Evidence for structural and electronic instabilities at intermediate temperatures in κ-(BEDT-TTF)$_2X$ for X=Cu[N(CN)$_2$]Cl, Cu[N(CN)$_2$]Br and Cu(NCS)$_2$: Implications for the phase diagram of these quasi-two-dimensional 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-two-dimensional (quasi-2D) salts κ-(BEDT-TTF)$_2X$ with X=Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, and Cu[N(CN)$_2$]Cl in the temperature range $T \leqslant 150$ 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, glasslike 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 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 $T^*=38$ K and 45 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^*, $\partial T^*/\partial p_i$ ($i=a,b,c$), are strictly anticorrelated with those of T_c. Based on comparative studies including the nonsuperconducting X=Cu[N(CN)$_2$]Cl salt as well as isotopically labeled compounds, we propose that T^* marks the transition to a density-wave 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, glasslike transition where, below a characteristic temperature T_g, disorder in the orientational degrees of freedom of the terminal ethylene groups becomes frozen in. Our results provide a natural explanation for the unusual time- and cooling-rate dependences of the ground-state properties in the hydrogenated and deuterated Cu[N(CN)$_2$]Br salts reported in the literature.

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I. INTRODUCTION

Organic charge-transfer salts based on the electron-donor molecule bis(ethylenedithio)-tetrathiafulvalene, commonly abbreviated BEDT-TTF or simply ET, are characterized by their quasi-two-dimensional 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 $\cdots$ anion contacts of the terminal ethylene groups of the ET's. In forming the solid, these [(CH$_2$)$_2$] end groups 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 [(CH$_2$)$_2$] system is thermally disordered, a preferential orientation in 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.[1–3]

Within this class of materials, the κ-phase (ET)$_2X$ salts are distinct because of their interesting superconducting and normal-state properties—some of which are similar to those of the high-T_c cuprates.[4,5] The compounds with the complex anions $X^- = [\mathrm{Cu(NCS)_2}]^-$ and $[\mathrm{Cu\{N(CN)_2\}Br}]^-$, which will be abbreviated as κ-Cu(NCS)$_2$ and κ-Br, are superconductors with T_c values of 10.4 K and 11.6 K, respectively. On the other hand, the system κ-(ET)$_2$Cu[N(CN)$_2$]Cl, in short κ-Cl, is an antiferromagnetic insulator ($T_N = 27$ K) which can be transformed into a superconductor with $T_c = 12.8$ K upon applying a small hydrostatic pressure of only 300 bars.[6] Kanoda[7] 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., U_{eff}/W with an effective on-site (dimer) Coulomb interaction U_{eff} and a bandwidth W: with increasing U_{eff}/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 are determined by their ambient-pressure ground-state properties. In this picture, the deuterated salt κ-(D$_8$-BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, denoted as κ-D$_8$-Br, is situated right at the AFI/SC border in between the antiferromagnetic insulating κ-Cl and the superconducting hydrogenated κ-H$_8$-Br salts. The close proximity of an antiferromagnetic insulating to a superconducting phase has been considered—in analogy to the high-T_c cuprates—as a strong indication that both phenomena are closely connected to each other.[5] A theoretical approach to the above proposal has been given by Kino and Fukuyama[8] 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.[7,9]

In fact, various properties of the normal state show anomalous behavior: the spin-lattice-relaxation rate $(T_1T)^{-1}$ of the superconducting κ-H$_8$-Br and κ-Cu(NCS)$_2$ salts studied by ^{13}C-NMR shows a maximum around 50 K which has been ascribed to antiferromagnetic spin fluctuations.[10] For both compounds, a decrease of the spin susceptibility χ_{spin} in the same temperature range,[11,12] together with a distinct peak in the temperature derivative of the electrical resistivity, dR/dT,[13–15] has been interpreted as a reduction of the density of states at the Fermi level, i.e., the opening of a pseudogap.[16,17,7] The softening of ultrasound modes exhibiting pronounced minima at 38 K and 46 K for κ-H$_8$-Br and κ-Cu(NCS)$_2$, respectively, was attributed to the same effect.[18]

Besides these anomalies around 50 K, unusual time dependences in magnetic and transport properties have been reported for both deuterated and hydrogenated κ-Br near 80 K.[19–22] For κ-H$_8$-Br, the superconducting properties have been found to depend on the thermal history, in particular on how fast the sample had been cooled through 77 K. As mentioned above, the ground state of κ-D$_8$-Br is strongly sample dependent: both superconducting and nonsuperconducting crystals are found. Furthermore, superconducting as well as insulating (possibly antiferromagnetic) phases in separated volume parts of the *same* sample have been reported. Their relative volume fraction was found to depend on the cooling rate q_c employed at around 80 K:[19,23] in quenched-cooled crystals ($q_c \sim -100$ K/min), a strong decrease of the diamagnetic signal has been observed, which has been interpreted as indicating a suppression of the superconducting in favor of the magnetic phase.

Concerning both the pairing mechanism and the symmetry of the superconducting order parameter, 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.[24–26] This conflicts sharply with the results of other experiments, notably NMR measurements performed in finite magnetic fields,[27–29] which 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, Refs. 4 and 30. In connection with the above controversy on the state below T_c, questions arise about the origin of the anomalous properties at $T > T_c$ and their interrelation to the superconducting state. In addition, one may ask to what extent a comparison can be drawn to the high-T_c 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 covering a wide temperature range. These studies supplement recent thermal expansion investigations aiming at a determination of the uniaxial-pressure coefficient of T_c, $\partial T_c/\partial p_i$, for various (ET)$_2X$ compounds.[31,32]

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

$$\alpha(T) = \frac{1}{l(T)} \frac{\partial l(T)}{\partial T}$$

is approximated by the differential quotient

$$\alpha(T) \approx \frac{\Delta l(T_2) - \Delta l(T_1)}{l(300\ \mathrm{K}) \cdot (\mathrm{T_2} - \mathrm{T_1})},$$

with $T = (T_1 + T_2)/2$.

