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Comparative Thermal-Expansion Study of β"-(ET)2SF5CH2CF2SO3 and κ-(ET)2Cu(NCS)2: Uniaxial Pressure Coefficients of Tc and Upper Critical Fields

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Comparative thermal-expansion study of β''-$(ET)_2SF_5CH_2CF_2SO_3$ and κ-$(ET)_2Cu(NCS)_2$: Uniaxial pressure coefficients of T_c and upper critical fields

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We report high-resolution measurements of the coefficient of thermal expansion, $\alpha = l^{-1} \times (\partial l/\partial T)$, on single crystals of the organic superconductors β''-$(ET)_2SF_5CH_2CF_2SO_3$ and κ-$(ET)_2Cu(NCS)_2$. For both salts we find large and highly anisotropic phase-transition anomalies at T_c. Combining these data with literature results on the specific heat via the Ehrenfest relation, the uniaxial pressure coefficients of T_c can be determined. Most remarkably, a strikingly similar in-plane vs out-of-plane anisotropy is found for both compounds: the strong suppression of T_c observed in hydrostatic-pressure experiments is dominated by a huge negative uniaxial stress effect perpendicular to the conducting planes. Therefore we expect that an increase of T_c in this class of superconductors can be obtained by enlarging the distance between the conducting layers. Application of magnetic fields perpendicular to the planes for the β''-$(ET)_2SF_5CH_2CF_2SO_3$ salt were found to result in pronounced superconducting fluctuation effects and scaling behavior in $\alpha(T,B)$. Owing to the pronounced phase-transition anomalies in $\alpha(T,B)$ at T_c, our measurements allow for an accurate determination of the upper critical fields. We find $B_{c_2}^{\perp}(0) = (1.4 \pm 0.2)$ T and $B_{c_2}^{\parallel}(0) = (10.4 \pm 0.5)$ T for fields perpendicular and parallel to the conducting planes, respectively.

I. INTRODUCTION

Among the radical cation organic charge-transfer salts the majority of superconductors is based on the electron donor molecule bis(ethylenedithio)tetrathiafulvalene, commonly abbreviated BEDT-TTF or simply ET. Of particular interest in this class of materials are the κ-phase $(ET)_2X$ salts with the complex anions $X^- = [Cu(NCS)_2]^-$ and $[Cu\{N(CN)_2\}Br]^-$. These salts have a layered structure consisting of alternating sheets of conducting $(ET)_2^+$ cations and insulating X^- anions. Besides their high T_c values around 10 K, the strong interest in this class of superconductors originates in their normal- and superconducting-state properties which are similar to those of the high-T_c cuprates.[1]

As the delocalization of the charge carriers within the ET layers is provided by the overlap of π orbitals of sulfur atoms of adjacent ET molecules, the anion structure is crucial in determining the packing pattern of the ET molecules and thereby the electronic properties. While the above mentioned κ-phase salts contain polymeric charge-compensating anions, large discrete counter ions such as $M(CF_3)_4^-$ + solvent molecules (M = Cu, Ag, Au) were found to produce similarly high-T_c values.[2] In the course of this line of synthesis the superconductor β''-$(ET)_2SF_5CH_2CF_2SO_3$ with T_c around 5 K has recently been found.[3] This salt, which contains large discrete anions without solvent molecules, is unique in being the first superconductor of this class free of any metal atoms.

A generally accepted picture of the nature of superconductivity in this class of materials is still lacking. A way to find out the relevant microscopic parameters is to look for systematics that correlate T_c with other physical parameters such as the unit-cell dimensions. To this end, comparative studies of the directional-dependent uniaxial pressure dependencies on various, well-characterized members of these quasi-two-dimensional superconductors are most useful.

