Evidence for structural and electronic instabilities at intermediate temperatures in $\kappa$-(BEDT-TTF)$_2$X for X=Cu[N(CN)$_2$]Cl, Cu[N(CN)$_2$]Br and Cu(NCS)$_2$: Implications for the phase diagram of these quasi-2D organic superconductors

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We present high-resolution measurements of the coefficient of thermal expansion $\alpha(T) = \partial \ln l(T) / \partial T$ of the quasi-twodimensional (quasi-2D) salts $\kappa$-(BEDT-TTF)$_2$X with X = Cu(NCS)$_2$, Cu[N(CN)$_2$]Br and Cu[N(CN)$_2$]Cl in the temperature range $T \leq 150 \text{K}$. Three distinct kinds of anomalies corresponding to different temperature ranges have been identified. These are (A) phase-transition anomalies into the superconducting, X = Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, and antiferromagnetic, X = Cu[N(CN)$_2$]Cl, ground state, (B) phase-transition-like anomalies at intermediate temperatures (30 - 50) K for the superconducting salts and (C) kinetic, glass-like transitions at higher temperatures, i.e. (70 - 80) K for all compounds. By a thermodynamic analysis of the discontinuities at the second-order phase transitions that characterize the ground state of the system (A), the uniaxial-pressure coefficients of the respective transition temperatures could be determined. We find that in contrast to what has been frequently assumed, the intraplane-pressure coefficients of $T_c$ for this family of quasi-2D superconductors do not reveal a simple form of systematics. This demonstrates that attempts to model these systems by solely considering in-plane electronic parameters are not appropriate. At intermediate temperatures (B), distinct anomalies reminiscent of second-order phase transitions have been found at $T^* = 38 \text{K}$ and $45 \text{K}$ for the superconducting X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts, respectively. Most interestingly, we find that the signs of the uniaxial pressure coefficients of $T^*$, $dT^* / dp_i \ (i = a, b, c)$, are strictly anticorrelated with those of $T_c$. Based on comparative studies including the non-superconducting X = Cu[N(CN)$_2$]Cl salt as well as isotopically labeled compounds, we propose that $T^*$ marks the transition to a spin-density-wave (SDW) state forming on minor, quasi-1D parts of the Fermi surface. Our results are compatible with two competing order parameters that form on disjunct portions of the Fermi surface. At elevated temperatures (C), all compounds show $\alpha(T)$ anomalies that can be identified with a kinetic, glass-like transition where, below a characteristic temperature $T_g$, disorder in the orientational degrees of freedom of the terminal ethylene groups becomes frozen in. We argue that the degree of disorder increases on going from the X = Cu(NCS)$_2$ to Cu[N(CN)$_2$]Br and the Cu[N(CN)$_2$]Cl salt. Our results provide a natural explanation for the unusual time- and cooling-rate dependencies of the ground-state properties in the hydrogenated and deuterated Cu[N(CN)$_2$]Br salts reported in the literature.
I. INTRODUCTION

Organic charge-transfer salts based on the electron-donor molecule bis(ethylendithio)-tetrathiafulvalene, commonly abbreviated BEDT-TTF or simply ET, are characterized by their quasi-twodimensional electronic properties. They consist of alternating conducting ET layers and insulating anion sheets. Within the conducting layers, the delocalization of the charge carriers is provided by the overlap of the π orbitals of sulfur atoms of adjacent ET molecules. The packing pattern of the ET molecules, and thereby the electronic properties, are determined by the anion structure via short C-H···anion contacts of the terminal ethylene groups of the ETs. In forming the solid, these [(CH₂)₂] endgroups can adopt two possible out-of-plane configurations, with the relative orientation of the outer C-C bonds being either eclipsed or staggered. While at high temperatures the [(CH₂)₂] system is thermally disordered, one of the two configurations, depending on the anion and crystal structure, is adopted upon lowering the temperature. This points to the fact that the ethylene conformation is an important parameter determining the structural and physical properties of the ET compounds.

Within this class of materials, the κ-phase (ET)₂X salts are of particular interest because of their interesting superconducting and normal-state properties - some of which are similar to those of the high-Τc cuprates. The compounds with the complex anions X−={Cu(NCS)₂}− and {Cu{N(CN)₂}Br}−, which will be abbreviated as κ-Cu(NCS)₂ and κ-Br, are superconductors with Tc values of 10.4 K and 11.6 K, respectively. On the other hand, the system κ-(ET)₂Cu(N(CN)₂)Cl, in short κ-Cl, is an antiferromagnetic insulator (TΝ=27 K) which can be transformed into a superconductor with Tc = 12.8 K upon applying a small hydrostatic pressure of only 300 bar. Kanoda proposed a conceptual phase diagram for the dimeric κ-type BEDT-TTF salts where the application of hydrostatic pressure has been linked to a variation of in-plane electronic parameters only, i.e. Ueff/W with an effective on-site (dimer) Coulomb interaction Ueff and a bandwidth W: with increasing Ueff/W the ground state changes from a paramagnetic metal (PM) to a superconductor (SC) and further to an antiferromagnetic insulator (AFI). The positions of the various salts with different anions in the phase diagram is determined by their ambient-pressure ground-state properties. In this picture, the deuterated salt κ-(D₈-BEDT-TTF)₂Cu(N(CN)₂)Br, denoted as κ-D₈-Br, is situated right at the AFI/SC border in between the antiferromagnetic insulating κ-Cl and the superconducting hydrogenated κ-H₈-Br salts. The close proximity of an antiferromagnetic insulating to a superconducting phase has been considered - in analogy to the high-Τc cuprates - as a strong indication that both phenomena are closely connected to each other. A theoretical approach to the above proposal has been given by Kino and Fukuyama on the basis of a two-dimensional (2D) Hubbard model. In this picture, the AFI state of κ-(ET)₂X is a Mott insulating phase. The Mott-Hubbard scenario for the title-compound family implies a half-filled conduction band together with strong electron correlations leading to unusual normal-state properties in the metallic phase (pseudogap behavior) close to the magnetic insulating phase and a spin-fluctuation mediated superconductivity.

In fact, various properties of the normal state show anomalous behavior: the spin-lattice-relaxation rate (T1T)⁻¹ of the superconducting κ-H₈-Br and κ-Cu(NCS)₂ salts studied by ¹³C-NMR shows a maximum around 50 K which has been ascribed to antiferromagnetic spin fluctuations. For both compounds, a decrease of the spin susceptibility χSpin in the same temperature range, together with a distinct peak in the temperature derivative of the electrical resistivity, dR/dΤ, has been interpreted as a reduction of the density of states at the Fermi level, i.e. the opening of a pseudogap. The softening of ultrasound modes exhibiting pronounced minima at 38 K and 46 K for κ-H₈-Br and κ-Cu(NCS)₂, respectively, was attributed to the same effect. Besides these anomalies around 50 K, unusual time dependencies in magnetic and transport properties have been reported for both deuterated and hydrogenated κ-Br near 80 K. The experimental situation is still unsettled: a number of recent experiments provide strong arguments for an isotropic gap structure and indicate the particular role of lattice degrees of freedom in the pairing interaction. This conflicts sharply with the results of other experiments, notably NMR measurements performed in infinite magnetic fields, that reveal low energy excitations indicative of an anisotropic pairing state with nodes in the gap. For a review on the controversy on the superconducting state, see for example. In connection with the above controversy on the state below Tc, questions arise about the origin of the anomalous properties at T > Tc and their interrelation to the superconducting state. In addition, one may ask to what extent a comparison can be drawn to the high-Τc cuprates and...
- an obvious concern for the present molecular systems
- what the role of lattice degrees of freedom is for the above-mentioned anomalies.

A most sensitive tool, to probe the lattice properties and their coupling to the electronic degrees of freedom, is provided by measurements of the linear thermal expansion coefficient \( \alpha(T) = \partial \ln l(T) / \partial T \), where \( l(T) \) is the sample length. To this end we have initiated a systematic thermal expansion study on the title compounds. In recent comparative thermal expansion experiments focusing on the uniaxial-pressure coefficients of \( T_c, \partial T_c / \partial p \), for various (ET)\(_2\)X compounds, we found that the interlayer-pressure effect is of crucial importance for \( T_c \). We present here the extension of that work to higher temperatures covering also the unusual normal-state properties. Our thorough comparative studies have enabled us to distinguish three different kinds of anomalies in \( \alpha(T) \) in the temperature range \( 1.5 \text{ K} \leq T \leq 80 \text{ K} \). These are (A) the phase transitions at \( T_c \) or \( T_N \) determining the actual ground state of the system, (B) well-defined \( \alpha(T) \) maxima at intermediate temperatures around \( 30 \text{ K} - 50 \text{ K} \) for the superconducting salts and (C) second-order phase-transition-like jumps in \( \alpha(T) \) due to a kinetic, glass-like transition at higher temperatures around \( 70 \text{ K} - 80 \text{ K} \). As will be shown below, the latter originate in relaxation effects of the ethylene endgroups of the ET molecules. Such a glass-like freezing process of the terminal ethylene moieties provides a natural explanation for the above-mentioned time-dependent transport and magnetic properties found for \( \kappa\)-Br. We will also discuss possible implications of disorder for the ground-state properties. Furthermore, our results hint at a phase transition, i.e. a real gap formation that involves only a minor part of the Fermi surface, in the superconducting salts \( \kappa\)-Br and \( \kappa\)-Cu(NCS)\(_2\) at \( T^* = 38 \text{ K} \) and \( 45 \text{ K} \), respectively, as opposed to a pseudogap on the whole Fermi surface. Concerning the ground-state properties, we will present results on the anisotropy of the uniaxial-pressure coefficients of \( T_c \) for \( \kappa\)-Br that supplement our previous studies \([31,32]\) and give clear thermodynamic evidence for a second-order phase transition at \( T_N \) for \( \kappa\)-Cl.

II. EXPERIMENT

The coefficient of thermal expansion has been measured utilizing a high-resolution capacitance dilatometer \([33]\) with a maximum sensitivity corresponding to \( \Delta l/l = 10^{-10} \). Length changes \( \Delta l(T) = l(T) - l(T_0) \), where \( T_0 \) is the base temperature, were detected upon both heating and cooling the sample. The coefficient of thermal expansion \( \alpha(T) = \frac{\partial ln(l)}{\partial T} \) is approximated by the differential quotient \( \alpha(T) \approx \frac{\Delta l(T) - \Delta l(T_1)}{(T_2 - T_1) \Delta \ln l} \) with \( T = (T_1 + T_2)/2 \).

