Exploring the Phase Diagram of the Quasi-2D Organic Superconductors κ-(BEDT-TTF)$_2$*X*

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Introduction

The organic charge-transfer salts of the (BEDT-TTF)$_2$***X*** family (BEDT-TTF or simply ET denotes bis(ethylenedithio)-tetrathiafulvalene and ***X*** a monovalent anion) represent fascinating model systems for exploring the interplay of strong electron-electron and electron-phonon interactions in reduced dimensions. Of particular interest are the κ-phase (ET)$_2$***X*** salts with various monovalent anions such as ***X***$^-$ = [Cu(NCS)$_2$]$^-$, [Cu[N(CN)$_2$]Br]$^-$ and [Cu[N(CN)$_2$]Cl]$^-$. They exhibit unusual normal (N)- and superconducting (SC)-state properties which resemble in some aspects those of the layered high-T_c cuprates. Apparent similarities include the quasi-twodimensional (quasi-2D) electronic structure and the proximity to an antiferromagnetically (AFM) ordered state, cf. Fig. 5. Moreover, the presence of strong AFM spin fluctuations above T_c as inferred from various magnetic and thermal properties has been associated with a magnetically mediated non-***s***-wave type of SC not only for the cuprates but also for the present organic systems [1]. For the latter, however, such a scenario is at variance with the results of numerous other studies, see, e.g., [2,3] and references cited therein.

Here we summarize our recent results of a detailed thermodynamic study employing thermal expansion and specific heat measurements on the above κ-type salts. Particular attention is paid to the anomalous properties at elevated temperatures and their interrelation to the SC state. A full account of the work is given in [2,4,5].

Experiments

The coefficient of thermal expansion was mesured by means of an ultra-high-resolution capacitance dilatometer with a maximum sensitivity corresponding to $\Delta l/l = 10^{-10}$. Specific heat measurements on high-quality single crystals with masses $m < 1$ mg have been performed utilizing an ac-modulation technique. High-quality single crystals of κ-(ET)$_2$Cu(NCS)$_2$ were grown in our Institute. Here we strongly benefited from the collaboration with and the advice of Prof. T. Sasaki (Institute of Materials Research, Tohoku University, Sendai, Japan). Most important for this projekt is also the close collaboration with Dr. J.A. Schlueter (Argonne National Laboratory, USA) who provided most of the (ET)$_2$***X*** salts studied within this project.

Classification of anomalies and discussion

Figure 1 compiles the results of the coefficient of thermal expansion measured perpendicular to the conducting planes, $\alpha_\perp$, for the various κ-(ET)$_2$***X*** salts investigated: ***X*** = Cu(NCS)$_2$ (in short κ-Cu(NCS)$_2$), Cu[N(CN)$_2$]Br (κ-Br) and Cu[N(CN)$_2$]Cl (κ-Cl). For all compounds, a variety of anomalies can be discerned and classified as (A) step-like changes in $\alpha(T)$ at temperatures T_g around 50 K – 80 K, (B) phase-transition-like anomalies at an intermediate temperature T^* around 40 K only for the SC salts and (C) phase-transition anomalies into the SC (κ-Cu(NCS)$_2$, κ-H$_8$-Br) and AFM (κ-Cl) ground states. In what follows, we will discuss all three kinds of anomalies and their implications for the SC state.

(A) Glass-like transitions at T_g

Figure 2 shows on expanded scales the anomalies in $\alpha_\perp$ for all three compounds near T_g. The distinct hysteresis between heating and cooling curves, the particular shape of the anomalies, as well as their characteristic cooling-rate dependence (not shown) are clear manifestations of the glassy nature of these anomalies [4]. It is well known that in positionally and/or orientationally disordered systems, relaxation processes can lead to glass-like transitions where below the glass-transition temperature T_g a short-range order characteristic for this temperature becomes frozen, see [4] and references cited therein.

