The dependence of the superconducting transition temperature T_c on the quasi-two-dimensional carrier concentration in the organic superconductor κ-$(BEDT\text{-}TTF)_2Cu(SCN)_2$ (BEDT-TTF ≱ bis(ethylene-dithio)tetrathiafulvalene)

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The dependence of the superconducting transition temperature T_c on the quasi-two-dimensional carrier concentration in the organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ (BEDT-TTF $\equiv$ bis (ethylene-dithio)tetrathiafulvalene)

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Abstract
In this paper we discuss the effect of the quasi-two-dimensional carrier concentration, n_{Q2D} on the superconducting transition temperature, T_c, of the organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. Recent ac susceptibility as well as magnetotransport measurements on the organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ under pressure with different pressure media are compared. The exact results of the individual pressure experiments are pressure media dependent, thus making the experimentally determined pressure an unsuitable parameter for describing the physical properties of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. The pressure media dependence is thought to originate from the difference in thermal contraction between the isotropic pressure medium and the highly anisotropic and very soft sample. However, comparison of pressure measurements with different media reveals a pressure medium independent correlation between the superconducting transition temperature, T_c, and the size of the quasi-two-dimensional Fermi surface pocket and thus the quasi-two-dimensional carrier density in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. The observed pressure-induced increase in the quasi-two-dimensional carrier density can be interpreted as a transfer of carriers from quasi-one-dimensional Fermi surface sections, reminiscent of a mechanism in cuprate superconductors, where pressure is known to transfer carriers from the insulating charge reservoir layers into the conducting cuprate sheets. In further analogy with the cuprate superconductors, it is seen that the highest T_c is achieved at carrier concentrations of $\sim$0.15 holes/dimer, which is very similar to the value found consistently for optimal doping in cuprate superconductors.

1. Introduction

κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ is the archetypical quasi-two-dimensional organic superconductor. Its ambient pressure properties are very well characterized [3–5] and the resemblance of its pressure–temperature phase diagram [6] to that of the carrier density–temperature phase diagram in cuprate superconductors [7] has frequently been taken as evidence for similar interaction mechanisms governing superconductivity [8, 9]. In cuprate superconductors, magnetic ordering, metallic behaviour and superconductivity are determined by the carrier concentration in the conducting cuprate layers [7]. The carrier concentration in cuprates can be regulated through chemical doping [7] and/or pressure [10, 11]. In most organic superconductors, however, the overall carrier concentration per unit cell is kept at a constant value of 2 holes/(unit cell) by the chemically determined charge transfer between the organic, conducting and the mainly insulating and inorganic layer [3]. Thus, in organic superconductors evidence for a correlation between carrier concentration and the superconducting transition temperature, T_c, has been lacking.

κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ is a strongly anisotropic material in which conducting layers of (BEDT-TTF)$_2^{+1}$ in the crystallographic *bc*-plane are separated by insulating layers of polymorphic Cu(SCN)$_2^{-1}$ [3–5] (see figure 1). The resulting strong anisotropy is reflected in all physical properties of the material, including its electrical conductivity [3–5], its quasi-two-dimensional band structure [4, 5], its compressibility [12] and its uniaxial pressure dependence of T_c [13].

The conduction bands in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ are formed due to the molecular π-overlap of the organic BEDT-TTF molecules [3–5]. Thus, the Fermi surface of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ reflects the structural anisotropy: it consists of a quasi-two-dimensional Fermi surface pocket and two quasi-one-dimensional Fermi surface sections. The quasi-two-dimensional Fermi surface pocket, also known as the α-pocket, gives rise to Shubnikov–de Haas oscillations of ~600 T at ambient pressure. At high magnetic fields and low temperatures, magnetic breakdown between the α-pocket and the quasi-one-dimensional Fermi surface sections can give rise to a semiclassical orbit, the β-orbit, which has the same cross sectional area as the Brillouin zone. Thus, the knowledge of this orbital size is a measure of the low temperature in-plane compressibility of the material. In conjunction with the size of the α-orbit, it also allows one to calculate the exact shape of the quasi-two-dimensional Fermi surface according to the effective dimer model [14]. The inter-layer transfer integral, $t_\perp \approx 0.04$ meV, was found to be a factor $\leqslant 10^3$ smaller than that observed for the intra-layer components, $t_b \approx 16$ meV and $t_c \approx 22$ meV [14], indicating that κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ is predominantly quasi-two-dimensional in its electronic properties, even though there is a small degree of coherent inter-layer transport [14]. Considering this huge difference between the inter-layer and intra-layer transfer integrals, κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ can, to a first approximation, be treated as an electronically two-dimensional (2D) system. For a 2D material, simple Fermi statistics dictates that the area of the 2D Fermi surface, A_{FS}, is directly proportional to the 2D carrier density, n_{2D}, according to

