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LETTER TO THE EDITOR

A statistical model for the intrinsically broad superconducting-to-normal transition in quasi-two-dimensional crystalline organic metals

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Abstract

Although quasi-two-dimensional organic superconductors such as κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF $\equiv$ bis(ethylene-dithio)tetrathiafulvalene) seem to be very clean systems, with apparent quasiparticle mean free paths of several thousand ångströms, the superconducting transition is intrinsically broad (e.g. $\sim$1 K wide for $T_c \approx 10$ K). We propose that this is due to the extreme anisotropy of these materials, which greatly exacerbates the statistical effects of spatial variations in the potential experienced by the quasiparticles. Using a statistical model, we are able to account for the experimental observations. A parameter $\bar{x}$, which characterizes the spatial potential variations, may be derived from Shubnikov–de Haas oscillation experiments. Using this value, we are able to predict a transition width which is in good agreement with that observed in megahertz penetration-depth measurements on the same sample.

The large number of Shubnikov–de Haas and de Haas–van Alphen oscillation experiments which have been carried out on crystalline organic superconductors demonstrate the high quality of these materials [1]; oscillations are resolved down to $\sim$2 T [2], and apparent scattering times extracted by Dingle analysis [1, 3] are well in excess of a picosecond, suggesting intralayer mean free paths $\gtrsim$1000 Å [4]. Support for the cleanliness of the organics also comes from magneto-optical measurements of cyclotron and Fermi-surface-traversal resonances, which again yield apparent scattering times $\gtrsim$1 ps [4, 5].

In spite of this, the superconducting transition at the critical temperature T_c seems to be rather broad, whatever the measurement method used. Resistivity measurements are the most prone to complications [6, 7], especially in an applied magnetic field. However, even

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when reliable perturbative techniques such as thermal conductivity [6] or GHz and MHz penetration-depth experiments [6, 8, 9] are employed in zero field, the transition has a significant width ΔT_c. Figure 1 shows a typical example; a κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ sample was placed in a coil forming part of a tank circuit oscillating at around 38 MHz (see reference [9]). The superconducting-to-normal transition is observed because the change from skin depth to penetration depth limited coupling of the sample to the MHz fields [8, 9], which results in a shift in the resonant frequency f of the tank circuit. For the purpose of making quantitative comparisons below, we choose two methods for defining the temperature (T) width of the transition. Firstly, by fitting the differential $\mathrm{d}f/\mathrm{d}T$ of the data to a Gaussian centred on $T_c^{\mathrm{Gauss}} = 9.38$ K (figure 1, inset), a full width of $\Delta T_c^{\mathrm{Gauss}} \approx 0.7$ K is obtained. Alternatively, ΔT_c may be defined using straight-line extrapolations (see figure 1), to give $\Delta T_c^{\mathrm{linear}} \approx 0.9$ K. Note that both methods yield $\Delta T_c/T_c \sim 0.1$; it is likely that this significant intrinsic broadening of the transition region is responsible for the wide range of T_c-values quoted for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [1, 7].

