1) a purely structural gain in the OD phase compared to the SS phase decreases, and (2) an electronic energy gain increases due to an increase in the density of states. Therefore, it is natural to expect a sub-phase transformation at higher temperature with pressure decrease, as is indeed observed in the insulating phase. Similarly to the ordering transformation, the sub-phase transformation should proceed through coexistence of two phases in some temperature range, giving the characteristic transformation 'halo'. Thus the net effect of the transformation is spread through the 100 to 50 K range, which could explain the lack of sharp changes in electronic properties. In addition, in line with the data of Fig.3, the characteristic energy of SS to SS' transformation should be essentially reduced compared to that of SS to OD, since only a small number of the molecules change their conformational state.

In view of this, it seems reasonable to interpret the 80 K transformation in Cl (and I) salt as a sub-phase transition in the superstructure phase, while in metallic Br and D-Br salts the transformation heads towards an ordered state. This interpretation supposes that in Br salt SS-OD transformation takes place at a higher temperature than the sub-phase transformation. The latter can still be observed in a metallic state if either ordering transformation is incomplete, or the SS' phase becomes more stable than the OD on further cooling. In Cl (and I) salts sub-phase transformation takes place at a higher temperature than the ordering, resulting in a stable superstructure phase at low temperatures.

Conclusion

Second order phase transition observed at around 80 K in the family of organic superconductors κ -(BEDT-TTF)₂Cu[N(CN)₂]X is accompanied by notable difference in lattice relaxation and the annealing effect, depending on whether it is an insulating (Cl and I) or a superconducting (Br and D-Br) salt. We relate this difference to the difference of ethylene ordering in the ground state as a result of competition between sub-phase and ordering transformations of the superstructure phase.

Acknowledgement

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