$$n_{2D}\ (\mathrm{m}^{-2}) = \frac{A_{FS}}{2\pi^2} \qquad (1)$$

with

$$A_{FS} = \frac{2\pi e}{\hbar} F_\alpha,$$

where A_{FS} is the area of the 2D Fermi surface section and F_α is the frequency of the quantum oscillations due to A_{FS}. Recent studies [14, 15] have discussed and investigated the importance

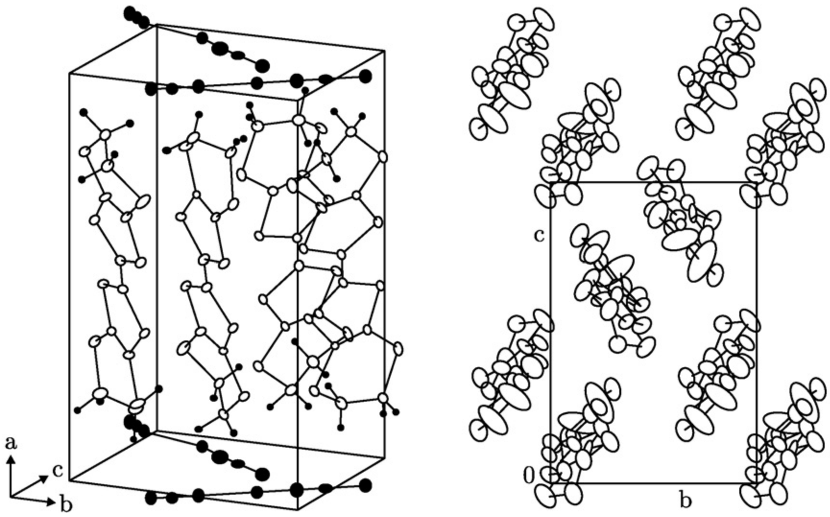

Figure 1. The structure of the organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$, after [1, 2], with $a = 16.37$ Å, $b = 8.38$ Å, $c = 12.78$ Å and $\beta = 111.5°$ at 15 K. (a) Side view: the organic molecules of BEDT-TTF form conducting layers that are separated by insulating layers of Cu(SCN)$_2$. (b) Top view onto the organic layer: the BEDT-TTF molecules are arranged in pairs (*dimers*). Each dimer transfers on average one electron to the Cu(SCN)$_2$ layer, thus leaving it with an average charge of one hole per dimer.

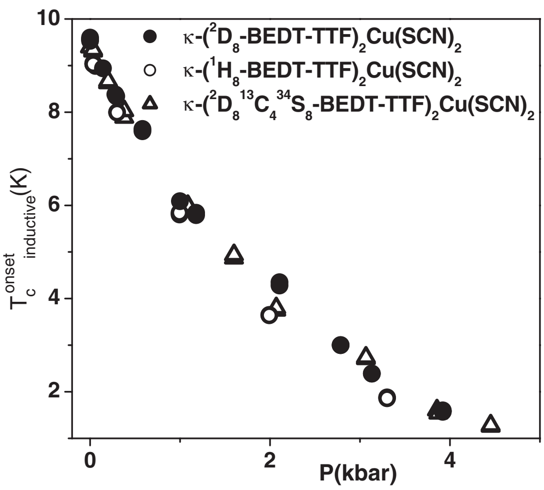

Figure 2. The pressure dependence of T_c for single crystals of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ with different isotope compositions using helium as a pressure medium. The pressure dependence of T_c is independent of the isotope composition [19].

of the out-of-plane direction, the crystallographic a'-direction perpendicular to the bc-plane, for a more general understanding of the general physical properties of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$.