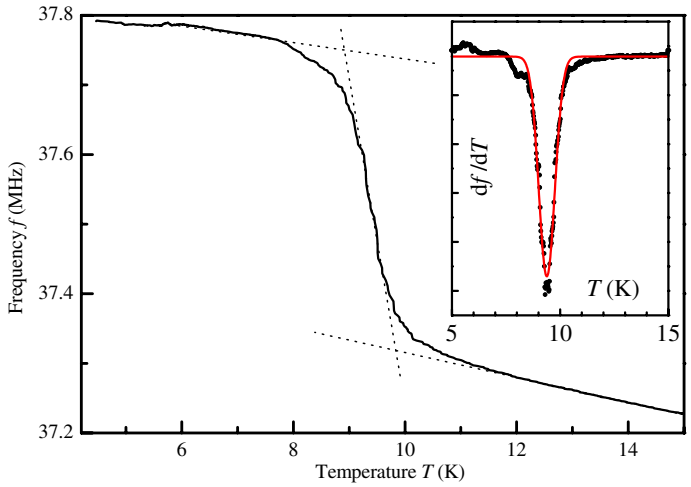

Figure 1. MHz penetration data for a single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, shown as resonant frequency f versus temperature T. The superconducting transition is the steeply sloping region between the more gentle variations characteristic of superconductivity (low T) and the normal state (high T); note that the complete transition region occupies a temperature range from around 8 K to 11 K. The dotted lines are extrapolations of the normal-state, transition-region and superconducting-state behaviours. The intersections of the extrapolations occur at 8.9 T and 9.8 T, giving $T_c^{\mathrm{linear}} \approx 9.35$ K (mid-point) and $\Delta T_c^{\mathrm{linear}} \approx 0.9$ K. The inset shows the differential $\mathrm{d}f/\mathrm{d}T$ of the data (points) fitted to a Gaussian (curve) centred on $T_c^{\mathrm{Gauss}} = 9.38$ K, with a full width of $\Delta T_c^{\mathrm{Gauss}} \approx 0.7$ K.

In this letter, we show how a superconducting transition can be broadened due to charged impurities (or vacancies) randomly dispersed throughout a crystal, even when the potential associated with the impurity (or vacancies) is of extremely short range. When averaged over the coherence volume $\Lambda_v = \pi\xi_{0x}\xi_{0y}\xi_{0z}/6$, where the ξ are Pippard coherence lengths[5], statistical variations in the density of impurities (or vacancies) lead to a spatially varying order parameter Δ_0 and consequently a Gaussian-broadened transition. The effects of these statistical variations are shown to become more pronounced when the dimensionality of the superconductor is

[5] As the following paragraph will show, we are dealing with a situation in which mean-field theory breaks down because of spatial variations of the order parameter. It is therefore inappropriate to use the Ginzburg–Landau temperature-dependent coherence lengths to parametrize the coherence volume, as these diverge at T_c.

reduced, as is the case in quasi-two-dimensional crystalline organic superconductors such as κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

Our treatment is closely related to the Ginzburg criterion [10, 11], a quantitative guide to the circumstances under which mean-field theory can be expected to break down due to fluctuations[6]. The Ginzburg criterion has in the past been invoked to explain the broad superconducting transitions in the 'high-T_c' cuprates [12]. However, in contrast to the situation in the cuprates, details of the band-structures of the organic superconductors are often known to great precision [1], whereas the interpretation of heat capacity data (necessary to derive the Ginzburg criterion) in the latter systems is still somewhat contentious [7]. We have therefore used an alternative statistical method to treat the spatial variations of the potential, based on a good quantitative knowledge of $g(E_F)$, the density of quasiparticle states close to the Fermi energy E_F.

The introduction of impurities in an ideal metal leads to potential variations (of typical length scale R) and a finite scattering rate τ^{-1} for *normal* quasiparticles [1, 13]. By contrast, the spatial extent ξ_0 of the *superconducting* wavefunction often greatly exceeds R, with the result that theoretical studies fail to yield a direct correlation between τ^{-1} and the order parameter Δ_0 [15][7]. Nevertheless, nonmagnetic impurities can have an effect because the superconducting state is sensitive to changes in $g(E_F)$. As an example of this, let us consider the weak-coupling BCS formula

$$\Delta_0 \approx \hbar\omega_0 \exp\left[-\frac{1}{g(E_F)V}\right] \tag{1}$$

where V is an interaction strength [15]. If a small (local) fraction x of the host atoms or molecules are replaced by impurities, then the variation of $g(E_F, x)$ can be written as [13]

$$g(E_F, x) = g(E_F) + g'(E_F)x. \tag{2}$$

If we assume that each impurity introduces one extra charge $(-e)$, the derivative $g'(E_F) = \mathrm{d}g(E_F, x)/\mathrm{d}x$ can be obtained from band-structure calculations in the limit $x \to 0$.