Here we report on the determination of the uniaxial-pressure coefficients of T_c in the limit of vanishing pressure by means of thermal-expansion measurements. According to quantum-oscillation studies β''-$(ET)_2SF_5CH_2CF_2SO_3$,[4] as well as κ-$(ET)_2Cu(NCS)_2$,[5] selected for this study are characterized as quasi-two-dimensional superconductors with a high degree of crystalline order. For both compounds pronounced phase-transition anomalies were observed in the coefficient of thermal expansion at T_c, indicative of a substantial coupling of superconductivity to the lattice degrees of freedom. Most interestingly, we find an in-plane vs out-of-plane anisotropy which is identical in both cases. In addition, owing to the pronounced lattice response at T_c, our measurements allow for a very accurate determination of the upper critical fields for the β''-$(ET)_2SF_5CH_2CF_2SO_3$ salt.

II. EXPERIMENT

The coefficient of thermal expansion was measured by means of an ultra-high-resolution capacitance dilatometer[6] with a maximum sensitivity corresponding to $\Delta l/l = 10^{-10}$. Length changes $\Delta l(T) = l(T) - l(1.4\,\mathrm{K})$ were detected upon both heating and cooling the sample with a rate $|dT/dt| \leqslant 2$ K/h. The coefficient of thermal expansion $\alpha(T) = l^{-1} \times (\partial l/\partial T)$ is approximated by the differential quotient $\alpha(T) \approx [\Delta l(T_2) - \Delta l(T_1)]/[l(300\ \mathrm{K}) \cdot (T_2 - T_1)]$ with $T = (T_1 + T_2)/2$. Measurements were performed along both in-plane principal axes and perpendicular to the highly conducting planes, i.e., along a^* and almost parallel to c for κ-$(ET)_2Cu(NCS)_2$ and β''-$(ET)_2SF_5CH_2CF_2SO_3$, respectively. A small misalignment of about 5° cannot be excluded. The magnetic fields were aligned parallel to the measuring direction.

The single crystals used were synthesized by the standard electrocrystallization technique as described elsewhere.[3,7] For the measurements on the β''-$(ET)_2SF_5CH_2CF_2SO_3$ salt (triclinic crystal structure), two crystals were used, both of which have dimensions $(a \times b \times c)$ axis $\approx (5 \times 1.2 \times 0.5)\mathrm{mm}^3$. While the *a*- and *b*-axis thermal-expansion coefficients α_a and α_b were measured on crystal 4 ($T_c = 4.75$ K), the α_c data were taken on crystal 2 ($T_c = 4.6$ K). The single crystal of κ-$(D_8\text{-}ET)_2Cu(NCS)_2$ (monoclinic structure) with $T_c = 9.95$ K had dimensions $(a^* \times b \times c)$ axis $= (0.65 \times 2.3 \times 1.2)$ mm^3. In the D_8-ET molecule the terminal ethylene groups of the ET molecule are deuterated. Except a slightly higher transition temperature for the deuterated compound compared to the hydrogenated one, the two systems are considered identical as for the properties discussed in the present paper. For the determination of T_c we use the standard ''equal-areas'' construction in a plot $\alpha(T)/T$ vs T.

III. RESULTS AND DISCUSSION

A. Uniaxial pressure coefficients of T_c

Figure 1 shows the linear thermal-expansion coefficients $\alpha_i(T)$ of β''-$(ET)_2SF_5CH_2CF_2SO_3$ along the $i = a$, b, and c axes for temperatures up to 40 K. The inset contains data of the in-plane coefficients α_a and α_b up to 220 K. In accordance with the crystal structure the lattice response to temperature changes is strongly anisotropic in the whole temperature range investigated. At T_c we observe pronounced second-order phase-transition anomalies with opposite signs in α_b and α_c. This contrasts with α_a where no significant anomaly is visible at T_c. While the linear expansion coefficient along the in-plane b direction grows monotonically with increasing temperature, we find a broad minimum structure with negative values of α centered around 8.3 K for α_a and 12.5 K for α_c, respectively. It is remarkable that the in-plane anisotropy in α, i.e., α_a vs α_b, grows with increasing temperature. This corresponds to a progressive triclinic distortion of the ab plane upon warming. Furthermore, the