Superconductivity in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ is thought to be determined by the detailed warping of the Fermi surface [8, 16], with the pairing of the electrons in the quasi-two-dimensional band being mediated by the exchange of spin fluctuations within the quasi-one-dimensional band [16]. In κ-(BEDT-TTF)$_2$Cu(SCN)$_2$, the relevant intra-layer parameters for describing the shape of the Fermi surface can be easily calculated, if the size of the quasi-two-dimensional Fermi surface pocket and the size of the Brillouin zone are known [14]. The ratio of the inter-dimer transfer integrals, t_b/t_c, is thought to be the critical parameter determining the ground state of the material [8, 16].

2. Experimental details

Single crystals of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ were grown by standard electrocrystallization techniques [17]. The measurements compared in this paper have been published previously [15, 18–20] and details about the measurement techniques can be found in those publications; details of the measurements on κ-(h$_8$-BEDT-TTF)$_2$Cu(SCN)$_2$ with petroleum spirit as a pressure medium can be found in [18]. The corresponding measurements on κ-(d$_8$-BEDT-TTF)$_2$Cu(SCN)$_2$ with helium and Fluorinert are described in detail in [20] and [15], respectively. The ac susceptibility measurements are published in [19]. The sample of κ-(d$_8$-BEDT-TTF)$_2$Cu(SCN)$_2$ investigated in the magnetotransport measurements in [20] is from the same batch as that investigated in [19].

3. The ac susceptibility measurements under pressure

The ac susceptibility measurements were performed on single crystals with different isotope compositions. The oscillating magnetic field $H_{ac}^{(rms)} = 1$ Oe was oriented parallel to the crystallographic bc-plane, the quasi-two-dimensional conducting plane of the crystal in all measurements, thus inducing shielding currents along the inter-plane and one in-plane direction. Further details of these ac susceptibility measurements can be found in [19].

Isotopic substitution in the organic molecule BEDT-TTF has the effect of changing the ambient pressure value of T_c [17]. Those ambient pressure values of T_c agreed well with the ones quoted in the literature [17]. These ac susceptibility measurements under pressure [19] demonstrated that the pressure dependence of T_c of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ is independent of its isotope composition (see figure 2). $T_c(P)$ can be described using a common pressure dependence:

$$T_c\ (\mathrm{K}) = T_c(0) - (3.93 \pm 0.26) \cdot P\ (\mathrm{kbar}) + (0.76 \pm 0.11) \cdot P\ (\mathrm{kbar})^2 - (0.06 \pm 0.03) \cdot P\ (\mathrm{kbar})^3. \quad (2)$$

This pressure dependence of T_c agrees well with literature values where helium was used as a pressure medium [21, 22].

Figure 3 shows a selection of ac susceptibility signals for the deuterated, protonated and 'heavy' single crystal of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ as a function of pressure. In all three samples the size of the superconducting transition, $\Delta\chi'$, is increasing with increasing pressure. This increase of the ac signal with increasing pressure is opposite to what one would expect due to the compression of the crystal under pressure. This enlargement of the signal is thought to be a direct result of a pressure-induced reduction in the large inter-plane London penetration length ($\lambda_a(0)_{P=0\ \mathrm{kbar}} = 40\ \mu$m [23]), which is a significant fraction ($\geqslant$10%) of the inter-plane sample dimension ($\approx$0.3–0.7 mm); in contrast, the in-plane London penetration length ($\lambda_\parallel(0)_{P=0\ \mathrm{kbar}} = 1.4\ \mu$m [23]) is very small compared to the smallest in-plane dimension of our crystals ($\geqslant$1 mm).