As discussed in detail in ref. [4], the relevant entities involved in the freezing process for the present κ-(ET)$_2$***X*** salts are the terminal ethylene groups [(CH$_2$)$_2$] of the ET molecules. From these results

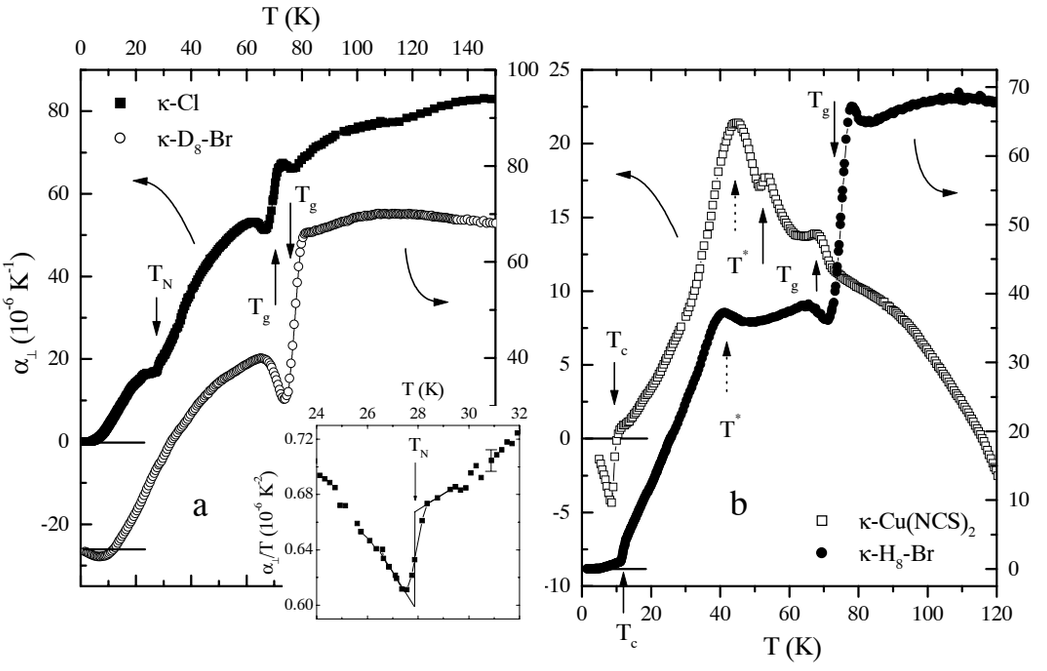

Fig. 1: Cross-plane thermal expansion coefficient for various κ-$(ET)_2X$ salts; H_8 (D_8) indicate protonated (deuterated) ethylene endgroups. Inset shows the phase transition into the AFM ground state for κ-Cl.

together with earlier X-ray-diffraction studies [6], we infer that, upon cooling from room temperature, the gradual ordering in the relative orientation of the ethylene groups in one of two possible conformations becomes interrupted at T_g leaving a residual frozen disorder at low temperatures. The amount of disorder depends on the cooling rate employed at T_g and is expected to be at a 10-20 % level. Its implications for the ground-state properties can be discerned by recalling the results of magnetic and transport measurements on protonated (H_8) and deuterated (D_8) κ-Br: rapid cooling of the latter salt through a temperature around 75 K – 80 K (T_g) was found to cause a strong reduction of