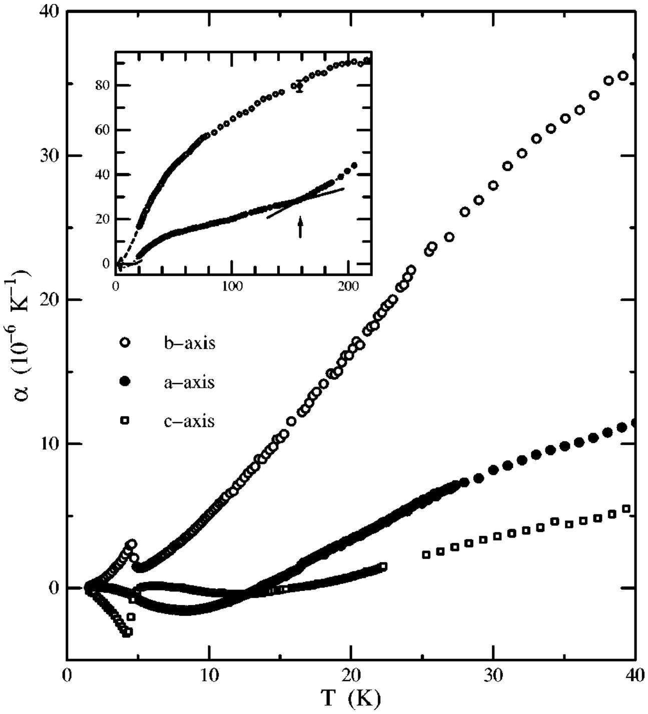

FIG. 1. Coefficient of thermal expansion α vs T for β''-$(ET)_2SF_5CH_2CF_2SO_3$ along the *a*, *b*, and *c* axes. The *c* axis is almost perpendicular to the highly conducting ab plane. The inset shows the in-plane thermal-expansion coefficients α_a and α_b up to 220 K.

data in the inset of Fig. 1 reveal an abrupt change in slope of α_a around 160 K. The origin of this feature is unclear, but might be related to a conformational ordering of the terminal ethylene groups of the ET molecules. We note that a similar anomaly, i.e., a sudden change of slope is found also in the $\alpha_i(T)$ data of κ-$(ET)_2Cu(NCS)_2$ at temperatures $170 \leqslant T \leqslant 190$ K.[8] Apart from the superconducting transition there are no further anomalies visible in the $\alpha_i(T)$ data shown in the main panel of Fig. 1. In particular, we observe a smooth variation of α_i with T in the temperature range $30 < T < 90$ K, where a sequence of rather sharp maxima, reminiscent of structural anomalies, was found in the κ-$(ET)_2Cu(NCS)_2$ salt.[9]

The volume thermal expansion $\beta(T) = \Sigma_i \alpha_i(T)$ is related to the specific heat via the Grüneisen relation

$$\beta(T) = \gamma \cdot \frac{\kappa_T}{V_{mol}} \cdot C_V(T), \tag{1}$$

where κ_T denotes the isothermal compressibility, V_{mol} the molar volume, and γ the volume Grüneisen parameter. Using literature data for the specific heat[10,11] and assuming that the bulk modulus $B = 1/\kappa_T = 122$ kbars for κ-$(ET)_2Cu(NCS)_2$ (Ref. 12) is appropriate also for the β''-$(ET)_2SF_5CH_2CF_2SO_3$ salt, we can estimate the Grüneisen parameter γ. We find $\gamma \approx 3.5$ for the former and $\gamma \approx 1$ for the latter salt. Since γ is a measure of the anharmonicity of the lattice vibrations these results may indicate that anharmonic lattice vibrations are favorable for superconductivity in this class of materials.