The London penetration length, λ_i, is a measure of the distance over which an external magnetic field is expelled from the interior of a superconductor. The sample is thus not exhibiting perfect diamagnetism over a circumference of the order of λ_i and thus in those parts not contributing fully to the diamagnetic signal measured by $\Delta\chi'$. With λ_a being a significant

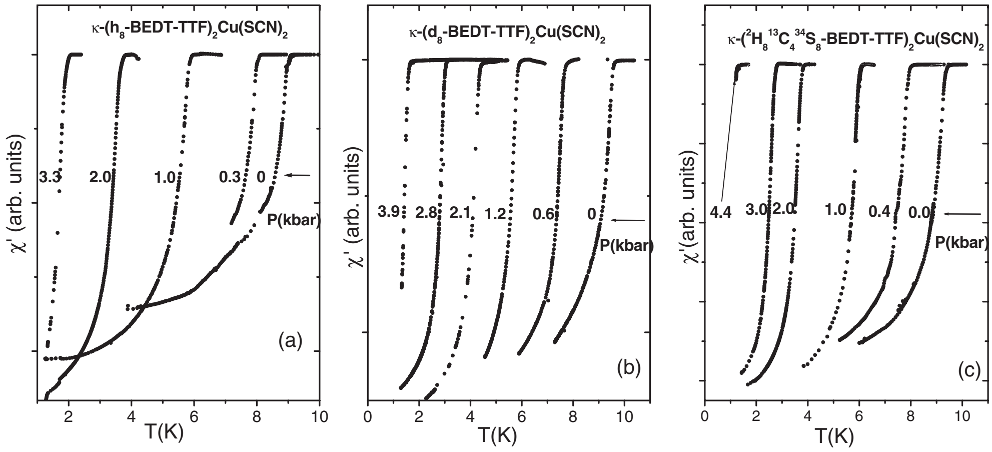

Figure 3. The temperature dependence of the real part, χ', of the ac susceptibility for the protonated (a), deuterated (b) and 'heavy' (c) crystals of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ for a selection of pressures with $H_{ac}^{(rms)} = 1$ Oe and $\nu = 1.023$ kHz, $H_{ac} \parallel bc$-plane. $\Delta\chi'$, which is proportional to the volume fraction of the sample exhibiting perfect diamagnetism, is seen to increase with increasing pressure and decreasing T_c [19].

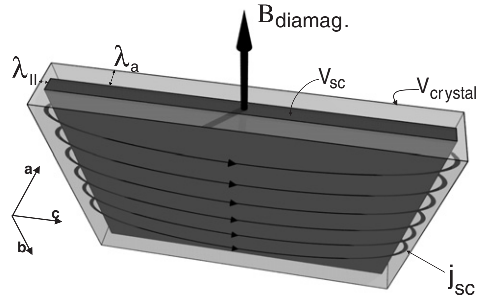

Figure 4. A sketch of the penetration of the magnetic field in the crystal. The crystal is oriented with the magnetic field oriented perpendicular to the inter-plane direction. $B_{diamagn}$ is the magnetic field created by the superconducting currents, j_{SC}, that are flowing in an outer layer of the sample, of thickness $\lambda_\parallel$ and λ_a. λ_a is a significant fraction of the inter-plane dimension of the crystal, whereas $\lambda_\parallel$ is very small compared to the crystal dimension in that direction.

fraction of the inter-plane sample dimension, the volume fraction of the sample not exhibiting perfect diamagnetism is significant and the signal size is visibly reduced. $\Delta\chi'$ is proportional to the part of the sample exhibiting perfect diamagnetism, V_{SC}. Given our samples' geometry and their alignment in the magnetic field, the latter can be estimated as (see figure 4)

$$V_{SC} = V_{crystal} - 2\lambda_a \times (bc)$$

with bc = in-plane sample dimension. Thus,

$$\frac{d\ln(V_{SC})}{dT_c} = -2\frac{d\ln(\lambda_a)}{dT_c}.$$

Given the data in figure 3, $\frac{d\ln(\lambda_a)}{dT_c}$ can be estimated to be $\approx -(1\text{–}3)\%\ K^{-1}$, i.e. a change of T_c by 5 K is accompanied by a change in the inter-plane London penetration length of (5–15)%.