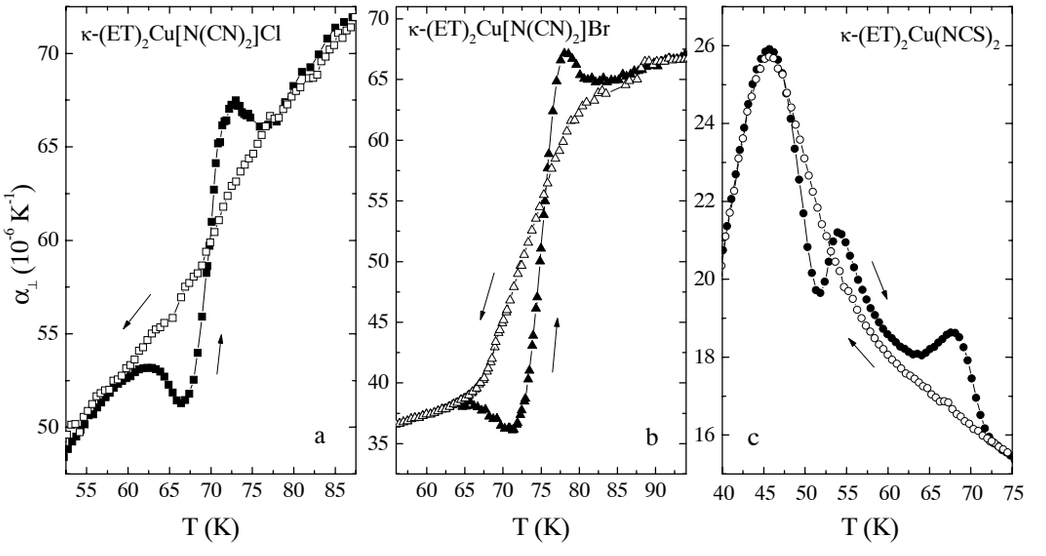

Fig. 2: Blow-up of the cross-plane thermal expansion coefficient around the glass-like transition(s) at T_g for various κ-$(ET)_2X$ salts. Arrows indicate cooling and heating runs.

the SC volume fraction and may even transform a SC into an insulator [7].

(B) Phase-transition anomalies at T^*

For the SC salts, i.e. κ-H_8-Br and κ-Cu(NCS)$_2$, the $\alpha_\perp$ data (Fig. 1b) reveal distinct local maxima at T^* = 38 and 45 K, respectively. In addition, directional-dependent measurements (not shown) disclose a strongly anisotropic lattice response at T^*. In an attempt to extract the anomalous contributions to the uniaxial coefficients of thermal expansion α_i at T^*, $\delta\alpha_i$, we use a smooth interpolation of the data away from the α_i anomalies. The so-derived α_{ib} serve as rough estimates of the background expansivities.

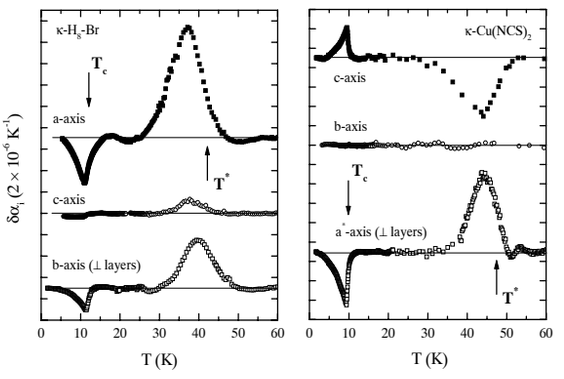

Fig. 3: Anomalous contributions to the uniaxial thermal expansion coefficients at T_c and T^* derived by subtracting a smooth background contribution.

In Fig. 3 we display the quantities $\delta\alpha_i(T) = \alpha_i(T) - \alpha_{ib}(T)$ over an extended temperature range which also covers the SC transition [8]. We find pronounced 2nd-order phase-transitions-like anomalies at slightly different temperatures T^* for both compounds. We note that the overall shape of these anomalies, i.e. their width and asymmetry, but not the peak itself, depends somewhat on the interpolation procedure used to determine the background expansivities. An important piece of information enclosed in Fig. 3 is a striking interrelation between the $\alpha(T)$ anomalies at T^* and those at T_c for both compounds: for each axis, a large (small) feature at T^* is accompanied by a large (small) discontinuity at T_c, while the signs of both anomalies are just reversed. According to the Ehrenfest relation

$$\left(\frac{\partial T_0}{\partial p_i}\right)_{p_i \to 0} = V_{mol} \cdot T_0 \cdot \frac{\Delta\alpha_i}{\Delta C}$$

the uniaxial-pressure dependence of a 2nd-order phase transition at T_0 is related to the discontinuities at T_0 by the coefficients of thermal expansion, $\Delta\alpha_i$, and specific heat ΔC. Thus, the data of Fig. 3 imply that for both compounds the uniaxial-pressure coefficients of T^* and those of T_c are strictly anticorrelated in their signs but correlated in their magnitudes. In the case of the κ-Cu(NCS)$_2$ salt, for example, we infer that uniaxial pressure applied perpendicular to the planes causes a substantial shift of T^* to higher temperatures and, at the same time, a strong reduction of T_c. Likewise, uniaxial pressure along the in-plane ***b***-axis neither affects T^* nor does it have any effect on T_c.