The single crystals used were synthesized by the standard electrocrystallization technique with typical dimensions of

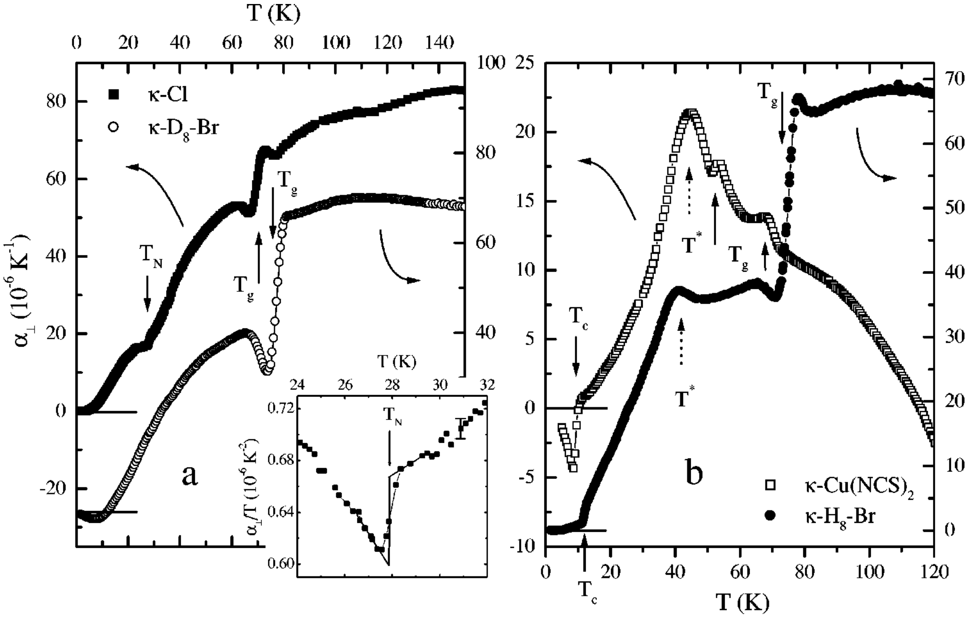

FIG. 1. Linear thermal expansion coefficient perpendicular to the planes, $\alpha_\perp$, vs T for various salts κ-(ET)$_2X$. (a) Nonsuperconducting κ-Cl and κ-D$_8$-Br, (b) superconducting κ-H$_8$-Br and κ-Cu(NCS)$_2$. For clarity, different scales have been used along the ordinates. The inset shows 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.

(0.5–1.5) mm perpendicular to the highly conducting planes and (0.5–2.5) mm along both in-plane axes. In the present work ten crystals have been studied: one κ-Cl sample ($T_N=27.8$ K), four crystals of κ-Br, and five of κ-Cu(NCS)$_2$ including samples with various isotope substitutions. Due to the particular shape of the κ-Cl and κ-Br crystals used,[34] it was not possible to measure $\alpha(T)$ along all three principal axes on the *same* sample. For κ-H$_8$-Br measurements perpendicular to the planes (b axis) and along one not specified in-plane axis were performed on crystal No. 2 ($T_c=11.8$ K), while measurements along the in-plane a and c axes were performed on crystal No. 3 ($T_c=11.5$ K). The excellent quality of both crystals is reflected by both the high transition temperatures and relatively small transition widths of $\Delta T_c=500$ 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 κ-H$_8$-Br, No. 1, along the out-of-plane axis, and found (besides a slightly lower T_c value of 11.5 K) almost identical expansivity behavior to that for crystal No. 2 in the whole temperature range investigated, i.e., up to 200 K. Crystals No. 1 and No. 2 have also been used in our previous study on the uniaxial-pressure coefficients of T_c.[32] For a deuterated crystal, κ-D$_8$-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 K/h up to -300 K/h. For κ-Cu(NCS)$_2$, measurements along the out-of-plane a^* axis were performed on two crystals of the pure compound ($T_c=9.2$ 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 κ-(D$_8$-ET)$_2$Cu(NCS)$_2$ ($T_c=9.95$ K), anion-labeled κ-(ET)$_2$Cu(^{15}N^{13}CS)$_2$ ($T_c=9.3$ K), and κ-(D$_8^{13}$C$_4^{34}$S$_8$-ET)$_2$Cu(NCS)$_2$ ($T_c=9.8$ K) where eight sulfur atoms of the ET molecule have been labeled with ^{34}S, the four ethylene carbon atoms with ^{13}C, and the eight hydrogen atoms with deuterium. As pointed out in Ref. 24, the latter compound shows a "normal" BCS-like mass isotope effect on T_c for the ^{13}C^{34}S substitution and an "inverse" isotope effect upon replacing the hydrogen atoms of the ethylene end groups by deuterium; no isotope effect on T_c is observed for the anion-labeled salt.[35] In the present paper we refrain from comparing superconducting properties for the aforementioned κ-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 Ref. 31. 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 ±5° from the exact alignment cannot be excluded.

III. CLASSIFICATION OF THERMAL EXPANSION ANOMALIES

Figure 1 shows the thermal expansion coefficient measured perpendicular to the highly conducting planes, $\alpha_\perp$, for κ-(ET)$_2X$ with $X=$Cu[N(CN)$_2$]Cl, $X=$Cu[N(CN)$_2$]Br, and $X=$Cu(NCS)$_2$ over an extended temperature range. Figure 1(a) compares $\alpha_\perp(T)$ of the nonsuperconducting salts κ-Cl and κ-D$_8$-Br. In Fig. 1(b) we show the expansivity data of superconducting κ-H$_8$-Br and κ-Cu(NCS)$_2$. Note the different scales of the ordinate for each case. For the various compounds, a number of anomalies is observed for temperatures $T\leqslant 80$ K 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 70–80 K (C), large steplike anomalies are found for κ-Cl and both kinds of κ-Br salts. Their characteristic temperatures are labeled as T_g. For κ-Cu(NCS)$_2$, a smaller but distinct 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, glasslike transition where, below T_g, a certain disorder in the positional degrees of freedom of the $[(\mathrm{CH}_2)_2]$ end groups of the ET molecules becomes frozen in.