The single crystals used were synthesized by the standard electrocrystallization technique with typical dimensions of \( (0.5 - 1.5) \text{ mm} \) perpendicular to the highly conducting planes and \( (0.5 - 2.5) \text{ mm} \) along both in-plane axes. In the present work ten crystals have been studied: one \( \kappa\)-Cl sample \( (T_N = 27.8 \text{ K}) \), four crystals of \( \kappa\)-Br and five of \( \kappa\)-Cu(NCS)\(_2\) including samples with various isotope substitutions. Due to the particular shape of the \( \kappa\)-Cl and \( \kappa\)-Br crystals used \([34]\), it was not possible to measure \( \alpha(T) \) along three principal axes on the same sample. For \( \kappa\)-Br measurements perpendicular to the planes \( (b\text{-axis}) \) and along one not specified in-plane axis were performed on crystal \# 2 \( (T_c = 11.8 \text{ K}) \), while measurements along the in-plane \( a \)- and \( c \)-axis were performed on crystal \# 3 \( (T_c = 11.5 \text{ K}) \). The excellent quality of both crystals is reflected by both the high transition temperatures and relatively small transition widths of \( \Delta T_c = 500 \text{ mK} \), as determined by a thermodynamic measurement as well as the pronounced anisotropy in the uniaxial thermal expansion coefficients. To check for reproducibility, we measured another crystal of \( \kappa\)-Br, \# 1, along the out-of-plane axis and found (besides a slightly lower \( T_c \) value of \( 11.5 \text{ K} \)) almost identical expansivity behavior to that for crystal \# 2 in the whole temperature range investigated, i.e. up to \( 200 \text{ K} \). The crystals \# 1 and \# 2 have also been used in our previous study on the uniaxial-pressure coefficients of \( T_c \). For a deuterated crystal, \( \kappa\)-D\(_2\)-Br, which was measured along the \( b \)-axis, no superconducting phase-transition anomaly was found. Regarding the above-mentioned cooling-rate dependence of the ground state, we note that for all samples investigated no changes of the low-temperature expansivity behavior were observed within the parameters accessible with our experimental setup, allowing cooling rates \( q_c \), ranging from \(-1 \text{ K/h} \) up to \(-300 \text{ K/h} \). For \( \kappa\)-Cu(NCS)\(_2\), measurements along the out-of-plane \( a \)-axis were performed on two crystals of the pure compound \( (T_c = 9.2 \text{ K}) \) and three crystals with isotope substitutions either on the ET or anion sites. In each case, a pronounced and relatively sharp phase-transition anomaly was found at \( T_c \). For comparison, we studied deuterated \( \kappa\)-(D\(_8\)-ET)\(_2\)Cu(NCS)\(_2\) \( (T_c = 9.95 \text{ K}) \), anion-labeled \( \kappa\)-(ET)\(_2\)Cu(\( ^{15}\text{N}\)\(^{31}\text{CS})\(_2\) \( (T_c = 9.3 \text{ K}) \) and \( \kappa\)-(D\(_8\)-C\(_4\)S\(_8\)-ET)\(_2\)Cu(NCS)\(_2\) \( (T_c = 9.8 \text{ K}) \) where eight sulfur atoms of the ET molecule have been labeled with \(^{34}\text{S}\), the four ethylene carbon atoms with \(^{13}\text{C}\) and the eight hydrogen atoms with deuterium. As pointed out in \([24]\), the latter compound shows a 'normal' BCS-like mass isotope effect on \( T_c \) for the \(^{13}\text{C}\)\(^{34}\text{S}\) substitution and an 'inverse' isotope effect upon replacing the hydrogen atoms of the ethylene endgroups by deuterium: no isotope effect on \( T_c \) is observed for the anion-labeled salt \([32]\). In the present paper we refrain from comparing superconducting properties for the afore-mentioned \( \kappa\)-Cu(NCS)\(_2\) samples containing isotope substitutions, but have tended to focus on the effect of isotope substitution on the expansivity anomalies at intermediate temperatures (B). For the deuterated sample, the in-plane \( b \)- and \( c \)-axis thermal expansion coefficients have also been measured. This crystal of excellent quality is identical to that studied in
For the determination of $T_c$ and $T_N$, we use the standard "equal-areas" construction in a plot $\alpha(T)/T$ vs $T$. A small misalignment of the crystal orientation of about $\pm 5^\circ$ from the exact alignment cannot be excluded.

### III. CLASSIFICATION OF THERMAL EXPANSION ANOMALIES

Fig. 2 shows the thermal expansion coefficient measured perpendicular to the highly conducting planes, $\alpha_{||}$, for $\kappa-(ET)_2X$ with $X=\text{Cu}[\text{N(CN)}_2]\text{Cl}$, $X=\text{Cu}[\text{N(CN)}_2]\text{Br}$ and $X=\text{Cu}(\text{NCS})_2$ over an extended temperature range. Fig. 2(a) compares $\alpha_{\perp}(T)$ of the non-superconducting salts $\kappa-\text{Cl}$ and $\kappa-\text{D}_{8}-\text{Br}$. In Fig. 2(b) we show the expansivity data of superconducting $\kappa-H_8-\text{Br}$ and $\kappa-\text{Cu}(\text{NCS})_2$. Note the different scales of the ordinate for each case. For the various compounds, a number of anomalies is observed for temperatures $T \leq 80K$ as indicated by the arrows. As will be discussed in more detail below, three different kinds of anomalies can be distinguished that correspond to different temperature ranges:

At temperatures around 70 K – 80 K (C), large second-order phase-transition-like anomalies are found for $\kappa-\text{Cl}$ and both kinds of $\kappa-\text{Br}$ salts. Their characteristic temperatures are labeled as $T_g$. For $\kappa-\text{Cu}(\text{NCS})_2$, a smaller but distinct step-like anomaly at 70 K and a second one at around 53 K can be observed. As will be shown below, these anomalies are of the same origin, namely due to a kinetic, glass-like transition where, below $T_g$, a certain disorder in the positional degrees of freedom of the [(CH$_2$)$_2$] endgroups of the ET molecules becomes frozen in.

In the intermediate temperature range around 40 K – 50 K (B) both superconducting compounds exhibit a pronounced local maximum in $\alpha(T)$ at a temperature labeled as $T^\ast$, Fig. 2(b), while the features are absent in both non-superconducting salts, see Fig. 2(a). These anomalies have been reproduced in detail for all five crystals of $\kappa-\text{Cu}(\text{NCS})_2$ and both of the crystals of $\kappa-H_8-\text{Br}$ measured (see section V). They can thus be regarded as intrinsic properties. Most pronounced is the sharp maximum in $\alpha_{\perp}(T)$ for the $\kappa-\text{Cu}(\text{NCS})_2$ compound at 45 K indicating a significant change in the temperature dependence of the interlayer lattice parameter at this temperature, i.e. an additional strong contraction of the interlayer lattice parameter $\alpha^*$ upon cooling through $T^\ast$. While the overall expansivities of $\kappa-\text{Cl}$ and $\kappa-\text{Br}$ show the usual increase in $\alpha$ as $T$ increases, for $\kappa-\text{Cu}(\text{NCS})_2$ an anomalous temperature dependence is revealed for temperatures $T > T^\ast$, i.e., $\alpha_{\perp}(T)$ decreases with increasing temperature. Above $T \approx 120K$, it even becomes negative corresponding to a progressive reduction of the interlayer distance upon warming. Then, at $T \approx 175K$, $\alpha_{\perp}(T)$ passes through a broad minimum and becomes positive again above 220 K (not shown). The latter findings have been pointed out already in a previous thermal expansion study [30]. In the following, we concentrate on the anomalies at $T^\ast$ found for the superconducting salts. Subtracting the interpolated lattice background and judging from the shape of the separated anomalies, i.e., their sharpness and magnitude, it is tempting to attribute these effects to a true phase transition. We will discuss its relation to the various anomalies reported for these compounds in the literature and propose a generalized scenario for the $\kappa-(ET)_2X$ title compounds in terms of two competing order parameters associated with $T_c$ and $T^\ast$, forming on disjoint parts of the Fermi surface.

At low temperatures, i.e. in the temperature range (A), the thermal expansion behavior is dominated by the phase-transition anomalies characterizing the respective ground state of the system: the ambient-pressure superconductors $\kappa-H_8-\text{Br}$ and $\kappa-\text{Cu}(\text{NCS})_2$ show pronounced negative second-order phase-transition anomalies in $\alpha_{\perp}(T)$ at $T_c = 11.8K$ and 9.3K, respectively. Since the discontinuities in $\alpha_{\perp}^\ast$, $\Delta\alpha_{\perp}$, at $T^\ast$, typical for a second-order phase transition, are related via the Ehrenfest relation to the uniaxial-pressure dependences of $T^\ast$ along the $i$-axis in the limit of vanishing pressure:

$$\left(\frac{\partial T^\ast}{\partial p_i}\right)_{p_i \to 0} = V_{\text{mol}} \cdot T^\ast \cdot \frac{\Delta\alpha_i}{\Delta C}$$

where $V_{\text{mol}}$ denotes the molar volume and $\Delta C$ the discontinuity in the specific heat at $T^\ast$, the large negative discontinuities in $\alpha_{\perp}(T)$ at $T_c$ demonstrate that uniaxial stress perpendicular to the planes causes a strong suppression of $T_c$. In section VI we will discuss the anisotropy of the lattice response at $T_c$ for the superconducting $\kappa-H_8-\text{Br}$ and $\kappa-\text{Cu}(\text{NCS})_2$ salts.

The inset of Fig. 2(a) gives details of $\alpha_{\perp}(T)$ for $\kappa-(ET)_2\text{Cu}[\text{N(CN)}_2]\text{Cl}$ in a representation $\alpha/T$ vs $T$. A distinct negative jump reminiscent of a second-order phase transition can be resolved at 27.8 K. This is about the same temperature at which $^1H$-NMR and magnetization measurements revealed the onset of 3D antiferromagnetic order [37]. Our data thus provide, for the first time in a thermodynamic quantity beyond magnetization, clear evidence for a second-order phase transition in $\kappa-(ET)_2\text{Cu}[\text{N(CN)}_2]\text{Cl}$ at $T_N$.

After analyzing the glassy anomalies at higher temperatures (C) in the following section V we will focus on the expansivity properties in the low- (A) and intermediate-temperature range (B) in sections IV and VI. A conclusion is given in section VII.