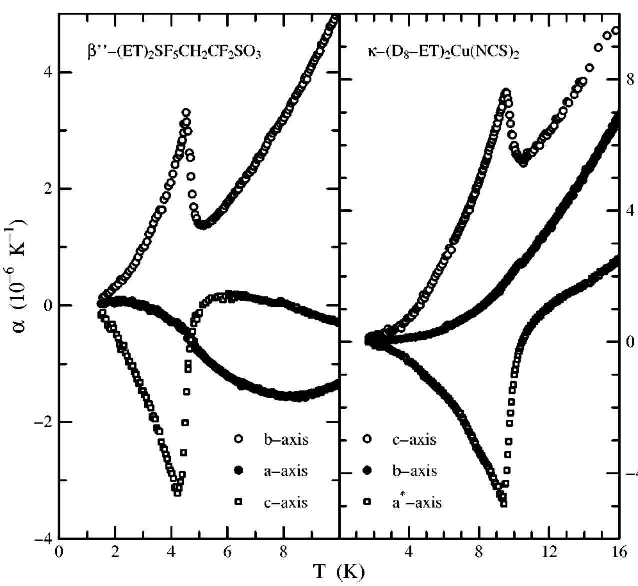

FIG. 2. Thermal-expansion coefficients α_i vs T close to the superconducting transition measured parallel and perpendicular to the conducting planes for β''-$(ET)_2SF_5CH_2CF_2SO_3$ (left panel) and κ-$(D_8\text{-}ET)_2Cu(NCS)_2$ (right panel).

Figure 2 compares details of α_i close to the superconducting phase transition of β''-$(ET)_2SF_5CH_2CF_2SO_3$ (left panel) with those of κ-$(D_8\text{-}ET)_2Cu(NCS)_2$ (right panel). Strangely enough, both systems, though structurally different, behave very similar with respect to the in-plane vs out-of-plane anisotropy in the lattice response at the superconducting transition. Via the Ehrenfest relation, the discontinuities in α_i at T_c, $\Delta\alpha_i$, provide information on the uniaxial-pressure dependencies of T_c along the i axis in the limit of vanishing pressure:

$$\left(\frac{\partial T_c}{\partial p_i}\right)_{p_i\to 0} = V_{mol}\cdot T_c \cdot \frac{\Delta\alpha_i}{\Delta C}, \tag{2}$$

where ΔC denotes the discontinuity at T_c in the specific heat. Using the jump heights ΔC reported in literature for the two salts[10,11] one finds for both systems a huge negative pressure effect for stress perpendicular to the planes, i.e., $\partial T_c/\partial p_\perp = -(5.9\pm 0.25)$ K/kbars for β''-$(ET)_2SF_5CH_2CF_2SO_3$ and $\partial T_c/\partial p_\perp = -(6.2\pm 0.25)$K/kbars for κ-$(D_8\text{-}ET)_2Cu(NCS)_2$.[13] We note that measurements on hydrogenated crystals reveal $\partial T_c/\partial p_\perp$ values of similar size ranging from $-(4.8\pm 0.8)$ K/kbars (Ref. 14) to $-(3.2\pm 0.36)$ K/kbars.[8] These numbers are somewhat larger than $\partial T_c/\partial p_\perp = -2$ K/kbars obtained in an uniaxial stress experiment.[15] In accordance with previous studies on hydrogenated κ-$(ET)_2Cu(NCS)_2$ (Refs. 14, 16, 8) considerably smaller effects are found in the thermal-expansion experiments for in-plane stress. For both salts we find $\partial T_c/\partial p > 0$ for stress along one in-plane axis while $\partial T_c/\partial p \approx 0$ along the second one. The so-derived uniaxial-pressure coefficients for both samples are collected in Table I.

We note that the hydrostatic-pressure dependencies of T_c determined from the present study (bottom line of Table I) are in good agreement with the values found in hydrostatic-pressure experiments, i.e., $(\partial T_c/\partial p)_{hydr.} = -1.34$ K/kbars for β''-$(ET)_2SF_5CH_2CF_2SO_3$ (Ref. 17) and -3 K/kbars for κ-$(ET)_2Cu(NCS)_2$,[18] respectively. The above pressure coefficients are much larger than those found in any other superconductor as, e.g., conventional metals or high-T_c cuprates. At first glance this is not surprising in view of the weak van-der-Waals bondings between the ET molecules that result in a large isothermal compressibility κ_T. To account for this effect one should therefore consider the volume dependence of T_c, $\partial \ln T_c/\partial \ln V = V/T_c\cdot \partial T_c/\partial V = -1/(\kappa_T\cdot T_c)\cdot(\partial T_c/\partial p)$. Using again the compressibility data of κ-$(ET)_2Cu(NCS)_2$,[12] one finds for both salts $\partial \ln T_c/\partial \ln V \approx 40$. This is substantially larger than what is found for other classes of superconductors as, e.g., $\partial \ln T_c/\partial \ln V = 2.4$ for Pb (Ref. 19) and $-(0.36-0.6)$ for $YBa_2Cu_3O_7$ (Ref. 20) and underlines the role of the lattice degrees of freedom for the superconducting instability in this class of materials.