In the intermediate temperature range around 40–50 K (B) both superconducting compounds exhibit a pronounced local maximum in $\alpha(T)$ at a temperature labeled as T^*, Fig. 1(b), while the features are absent in both nonsuperconducting salts; see Fig. 1(a). While the overall expansivities of κ-Cl and κ-Br show the usual increase in α as T increases, for κ-Cu(NCS)$_2$ an anomalous temperature dependence is revealed for temperatures $T>T^*$; i.e., $\alpha_\perp(T)$ decreases with increasing temperature. Above $T\approx 120$ K, it even becomes negative, corresponding to a progressive reduction of the interlayer distance upon warming. Then, at $T\approx 175$ K, $\alpha_\perp(T)$ 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.[36]

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 κ-H$_8$-Br and κ-Cu(NCS)$_2$ show pronounced negative second-order phase-transition anomalies in $\alpha_\perp(T)$ at $T_c = 11.8$ K and 9.3 K, respectively.

The inset of Fig. 1(a) gives details of $\alpha_\perp(T)$ for κ-(ET)$_2$Cu[N(CN)$_2$]Cl in a representation α/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 ^{1}H-NMR and magnetization measurements revealed the onset of 3D antiferromagnetic order.[37] Our data thus provide, in a thermodynamic quantity beyond magnetization, clear evidence for a second-order phase transition in κ-(ET)$_2$Cu[N(CN)$_2$]Cl at T_N.

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

IV. GLASSLIKE TRANSITION

In positionally and/or orientationally disordered systems, relaxation processes can lead to glasslike 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: the corresponding orientational degrees of freedom can lead to glasslike transitions also in polymeric or crystalline materials with large organic molecules[38] such as, e.g., single-crystalline C$_{60}$.[39] 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: $C^{\mathrm{glass}}(T)=0$ for $T<T_g$ and $C^{\mathrm{glass}}(T)>0$ for $T>T_g$ with C^{glass} representing the additional contribution to the heat capacity. As the volume thermal expansion coefficient $\beta(T)=\Sigma_i \alpha_i(T)$, with $i=a,b,c$, is related to the specific heat via the Grüneisen relation

$$\beta(T)=\Gamma \frac{\kappa_T}{V_{\mathrm{mol}}} C_V(T), \qquad (1)$$

where κ_T denotes the isothermal compressibility, V_{mol} the molar volume, and Γ a generalized Grüneisen parameter, both methods are very well suited for studying glassy phenomena. In particular, the thermal expansion coefficient is extremely sensitive to structural rearrangements and allows for studying the anisotropy of the glassy effects. Glasslike transitions can be identified by the following characteristics: (i) a steplike increase of C_V and β upon heating through T_g, (ii) the occurrence of hysteresis around T_g, and (iii) a cooling-rate-dependent T_g value.[40]

In a recent ac-calorimetry study of the κ-Br and κ-Cl salts, glass transitions have been reported for both compounds.[41,42] The authors observed steplike anomalies in the heat capacity around 100 K, which were attributed to a freezing-out of the intramolecular motion of the ethylene end groups 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 κ-Br and κ-Cl salts:[43,44] 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 glasslike transition in the κ-Br and κ-Cl salts. This confirms, on the one hand, the above-mentioned specific heat results[41,42] and clarifies, on the other, the nature of the thermal expansion anomalies previously reported by Kund *et al.*[43,44] In addition we disclose a glasslike transition also for κ-(ET)$_2$Cu(NCS)$_2$.

A. Phenomena and analysis

Figure 2 shows on expanded scales the anomalies in $\alpha_\perp(T)$ in the temperature range (C) for the κ-Cl, κ-H$_8$-Br, and κ-Cu(NCS)$_2$ salts. A distinct hysteresis is seen between the heating (solid symbols) and cooling curves (open symbols). In the heating curves, the former two salts reveal pronounced jumplike anomalies at $T_g\approx 70$ K (κ-Cl) and 75 K (κ-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

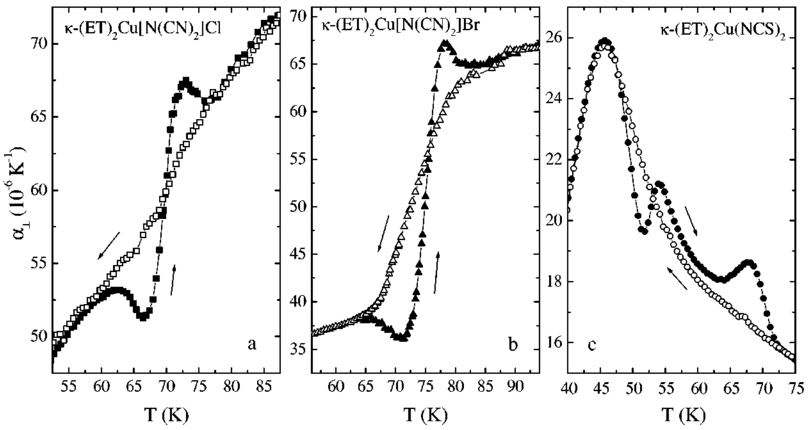

FIG. 2. Coefficient of thermal expansion perpendicular to the planes, $\alpha_\perp$, vs T close to the glasslike transition for κ-(ET)$_2X$ with $X=\mathrm{Cu[N(CN)_2]Cl}$ (a), Cu[N(CN)$_2$]Br (b), and Cu(NCS)$_2$ (c). Solid and open symbols denote heating and cooling curves, respectively.

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 glasslike transitions, where instead of a well-defined transition temperature, one meets a "glass-transformation temperature interval."[40,45] In contrast to the isostructural κ-Cl and κ-Br salts where a single anomaly occurs, the heating curve for the κ-Cu(NCS)$_2$ compound shows a sequence of two somewhat smaller steplike 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.[40]

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 at low temperatures. To this end it is helpful to evaluate the activation barrier for the relevant relaxation process from the cooling-rate (q_c) dependence of T_g.[45]

1. κ-(ET)$_2$Cu[N(CN)$_2$]Br and κ-(ET)$_2$Cu[N(CN)$_2$]Cl

Figure 3 shows the linear thermal expansion coefficient $\alpha(T)$ measured along one nonspecified in-plane axis of the κ-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 steplike 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 ΔT interrupted by intervals of duration $\Delta t=\Delta T/q$ at which $T=\mathrm{const}$. The system remains in equilibrium as long as Δt is much longer than the relaxation time τ which, for structural rearrangement processes in solids, is known to grow exponentially upon lowering the temperature.[40] At high temperatures, τ is small and, thus, $\tau\ll\Delta t$. 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.[40] 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]

$$\tau(T)=\nu_0^{-1}e^{E_\mathrm{a}/k_BT}, \tag{2}$$

where E_a denotes the activation energy barrier and k_B the Boltzmann constant. The prefactor represents an attempt frequency ν_0.