### IV. THE GLASS-LIKE TRANSITION

In positionally and/or orientationally disordered systems, relaxation processes can lead to glass-like transitions where, below a certain temperature $T_g$, a short-range order characteristic for this temperature is frozen in. These relaxation phenomena are not limited to "classical” glass-forming materials like undercooled liquids:
corresponding orientational degrees of freedom can lead to glass-like transitions also in polymeric or crystalline materials with large organic molecules as, e.g., single-crystalline C$_{60}$. Such transitions occur when the (structural) relaxation time of the relevant molecular movements, which is growing exponentially with decreasing temperature, exceeds the characteristic time scale of the experiment. Then the system cannot reach its equilibrium state before the temperature further decreases. As a result, the relevant degrees of freedom cannot be thermally excited and, thus, no longer contribute to quantities such as the specific heat: $C^{\text{glass}}(T) = 0$ for $T < T_g$ and $C^{\text{glass}}(T) > 0$ for $T > T_g$ with $C^{\text{glass}}$ representing the additional contribution to the heat capacity. As the volume thermal expansion coefficient is extremely sensitive to glassy effects. Glass-like transitions can be identified by the following characteristics: (i) a step-like increase of $C_V$ and $\beta$ upon heating through $T_g$, (ii) the occurrence of hysteresis around $T_g$, and (iii) a cooling-rate dependent $T_g$ value. Due to the general nature of the molecular motions involved in the relevant relaxation processes, the phenomenology of glass transitions as observed in undercooled liquids applies in certain limits also to the glass-forming subsystems in polymeric or crystalline materials like in the quasi-2D organic superconductors studied in this work.

In a recent ac-calorimetry study of the $\kappa$-Br and the $\kappa$-Cl, salt glass transitions have been reported for both compounds. The authors observed step-like anomalies in the heat capacity around 100 K. The activation energy for the relevant relaxation process has been deduced by analyzing the frequency dependence of the glass-transition temperature. The transition was attributed to a freezing out of the intramolecular motion of the ethylene endgroups of the ET molecules. It was claimed that an extrapolation of the frequency-dependent glass-transition temperatures to frequencies corresponding to "the time scale of our daily life" ($\sim 10^3$ s) would give a $T_g$ value of about 80 K. At about the same temperature, Kund et al. reported an anomalous thermal expansion behavior of the $\kappa$-Br and $\kappa$-Cl salts; these authors found abrupt changes of $\alpha_i(T)$ at 80 K and 73 K, respectively, which they attributed to second-order phase transitions. An explanation was given in terms of an order-disorder phase transition of the terminal ethylenes. The high-resolution thermal expansion results presented here provide convincing evidence for a glass-like transition in the $\kappa$-Br and $\kappa$-Cl salts. This confirms, on the one hand, the above-mentioned specific heat results and clarifies on the other, the nature of the thermal expansion anomalies previously reported by Kund et al. For the first time, we report a glass-like transition also for $\kappa$-(ET)$_2$Cu(NCS)$_2$. A careful study of the cooling-rate dependence of $T_g$ enables us to evaluate the activation energy for the relevant relaxation process. For the $\kappa$-Br compound, we discuss the effect of H-D isotope substitution in the terminal ethylenes. We further discuss the systematics of the glassy behavior for the title compounds and the relation to various time dependencies reported in literature including possible implications for the low-temperature properties.

A. Phenomena and analysis

Fig. 2 shows on expanded scales the anomalies in $\alpha_\perp(T)$ in the temperature range (C) for the $\kappa$-Cl, $\kappa$-H$_8$-Br and $\kappa$-Cu(NCS)$_2$ salts. A distinct hysteresis is seen between the heating (closed symbols) and cooling curves (open symbols). In the heating curves, the former two salts reveal pronounced jump-like anomalies at $T_g \approx 70$ K ($\kappa$-Cl) and 75 K ($\kappa$-Br) with characteristic under- and overshoots at the low- and high-temperature sides of the $\alpha(T)$ discontinuity, respectively. While the heating and cooling data coincide further outside the transition region, they differ markedly close to $T_g$: upon cooling no under- and overshoot behavior can be observed and the $\alpha_\perp(T)$ curves are reminiscent of broadened second-order phase-transition anomalies. Such a hysteretic behavior is not expected for thermodynamic phase transitions but, as mentioned above, it is characteristic of glass-like transitions, where instead of a well-defined transition temperature, one meets a "glass-transformation temperature interval". In contrast to the isostructural $\kappa$-Cl and $\kappa$-Br salts where a single anomaly occurs, the heating curve for the $\kappa$-Cu(NCS)$_2$ compound shows a sequence of two somewhat smaller step-like anomalies at around 70 K and 53 K, cf. Fig. 2(c). The hysteretic behavior indicates that both features are glassy in nature, with the transition region extending over a wide range from about 48 K up to 73 K.

We note that, besides the actual value of $T_g$, which will be discussed below, the details of the heating curves, especially the characteristics of the under- and overshoot behavior, also depend on the thermal history: for all three systems, the overshoot on reheating was found to be more pronounced when the heating rate $|q_h|$ was larger than the preceding cooling rate $|q_c|$. On the other hand, if $|q_h| < |q_c|$, there was relatively little overshoot above $T_g$ but undershoot for $T < T_g$. This is precisely what one expects for "classical" glass-forming systems. The question at hand is which molecular motions are involved in the relaxation process, i.e., what kind of structural degrees of freedom are frozen in at low temperatures. To this end it is helpful to evaluate the activa-
tion barrier for the relevant relaxation process from the cooling-rate \( (q_c) \) dependence of \( T_g \) [49].

1. \( \kappa-(ET)_2 Cu[N(CN)_2]Br \) and \( \kappa-(ET)_2 Cu[N(CN)_2]Cl \)

Fig. 3 shows the linear thermal expansion coefficient \( \alpha(T) \) measured along one non-specified in-plane axis of the \( \kappa-Br \) salt at different cooling rates \( q_c \). The inset on the left side illustrates the hysteretic behavior around \( T_g \). For the transition temperature \( T_g(q_c) \), we use the midpoints of the somewhat broadened step-like anomalies in the respective cooling curves. The figure clearly shows that the transition shifts to higher temperatures with increasing cooling rate \( |q_c| \), whereas the shape of the curves remains unchanged. This behavior is well understood for a glass transition: cooling or heating at a continuous rate, \( q = dT/dt \), may be thought of as a sequence of differential temperature steps, \( \Delta T \), interrupted by intervals of duration \( \Delta t = \Delta T/q \) at which \( T = \text{const} \). The system remains in equilibrium as long as \( \Delta T \) is much longer than the relaxation time \( \tau \) which, for structural rearrangement processes in solids, is known to grow exponentially upon lowering the temperature [3]. At high temperatures, \( \tau \) is small and thus, \( \tau < \Delta t \). As soon as \( \tau \approx \Delta t \) upon cooling, the relaxation of one step is not completed before the temperature further decreases. The greater the cooling rate, the less time remains for relaxation; since, upon increasing \( |q_c| \), \( \Delta T \sim 1/|q_c| \) becomes smaller, the transition defined by \( \tau \approx \Delta t \) occurs at higher temperatures [3].

The inset on the right side of Fig. 3 shows an Arrhenius plot of the inverse of the so-derived glass-transition temperatures, \( T_g^{-1} \), vs \( |q_c| \). The data nicely follow a linear behavior as expected for a thermally activated relaxation time [45][46]

\[
\tau(T) = \nu_0^{-1} \cdot e^{E_a/k_B T}, \tag{3}
\]

where \( E_a \) denotes the activation energy barrier and \( k_B \) the Boltzmann constant. The prefactor represents an attempt frequency \( \nu_0 \).

Based on a simple two-state model [47], Nagel et al. have quantified the above-sketch idea of relating the cooling rate with the relaxation time [46]. They derived a criterion for the glass-transition temperature that allows for a determination of \( \nu_0 \) and \( \tau \) (see below) of \( T_g \).

In a first approximation we set \( \tau(T_g) \approx 1/|q_c| \), yielding:

\[
\ln |q_c| = -E_a/k_B T_g + \text{const}.
\]

This is in excellent agreement with the observed cooling-rate dependence of \( T_g \) cf. right inset of Fig. 3. A linear fit to the data of Fig. 3 yields \( E_a = (3200 \pm 300) \) K and \( \nu_0 = 5 \times 10^{15 \pm 1.5} \) Hz. As mentioned above, there are positional/orientational degrees of freedom for the \( \{\text{CH}_2\}_2 \) endgroups which represent the most deformable parts of the ET molecules [48]. For \( \kappa-Br \), the ethylene groups are known to be partially disordered at room temperature and to become ordered in the eclipsed conformation below 127 K [2]. The characteristic activation energy of the \( \{\text{CH}_2\}_2 \) conformational motion was determined as \( E_a = 2650 \) K by \( ^1\text{H-NMR} \) measurements [17]. This value has to be compared to 2400 K as estimated from ac calorimetry [12], (2000 \pm 500) K from resistance measurements of structural relaxation kinetics [49] and 2600 K also from resistance-relaxation measurements [23]. The similar size of the activation energy derived here, compared to the above numbers, suggests that the \( \{\text{CH}_2\}_2 \) endgroups are the relevant entities for the relaxation process observed in the thermal expansion. A direct check for this possibility is provided by measuring the mass-isotope effect on \( T_g \). For a deuterated \( \kappa-Br \) salt due to the higher mass of its \( \{\text{CD}_2\}_2 \) units, a shift of \( T_g \) is expected: for \( \kappa-\text{D}_8-Br \) the relaxation time \( \tau \) of the terminal \( \{\text{CD}_2\}_2 \) groups at a given temperature should exceed that for the \( \kappa-\text{H}_8-Br \) compound at the same temperature. Using the above criterion for \( T_g \), a longer relaxation time means that for a given cooling rate the system falls out of equilibrium at higher temperatures. Fig. 4 compares \( \alpha_1(T) \) for the hydrogenated compound, \( \kappa-\text{H}_8-Br \) (open symbols), with that for the deuterated one, \( \kappa-\text{D}_8-Br \) (closed symbols). For both compounds, two heating curves are shown taken after slow and fast cooling history \( (q_c^{\text{slow}} \approx -25 \text{K/h} \) and \( q_c^{\text{fast}} \approx -150 \text{K/h}) \). The figure clearly demonstrates that the \( T_g \) values for the deuterated \( \kappa-Br \) salt are shifted by about 3 K to higher temperatures compared to that for \( \kappa-\text{H}_8-Br \). To check for reproducibility, we measured a second sample of the hydrogenated salt from a different batch. We found that under similar conditions, the \( T_g \) value was reproduced within about 250 mK. If one simply assumes that the ratio of the relaxation times for the terminal \( \{\text{CD}_2\}_2 \) and \( \{\text{CH}_2\}_2 \) units scale with the square root of their mass ratios one would expect a positive shift of \( T_g \) of 3.4 % upon \( ^1\text{H} \rightarrow ^2\text{D} \) substitution (here we consider the activation barrier \( E_a \) to be identical for both isotopes). Thus the observation of a \( ^1\text{H} \rightarrow ^2\text{D} \) isotope effect on \( T_g(q_c) \) of about 4% provides clear evidence for a relaxation of the ethylene moieties as the origin of the observed glassy phenomena.