As demonstrated in Table I the large negative hydrostatic-pressure derivatives of T_c for the two title organic salts are dominated by a huge negative pressure effect for stress perpendicular to the highly conducting planes. As discussed in Ref. 1, this may arise from several factors: (i) pressure-induced changes in the interlayer interaction. This effect includes changes of both the interlayer coupling, i.e., the degree of two-dimensionality, and changes in the electron-electron as well as the electron-phonon coupling constants and (ii) changes in the phonon frequencies. Likewise, changes in the vibrational properties could be of relevance for the intraplane-pressure effect on T_c. In addition, in-plane stress effectively modifies the electronic degrees of freedom by changing the transfer integrals between the highest occupied molecular orbitals (HOMO's) of the nearest neighbor ET molecules. To clarify the relative role of the above various factors further material-specific investigations from both theory as well as experiment are needed. Yet, without such

TABLE I. Uniaxial pressure dependencies of T_c. The hydrostatic-pressure coefficients in the bottom line were determined by $(\partial T_c/\partial p)_{hydr.} = \Sigma_i(\partial T_c/\partial p_i)$. Note that for the determination of $(\partial T_c/\partial p)_{hydr.}$ of the β'' salt the jump heights $\Delta\alpha_a$ and $\Delta\alpha_b$ of crystal 4 and $\Delta\alpha_c$ of crystal 2 were used.

β''-$(ET)_2SF_5CH_2CF_2SO_3$	$\partial T_c/\partial p_i$ [K/kbars]	κ-$(D_8\text{-}ET)_2Cu(NCS)_2$	$\partial T_c/\partial p_i$ [K/kbars]
b axis (in plane)	3.9 ± 0.15	c axis (in plane)	3.44 ± 0.15
a axis (in plane)	0.39 ± 0.1	b axis (in plane)	$-(0.14\pm 0.1)$
c axis ($\perp$ planes)	$-(5.9\pm 0.25)$	a^* axis ($\perp$ planes)	$-(6.2\pm 0.25)$
volume	$-(1.6\pm 0.5)$	volume	$-(2.9\pm 0.5)$