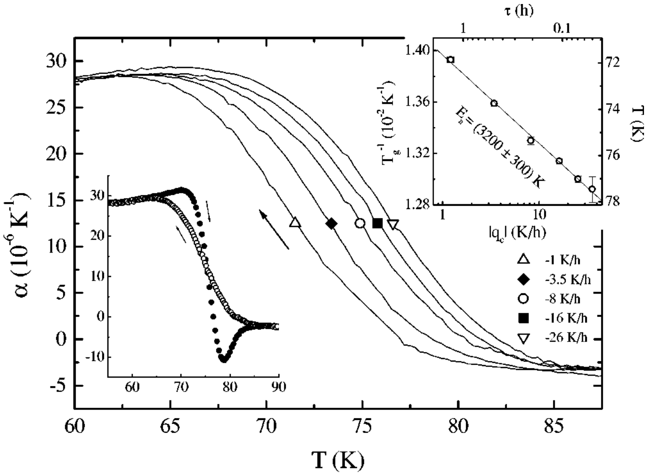

FIG. 3. Linear thermal expansion coefficient, α, vs T measured along one nonspecified in-plane axis of κ-(ET)$_2$Cu[N(CN)$_2$]Br in the vicinity of the glass transition for varying cooling rates q_c. The definition of the glass-transition temperature T_g is given in the text. Insets: hysteresis between heating and cooling curves around T_g (left side) and Arrhenius plot of T_g^{-1} vs $|q_c|$ and τ (right side).

Based on a simple two-state model,[47] Nagel *et al.* have quantified the above-sketched 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 ν_0 and τ:

$$\tau(T_g)=\frac{T_g}{|q_c|}\frac{k_B T_g}{E_a}.$$

In a first approximation we set $\tau(T_g)\sim 1/|q_c|$, 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 and orientational degrees of freedom for the $[(CH_2)_2]$ end groups which represent the most deformable parts of the ET molecules.[48] The characteristic activation energy of the $[(CH_2)_2]$ conformational motion was determined as $E_a=2650$ K by ^{1}H-NMR measurements.[17] This value has to be compared to 2400 K as estimated from resistivity and ac-calorimetric measurements,[49,42] (2000 ± 500) K from resistivity measurements of structural relaxation kinetics,[50] and 2600 K also from resistivity-relaxation measurements.[21] The similar size of the activation energy derived here, compared to the above numbers, suggests that the $[(CH_2)_2]$ end groups 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 κ-Br salt due to the higher mass of its $[(CD_2)_2]$ units, a shift of T_g is expected: for κ-D$_8$-Br the relaxation time τ of the terminal $(CD_2)_2$ groups at a given temperature should exceed that for the κ-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. Figure 4 compares $\alpha_\perp(T)$ for the hydrogenated compound, κ-H$_8$-Br (open symbols), with that for the deuterated one, κ-D$_8$-Br (solid symbols). For both compounds, two heating curves are shown taken after slow and fast cooling history ($q_c^{\text{slow}}\approx -25$ K/h and $q_c^{\text{fast}}\approx -150$ K/h). The figure clearly demonstrates that the T_g values for the deuterated κ-Br salt are shifted by about 3 K to higher temperatures compared to that for κ-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 $[(CD_2)_2]$ and $[(CH_2)_2]$ units scale with the square root of their mass ratios, one would expect a positive shift of T_g of 3.4% upon ^{1}H→^{2}D substitution (here we consider the activation barrier E_a to be identical for both isotopes). Thus the observation of a ^{1}H-^{2}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.

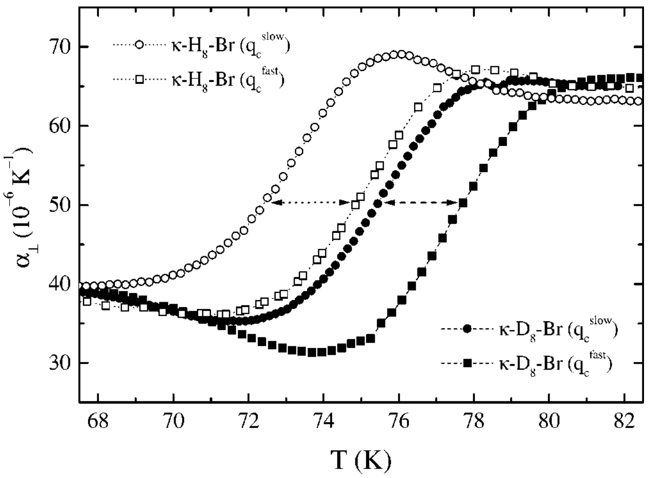

FIG. 4. Coefficient of thermal expansion perpendicular to the planes, $\alpha_\perp$, vs T of hydrogenated (open symbols) and deuterated (solid symbols) κ-(ET)$_2$Cu[N(CN)$_2$]Br. Data were taken upon heating after cooling the crystals with two different rates q_c^{slow} and q_c^{fast} (see text) which 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.