On the basis of these ac susceptibility measurements, no information is available on the pressure or T_c dependence on the in-plane London penetration length. The London penetration

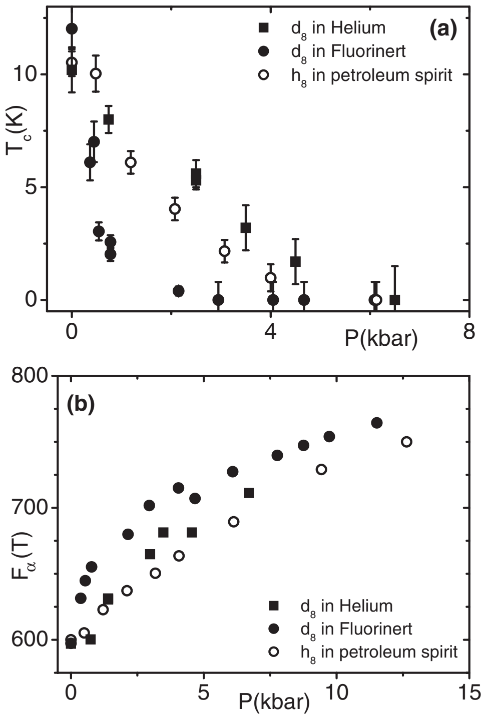

Figure 5. (a) T_c and (b) α-frequency, $F_\alpha(T)$, as a function of pressure for κ-(d_8-BEDT-TTF)$_2$Cu(SCN)$_2$ using helium (■) [20], using Fluorinert (●) [15] and for κ-(h_8-BEDT-TTF)$_2$Cu(SCN)$_2$ using petroleum spirit (○) [18] as a pressure medium.

length is related to the mass of the superconducting carriers, m_s, and the superconducting carrier density, n_S, via $\lambda_i \sim (m_s/n_S)^{1/2}$. Thus, given that m_s^{bc} is known to decrease strongly under pressure [18, 15], one might expect also an associated decrease of λ_{bc}.

4. The pressure medium dependence of T_c and F_α in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$

Several magnetotransport measurements under pressure using different pressure media [18, 15, 20] were performed on single crystals of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ with different isotope compositions [20] and from different growers [15]. It is known, that neither the crystal grower [15] nor the isotope composition [19] has an effect on the pressure dependence of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. Figures 5 (a) and (b) [20] compare measurements with three different pressure media: helium, Fluorinert and petroleum spirit.

There are three trends evident:

(1) T_c decreases as a function of pressure.
(2) $F_\alpha(T)$ increases as a function of pressure.
(3) The exact pressure dependence measured depends on the pressure medium used.

There was no evidence for shear stresses on the sample in any of those measurements, i.e. the superconducting transitions did not broaden under pressure nor could a reduction of the amplitude of quantum oscillations as a function of pressure history be observed. There was also no evidence in any of those measurements of any sample deterioration after the pressure measurements, which could have indicated a chemical reaction between the sample

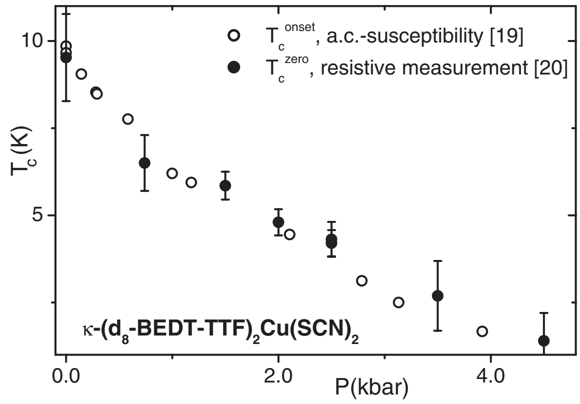

Figure 6. T_c as a function of pressure using helium as a pressure medium. Compared are T_c^{onset} from an ac susceptibility measurement [19] and T_c^{zero}, the temperature below which the resistance the sample has dropped to zero within the accuracy of the measurement [20].

and pressure medium. One thus has to conclude that the difference between the different measurements originates in the choice of pressure medium.