The anomaly at T^* is particularly interesting because it coincides with the temperature where magnetic, transport, and elastic properties exhibit anomalous behavior: a sharp peak in the spin-lattice relaxation rate $(T_1T)^{-1}$ [9,10] accompanied by a reduction of the spin susceptibility as determined by Knight-shift [9] or ESR [11] measurements as well as pronounced softening of ultrasonic modes [12,13]. In addition, our analysis yields an increase of T^* under hydrostatic pressure conditions for both compounds, in accordance with the results of pressure studies [9,12].

Concerning the nature of the anomaly at T^* we note that it is independent of the crystal structure as κ-Cu(NCS)$_2$ is not isomorphic to κ-Br, but it appears to be related to the electronic structure which is very similar for the two SC compounds [6].

Based on the above results, we propose that T^* marks a density-wave instability that involves only the minor 1D parts of the Fermi surface while leaving the major 2D portions unaffected. This implies that cooling through T^* is accompanied by the formation of a ***real*** gap on a small fraction of the Fermi surface as opposed to a ***pseudogap*** on the major parts [1]. The above interpretation is consistent with recent results of both magnetic and transport measurements on the SC salts yielding the onset of a small but distinct anisotropy below T^* [14].

(C) Transitions into the magnetic and superconducting ground states

The phase transitions into either the AFM ordered (κ-Cl), (cf. Fig. 1a) or SC (κ-H_8-Br, κ-Cu$(NCS)_2$), (cf. Figs. 1 and 3) ground state manifest themselves in distict and strongly anisotropic phase-transition anomalies in α_i. As for the transition at $\boldsymbol{T}_N$, our directional-dependent measurements (not shown) reveal a finite discontinuity only along the axis perpendicular to the conducting planes ($\Delta\alpha_\perp < 0$), cf. inset Fig. 1a, while $\Delta\alpha_\parallel$ 0 for both in-plane expansion coefficients [4,5]. Applying the Ehrenfest relation, we thus conclude that uniaxial pressure applied perpendicular to the conducting planes causes a reduction of $\boldsymbol{T}_N$ whereas in-plane pressure leaves $\boldsymbol{T}_N$ unaffected. Taking these uniaxial-pressure coefficients together results in a negative pressure dependence of $\boldsymbol{T}_N$ under hydrostatic-pressure conditions in accordance with the results of pressure studies [15]. As for the nature of the AFM state, our results seem difficult to reconcile with existing models. Neither for the nesting-induced itinerant magnetism [16,17,18] nor for a Mott-Hubbard-type magnetic state of localized spins [19,1] - even when next nearest neighbor couplings are included - is a vanishingly small in-plane pressure coefficient expected.

Applying the same thermodynamic analysis to the directional-dependent $\alpha_i(\boldsymbol{T})$ anomalies at the SC transition for the κ-$(ET)_2\boldsymbol{X}$ series clearly demonstrates the lack of a simple form of systematics regarding the in-plane pressure coefficients of $\boldsymbol{T}_c$: While for the κ-H_8-Br salt both in-plane pressure coefficients of $\boldsymbol{T}_c$ are negative, an either zero or even positive in-plane pressure effect is found for κ-Cu$(NCS)_2$ [20,3]. Such a non-universal behavior is in clear contrast to the predictions of the purely 2D electronic model proposed by Kino et al. [21] yielding in all cases a suppression of $\boldsymbol{T}_c$ under in-plane stress. On the contrary, our studies reveal that it is the extraordinarily large negative inter-layer pressure coefficient of $\boldsymbol{T}_c$ which is common to all κ-$(ET)_2\boldsymbol{X}$ systems investigated so far including the $\boldsymbol{X} = I_3$ salt [5]. Apparently, it is this component which predominates the reduction of $\boldsymbol{T}_c$ under hydrostatic pressure.