Directional-dependent measurements reveal a strongly anisotropic lattice response at T_g (not shown) with contributions $\alpha_i^{\text{glass}}(T_g)=\alpha_i(T\to T_g^+)-\alpha_i(T\to T_g^-)$ of $\alpha_b^{\text{glass}}=+20\times 10^{-6}$ K^{-1}, $\alpha_a^{\text{glass}}=-52\times 10^{-6}$ K^{-1}, and $\alpha_c^{\text{glass}}=+22\times 10^{-6}$ K^{-1}. The resulting glass contribution to the volume expansivity above T_g, $\beta^{\text{glass}}(T)=\Sigma_i\alpha_i^{\text{glass}}(T)$, caused by the excitation of the motional $[(CH_2)_2]$ degrees of freedom is thermodynamically related to the pressure dependence of the entropy associated with the ordering of the ethylene end groups:

$$\left.\frac{\partial S_{\text{ethy}}}{\partial p_i}\right|_T=-V_{\text{mol}}\alpha_i^{\text{glass}}(T). \qquad (3)$$

Early x-ray diffraction studies revealed that the terminal ethylene groups for the κ-Br and κ-Cl salts are disordered with the tendency towards the eclipsed orientation at room temperature[51] but ordered—within the experimental resolution—in the eclipsed conformation at 127 K,[2] which was confirmed to be the case also at 20 K.[52] A complete ordering at temperatures above 127 K would be in contradiction to a glasslike freezing below 80 K. However, these x-ray diffraction measurements gave only an average structure, and disorder at the 10%–20% level could not be resolved.[53] Our results and those of the specific heat studies[41,42] imply that the ordering process of the $[(CH_2)_2]$ units which starts at room temperature is not completed at T_g leaving a considerable degree of disorder that becomes frozen below T_g. Combining the discontinuities in the linear thermal expansion coefficients at T_g, we find $\beta^{\text{glass}}=-10\times 10^{-6}$ K^{-1} and $\partial S_{\text{ethy}}/\partial p_{hydr}=\Sigma_i\partial S_{\text{ethy}}/\partial p_i=+0.5$ 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 $S_{\text{ethy}}^{\max}=Nk_B\ln 2=2R\ln 2=11.53$ J/(mol K) where $N=2N_A$ denotes the number of relevant ethylene moieties per mole. Given that about 10%–20% of the ethylenes are still disordered at T_g, i.e., that the major part of $S_{\text{ethy}}^{\max}$ has already been released at higher temperatures, the above estimated value of $\partial S_{\mathrm{ethy}}/\partial p_{hydr}$ underlines the extraordinary large pressure and 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^{-1} follows well a linear $\ln|q_c|$ dependence in the Arrhenius plot yielding $E_{\mathrm{a}}=(2650\pm 300)$ K and $\nu_0 = 2\times 10^{13\pm 1.5}$ Hz. The value for E_{a} agrees well with those reported in the literature: (2600 ± 100) K from ^{1}H-NMR (Ref. 37) and 2700 K from ac-calorimetry.[42] The value found for the discontinuity of the volume expansion coefficient at T_g is $\Delta\beta \approx -3.25 \times 10^{-6}$ K^{-1}.[54] Using $V_{\mathrm{mol}} = 496.66$ cm^3, we find $\partial S_{\mathrm{ethy}}/\partial p_{hydr} = +0.16$ J/(mol K kbar), a value which is significantly smaller than that found for κ-Br. The correspondingly smaller pressure and volume effects on the $[(\mathrm{CH}_2)_2]$ disorder may be due to the fact that the short C-H $\cdots$ H and C-H $\cdots$ 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 glasslike 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, ribbonlike 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 $\cdots$ donor and C-H $\cdots$ anion contacts which supports an ethylene–end-group ordering in the staggered instead of the eclipsed conformation.[55] Figure 2(c) clearly shows that in κ-Cu(NCS)$_2$, *two* closely spaced glasslike transitions occur with small but distinct anomalies around $T_{\mathrm{g}_1} = 70$ K and $T_{\mathrm{g}_2} = 53$ 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 $T_g(q_c)$ 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 end groups of the donor molecules are the relevant relaxation units.

B. Discussion

The size of T_g suggests that the energy difference E_{S} between the eclipsed and staggered conformation is quite small, i.e., of the order of 100 K. Both E_{S} and 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.

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 glasslike transition may cause anomalies in physical quantities which depend on the transfer integrals such 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 κ-H$_8$-Br salt.[56] According to our $\alpha(T)$ data, hysteretic behavior in the resistivity at T_g might also be expected for the κ-Cl as well as the κ-Cu(NCS)$_2$ salt. Because of the small number of carriers for the κ-Cl and the weak effect in $\alpha(T)$ for the κ-Cu(NCS)$_2$ salt, the response in the resistivity is probably very weak and has not been seen yet.

Besides the kink structure in the resistivity, the H$_8$ and D$_8$ salts of κ-Br show interesting time dependences affecting both the electronic properties at temperatures below $T^{\ddagger} \approx (75\text{–}80)$ K and the actual ground-state properties. For superconducting κ-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 T_c decreases on increasing $|q_c|$. These phenomena have been ascribed to a structural transformation leading to lattice disorder. We note that the quenching rates which were found to influence T_c in those studies ($|q_c| \geqslant 600$ K/h) are much higher than the cooling rates employed in our experiments. A sequence of first-order phase transitions around 75 K due to ethylene–end-group ordering was claimed based on resistance measurements of structural relaxation kinetics.[50] Magnetization measurements revealed that a growing amount of disorder with increasing values of $|q_c|$ leads to larger penetration depths and lower superconducting transition temperatures.[57] Besides these cooling-rate-dependent effects on T_c for κ-H$_8$-Br, it has been reported that rapid cooling through $T^{\ddagger} \lesssim 80$ K drives the superconducting ground state of the deuterated salt κ-D$_8$-Br into an insulating antiferromagnetic state.[19,23]

The above temperature $T^{\ddagger}$, below which time dependences affecting the ground-state properties become important, coincides with the glass-transition temperature T_g determined from our $\alpha(T)$ measurements. This suggests that the cooling-rate-dependent metal-insulator transition in κ-D$_8$-Br and the shift of T_c in κ-H$_8$-Br are related to the above relaxation phenomena.