Fig. 5 displays the linear thermal expansion coefficient for the three principal axes, \( \alpha_i(T) \), of \( \kappa-\text{H}_8-Br \). In accordance with the low symmetry of the crystal structure, the lattice response at \( T_g \) is strongly anisotropic (note the different scales of the ordinates). The additional glass contribution to the volume expansivity above \( T_g \), \( \beta^{\text{glass}}(T) = \sum_i \alpha_i^{\text{glass}}(T) \), caused by the excitation of the motional \( \{\text{CH}_2\}_2 \) degrees of freedom is thermodynamically related to the pressure dependence of the entropy associated with the ordering of the ethylene endgroups:

\[
\frac{\partial S_{\text{ethy}}}{\partial p_i} \bigg|_T = -V_{\text{mol}} \cdot \alpha_i^{\text{glass}}(T). \tag{4}
\]

According to room-temperature X-ray diffraction studies, the terminal ethylene groups for the \( \kappa-Br \) and \( \kappa-\text{Cl} \) salts are disordered with the tendency towards the eclipsed orientation [50]. The crystal structure taken at
127 K revealed an ordering in the eclipsed conformation which was confirmed to be the case also at 20 K [51]. Since the X-ray diffraction measurements give only an average structure, disorder at the 10% level cannot be resolved. So, below 100 K there may still be a considerable degree of ethylene disorder. Since the background expansivity is unknown, the temperature dependence of the additional glassy contribution is difficult to determine. Yet, the discontinuities in the α’s can be used to estimate this contribution just above the transition temperature where equilibrium can be established, i.e., at about 90 K: α\text{glass}^\alpha(90 K) ≈ α\text{glass}^\alpha(T_g) = α_\alpha(T → T_g⁻) − α_\alpha(T → T_g⁺). This procedure, as exemplarily indicated in Fig. 2(c) for the c-axis, yields α\text{glass}^\alpha = +20 · 10^{-6} K⁻¹, α\text{glass}^\beta = −52 · 10^{-6} K⁻¹ and α\text{glass}^\gamma = +22 · 10^{-6} K⁻¹ [52]. Using equation (4) and V\text{mol} = 499.37 cm³, we estimate ∂S\text{ethy}/∂p\text{b} = −1.1 J/(mol K kbar), ∂S\text{ethy}/∂p\text{a} = +2.6 J/(mol K kbar) and ∂S\text{ethy}/∂p\text{c} = −1.1 J/(mol K kbar). Consequently, pressure along the b- and c-axes should increase the degree of [(CH₂)₂] order, whereas for uniaxial stress along the a-axis the opposite effect is expected. The uniaxial-pressure effects for stress along the in-plane a- and c-axes are in accordance with the expectation: in the eclipsed conformation, the ethylene moieties of the donor molecules making short C-H···H and C-H···anion contacts are aligned parallel to the a-axis [2]. Therefore, stress along the orthogonal in-plane c-axis should stabilize this conformation and thus should increase the degree of order. On the other hand, the position of a few still disordered ethylenes in the staggered conformation should be stabilized for a-axis stress, as the alignment of the staggered [(CH₂)₂] endgroups is parallel to c (see, e.g., Fig. 8 and Fig. 9 in [2]). Combining the uniaxial-pressure coefficients we find β\text{glass} = −10 · 10^{-6} K⁻¹ and ∂S\text{ethy}/∂p\text{hydr} = ∑ i ∂S\text{ethy}/∂p\text{i} = +0.5 J/(mol K kbar), i.e., a reduction of the degree of ethylene order upon the application of hydrostatic pressure. In a simple two-level model, the difference in the molar entropy between the totally ordered and totally disordered ethylene conformations amounts to S\text{max}^\text{ethy} = Nk_B ln 2 = 2Rln 2 = 11.53 J/(mol K) where N = 2N_A denotes the number of relevant ethylene moieties per mol. Given that only a few per cent of the ethylenes are still disordered at T_g, i.e., that the major part of S\text{max}^\text{ethy} has already been released at higher temperatures, the above estimated value of ∂S\text{ethy}/∂p\text{hydr} underlines the extraordinary large pressure/volume dependence of the ethylene-ordering effects in κ-Br.

In order to estimate the activation energy E_a for the κ-Cl salt, the cooling-rate dependence of T_g was measured in the same way as described above for the κ-Br salt. Again, T_g⁻ follows well a linear ln |q| dependence in the Arrhenius plot yielding E_a = (2650 ± 300) K and ν_0 = 2 × 10^{13±1.5} Hz. The value for E_a agrees well with those reported in the literature: (2600 ± 100) K from ³H-NMR [57] and 2700 K from ac-calorimetry [12]. Due to the particular shape of the κ-Cl crystal used in this work, α could be measured only along the interlayer direction, α_\alpha, and one in-plane diagonal, α_d. The values found for the discontinuities at T_g are Δα_\alpha = +3.75 · 10^{-6} K⁻¹ and Δα_d = −3.5 · 10^{-6} K⁻¹. With α_d = α_\alpha cos² φ + α_\alpha sin² φ for the present orthorhombic crystal structure and φ = 45°, we get Δα_\alpha + Δα_\alpha = 2 × Δα_d yielding Δβ ≈ −3.25 · 10^{-6} K⁻¹ [22]. Using V\text{mol} = 496.66 cm³, we find ∂S\text{ethy}/∂p\text{hydr} = +0.16 J/(mol K kbar), a value which is significantly smaller than that found for κ-Br. The correspondingly smaller pressure/volume effects on the [(CH₂)₂] disorder may be due to the fact that the short C-H···H and C-H···anion contacts are stronger strained for the κ-Cl salt which corresponds to a harder lattice [2].

2. κ-(ET)₂Cu(NCS)₂

The shape of the glass-like transition for the monoclinic κ-Cu(NCS)₂ salt differs substantially from that of the orthorhombic κ-Br and κ-Cl salts. Although these compounds are similar in sharing polymeric, ribbon-like anion chains, the donor molecules of the κ-Br and κ-Cl compounds lean along the anion chain while they are perpendicular to the anion chains for the κ-Cu(NCS)₂ salt. This results in a different network of short C-H···H and C-H···anion contacts which supports an ethylene-endgroup ordering in the staggered instead of the eclipsed conformation [53]. Fig. 2(c) clearly shows that in κ-Cu(NCS)₂, two closely spaced glass-like transitions occur with small but distinct anomalies around T_g = 70 K and T_g = 53 K indicating that, in this case, a simple two-state model is not adequate. Rather it appears that the transition occurs in two steps characterized by different activation energies E_a. Due to the fact that the cooling-curve anomalies can hardly be distinguished from the unknown background expansivity, our data do not allow for a reliable determination of T_g(q_g) and thus E_a. Although the freezing-in process seems to be more complicated as it occurs in two steps, it is likely that also for κ-Cu(NCS)₂ the ethylene endgroups of the donor molecules are the relevant relaxation units. Concerning the effect on the volume expansivity at T_g, we find that the uniaxial effects nearly compensate each other so that the hydrostatic-pressure dependence of the degree of ethylene ordering is rather small. This may be due to the fact that the lattice of κ-Cu(NCS)₂ is harder than that of κ-Br [54]. The rather weak lattice response to the structural rearrangement process occurring at T_g indicates that the occupancy of the staggered conformation is almost complete, i.e., the frozen-in degree of disorder at low temperatures appears to be small for κ-Cu(NCS)₂ compared to that for κ-Br and κ-Cl salts.
B. Discussion

The size of $T_g$ suggests that the energy difference $E_3$ between the eclipsed and staggered conformation is quite small, i.e. of the order of about 100 K. Both $E_3$ as well as the energy barrier $E_a$ depend on the details of the crystal structure, i.e., how the ethylene groups interact with the anion and neighboring ET molecules, and also on how the charge is distributed on the ET molecule because of the electrostatic interaction between the positive protons and the electronegative anions. Considering the slightly smaller unit-cell volume of $V_{uc} = 3223 \text{Å}^3$ (at 127 K) for $\kappa$-Cl compared to 3243 Å$^3$ for $\kappa$-Br [2] as a slightly higher chemical pressure for the former compound, the large positive values of $\partial S_{ethy}/\partial p_{hyd}$ estimated for this salt suggest that the degree of ethylene disorder is higher for the insulating $\kappa$-Cl salt. A rough estimate gives an entropy difference of $(0.2 - 0.3) \text{J/(mol K)}$ between the two salts which is significant compared to the approximated estimated value of $S_{ethy}(T_g) \approx 1.3 J/(mol K)$.

The transfer integrals $t_{eff}$ between adjacent ET molecules determining the electronic structure, depend strongly on the intermolecular distance. Thus, changes in the lattice parameters due to the above-identified glass-like transition may cause anomalies in physical quantities which depend on the transfer integrals as, e.g., transport properties. Indeed, a pronounced kink in the resistivity at 75 K accompanied by hysteresis between heating and cooling has been reported for the $\kappa$-H$_8$-Br salt [54], consistent with our thermal expansion results. Besides the kink structure in the resistivity, the $\text{H}_8$ and D$_8$ salts of $\kappa$-Br show interesting time dependencies affecting both the electronic properties at temperatures below $T^\dagger \approx (75 - 80)$ K and the actual ground-state properties. For superconducting $\kappa$-Br, Su et al. reported relaxation effects in $R(T)$ and a separation of the curves below 80 K as a function of the cooling rate $q_c$ [20,21].