All the pressure media were selected due to their hydrostatic or quasi-hydrostatic properties, but all these pressure media will have solidified at the low temperatures of the magnetoresistance and T_c measurements. The soft and highly anisotropic sample of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ [12] is thus submerged in a solid medium. Both sample and medium will experience thermal contraction during cool-down, and the resulting pressure on the sample will depend on the difference in thermal contraction between the sample and the medium [24]. The difference of the anisotropic thermal contraction of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ from that of the uniformly contracting pressure medium results in non-hydrostatic stresses on the sample upon cooling. Evidence for this effect of non-hydrostatic, pressure medium-induced stresses on a soft sample with an anisotropic compressibility [25] are well documented for zinc [24, 26]. Thus, similar effects of a frozen pressure medium on the soft and highly anisotropic [12] κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ are not surprising.

However, independent measurements by different groups using the same pressure medium, i.e. Fluorinert [15, 27] or helium [19, 20], demonstrate that the non-hydrostatic pressure conditions caused by the difference in thermal contraction between a very soft, anisotropic sample and the pressure medium can be reproducible. Figure 6 shows measurements of $\mathrm{d}T_c/\mathrm{d}P$ for κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ using helium as a pressure medium [19, 20]: within the error bars, identical results are obtained, but they are different from those obtained with the other pressure media.

In summary, it is evident that the experimentally determined pressure is not a suitable parameter for describing the physical properties of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ reliably. The experimentally determined pressure alone is not sufficient for parametrizing the sample's behaviour, as it is impossible to distinguish between intrinsic and pressure medium-induced effects.

5. The pressure medium independent correlation between T_c and the quasi-two-dimensional carrier density, n_{Q2D}

In the measurements above, however, each measurement of T_c has been accompanied by magnetoresistive measurements, determining F_α. The inset of figure 7 shows the correlation

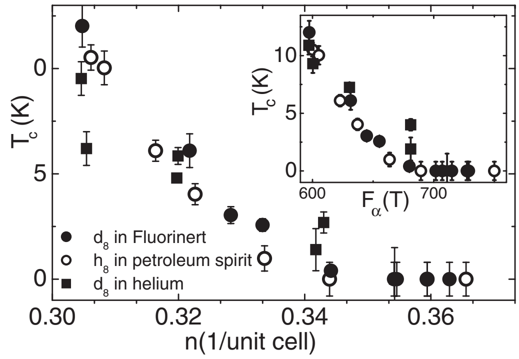

Figure 7. The correlation between T_c and the Q2D carrier density, n_{Q2D}. The inset shows T_c and F_α from figure 5, indicating their correlation. The correlation is independent of the individual pressure dependence observed, and thus of the individual pressure scale.

between these two parameters. Even though each of the measurements in figure 5 exhibits its own, individual pressure dependence of T_c and F_α, these parameters demonstrate a strong correlation with each other, seemingly independent of the pressure medium used and thus independent of the possible degree of shear on the sample. Thus, the strong correlation between the bulk property of superconductivity, as indicated by T_c, and the two-dimensional Fermi surface parameter, F_α, suggests that superconductivity in this organic superconductor is fully determined by processes in the quasi-two-dimensional conducting planes. Hence, warping effects of the Fermi surface in the inter-plane direction [15, 28] cannot be of major significance for the superconducting properties of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$.

According to the inset in figure 7, a smaller F_α leads to a higher T_c. This is observed upon deuteration of the organic BEDT-TTF molecule in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$: T_c increases by $\approx$0.5 K upon deuteration, while F_α decreases from 600 ± 1 T for h$_8$ to 597 ± 1 T for d$_8$ [15, 29][1]. In addition, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl with $T_c \approx 12.7$ K has a Q2D Fermi surface pocket with $F_\alpha \approx 577$ T [30]. This is again in agreement with the tendency that smaller quasi-two-dimensional Fermi surface areas result in higher T_c.