As the motional degrees of freedom of the $[(\mathrm{CH}_2)_2]$ 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 $\cdots$ donor and C-H $\cdots$ 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 κ-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 κ-Br salt.[58] The so-derived lattice contribution was found to differ substantially from the one observed in slowly cooled (superconducting) κ-H$_8$-Br.[26]

It is obvious that the random potential induced by large cooling rates is unfavorable for superconductivity and may thus account for the cooling-rate-dependent superconducting properties in the present materials.[2]

V. ANTIFERROMAGNETIC TRANSITION IN INSULATING $\boldsymbol{\kappa}$-(ET)$_2$Cu[N(CN)$_2$]Cl

Although being isostructural to the superconducting κ-Br salt, the small modification of the anion composition of κ-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.[59] In addition, these studies revealed indications for a weakly ferromagnetic state with a small saturation moment of $8\times10^{-4}\ \mu_B$/dimer below 22 K. Subsequently, the spin structure has been studied by ^{1}H-NMR measurements,[37] yielding a commensurate antiferromagnetic order at $T_N=27$ K with a moment of $(0.4–1.0)\mu_B$/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.

Figure 1(a) clearly demonstrates that $\alpha_\perp(T)$ of κ-Cl exhibits another distinct feature besides the glasslike 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 ^{1}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 κ-Cl: (i) lattice disorder due to conformational ethylene-end group disarrangements[60]—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;[17,61] and (iii) a Mott-Hubbard-type metal-insulator transition leading to a magnetic state characterized by localized spins.[37]

As our measurements provide clear thermodynamic evidence for a phase transition at T_N, the first proposal can be discarded. To check for proposals (ii) and (iii) it would 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., $\Delta\alpha_\parallel\simeq0$ (not shown).[62] According to the Ehrenfest relation

$$\left(\frac{\partial T^\star}{\partial p_i}\right)_{p_i\to0}=V_{\mathrm{mol}}T^\star\frac{\Delta\alpha_i}{\Delta C},\tag{4}$$

which relates the uniaxial-pressure dependence of a second-order phase-transition temperature $T^\star$ to the discontinuities in α_i, $\Delta\alpha_i$, and those of the specific heat, ΔC, 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.[63] Using the jump height for the volume expansivity $\Delta\beta\simeq\Delta\alpha_\perp=-2\times10^{-6}\ \mathrm{K}^{-1}$ and available literature data on the response of T_N to hydrostatic pressure varying between -150 K/kbar (Ref. 64) and -25 K/kbar (Ref. 65), the Ehrenfest relation allows us to estimate the expected discontinuity in the specific heat at T_N. We find $\Delta C_m\approx(20–100)$ mJ/(mol K), which is much below the experimental resolution of the specific heat measurements reported in Ref. 63.

The above findings of a highly anisotropic lattice response at T_N and, related to this, strongly directional-dependent uniaxial-pressure coefficients provide a crucial test for models attempting to describe the nature of the antiferromagnetism in κ-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 $J^\parallel\sim460$ K.[63] Accordingly, most of the entropy of $R\ln2$ is released at temperatures far above T_N. 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 $\partial T_N/\partial p_i$ 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 $\partial T_N/\partial p_\parallel$. On the other hand, from the negative pressure coefficient of T_N for uniaxial stress perpendicular to the planes we infer $\partial J^\perp/\partial p_\perp<0$, $J^\perp$ being the interplane coupling constant. 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. However, for the complex crystal structures of the title compounds there are additional, frustrating magnetic couplings.[66] 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 (FS) 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

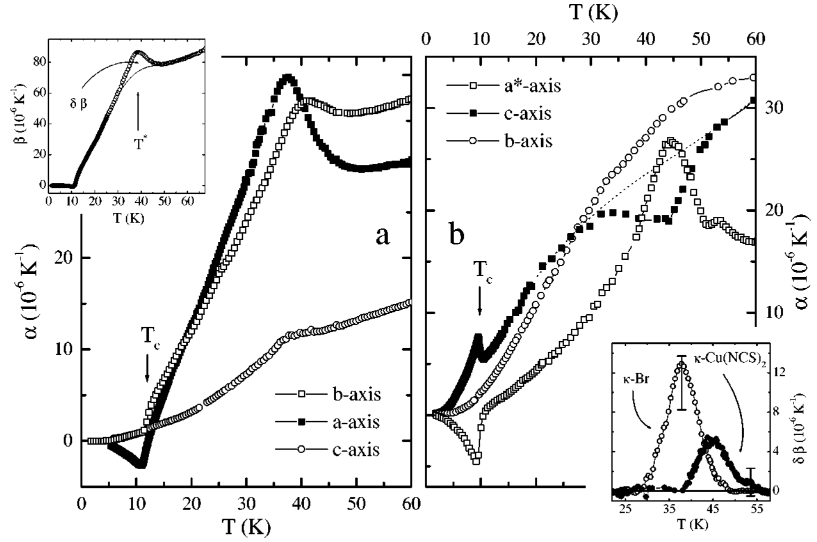

FIG. 5. Linear thermal expansion coefficients $\alpha_i(T)$ for the three principal axes of (a) κ-(H$_8$-ET)$_2$Cu[N(CN)$_2$]Br and (b) κ-(D$_8$-ET)$_2$Cu(NCS)$_2$. The same symbols indicate related symmetry axes for both salts: the interlayer direction, i.e., the b axis for the former and the a^* axis for the latter salt, the in-plane axis along which the polymeric anion chains run, i.e., the a-[κ-Br] and c-axis [κ-Cu(NCS)$_2$], and the second in-plane axis perpendicular to the anion chains, i.e., c-[κ-Br] and b-axis [κ-Cu(NCS)$_2$]. The inset in the left panel shows the volume thermal expansion coefficient $\beta(T)$ of κ-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 κ-Br and κ-Cu(NCS)$_2$ estimated as explained in the text. For κ-Br (a) the α_b data have been taken on crystal No. 2 while crystal No. 3 was used for α_a and α_c.

α-(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}.[67] Thus, the absence of any in-plane pressure effect on the antiferromagnetic phase transition in κ-Cl appears to be in conflict with a simple spin-density-wave (SDW) 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 α-(ET)$_2$KHg(SCN)$_4$.[68,67]

Our results indicate that none of the above proposals is suited to describe the magnetic state in κ-Cl satisfactorily. However, certain elements of both models—i.e., of a magnetism of localized moments as found for the high-T_c cuprates and of an itinerant, nesting-driven magnetism as in the Bechgaard salts—seem to apply for κ-Cl. This suggests a more complicated magnetic behavior than has been supposed up to now.