The way of cooling through 80 K was found to influence the low-temperature properties such that the way of cooling through 80 K was found to influence the low-temperature properties such that the way of cooling through 80 K was found to influence the low-temperature properties such that the way of cooling through 80 K was found to influence the low-temperature properties such that the way of cooling through 80 K was found to influence the low-temperature properties such that

$T_c$ for $\kappa$-H$_8$-Br, it has been reported that rapid cooling through $T^\dagger \lesssim 80$ K drives the superconducting ground state of the deuterated salt $\kappa$-D$_8$-Br into an insulating antiferromagnetic state [19,23]. This has been taken as a strong indication for $\kappa$-D$_8$-Br being located right at the border between a superconducting and a Mott-insulating phase.

However, the above temperature $T^\dagger$, below which time dependencies affecting the ground-state properties become important, coincides with the actual glass-transition temperature $T_g$. This suggests that the cooling-rate dependent metal-insulator transition in $\kappa$-D$_8$-Br and the shift of $T_c$ in $\kappa$-H$_8$-Br are related to the above relaxation phenomena.

As the motional degrees of freedom of the [(CH$_2$)$_2$] units become frozen-in below $T_g$ a direct interaction, i.e. a scattering of the charge carriers off that motion is not expected. Rather at $T_g$, the freezing-in process introduces, via the C-H⋯donor and C-H⋯anion contact interactions, a random potential that may influence the effective transfer integrals $t_{eff}$. In fact, the comparison of two recent specific heat experiments on $\kappa$-Br give strong indications for cooling-rate dependent disorder: Nakazawa and Kanoda used the specific heat data of a rapidly cooled deuterated crystal (which is insulating) to determine the lattice specific heat for the $\kappa$-Br salt [56]. The so-derived lattice contribution was found to differ substantially from the one observed in slowly-cooled (superconducting) $\kappa$-H$_8$-Br [24].

It is obvious to assume that the random potential induced by large cooling rates is unfavourable for superconductivity in the present materials [2]. One can think of different mechanisms as to how the disorder affects the superconducting state: (i) Extended structural defects may act as non-magnetic scattering centers but can also have an effect on the density of states $N(E_F)$ due to the deformation of the lattice. (ii) Disorder can induce local magnetization and thus magnetic scattering (pair breaking). In a recent theoretical study, it was pointed out that the effect of disorder on the interplay between magnetism and superconductivity can be crucial for strongly correlated electron systems [57]. (iii) Lattice disorder can lead to Anderson localization and metal-insulator transition, in particular in low-dimensional systems.

To clarify the relative role of the above effects, further material-specific experimental and theoretical studies are necessary. From our experiments we only can state that the phenomenology of the glass-like transition in the ethylene-endgroup degrees of freedom leading to lattice disorder provides a natural explanation for the time dependences and cooling-rate dependent effects reported in literature. To give some numbers, for the deuterated $\kappa$-D$_8$-Br salt, an increase of the cooling rate to 100 K/min has been reported to cause a 13 % depression of $T_c$ (from 11.5 K to 10 K) and a substantial reduction of the superconducting volume fraction compared to slow cooling (0.2 K/min) [19]. According to our results (assuming $E_a$ to be identical to that for $\kappa$-H$_8$-Br) such an increase in
\[ \mid q_0 \mid \text{ is expected to cause an } 18 \% \text{ shift of } T_g \text{ to higher temperatures (from 79 K to 93 K). This would correspond to a considerably higher degree of frozen-in disorder in the rapidly cooled sample which may qualitatively explain the depression of } T_c. \]

To disclose the role of ethylene disorder for the superconducting properties, comparative pressure experiments with hydrostatic pressure applied at temperatures well above and below \( T_g \) would be helpful: due to the large pressure/volume dependence of \( S_{\text{sthy}} \), the degree of disorder is considerably increased for the former experiment compared to the latter, even for a small hydrostatic pressure. Subsequent measurements of the Meissner and shielding volume and the resistivity could provide valuable information about the implication of lattice disorder on the superconducting state of \( \kappa \)-Br. According to this, the latter compound may be considered as a reference system, where the influence of structural disorder on the superconducting properties can be studied in a controlled way on the \textit{same} sample.

\[ \text{V. THE ANTIFERROMAGNETIC TRANSITION IN INSULATING } \kappa-(\text{ET})_2\text{Cu[N(CN)]_2Cl} \]

Although being isostructural to the superconducting \( \kappa \)-Br salt, the small modification of the anion composition of \( \kappa \)-Cl leads to subtle changes of the donor arrangement and to an insulating low-temperature state. Early magnetic measurements revealed the onset of a shallow decrease in the magnetization upon cooling to below 45 K, which was regarded as a signature of antiferromagnetic ordering [1]. In addition, these studies revealed indications for a weakly ferromagnetic state with a small saturation moment of \( 8 \cdot 10^{-4} \mu_B/\text{dimer} \) below 22 K. Subsequently, the spin structure has been studied by \textsuperscript{3}H-NMR measurements [17], yielding a commensurate antiferromagnetic order at \( T_N = 27 \) K with a moment of \( (0.4 \pm 1.0) \mu_B/\text{dimer} \). From these measurements, the authors inferred that the easy axis of the ordered moments is perpendicular to the layers and that a small canting of the spins below 23 K gives rise to a ferromagnetic moment parallel to the layers.

Fig. \[ a \] clearly demonstrates that \( \alpha_{\perp}(T) \) of \( \kappa \)-Cl exhibits another distinct feature besides the glass-like transition: a negative second-order phase-transition anomaly slightly below 28 K. As the anomaly in \( \alpha_{\perp}(T) \) occurs at the same temperature below which \textsuperscript{3}H-NMR measurements revealed the onset of magnetic order, we regard the \( \alpha_{\perp}(T) \) jump as the bulk signature of the antiferromagnetic transition.

Three different proposals have been made for the origin of the magnetic moments and the character of the magnetic state in \( \kappa \)-Cl: (i) lattice disorder due to conformational ethylene-endgroup disarrangements [23] - here the localization of electron states with incomplete compensation of their spins is believed to cause an inhomogeneous, frozen-in magnetic state at low temperatures; (ii) nesting properties of the Fermi surface giving rise to itinerant, spin-density-wave (SDW) magnetism [17,30]; (iii) a Mott-Hubbard type metal-insulator transition leading to a magnetic state characterized by localized spins [17]. As our measurements provide clear thermodynamic evidence for a phase transition at \( T_N \), the first proposal can be discarded. To check for the proposals (ii) and (iii) it is be helpful to inspect the anisotropies in the \( \alpha(T) \) response at \( T_N \) that allows for a determination of the uniaxial-pressure effects on \( T_N \). Within our experimental resolution, there is no anomaly visible at \( T_N \) for both in-plane thermal expansion coefficients, i.e. \( \Delta \alpha_{\parallel} \approx 0 \) (not shown) [17]. According to the Ehrenfest relation, eq. \[ \], this corresponds to a vanishingly small in-plane pressure effect on \( T_N \). Taken together, the negative pressure coefficient of \( T_N \) for uniaxial stress perpendicular to the planes and the negligible in-plane-pressure effect imply a negative pressure effect on \( T_N \) under hydrostatic-pressure conditions, in agreement with the experimental observations.

In contrast to the above dilatometric studies, specific heat measurements have failed so far to detect a phase-transition anomaly [23]. Using the jump height for the volume expansivity \( \Delta \beta \approx \Delta \alpha_{\perp} = -2 \cdot 10^{-6} \text{ K}^{-1} \) and available literature data on the response of \( T_N \) to hydrostatic pressure varying between \(-150 \text{ K/kbar} \) and \(-25 \text{ K/kbar} \), the Ehrenfest relation allows to estimate the expected discontinuity in the specific heat at \( T_N \). We find \( \Delta C_m \approx (20 - 100) \text{ mJ/(mol K)} \), which is much below the experimental resolution of the specific heat measurements reported in [23].

The above findings of a highly anisotropic lattice response at \( T_N \) and, related to this, strongly direction-dependent uniaxial-pressure coefficients, provide a crucial test for models attempting to describe the nature of the antiferromagnetism in \( \kappa \)-Cl. The lack of a visible \( C(T) \) anomaly has been ascribed to the 2D character of the spin correlations, resulting in a short-range 2D ordering of the spins well above the 3D transition temperature. The magnetic exchange-coupling constant for nearest-neighbor interactions was estimated to \( J^\parallel \approx 400 \text{ K} \). Accordingly, most of the entropy of \( R \ln 2 \) is released at temperatures far above \( T_N \) this situation is strikingly similar to that in \( \text{La}_2\text{CuO}_4 \) where the expected jump height in specific heat at the 3D magnetic ordering, \( \Delta C_m(T_N) \), was below the experimental resolution due to the strong 2D antiferromagnetic correlations with \( J^\perp /J^\parallel \approx 10^{-5} \), \( J^\perp \) being the interplane coupling constant. Apart from the small jump in the specific heat which would be compatible with a 3D antiferromagnetic ordering among localized spins at \( T_N \), i.e. proposal (iii), this model is difficult to reconcile with the distinct anisotropy in \( \partial T_N /\partial p \) deduced from our measurements.

On the one hand, for such a scenario, one would expect that in-plane pressure affecting predominantly \( J^\parallel \) should also influence the 3D ordering temperature. This contrasts with our finding of a vanishingly small \( \partial T_N /\partial p \). On the other hand, from the negative pressure coefficient
of $T_N$ for uniaxial stress perpendicular to the planes we infer $\partial J^+ / \partial p_\perp < 0$. However, a decrease of the interlayer coupling constant upon reducing the interlayer distance cannot be understood regarding only nearest-neighbor magnetic couplings in a 3D spatially anisotropic Heisenberg model. The latter has been successfully applied to explain the experimental data of La$_2$CuO$_4$ [56]. However, for the complex crystal structures of the title compounds there are additional, frustrating magnetic couplings [57]. Possibly, these are relevant not only for the in-plane but also for the out-of-plane directions. A suppression of the magnetic order upon stress perpendicular to the planes could be understood if those frustrating interactions were to increase more strongly than the nearest-neighbor couplings. For in-plane pressure, both interactions would have to just cancel out in our case. An explanation in terms of frustrating magnetic couplings could account also for the low value of the transition temperature $T_N$. With respect to a SDW scenario, i.e. proposal (ii), the following aspects are of relevance: as it is likely that the nesting vector lies normal to the open sheets of the Fermi surface with the largest component along the $c$-axis in the conducting plane, in-plane stress is expected to affect the FS topology and thus the nesting properties. In fact, recent uniaxial-strain studies of the SDW transition in $\alpha$-(ET)$_2$KHg(SCN)$_4$ revealed that uniaxial pressure along both in-plane axes alter the nesting properties and, thereby, cause a strong suppression of $T_{SDW}$ [58]. Thus, the absence of any in-plane pressure effect on the antiferromagnetic phase transition in $\kappa$-Cl appears to be in conflict with a simple spin-density-wave scenario. Nevertheless, the fact that uniaxial pressure along the out-of-plane direction suppresses $T_N$ (and subsequently induces superconductivity) would be compatible with a SDW scenario. Uniaxial stress perpendicular to the planes is expected to increase the warping of the cylindrical FS which in turn reduces the nesting properties, thereby allowing superconductivity to form. In fact, such a behavior is observed for $\alpha$-(ET)$_2$KHg(SCN)$_4$ [81] [85].