According to equation (1) the observed correlation between T_c and F_α is synonymous with a correlation between T_c and the Q2D carrier density, n_{Q2D}: the effect of pressure is to increase the number of carriers in the Q2D hole pockets in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. The in-plane compression of the unit cell at low temperatures has been determined from the pressure dependence of the β-frequency to be $\sim$4% GPa^{-1} [15, 18]. This compares to an overall increase in F_α or n_{Q2D} (m^{-2}) of $\sim$30% in the same pressure region, indicating that n_{Q2D} (m^{-2}) increases beyond what would be expected from the compression of the Brillouin zone alone. n_{Q2D} (m^{-2}) is converted to the carrier density per unit cell, n_{Q2D} (1/unit cell), using this in-plane compressibility for all measurements. It appears from the inset of figure 7 that n_{Q2D} (1/unit cell) increases from $\sim$0.30 (holes/unit cell) to $\sim$0.34 (holes/unit cell) when T_c is suppressed. κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ has two dimers per unit cell, and thus the suppression of T_c is accompanied by an increase of the number of holes per dimer from $\sim$0.15 (holes/dimer) to $\sim$0.18 (holes/dimer). These values of carrier concentration against T_c are surprisingly close to those found for the cuprate superconductors, when T_c is changed through doping from its optimal value to zero.

κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ has two holes per unit cell [3] due to the transfer of two electrons from the four BEDT-TTF molecules per unit cell to the polymorphic Cu(SCN)$_2$ layer.

[1] The origin of the decrease in F_α upon deuteration, however, is unknown.

At the small pressures used in our experiments, this overall carrier density per unit cell has to be considered independent of pressure. In the conducting organic layer in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$, these holes are distributed between the Q2D Fermi surface pockets and the Q1D Fermi surface sheets:

$$n_{\text{total}}\ (1/\text{unit cell}) \equiv 2\ \text{holes/unit cell} = n_{\text{Q2D}}\ (1/\text{unit cell}) + n_{Q1\text{D}}\ (1/\text{unit cell}). \quad (3)$$

According to equation (3), the observed increase in n_{Q2D} is equivalent to an identical decrease in n_{Q1D}. Thus, the increase in n_{Q2D} can be understood as a simple, pressure-induced charge transfer of holes from the quasi-one-dimensional Fermi surface planes to the quasi-two-dimensional Fermi surface pockets in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$.

Again, this mechanism bears a resemblance to the mechanism observed in cuprate superconductors where the effect of pressure is to transfer holes from the insulating charge reservoir layers into the Q2D, conducting CuO_2 layers [10]. Thus, in organic superconductors, similar to the case for cuprate superconductors, pressure has the effect of increasing the Q2D carrier density by transferring holes from other parts of the Fermi surface to those bands that support superconductivity [16].

6. Conclusion

We discovered that the quasi-two-dimensional carrier concentration, n_{Q2D} (holes/unit cell), in the organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ seems to be a determining parameter for its superconducting transition temperature, T_c, by comparing pressure measurements with different pressure media. Pressure can be understood to increase n_{Q2D} by transferring carriers from the Q1D sections of the Fermi surface to the Q2D sections. The correlation between T_c and the hole concentration is reminiscent of that in cuprate superconductors: in both materials pressure causes the transfer of holes from other sections of the band structure to the superconducting sections of the Fermi surface; in both materials the maximum T_c is achieved at hole concentrations of $\sim$0.15 (holes/unit) and T_c is suppressed if the hole concentration exceeds $\sim$0.3 (holes/unit), hinting that the resemblance between the superconductivity in organics and cuprates is based an intrinsic similarities.

Experimentally determined pressure in general is not a reliable parameter for describing κ-(BEDT-TTF)$_2$Cu(SCN)$_2$. This is thought to be due to the strong anisotropy of all physical properties in κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ and the possible departure from fully hydrostatic conditions when the sample is cooled in the frozen pressure medium.

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