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

A. Uniaxial-pressure coefficients of T_c

Figure 5 shows the linear thermal expansion coefficients $\alpha_i(T)$ for $T \leqslant 60$ K of (a) κ-Br and (b) κ-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 of T_c we found that the latter system exhibits a strikingly similar anisotropy of $\partial T_c/\partial p_i$ as the compound β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$, namely, either a positive or vanishingly small pressure coefficient for uniaxial pressure along both in-plane axes, but a huge negative interplane coefficient $\partial T_c/\partial p_\perp$.[31] Pronounced negative cross-plane pressure effects $\partial T_c/\partial p_\perp < 0$ were found also for the κ-(ET)$_2X$ salts with $X=$I$_3$ and Cu[N(CN)$_2$]Br.[32] The results for the latter salt are in conflict with those reported by Kund *et al.*,[69] where a vanishingly small cross-plane pressure coefficient of (0 ± 0.2) K/kbar was claimed. Here we present high-resolution measurements of the linear expansivities for the three principal axes for the κ-Br salt which clearly reveal negative discontinuities at T_c along all three axes: $\Delta\alpha_b = -(2.1\pm0.3)\times10^{-6}$ K^{-1} (out-of-plane) and for the in-plane a and c axes $\Delta\alpha_a = -(1.93\pm0.3)\times10^{-6}$ K^{-1} and $\Delta\alpha_c = -(0.2\pm0.08)\times10^{-6}$ 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 dependences, we studied a second crystal from a different batch and found almost identical behavior.[32] Using the Ehrenfest relation, Eq. (4), and the jump height ΔC reported in literature[70] we find for the uniaxial-pressure coefficients of T_c for the κ-Br system $\partial T_c/\partial p_b = -(1.26\pm0.25)$ K/kbar (out-of-plane) and for the in-plane coefficients $\partial T_c/\partial p_a = -(1.16\pm0.2)$ K/kbar and $\partial T_c/\partial p_c = -(0.12\pm0.05)$ K/kbar. For the hydrostatic-pressure coefficient we get $\partial T_c/\partial p_{hydr} = \Sigma_i(\partial T_c/\partial p_i) = -(2.58\pm0.5)$ K/kbar,[71] in excellent agreement with the values found in hydrostatic-pressure experiments, i.e., $-(2.4-2.8)$ K/kbar.[72,13] We stress that these uniaxial-pressure results for the various (ET)$_2X$ superconductors *do not* yield a uniform behavior as for the intralayer pressure effects on T_c. In particular, the results on κ-Cu(NCS)$_2$ show that in-plane pressure can even cause an increase of T_c.[31] Note that this is in contrast to what is assumed in the 2D electronic model[8] and demonstrates that an attempt to model these systems by solely considering in-plane electronic degrees of freedom is not appropriate.

However, a large negative *inter*layer pressure coefficient of T_c that predominates the hydrostatic pressure effect is common to all κ-(ET)$_2X$ salts investigated so far. As we discussed in Refs. 31 and 32 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 behavior in the range 30–50 K (B). For κ-H$_8$-Br [cf. Fig. 5(a)], we find anomalous expansivity contributions $\delta\alpha_i$, i.e., a pronounced local maximum and a shoulder around 37.5 K for the in-plane *a* and *c* axes, respectively, and a maximum at 41.5 K for the out-of-plane *b* axis. The slight differences in the characteristic temperatures of these anomalies are most likely an artifact 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^*. We note that for κ-Br these anomalous contributions at T^*, $\delta\alpha_i(T^*)$, 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 α_c where also the lattice response at T_c is smallest. The inset of Fig. 5(a) shows the volume thermal expansion coefficient $\beta(T)=\Sigma_i\alpha_i(T)$ of κ-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 κ-Cu(NCS)$_2$ salt; see Fig. 5(b). Here, the background expansivity along the out-of-plane direction a^* is rather difficult to estimate due to both the nearness of the glasslike anomaly around 53 K and the unusual overall temperature dependence of the a^* 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 α_b but a distinct negative anomaly for α_c; cf. the dotted line representing the approximate background contribution. The largest effect, i.e., a sharp maximum at $T^*=45$ K, is found for α_{a*}. Again, as for κ-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 α_b both around T^* and at T_c; a positive jump in α_c at T_c is accompanied by a negative contribution at T^* and the large negative $\Delta\alpha_{a*}$ at T_c complies with the large positive peak structure at T^*. These results imply that for both compounds, the uniaxial-pressure coefficients of the anomaly at T^* and those at T_c are strictly anticorrelated in their signs but correlated in their magnitudes: for κ-Cu(NCS)$_2$, for example, uniaxial pressure applied perpendicular to the planes causes a substantial shift of the 45 K anomaly to higher temperatures while at the same time it strongly reduces T_c. The inset of Fig. 5(b) compares the corresponding contributions to the volume expansion coefficient for both salts. We find sharp peaks in $\delta\beta$ at $T^*=38$ K and 45 K for κ-H$_8$-Br and κ-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,[10] yielding a pronounced maximum in $(T_1T)^{-1}$ at around 50 K for κ-Cu(NCS)$_2$ and at somewhat lower temperatures for the κ-Br salt. The rapid decrease of $(T_1T)^{-1}$ below 50 K has been ascribed to the opening of a pseudogap in the spin-excitation spectrum[7,9]—an interpretation that was proposed by Kataev *et al.* based on their analysis of ESR data.[16] At about the same temperature, anomalous behavior has been reported also from various other quantities, such as the decrease of the spin susceptibility studied by Knight-shift and dc-magnetization measurements,[11,12] 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.[13–15] The coincidence of these features in the electronic and magnetic properties with the $\alpha(T)$ anomalies described above suggests 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. 5(b)], a shift of T^* to higher temperatures is expected under hydrostatic pressure. In fact, a positive hydrostatic-pressure coefficient has been found in the magnetic and transport measurements.[11,15,13] 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 K and 46 K for κ-Br and κ-Cu(NCS)$_2$, respectively.[18,73] These sound velocity anomalies have been assigned to a magnetic origin due to their phenomenological relation to the NMR results.[18] However, an alternative interpretation in terms of a structural phase transition could not be excluded.[73] 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 various related $(\mathrm{ET})_2X$ compounds is helpful to find out the relevant structural and/or electronic parameters involved. Interestingly enough, corresponding features are absent in β''-$(\mathrm{ET})_2\mathrm{SF}_5\mathrm{CH}_2\mathrm{CF}_2\mathrm{SO}_3$ ($T_c = 5$ K, large discrete anions),[31] κ-$(\mathrm{ET})_2\mathrm{I}_3$ ($T_c = 3.5$ K, linear anions) as well as α-$(\mathrm{ET})_2\mathrm{KHg(SCN)}_4$ (nonsuperconducting; thick, polymeric anions),[74] showing smooth, Debye-like temperature dependences of $\alpha(T)$ along all crystal axes for temperatures up to 200 K. Accordingly, purely *intra*molecular changes of the ET molecule can be ruled out to account for the T^* anomalies in the κ-Br and κ-$\mathrm{Cu(NCS)}_2$ 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 nonmetallic κ-Cl as well as in the deuterated κ-D_8-Br (cf. Fig. 1), and is also corroborated by our supplementary investigations on the isotope effect: For the κ-$\mathrm{Cu(NCS)}_2$ 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 κ-$(\mathrm{D}_8^{13}\mathrm{C}_4^{34}\mathrm{S}_8\text{-ET})_2\mathrm{Cu(NCS)}_2$ crystal yielding a mass change of 28 amu per ET molecule has been investigated. For all isotopically labeled 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 end groups as well as in the anion or *inter*molecular 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 κ-Br and κ-$\mathrm{Cu(NCS)}_2$ salts.[55] The presence of strong antiferromagnetic interactions as seen in the NMR experiments then would hint at a spin density wave although such a state seems to be incompatible with the width of the NMR line.[75] We propose that below T^* some kind of density wave forms which—for $T < T_c$—coexists with superconductivity. The density-wave state is likely to involve the small, quasi-one-dimensional portions while leaving the major two-dimensional parts of the FS unaffected. The latter is subject to the superconducting instability in the κ-Br and κ-$\mathrm{Cu(NCS)}_2$ salts. We suppose that a relative shift of one of these FS portions in favor 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-one-dimensional parts, thereby destabilizing the density-wave state and causing a negative-pressure coefficient of T^*. As a consequence, the remaining quasi-two-dimensional 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. 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 κ-$(\mathrm{ET})_2X$ salts which, in fact, confirms our expectation.[76]