Our results indicate that none of the above proposals is suited to describe the magnetic state in $\kappa$-Cl satisfactorily. However, certain elements of both models, i.e. of a magnetism of localized moments like it is found for the high-$T_c$ cuprates and of an itinerant, nesting-driven magnetism like in the Bechgaard salts seem to apply for $\kappa$-Cl. This suggests a more complicated magnetic behavior than supposed up to now. In section VI.14 we will discuss a spin-density-wave scenario as for the origin of the phase-transition-like anomalies at $T^*$ in the superconducting salts. In this context we will speculate that the same magnetic interactions cause an antiferromagnetic order among localized spins in insulating $\kappa$-Cl.

VI. INSTABILITIES IN SUPERCONDUCTING $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br AND $\kappa$-(ET)$_2$Cu(NCS)$_2$

A. Uniaxial-pressure coefficients of $T_c$

Fig. 6 shows the linear thermal expansion coefficients $\alpha_i(T)$ for $T \leq 60$ K of (a) $\kappa$-Br and (b) $\kappa$-Cu(NCS)$_2$. For both compounds the lattice response at $T_c$ is strongly anisotropic. In a comparative thermal expansion study aiming at a determination of the uniaxial-pressure coefficients $T_c$ we found that the latter system exhibits a strikingly similar anisotropy of $\partial T_c / \partial p_\perp$ as the compound $\beta$-(ET)$_2$SF$_6$CH$_2$CF$_2$SO$_4$, namely either a positive or vanishingly small pressure coefficient for uniaxial pressure along both in-plane axes, but a huge negative interplane coefficient $\partial T_c / \partial p_\perp$ [81]. Pronounced negative cross-plane pressure effects $\partial T_c / \partial p_\perp < 0$ were found also for the $\kappa$-(ET)$_2$X salts with X=I$_3$ and Cu[N(CN)$_2$]Br [82]. The results for the latter salt are in conflict with those reported by Kund et al. [70], where a vanishingly small cross-plane pressure coefficient of $(0 \pm 0.2)$ K/kbar was claimed. Here we present high-resolution measurements of the linear expansivities for the three principal axes for the $\kappa$-Br salt which clearly reveal negative discontinuities at $T_c$ along all three axes: $\Delta \alpha_a = -(2.1 \pm 0.3) \cdot 10^{-6}$ K$^{-1}$ (out-of-plane) and for the in-plane $a$- and $c$-axes $\Delta \alpha_a = -(1.93 \pm 0.3) \cdot 10^{-6}$ K$^{-1}$ and $\Delta \alpha_c = -(0.2 \pm 0.08) \cdot 10^{-6}$ K$^{-1}$, respectively. The values for the in-plane discontinuities agree well with those reported in a previous thermal expansion study by Kund et al. In order to rule out sample dependencies, we studied a second crystal from a different batch and found almost identical behavior [82]. Using the Ehrenfest relation, eq. (1), and the jump height $\Delta C$ reported in literature [71], we find for the uniaxial-pressure coefficients of $T_c$ for the $\kappa$-Br system: $\partial T_c / \partial p_\perp = -(1.26 \pm 0.25)$ K/kbar (out-of-plane) and for the in-plane coefficients $\partial T_c / \partial p_\perp = -(1.16 \pm 0.2)$ K/kbar and $\partial T_c / \partial p_\perp = -(0.12 \pm 0.05)$ K/kbar. For the hydrostatic-pressure coefficient we get $\partial T_c / \partial p_{hydr} = \sum_i (\partial T_c / \partial p_i) = -(2.58 \pm 0.5)$ K/kbar [72], in excellent agreement with the values found in hydrostatic-pressure experiments, i.e. $-(2.4 - 2.8)$ K/kbar [83,13]. We stress that these uniaxial-pressure results for the various (ET)$_2$X superconductors do not yield a uniform behavior as far as the intralayer pressure effects on $T_c$. In particular, the results on $\kappa$-Cu(NCS)$_2$ show that in-plane pressure can even cause an increase of $T_c$ [81]. Note that this is in contrast to what is assumed in a 2D electronic model [8] and demonstrates that an attempt to model these systems by solely considering in-plane electronic properties is not appropriate.

However, a large negative interlayer pressure coefficient of $T_c$ that predominates the hydrostatic pressure effect is common to all $\kappa$-(ET)$_2$X salts investigated so far. As we discussed in [84,82] the sensitivity of $T_c$ to changes of the cross-plane lattice parameter can arise from pressure induced changes of both the interlayer interaction, i.e., the strength of the 3D coupling and/or the vibrational properties of the lattice.
B. Phase-transition anomalies above $T_c$

1. Phenomena and analysis

Besides the discontinuities associated with the superconducting instability in temperature region (A), the linear thermal expansion coefficients of both compounds show unusual expansivity behaviour in the range $30 - 50\,\text{K}$ (B). For $\kappa$-H$_8$-Br, cf. Fig. 6(a), we find anomalous expansivity contributions $\delta\alpha_i$, i.e. a pronounced local maximum and a shoulder around $37.5\,\text{K}$ for the in-plane $a$- and $c$-axis, respectively, and a maximum at $41.5\,\text{K}$ for the out-of-plane $b$-axis. The slight differences in the characteristic temperatures of these anomalies are most likely an artefact due to the unknown background expansivities, which makes a separation of $\delta\alpha_i$ difficult. As will be shown below, the corresponding contribution to the volume expansivity, $\delta\beta$, can be estimated in a more reliable way allowing for a determination of the characteristic temperature $T^\ast$. We note that for $\kappa$-Br these anomalous contributions at $T^\ast$, $\delta\alpha_i(T^\ast)$, are positive along all three axes whereas the discontinuities at $T_c$, $\Delta\alpha_i(T_c)$, are all negative. Furthermore, we find the smallest effect for $\alpha_c$ where also the lattice response at $T_c$ is smallest. The inset of Fig. 6(a) shows the volume thermal expansion coefficient $\beta(T) = \sum_i \alpha_i(T)$ of $\kappa$-H$_8$-Br together with a smooth interpolation from temperatures below and above the range of anomalous expansivity behavior. This procedure allows for a rough estimate of the anomalous contribution $\delta\beta(T)$.

At slightly higher temperatures, anomalous expansivity behavior is found also for the $\kappa$-Cu(NCS)$_2$ salt, see Fig. 6(b). Here, the background expansivity along the out-of-plane direction $a^\ast$ is rather difficult to estimate due to both the nearness of the glass-like anomaly around $53\,\text{K}$ and the unusual overall temperature dependence of the $a^\ast$ lattice parameter. Yet, a determination of the sign and the approximate size of the anomalies for each axis is still possible: there is almost no anomalous contribution visible for $\alpha_0$ but a distinct negative anomaly for $\alpha_c$, cf. the dotted line representing the approximate background contribution. The largest effect, i.e. a sharp maximum at $T^\ast = 45\,\text{K}$ is found for $\alpha_{a^\ast}$. Again, as for $\kappa$-H$_8$-Br, the signs of these anomalies are strictly anticorrelated with those of the discontinuities at $T_c$: there is almost no anomaly in $\alpha_b$ both around $T^\ast$ and at $T_c$: a positive jump in $\alpha_c$ at $T_c$ is accompanied by a negative contribution at $T^\ast$ and the large negative $\Delta\alpha_{a^\ast}$ at $T_c$ complies with the large positive peak structure at $T^\ast$. These results imply that for both compounds, the uniaxial-pressure coefficients of the anomaly at $T^\ast$ and those at $T_c$ are strictly anticorrelated in their signs but correlated in their magnitudes: for $\kappa$-Cu(NCS)$_2$, for example, uniaxial pressure applied perpendicular to the planes causes a substantial shift of the $45\,\text{K}$ anomaly to higher temperatures while at the same time it strongly reduces $T_c$. The inset of Fig. 6(b) compares the corresponding contributions to the volume expansion coefficient for both salts. We find sharp peaks in $\delta\beta$ at $T^\ast = 38\,\text{K}$ and $45\,\text{K}$ for $\kappa$-H$_8$-Br and $\kappa$-Cu(NCS)$_2$, respectively, reminiscent of somewhat broadened second-order phase transitions. We note that the overall shape of the anomaly, i.e. its width and asymmetry, but not the peak itself depends somewhat on the interpolation procedure employed to determine the background expansivity. The error bars include the uncertainties in the interpolated lattice background and sample-to-sample variations.

