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Importance of interlayer effects for T_c in κ-$(ET)_2X$ superconductors

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Abstract

We report high-resolution measurements of the linear thermal-expansion coefficient perpendicular to the conducting planes, $\alpha_\perp(T)$, on single crystals of the superconductors κ-$(ET)_2X$ with X=I_3, $Cu(NCS)_2$ and $Cu[N(CN)_2]Br$. For all three compounds we find pronounced negative phase-transition anomalies at T_c. Using the Ehrenfest relation, the uniaxial-pressure coefficients of T_c can be determined. We find that *inter*layer effects are of crucial importance for T_c in this class of materials. Regarding also *intra*layer effects we compare our results with recent theories addressing the $p-T$ phase diagram.

Key words: Thermal expansion, Superconducting phase transition, Organic superconductors, BEDT-TTF salt

1. Introduction

Among quasi-twodimensional organic conductors based on the electron donor molecule BEDT-TTF (abbreviated as ET) the superconductors with the highest transition temperatures T_c belong to the κ-phase compounds κ-$(ET)_2X$. Within this family, different ground states are found: while the systems with X=I_3, $Cu(NCS)_2$ and $Cu[N(CN)_2]Br$ are superconductors with T_c values of 3.6 K, 10.4 K and 11.8 K, respectively, κ-$(ET)_2Cu[N(CN)_2]Cl$ is an antiferromagnetic insulator. However, the application of small hydrostatic pressure of only 300 bar drives the latter system to a superconductor with $T_c = 12.8$ K. A common feature of these systems is the high sensitivity to external pressure: the superconducting phase becomes rapidly suppressed with pressure giving way to a paramagnetic metallic phase. Recent theoretical investigations based on a 2D Hubbard model studied the effect of pressure considering stress induced changes of both the inter- and intradimer transfer integrals [1]. It was found there that *in-plane* pressure can drive an ambient-pressure antiferromagnetic insulator into a superconductor and, as pressure further increases, into a paramagnetic metallic ground state. It is argued in [1] that this is in accordance with the experimental observations. Considering the quasi-2D character of the title compounds it is important to study not only the hydrostatic- but also the uniaxial-pressure coefficients of T_c, $\partial T_c/\partial p_i$. In this context we initiated a systematic study of $\partial T_c/\partial p_i$ by means of thermal-expansion measurements.

2. Results and discussion

In a recent comparative study of the quasi-2D charge transfer salts β''-$(ET)_2SF_5CH_2CF_2SO_3$ and κ-$(ET)_2Cu(NCS)_2$ we found that the large negative hydrostatic-pressure coefficients of T_c for both salts are dominated by a huge negative pressure effect for stress perpendicular to the highly conducting planes [2]. We found, e.g., for κ-$(ET)_2Cu(NCS)_2$: $\partial T_c/\partial p_\perp = -(6.2 \pm 0.25)$ K/kbar and $\sum_i (\partial T_c/\partial p_i) = -(2.9 \pm 0.5)$ K/kbar, the latter being in excellent agreement with the value of -3 K/kbar found in a hydrostatic-pressure experiment [3]. These findings led us to extend our studies to the other κ-phase superconductors mentioned above. Fig. 1 shows the linear coefficient of thermal expansion perpendicular to the conducting planes, $\alpha_\perp(T)$, for

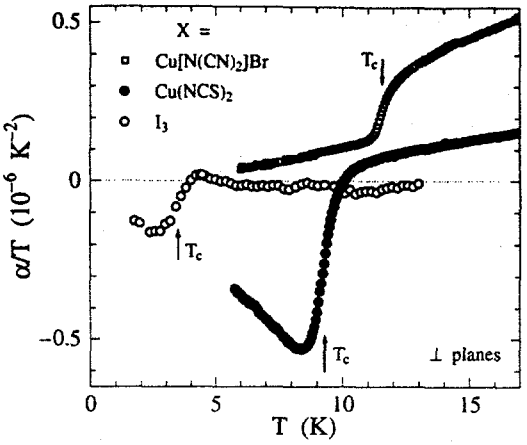

Fig. 1. Coefficient of thermal expansion perpendicular to the highly conducting planes of three different superconductors κ-(ET)$_2$X in a representation $\alpha_\perp/T$ vs. T.