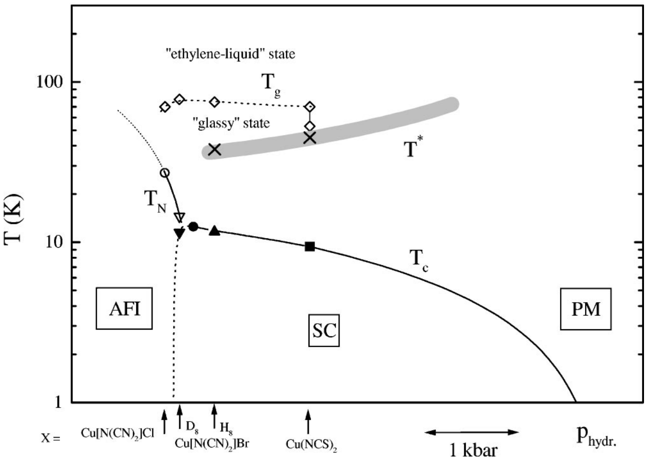

FIG. 6. Temperature/hydrostatic-pressure phase diagram for the κ-$(\mathrm{BEDT\text{-}TTF})_2X$ title compounds. Arrows indicate the location of different compounds at ambient pressure. Solid lines represent the hydrostatic pressure dependences of T_N and T_c taken from the literature. Circles denote κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Cl}$, down and up triangles denote deuterated and hydrogenated κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Br}$, respectively, and squares stand for κ-$(\mathrm{ET})_2\mathrm{Cu(NCS)}_2$. The superconducting and antiferromagnetic transitions are represented by solid and open symbols, respectively. Diamonds stand for the glasslike transitions and crosses for the maxima of the anomalous expansivity contributions $\delta\beta$ at intermediate temperatures 30–50 K. In the shaded area anomalies in magnetic, transport, and elastic properties have been observed (details are explained in the text).

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.

VII. CONCLUSION

Figure 6 summarizes our results on the various κ-$(\mathrm{ET})_2X$ compounds discussed in the present paper. To this end we use as the abscissa hydrostatic pressure following the suggestion of Ref. 7. The positions of the various salts at ambient pressure are indicated by the arrows. The solid lines representing the phase boundaries from the PM to the SC and AFI states refer to the results of hydrostatic-pressure studies of T_c and T_N.[77,72,64] 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 *intra*plane pressure coefficients of T_c. On the other hand, a feature common to all systems studied among the κ-(ET)$_2X$ salts is the large negative effect for uniaxial stress perpendicular to the planes on both T_c and 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 $T_N = 27.8$ K in κ-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 end groups can be excited and thus contribute to the specific heat and thermal expansion whereas below T_g a certain disorder is frozen in. The glasslike transition which is structural in nature has been shown to imply time dependences in electronic properties. We discussed possible implications on the ground-state properties of κ-Br in terms of frozen-in lattice disorder depending on the cooling rate employed at T_g.

At intermediate temperatures, an anomalous expansivity contribution $\delta\beta(T)$ has been observed at T^* for the superconducting salts, symbolized in Fig. 6 by crosses. These anomalies coincide with various features observed in magnetic, transport, and elastic properties (shaded area).

We proposed that, instead of a pseudogap on the whole Fermi surface, a real gap associated with a density wave on minor parts forms below T^*. This scenario implies that the density wave and superconductivity involve disjunct parts on the Fermi surface and compete for stability.

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 κ-Br and κ-Cl salts.[78] It has been found that one *single* parameter like the Coulomb repulsion U_{eff}, the effective transfer integrals t_{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 κ-(ET)$_2X$ title compounds.

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