2. Discussion

The above described anomalies in $\alpha(T)$ at intermediate temperatures are particularly interesting because magnetic, transport and elastic properties exhibit anomalous behavior in the same temperature range. As mentioned in the introduction, the presence of strong antiferromagnetic spin fluctuations preceding the superconducting transition has been inferred from measurements of the $^{13}$C-NMR, yielding a pronounced maximum in $(T_1T)^{-1}$ around $50\,\text{K}$ for $\kappa$-Cu(NCS)$_2$ and at somewhat lower temperatures for the $\kappa$-Br salt. The rapid decrease of $(T_1T)^{-1}$ below $50\,\text{K}$ has been ascribed to the opening of a pseudogap in the spin-excitation spectrum - an interpretation that has been proposed first by Kataev et al. based on their analysis of ESR data. At about the same temperature, anomalous behavior has been reported also from various other quantities, as, e.g., the decrease of the spin susceptibility studied by Knight-shift and dc-magnetization measurements, indicative of a depression of the density of states at the Fermi level and the resistivity, showing a pronounced peak in its temperature derivative dR/dT. The coincidence of these features in the electronic and magnetic properties with the $\alpha(T)$ anomalies described above suggest a common origin of the various phenomena. This is corroborated also by the response of these features to hydrostatic pressure. From the positive sign of the anomalous expansivity contribution $\delta\beta(T)$, cf. inset of Fig. 6(b), a shift of $T^\ast$ to higher temperatures is expected under hydrostatic pressure. In fact, a positive hydrostatic-pressure coefficient has been found in the magnetic and transport measurements. A similar, positive pressure effect has been observed also for the anomalies in the elastic constants. At ambient pressure, a pronounced softening of ultrasonic modes has been detected at $38\,\text{K}$ and $46\,\text{K}$ for $\kappa$-Br and $\kappa$-Cu(NCS)$_2$, respectively. These sound velocity anomalies have been assigned to a magnetic origin due to their phenomenological relation to the NMR results. However, an alternative interpretation in terms of a structural phase transition could not be excluded. Owing to the large response of the anomaly in $\alpha(T)$, thermal expansion measurements provide a most sensitive tool to investigate these effects in detail. In particular, a comparative study covering var-
ious related (ET)$_2$X compounds is helpful to find out the relevant structural and/or electronic parameters involved. Interestingly enough, corresponding features are absent in $\beta''$(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ ($T_c = 5$ K; large discrete anions) [24], $\kappa$-(ET)$_2$I$_3$ ($T_c = 3.5$ K; linear anions) as well as $\alpha$-(ET)$_2$KHg(SCN)$_4$ (non-superconducting; thick, polymeric anions) [22], showing smooth, Debye-like temperature dependences of $\alpha(T)$ along all crystal axes for temperatures up to 200 K. Accordingly, purely intramolecular changes of the ET molecule can be ruled out to account for the $T^*$ anomalies in the $\kappa$-Br and $\kappa$-Cu(NCS)$_2$ salts. Obviously, the peculiarities of the packing arrangement and the coupling to the charge compensating anions, both of which result in a very similar electronic structure for the latter two salts (but a slightly different one for the various others), are crucially important for the anomalies at $T^*$. An intimate relation to the electronic structure is in line with the absence of corresponding features in both the non-metallic $\kappa$-Cl as well as in the deuterated $\kappa$-D$_8$Br, cf. Fig. 4 and is also corroborated by our supplementary investigations on the isootope effect: For the $\kappa$-Cu(NCS)$_2$ salt we compared $\alpha_\perp(T)$ of the pure system to that of crystals with various isotope substitutions. This includes not only the deuterated $D_8$-counterpart but also isotope substitutions at the anion as well as the cation sites. For the latter, a $\kappa$-(D$_8$S$^{13}$C$_4$S$^{34}$S$_8$)-ET)$_2$Cu(NCS)$_2$ crystal yielding a mass change of 28 amu per ET molecule has been investigated. For all isotopically labelled crystals the maximum in $\alpha_\perp(T)$ could be reproduced in detail without any significant shift in $T^*$. From the absence of a measurable isotope shift, cooperative structural changes in the ethylene-endgroups as well as in the anion or intermolecular rearrangements in the cation system can be ruled out. Hence, we propose that the anomaly at $T^*$ is caused by the electronic structure, i.e. the Fermi-surface topology, which, according to band structure calculations, should be similar for the $\kappa$-Br and $\kappa$-Cu(NCS)$_2$ salts [23]. The presence of strong antiferromagnetic interactions as seen in the NMR experiments then hint at a spin-density-wave (SDW) rather than a pure charge-density-wave (CDW) formation. This scenario implies that the SDW and superconductivity form on disjoint parts of the Fermi surface (FS). The SDW state is likely to involve the small, quasi-onedimensional portions while leaving the major twodimensional parts of the FS unaffected. The latter is subject to the superconducting instability in the $\kappa$-Br and $\kappa$-Cu(NCS)$_2$ salts. We suppose that a relative shift of one of these FS portions in favour of the other can be induced by the application of uniaxial pressure: For instance, uniaxial pressure along certain crystallographic directions may destroy the nesting properties of the quasi-onedimensional parts, thereby destabilising the SDW state and causing a negative pressure coefficient of $T^*$. As a consequence, the remaining quasi-twodimensional parts of the FS will increase. Since this will reinforce superconductivity, an increase of $T_c$ is expected. On the other hand, those uniaxial-pressure conditions that improve the nesting properties and, by this, cause an increase in $T^*$ will result in a reduced remaining FS and, thus, in a drop of $T_c$. Such an anticorrelation of the uniaxial-pressure coefficients of $T^*$ and $T_c$ is exactly what we have found in our experiment.

The presence of two "subsets" of $\pi$-electrons in $k$-space corresponding to the quasi-1D and -2D parts of the FS would be compatible with the NMR results: while the quasi-2D parts cause an ordinary Korringa-type relaxation behavior, the good nesting properties of the quasi-1D portions give rise to a $(T_1T)^{-1}$ component that grows with decreasing $T$. Upon cooling through $T^*$, a real gap on that part of the FS opens and causes a rapid drop in the corresponding $(T_1T)^{-1}$ contribution. A loss of the minor part of the FS (say about 10%) is also capable to account for the change in the temperature dependence of the resistivity from a larger slope $(T > T^*)$ to a smaller slope $(T < T^*)$, i.e. a relative increase in $\rho(T)$ at $T < T^*$. Such a scenario implies that cooling through $T^*$ is accompanied not only by a reduction of the spin susceptibility, as has been seen in several of the above-mentioned experiments, but also by the development of a (weak) magnetic anisotropy. To check for this possibility, we have initiated a careful study of the spin susceptibility on the various $\kappa$-(ET)$_2$X salts which, in fact, confirm our expectation [26].

It remains to be seen, whether the disappearance of a minor part of the Fermi surface would be compatible with the results of the Fermi-surface studies on these materials. If we speculate a little further, it is tempting to associate the antiferromagnetism in the $\kappa$-Cl salt also with a SDW state. As a consequence, we propose that in the latter salt, the large gap seen in various quantities such as the optical conductivity [25], involves only the charge degrees of freedom but leaves the spins unaffected. Upon cooling down to $T_N = 27.8$ K in such a commensurate charge-ordered state, the same antiferromagnetic interactions between nearest neighbour spins that cause the SDW state in the $\kappa$-Br and $\kappa$-Cu(NCS)$_2$ salts then lead to a commensurate antiferromagnetic order in $\kappa$-Cl.

VII. CONCLUSION

Fig. 8 summarizes our results on the various $\kappa$-(ET)$_2$X compounds discussed in the present paper. To this end we use as the abscissa hydrostatic pressure following the suggestion of [24]. The positions of the various salts at ambient pressure is indicated by the arrows. The solid lines representing the phase boundaries from the paramagnetic (PM) to the superconducting (SC) and insulating antiferromagnetic (AFI) states refer to the results of hydrostatic-pressure studies of $T_c$ and $T_N$ [26]. It is important to keep in mind, however, that the pressure effects are highly anisotropic. In an attempt to find out the relevant directional dependent material-to-properties correlations, no simple systematics was found for the intraplane pressure coefficients of $T_c$. On the other hand,
a feature common to all systems studied among the \( \kappa-(ET)_2X \) salts is the large negative effect for uniaxial stress perpendicular to the planes on both \( T_c \) as well as \( T_N \). In both cases the pronounced interlayer effect dominates the \( T_c \) and \( T_N \) shifts found under hydrostatic-pressure conditions. Our results provide clear thermodynamic evidence for a second-order phase transition at \( T_N = 27.8 \text{ K} \) in \( \kappa-\text{Cl} \).

At elevated temperatures, a glass transition at \( T_g \) has been identified that defines the boundary between an ethylene-liquid at \( T > T_g \) and a glassy state at \( T < T_g \) (dotted line): at temperatures above \( T_g \), the motional degrees of freedom of the ethylene endgroups can be excited and thus contribute to the specific heat and thermal expansion whereas below \( T_g \) a certain disorder is frozen in. The glass-like transition which is structural in nature has been shown to imply time dependencies in electronic properties. We discussed possible implications on the ground-state properties of \( \kappa-\text{Br} \) in terms of frozen-in lattice disorder depending on the cooling rate employed at \( T_g \). Using similar cooling conditions, the degree of frozen-in disorder seems to be largest for \( \kappa-\text{Cl} \) and decreases from \( \kappa-\text{Br} \) to \( \kappa-\text{Cu(NCS)}_2 \). Considering the large pressure/volume dependence of \( S_{\text{ethy}} \) for the \( \kappa-\text{Br} \) salt we proposed a pressure experiment which could clarify the relative role of lattice disorder for the ground-state properties of hydrogenated and deuterated \( \kappa-\text{Br} \).

At intermediate temperatures, we observe an anomalous expansivity contribution, \( \delta \beta(T) \), at \( T^* \) for the superconducting salts, symbolized in Fig. 7 by crosses. These anomalies coincide with various features observed in magnetic, transport and elastic properties (shaded area). Among them are the peak in \( (T_1 T)^{-1} \) and the decrease of \( \chi_{\text{spin}} \) at that point to strong antiferromagnetic fluctuations and the decrease of the density of states at the Fermi level.

We proposed that, instead of a pseudogap on the whole Fermi surface as has been frequently discussed in the literature, a real gap associated with a SDW on minor parts forms below \( T^* \). This scenario implies that the SDW and superconductivity involve disjoint parts on the Fermi surface, i.e. that the antiferromagnetic fluctuations compete with rather than contribute to the superconducting instability. In a generalized picture including also the AFI phase, the nature of the magnetic state in \( \kappa-\text{Cl} \) might be that of an antiferromagnetic order among nearest-neighbor spins, i.e. a commensurate spin-density-wave.

Although electron correlations are important for the quasi-2D organic superconductors, we have shown that a phase diagram solely based on electronic degrees of freedom is not appropriate. This is supported by recent theoretical investigations of the 2D Hubbard model and its application to the \( \kappa-\text{Br} \) and \( \kappa-\text{Cl} \) salts [11]. It has been found that one single parameter like the Coulomb repulsion \( U_{\text{eff}} \), the effective transfer integrals \( t_{\text{eff}} \) or the orthorhombic distortion \( c/a \) cannot govern the physics of the AFI/SC interface. It is a combination of electronic correlations, electron-phonon coupling and interlayer effects as well as the influence of lattice disorder which have to be considered in order to understand more clearly the interesting physics of the \( \kappa-(ET)_2X \) title compounds.

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[1] P. C. W. Leung, T. J. Emge, M. A. Beno, H. H. Wang, J. M. Williams, V. Petriceck, and P. Coppens, J. Am. Chem. Soc. **107**, 6184 (1985).

[2] U. Geiser, A. J. Schultz, H. H. Wang, D. M. Watkins, D. L. Stupka, J. M. Williams, J. E. Schirber, D. L. Overmyer, D. Jung, J. J. Novoa, and M.-H. Whangbo, Physica C **174**, 475 (1991).