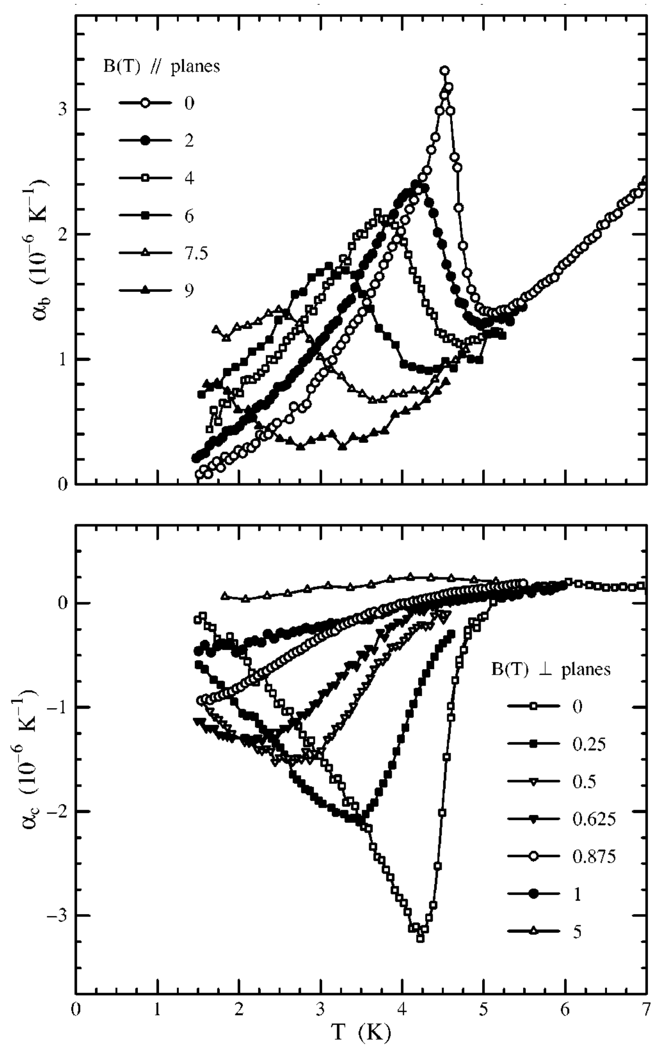

FIG. 3. Field dependence of α_b (parallel to the conducting planes, upper panel) and α_c (perpendicular to the conducting planes, lower panel) for β''-$(ET)_2SF_5CH_2CF_2SO_3$. Fields are parallel to the measuring direction.

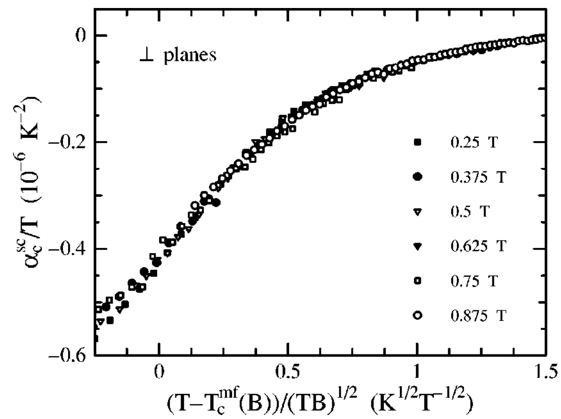

FIG. 4. Scaling behavior of the superconducting contribution to α_c, α_c^{sc}, for β''-$(ET)_2SF_5CH_2CF_2SO_3$ in magnetic fields aligned perpendicular to the planes.

supplementary information the following conclusions can be drawn on the basis of the presently available data: (i) T_c is most sensitive to changes of the cross-plane lattice parameter which may affect the interlayer interaction, i.e., the strength of the three-dimensional (3D) coupling and/or the vibrational properties of the lattice. (ii) An in-plane-stress effect which is either positive or zero for the present salts makes a purely density of states effect to account for the pressure-induced T_c shifts very unlikely: pressure-induced changes in the density-of-states should be strongest for in-plane stress owing to the quasi-2D electronic band structure. According to the simple BCS relation, an in-plane-stress-induced increase of the π-orbital overlap, i.e., a reduction of the density of states at the Fermi level, $n(E_F)$, should lead to a reduction of T_c. This is in contrast to the observation.

B. Fluctuation effects and scaling behavior

Figure 3 shows the linear coefficients of thermal expansion α_b and α_c of β''-$(ET)_2SF_5CH_2CF_2SO_3$ at varying magnetic fields B. Owing to the layered crystal structure the field-induced temperature shifts of T_c are strongly anisotropic: while for fields parallel to the planes (upper panel) the phase transition in $\alpha(T)$ is still visible even in $B=9$ T, a field of 1 T is sufficient to almost completely suppress superconductivity for B perpendicular to the conducting planes (lower panel of Fig. 3).

Furthermore, Fig. 3 illustrates the influence of thermal fluctuations of the amplitude of the order parameter which can be considerably strong in materials with reduced dimensionality. With increasing magnetic fields aligned perpendicular to the conducting planes, the phase-transition anomaly becomes substantially broadened. This is understood as a field-induced dimensional crossover: in high fields the confinement of the quasiparticles to their lower Landau levels leads to a reduction of the effective dimensionality from a quasi-2D system in small fields to a quasi-0D system in strong fields.[21,22] This enhances the effect of fluctuations in growing fields. As a result the rather sharp phase-transition anomaly in zero field becomes progressively rounded and smeared out with increasing fields. In higher fields the phase boundary in the B-T plane is replaced by a crossover line with a rather wide region of critical fluctuations. The effect of fluctuations on transport and thermodynamic properties has been studied by Ullah and Dorsey.[23] Assuming the lowest-Landau-level approximation and taking into account only noninteracting, Gaussian fluctuations they obtain an expression for the scaling functions of various thermodynamic quantities as, e.g., magnetization M and specific heat C:

$$\Xi_i = F_i\left(A\,\frac{T-T_c^{mf}(B)}{(TB)^n}\right), \tag{3}$$

with $\Xi_i = M/(TB)^n$ or C/T.[24] F_i is an unknown scaling function, A a temperature- and field-independent coefficient characterizing the transition width and $n=2/3$ for anisotropic 3D systems, and $n=1/2$ for a 2D system. $T_c^{mf}(B)$ is the mean-field transition temperature. Since the coefficient of thermal expansion is closely related to the specific heat via the Grüneisen relation, cf. Eq. (1), a scaling relation can be expected also for α/T. Figure 4 shows the α_c data in varying fields in a plot α_c^{sc}/T vs $[T-T_c^{mf}(B)]/(TB)^{1/2}$. α_c^{sc} denotes the superconducting contribution to α_c, i.e., the raw data corrected for the phonon background. As the latter is very

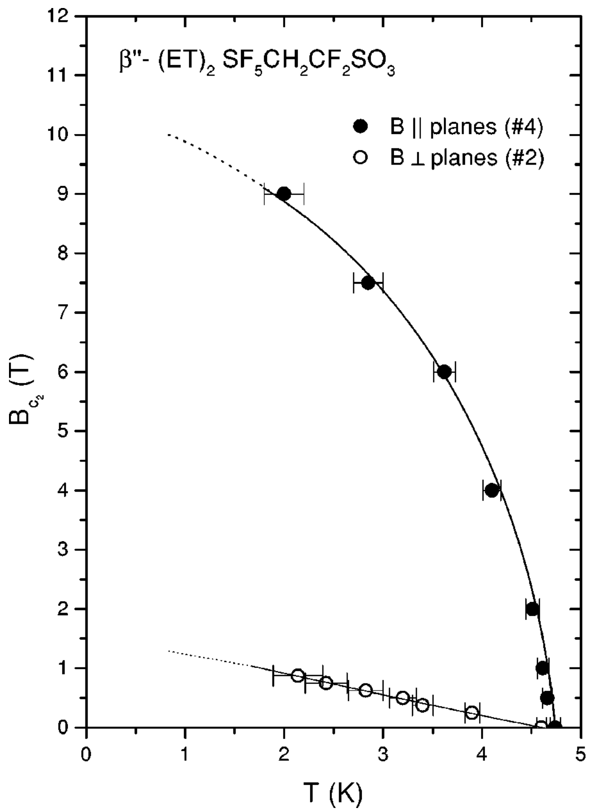

FIG. 5. Upper critical fields $B_{c_2}(T)$ for fields parallel and perpendicular to the conducting planes for β''-$(ET)_2SF_5CH_2CF_2SO_3$. The lines are guides for the eye. The data have been taken on two different crystals 4 and 2.

small in the temperature range of interest, i.e., $T \leqslant 5$ K, and field independent, we find that both the quality of the scaling as well as the mean-field transition temperatures $T_c^{mf}(B)$ derived from the scaling plot are not affected by the subtraction procedure. As shown in Fig. 4 the various field curves $\alpha_c^{sc}(T,B)$ show the 2D scaling over a rather wide temperature and field range. We note that a 3D scaling is found to work equally well. The same observation was made in a scaling analysis of magnetization and thermal-expansion data of κ-$(ET)_2Cu(NCS)_2$.[25,26] Another interesting feature shared not only by the above organic compounds, but also by the high-T_c cuprates, is that the actual scaling range is much wider than the field and temperature interval predicted by theory.[24,27] We note that the mean-field transition temperatures $T_c^{mf}(B)$ derived by using the above scaling relation, are identical within the experimental error with the values obtained by using the standard equal-areas construction in a plot α/T vs T.