the compounds κ-(ET)$_2$X with X=Cu[N(CN)$_2$]Br, Cu(NCS)$_2$ and I$_3$. All three systems show pronounced negative phase-transition anomlies at T_c. Via the Ehrenfest relation, the discontinuities in α_i at T_c, $\Delta\alpha_i$, provide informations on the uniaxial-pressure dependencies of T_c along the i-axis in the limit of vanishing pressure:

$$\left(\frac{\partial T_c}{\partial p_i}\right)_{p_i\to 0} = V_{mol}\cdot T_c\cdot\frac{\Delta\alpha_i}{\Delta C}, \qquad (1)$$

where ΔC denotes the discontinuity at T_c in the specific heat. Using literature results for the specific heat, one finds large negative pressure coefficients for stress perpendicular to the conducting planes: $\partial T_c/\partial p_\perp = -(2.2\pm 0.4)$ K/kbar for X=Cu[N(CN)$_2$]Br and $-(0.85\pm 0.2)$ K/kbar for X=I$_3$. A comparison with the hydrostatic-pressure coefficients of $(\partial T_c/\partial p)_{hydr.} = -2.8$ K/kbar for the former [4] and -2.3 K/kbar for the latter salt [5] indicates that interlayer effects are most important for T_c in these κ-phase compounds.

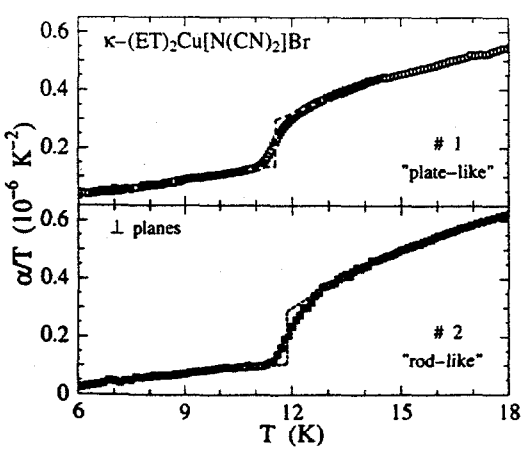

Fig. 2. $\alpha_\perp(T)/T$ of κ-(ET)$_2$Cu[N(CN)$_2$]Br. Upper panel: "plate-like", lower panel: "rod-like" morphology.

A cross-plane pressure coefficient of (0 ± 0.2) K/kbar for κ-(ET)$_2$Cu[N(CN)$_2$]Br has been claimed by Kund et al. based on their thermal-expansion measurements [6]. As shown in Fig. 1 our measurement clearly reveal a negative jump of $\alpha_\perp(T)$ at T_c. In order to rule out sample dependencies, we studied a second crystal from a different batch. While crystal # 1 is of the so-called "plate-like" morphology, crystal # 2 is of the "rod-like" variant. These are different habits of the same phase, whereas the "rod-like" character is more typical [7]. Fig. 2 shows almost identical behavior for both crystals, i.e., a negative discontinuity at T_c with a slightly higher T_c for the "rod-like" crystal (lower panel).

In summary, we determined $\partial T_c/\partial p_i$ for κ-(ET)$_2$X superconductors by thermal-expansion measurements. All systems studied here show pronounced negative effects for stress perpendicular to the planes. As discussed in [8,2] 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. As for the *intra*layer effects, there is no simple systematics: for κ-(ET)$_2$Cu(NCS)$_2$, for example, the in-plane pressure effect is either positive or zero [2]. This is in contradiction to the predictions of recent calculations based on the 2D-Hubbard model [1]. On the other hand, for the compounds with X=I$_3$ and X=Cu[N(CN)$_2$]Br negative pressure coefficients are found for both in-plane axes [5,6]. Owing to the lack of a simple correlation of in-plane geometrical parameters with T_c, a 2D-Hubbard model appears insufficient to explain the $T_c(p)$ dependence in these systems. Rather our results demonstrate the crucial importance of *inter*layer effects as the common feature of the materials studied. Thus, further theoretical investigations that incorporate also the 3D couplings and lattice degrees of freedom are highly desirable.

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