As for the symmetry of the SC state, arguments in favor of an unconventional order parameter with ***d***-wave symmetry for the investigated κ-$(ET)_2\boldsymbol{X}$ family have been derived from temperature dependent studies and, more recently, from orientational-dependent measurements aiming at a direct determination of the gap anisotropy. Conversely, there are numerous experimental investigations which indicate a SC state

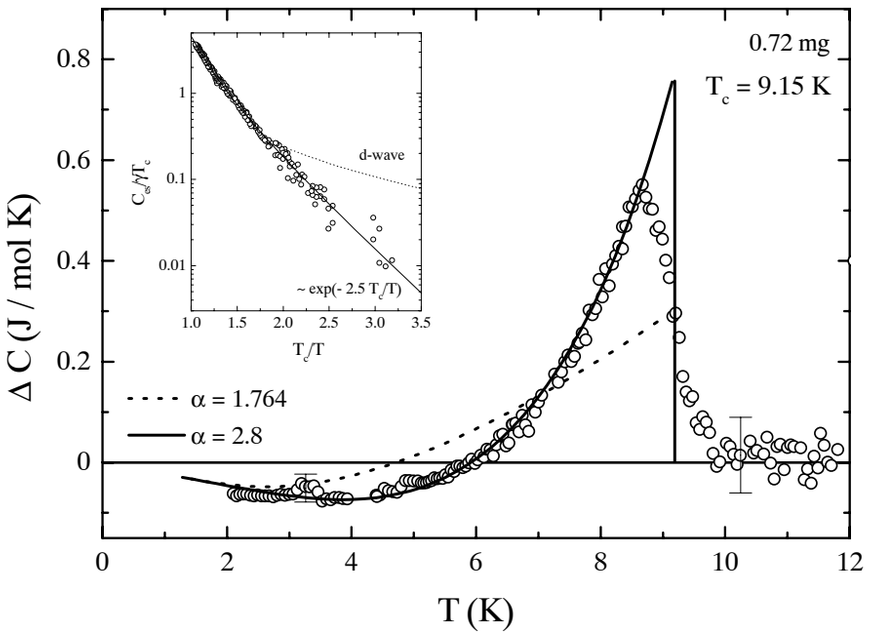

Fig. 4: Specific heat difference $\Delta C = C(0T) - C(8T) = C(0T) - C_n$, where C_n denotes the N-state specific heat. Dotted and solid thick lines represent BCS curves for weak and strong coupling, respectively. Inset shows the electronic contribution in a BCS-plot.

characterized by a finite gap. For a discussion of the present status of this controversy, see e.g. [2,3].

A decisive technique to probe certain aspects of the gap structure – in particular, the question whether gap zeroes exist or not – is provided by specific heat measurements. In case this integral thermodynamic probe were to detect an electronic quasiparticle contribution $\boldsymbol{C}_{es}(\boldsymbol{T})$ for $\boldsymbol{T} \ll \boldsymbol{T}_c$ that varies exponentially weakly with the temperature, the existence of a vanishing gap on parts of the Fermi surface could be definitely ruled out. In Fig. 4 we display the quantity $\Delta\boldsymbol{C}(\boldsymbol{T}) = \boldsymbol{C}(\boldsymbol{T},\boldsymbol{B} = 0) - \boldsymbol{C}(\boldsymbol{T},\boldsymbol{B} = 8\ \mathrm{T})$, where $\boldsymbol{C}(\boldsymbol{T},8\ \mathrm{T})$ is the specific heat in the N-state, measured on a tiny high-quality single crystal of κ-$Cu(NCS)_2$ with a mass of only 0.72 mg.

Given a $\boldsymbol{B}$-independent specific heat above $\boldsymbol{T}_c$ as proved experimentally [22,23], the analysis of $\Delta\boldsymbol{C}(\boldsymbol{T})$ has the advantage that the unknown phonon contribution and all other extraneous contributions cancel out each other. Figure 4 demonstrates that $\Delta\boldsymbol{C}(\boldsymbol{T})$ deviates markedly from a weak-coupling BCS-behavior (broken line) but is in excellent agreement with the so-called α-model, an empirical extension of the BCS formalism to strong-coupling superconductors [24]. As the inset of Fig. 4 clearly shows, $\boldsymbol{C}_{es} = \Delta\boldsymbol{C} + \gamma\boldsymbol{T}$, (where γ is the Sommerfeld coefficient), reveals an exponentially weak temperature dependence at low temperatures incompatible with a ***d***-wave order parameter. The same conclusions have been drawn recently from similar measurements on the κ-H_8-Br salt [23].