[3] T. Ishiguro, K. Yamaji, and G. Saito, Organic Superconductors, Second edition, Springer, Berlin (1997).

[4] M. Lang, Superconductivity Review **2**, 1 (1996).

[5] R. H. McKenzie, Science **278**, 820 (1997).

[6] H. H. Wang, K. D. Karlson, U. Geiser, A. M. Kini, A. J. Schultz, J. M. Williams, L. K. Montgomery, W. K. Kwok, U. Welp, K. G. Vandervoort, S. J. Boryshuk, A. V. Strelby Crouch, J. M. Kommers, D. M. Watkins, J. E. Schirber, D. L. Overmyer, D. Jung, J. J. Novoa, and M. H. Whangbo, Synth. Met. **41-43**, 1983 (1991).

[7] K. Kanoda, Hyperfine Int. **104**, 235 (1997); K. Kanoda, Physica C **282-287**, 299 (1997).

[8] H. Kino and H. Fukuyama, J. Phys. Soc. Japan **65**, 2158 (1996).

[9] Y. Nakazawa, H. Taniguchi, A. Kawamoto, and K. Kanoda, Phys. Rev. B **61**, R16295 (2000).

[10] A. Kawamoto, K. Miyaguchi, A. Kawamoto, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995).

[11] H. Mayaffre, P. Wzietek, C. Lenoir, D. Jérome, and P. Batail, Europhys. Lett. **28**, 205 (1994).

[12] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. B **52**, 15522 (1995).

[13] Y. V. Sushko, V. A. Bondarenko, R. A. Petrosov, N. D. Kushch, and E. B. Yagubskii, J. Phys. I France **1**, 1375 (1991).

[14] S. Gärten, E. Gogu, I. Heinen, H. J. Keller, T. Klutz, and D. Schweitzer, Solid State Commun. **65**, 1531 (1988).

[15] K. Murata, M. Ishibashi, Y. Honda, N. A. Fortune, M. Tokumoto, N. Kinoshita, and H. Anzai, Solid State Commun. **76**, 377 (1990).

[16] V. Kataev, G. Winkel, D. Khomskii, D. Wohlleben, W.
As mentioned in section IV A, due to the shape of our \(\kappa-(Et)_2Cu[N(CN)_2]Cl\) single crystal only the diagonal in-plane axis \(\alpha_d = \frac{1}{2} \times (\alpha_a + \alpha_c)\) could be measured. Since thermal expansion results on the same system performed by Kund et al. [4] reveal no discontinuity neither for \(\alpha_a\) nor for \(\alpha_c\), an accidental cancellation of the two intralayer effects, i.e. \(\Delta\alpha_a = -\Delta\alpha_c\) can be ruled out.

Y. Nakazawa, and K. Kanoda, Phys. Rev. B 53, R8875 (1996).

J. E. Schirber, D. L. Overmyer, K. D. Carlson, J. M. Williams, A. M. Kini, H. H. Wang, H. A. Charlier, B. J. Love, D. M. Watkins, and G. A. Yaconi, Phys. Rev. B 44, 4666 (1991).

S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérome, C. Mézière, M. Fourmigué, and P. Batail, Phys. Rev. Lett. 85, 5420 (2000).

K. Sun, J. H. Cho, F. C. Chou, W. C. Lee, L. L. Miller, D. C. Johnston, Y. Hidaka, and T. Murakami, Phys. Rev. B 91, 239 (1991).

L. Siurakshina, D. Ihle, and R. Hayn, Phys. Rev. B 61, 14601 (2000).

R. H. McKenzie, Comments Cond. Mat. Phys. 18, 309 (1998).

M. Maesato, Y. Kaga, R. Kondo, H. Hirai, and S. Kagoshima, Synth. Met. 120, 941 (2001).

C. E. Campos, J. S. Brooks, P. J. M. van Bentum, J. A. A. J. Perenboom, S. J. Klepper, P. S. Sandhu, S. Valfells, Y. Tanaka, T. Kinoshita, N. Kinoshita, M. Tokumoto, H. Anzai, Phys. Rev. B 52, R7014 (1995).

M. Kund, H. Veith, H. Müller, K. Andres, and G. Saito, Physica C 221, 119 (1994).

We used the value for the specific heat jump reported in [23]. These authors applied a BCS fit with strong coupling to their data giving \(\Delta C/\gamma T_c = 3.3\) and \(\Delta C \approx 0.95 \text{ J/(mol K)}\). A value of \(\Delta C \geq 0.8 \text{ J/(mol K)}\) can be directly read off the data; nevertheless, an uncertainty of 10% ... 20%, must be considered [J. Wosnitza, private communication]. The very good agreement of the calculated hydrostatic-pressure coefficient of \(T_c\) with the values found in pressure experiments suggests that using the above value of \(\Delta C\) is reasonable rather than using \(\Delta C/T_c = (45 \pm 10) \text{ mJ/(mol K}^2\) at \(T_c \sim 11.5 \text{ K}\) [B. Andraka et al., Solid State Commun. 79, 57 (1991)] which would give a much higher value for \(\partial T_c/\partial p_{hydr}\). Note that for the determination of \(\partial T_c/\partial p_{hydr}\) of the \(\kappa\)-Br salt the jump heights \(\Delta\alpha_a\) and \(\Delta\alpha_c\) of crystal # 3 and \(\Delta\alpha_b\) of crystal # 2 were used.

J. E. Schirber, D. L. Overmyer, J. M. Williams, A. M. Kini, and H. H. Wang, Physica C 170, 231 (1990).

T. Simizu, N. Yoshimoto, M. Nakamura, and M. Yoshizawa, Physica B 281 & 282, 896 (2000).

M. Köppen, M. Lang, and F. Steglich, unpublished results.

T. Sasaki et al., in preparation.

K. Kornelsen, J. E. Eldridge, H. H. Wang, H. A. Charlier, and J. M. Williams, Solid State Commun. 81, 343 (1992).

J. E. Schirber, E. L. Venturini, A. M. Kini, H. H. Wang, J. R. Witworth and J. M. Williams, Physica C 152, 157 (1988).

A. Painelli, A. Girlando, and A. Fortunelli, cond-mat/0011154 (2000).
FIG. 1. Linear thermal expansion coefficient perpendicular to the planes, $\alpha_\perp$, vs $T$ for various salts $\kappa$-(ET)$_2$X. (a) non-superconducting $\kappa$-Cl and $\kappa$-$D_8$-Br, (b) superconducting $\kappa$-$H_8$-Br and $\kappa$-Cu(NCS)$_2$. For clarity, different scales have been used along the ordinates. The inset shows details of $\alpha_\perp$ for X=Cu[N(CN)$_2$]Cl as $\alpha_\perp/T$ vs $T$. Arrows indicate different kinds of anomalies as explained in the text.
FIG. 2. Coefficient of thermal expansion perpendicular to the planes, $\alpha_\perp$, vs $T$ close to the glass-like transition for (a) $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, (b) $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br and (c) $\kappa$-(ET)$_2$Cu[NCS)$_2$. Closed and open symbols denote heating and cooling curves, respectively.
FIG. 3. Linear thermal expansion coefficient, $\alpha$, vs $T$ measured along one non-specified in-plane axis of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br in the vicinity of the glass transition for varying cooling rates $q_c$. The definition of the glass-transition temperature $T_g$ is given in the text. Insets: hysteresis between heating and cooling curves around $T_g$ (left side) and Arrhenius plot of $T_g^{-1}$ vs $|q_c|$ and $\tau$ (right side).
FIG. 4. Coefficient of thermal expansion perpendicular to the planes, $\alpha_\perp$, vs $T$ of hydrogenated (open symbols) and deuterated (closed symbols) $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. Data were taken upon heating after cooling the crystals with two different rates $q_c^{\text{slow}}$ and $q_c^{\text{fast}}$ (see text) which results in a lower and upper value of $T_g$ for the slow and fast cooling history, respectively, in each case, as indicated by the arrows.
Fig. 5. Linear thermal expansion coefficients $\alpha_i(T)$ for the three principal axes of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br in the vicinity of $T_g$. Note the different vertical scales. Closed and open symbols denote heating and cooling curves, respectively. In (c), the construction to estimate the additional glassy contribution just above $T_g$ is indicated (see text). The $\alpha_b$ data (a) have been taken on crystal #2 while crystal #3 was used for $\alpha_a$ (b) and $\alpha_c$ (c).
FIG. 6. Linear thermal expansion coefficients $\alpha_i(T)$ for the three principal axes of (a) $\kappa$-(H$_8$-ET)$_2$Cu[N(CN)$_2$]Br and (b) $\kappa$-(D$_8$-ET)$_2$Cu(NCS)$_2$. Same symbols indicate related symmetry axes for both salts: the interlayer direction, i.e. the $b$-axis for the former and the $a^*$-axis for the latter salt, the in-plane axis along which the polymeric anion chains run, i.e. the $a^*$-[$\kappa$-Br] and $c$-axis [$\kappa$-Cu(NCS)$_2$] and the second in-plane axis perpendicular to the anion chains, i.e. $c^*$-[$\kappa$-Br] and $b$-axis [$\kappa$-Cu(NCS)$_2$]. The inset in the left panel shows the volume thermal expansion coefficient $\beta(T)$ of $\kappa$-Br. The solid line indicates the interpolated lattice background. The inset in the right panel compares the anomalous additional contributions to the volume expansivity, $\delta \beta$, of $\kappa$-Br and $\kappa$-Cu(NCS)$_2$ estimated as explained in the text. For $\kappa$-Br (a) the $\alpha_b$ data have been taken on crystal # 2 while crystal # 3 was used for $\alpha_a$ and $\alpha_c$. 
FIG. 7. Temperature/hydrostatic-pressure phase diagram for the $\kappa$-(BEDT-TTF)$_2$X title compounds. Arrows indicate the location of different compounds at ambient pressure. Solid lines represent the hydrostatic pressure dependencies of $T_N$ and $T_c$ taken from literature. Circles denote $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, down and up triangles denote deuterated and hydrogenated $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br, respectively, and squares stand for $\kappa$-(ET)$_2$Cu(NCS)$_2$. The superconducting and antiferromagnetic transitions are represented by closed and open symbols, respectively. Diamonds stand for the glass-like transitions and crosses for the maxima of the anomalous expansivity contributions $\delta\beta$ at intermediate temperatures 30 K – 50 K. In the shaded area anomalies in magnetic, transport and elastic properties have been observed (details are explained in the text).