C. Upper critical fields

Figure 5 shows the temperature dependencies of the upper critical fields, $B_{c_2}(T)$, for fields parallel and perpendicular to the highly conducting ab plane of β''-$(ET)_2SF_5CH_2CF_2SO_3$. As shown in the figure, B_{c_2} is strongly anisotropic. An extrapolation of the data in Fig. 5 to $T=0$ yields $B_{c_2}^{\perp}(0) = (1.4\pm0.2)$ T and $B_{c_2}^{\parallel}(0)=(10.4\pm0.5)$ T for fields perpendicular and parallel to the conducting planes, respectively. The latter value is close to the Pauli-limiting field approximated by $H_p(\text{in Tesla}) = 1.84\times T_c(\text{in K}) = 8.74$ T. This strongly supports the pairing state's spin-singlet character for the present salt.

Measurements of $B_{c_2}^{\perp}(T)$ for the present salt have been previously reported by Wanka *et al.* based on specific-heat experiments.[10] Our results for $B_{c_2}^{\perp}(T)$ deviate from the values derived from their experiments where a somewhat weaker reduction of T_c with increasing field was claimed. From their data an upper critical field value at $T=0$ of $B_{c_2}^{\perp}(0) = (3.4\pm0.4)$ T was extrapolated. Since the crystals used in both experiments come from the same source and reveal T_c values of similar size, sample dependencies appear rather unlikely to account for the discrepancy in $B_{c_2}^{\perp}(0)$. We believe that owing to the pronounced $\alpha(T)$ discontinuities at T_c [a 100% effect in $\alpha(T)$ compared to a few percent in the specific heat], thermal-expansion measurements are better suited to follow the transition as a function of applied magnetic field for this material.

To determine the coherence lengths perpendicular and parallel to the conducting planes, $\xi_\perp$ and $\xi_\parallel$, respectively, the following relations are used: $B_{c_2}^{\perp\,\prime} = \phi_0/(2\pi\xi_\parallel^2 T_c)$ and $\sqrt{\Gamma} = B_{c_2}^{\parallel\,\prime}/B_{c_2}^{\perp\,\prime} = \xi_\parallel/\xi_\perp$,[28] where $B_{c_2}^{\perp\,\prime}$ and $B_{c_2}^{\parallel\,\prime}$ are the initial slopes of the upper critical fields for B perpendicular and parallel to the conducting planes, respectively. Γ is the anisotropy parameter and ϕ_0 the flux quantum. We find $\xi_\parallel = (144\pm9)$ Å, $\xi_\perp = (7.9\pm1.5)$ Å, and $\Gamma\approx330$. The cross-plane coherence length $\xi_\perp$ being smaller than the interlayer distance of 17.49 Å suggests a quasi-two-dimensional character of the superconducting state. This is supported by the huge anisotropy parameter $\Gamma\approx330$ that exceeds $\Gamma\approx100$ found for the κ-$(ET)_2Cu(NCS)_2$ salt.[1,29] A high degree of two dimensionality in the normal state was also observed in Shubnikov–de Haas measurements.[4]

IV. SUMMARY

In summary, a comparative thermal-expansion study of the quasi-2D charge-transfer salts β''-$(ET)_2SF_5CH_2CF_2SO_3$, a superconductor without any metal atoms, and κ-$(D_8\text{-}ET)_2Cu(NCS)_2$ is presented. The anisotropy of the uniaxial pressure dependencies of T_c is found to be strikingly similar for both compounds: a huge negative pressure effect for stress perpendicular to the conducting planes that dominates the large negative pressure effect on T_c. Our findings rule out models that solely consider intralayer interactions to account for the strong reduction of T_c under hydrostatic pressure. Rather we find that interlayer effects are most important. We expect that an increase of T_c can be obtained by enlarging the distance between the conducting layers. Since the superconducting contribution to the coefficients of thermal expansion parallel and perpendicular to the planes is so large for β''-$(ET)_2SF_5CH_2CF_2SO_3$, we were able to study the field dependency of T_c with a high degree of accuracy. For fields applied perpendicular to the planes we could study the effect of superconducting fluctuations on $\alpha(T,B)$ using a scaling relation. We find a pronounced anisotropy of the upper criti-cal fields. The resulting degree of two dimensionality is even higher than that of the κ-$(ET)_2Cu(NCS)_2$ salt.

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