Summary and outlook

The present study discloses important new aspects which impose clear constraints for both experimentalists and theoreticians attempting to unravel the nature of the states below and above $\boldsymbol{T}_c$ in these κ-$(ET)_2\boldsymbol{X}$ salts. At elevated temperatures, a glass transition has been identified that defines the boundary between an ethylene liquid at $\boldsymbol{T} > \boldsymbol{T}_g$ and a glassy state at $\boldsymbol{T} < \boldsymbol{T}_g$ where a certain amount of disorder in the terminal (C_2H_2)-units becomes frozen. With increasing cooling rate through $\boldsymbol{T}_g$, the level of disorder increases and may substantially influence the electronic properties at low temperatures, especially the SC state.

At intermediate temperatures $\boldsymbol{T}^*$, our studies disclose a second-order phase transition of the metallic/SC salts. We propose that instead of a pseudogap on the major 2D fractions of the Fermi surface, $\boldsymbol{T}^*$ is associated with the formation of a density wave, i.e., a real gap, on the minor 1D parts which competes with superconductivity for stability.

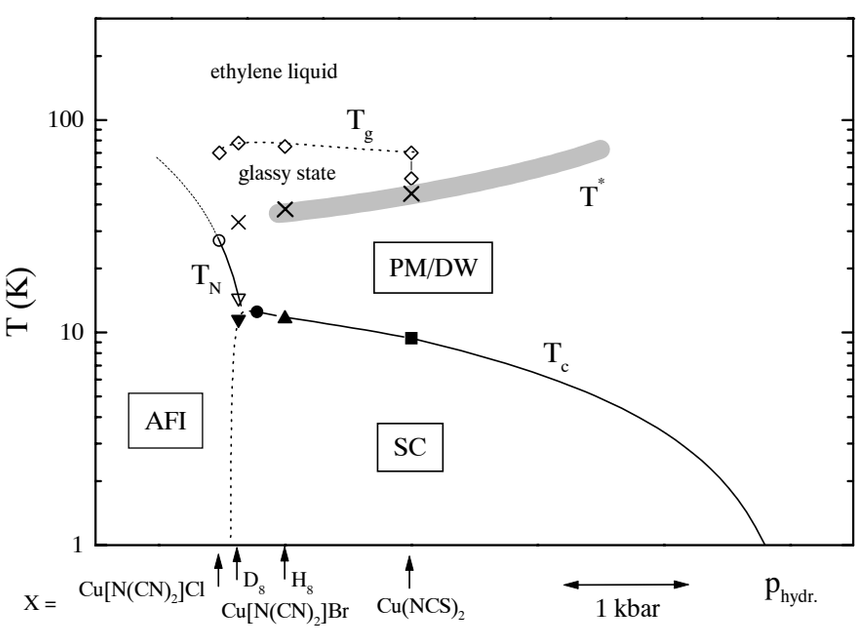

Fig. 5: Compilation of thermal expansion anomalies for the various κ-$(ET)_2X$ salts in a pressure-temperature phase diagram. Arrows indicate the location of the different salts at ambient pressure. AFI, PM/DW and SC denotes antiferromagnetic insulator, paramagnetic metal in coexistence with a density-wave state and superconductor, respectively. Solid lines represent the hydrostatic pressure dependences of T_N and T_c taken from the literature.

As for the response of T_c to pressure, our finding of an extraordinarily large interplane pressure effect but a non-universal behavior with respect to the in-plane pressure coefficients demonstrates that attempts to understand these quasi-2D organic superconductors merely on the basis of 2D electronic models are not appropriate. It is a combination of electronic correlations, electron-phonon interactions as well as interlayer-coupling effects which have to be considered in order to provide a realistic modeling of this family of superconductors.

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