The number of sites available for impurity substitution within Λ_v is $n = \Lambda_v/u_v$, where u_v is the formula-unit volume. However, the *local* number of impurities within such a volume, $m = xn$, will be subject to statistical variations via the binomial distribution (BD) [13]:

$$p(m, n) = \frac{\bar{x}[1-\bar{x}]^{n-m}n!}{m![n-m]!} \tag{3}$$

where $\bar{x}$ is the mean of x. Below we consider relatively large values of n ($43 \lesssim n \lesssim 10^{10}$); the skewness factor

$$\eta = 1/\sqrt{6\bar{x}[1-\bar{x}]n}$$

vanishes for large n, and the BD is well approximated by the normal distribution [13]. Hence, the mean value of m becomes $n\bar{x}$ while its standard deviation is

$$\sigma(m) = \sqrt{n\bar{x}[1-\bar{x}]}.$$

For a 'clean' metal, $\bar{x} \ll 1$, leading to a standard deviation in x of

$$\sigma(x) \approx \sqrt{\bar{x}/n}. \tag{4}$$

Using the fact that the standard deviation of a function of $\bar{x}$ is equal to the derivative of that function multiplied by the standard deviation of $\bar{x}$, we insert equations (2) and (4) into equation (1), yielding the standard deviation $\sigma(\Delta_0)$ of Δ_0:

$$\frac{\sigma(\Delta_0)}{\Delta_0} \approx \frac{g'(E_F)}{g(E_F)^2 V}\sqrt{\frac{\bar{x}u_v}{\Lambda_v}}. \tag{5}$$

[6] A useful introduction to the Ginzburg criterion is given in section 5.1 of reference [11].

[7] Except in the case of magnetic impurities [15].

Applying the relation $2\Delta = \alpha k_B T_c$, where $\alpha \approx 3.52$ in the weak-coupling BCS (Bardeen–Cooper–Schrieffer) limit [15], the broadening of the superconducting transition is

$$\frac{\Delta T_c}{T_c} \equiv 2\frac{\sigma(T_c)}{T_c} \approx 2\frac{\sigma(\Delta_0)}{\Delta_0}. \tag{6}$$

We now demonstrate the sensitivity of ΔT_c to the dimensionality of the superconductor.

Conventional three-dimensional (3D) superconductors have coherence lengths of approximately 10^2–10^4 Å and $u_v \sim 20$ Å^3 [14], yielding $10^4 \lesssim n \lesssim 10^{10}$. For reasonably pure metals, we expect $10^{-4} \lesssim \bar{x} \lesssim 10^{-2}$, while $g(E_F)V \sim 0.3$; finally we use the fact that $g'(E_F)/g(E_F) = \frac{1}{3}$ for a free-electron model [14]. These figures yield transition widths $10^{-3} \lesssim \Delta T_c/T_c \lesssim 10^{-7}$, in reasonable agreement with observations [15]. These sharp transitions are a consequence of the large size of the superconducting wavefunction, allowing inhomogeneities to be averaged out.

In *quasi-two-dimensional (Q2D) organic superconductors*, the intralayer coherence lengths are $\sim 10^2$ Å. However, the *interlayer* coherence length ξ_{0z} can be much less than the layer spacing a [7]; in κ-(BEDT-TTF)$_2$Cu(NCS)$_4$, ξ_{0z} can be estimated[8] to be $\sim$0.3 Å, whereas $a \approx 16$ Å [18]. The consequence of this extreme anisotropy is that Λ_v is replaced by a 'coherence area' $\Lambda_a = \pi\xi_{0x}\xi_{0y}/4$, because superconducting wavefunctions do not extend out of the layers. In enumerating n, the unit cell must also be represented by an area u_a ($\approx$106 Å^2 in κ-(BEDT-TTF)$_2$Cu(NCS)$_4$ [18]). Assuming BCS values for the intralayer coherence lengths ($\xi_{0x} \approx \xi_{0y} \approx 76$ Å) [18], we obtain $n \approx 43$, much less than typical values of n in 3D systems.

In the current context, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has the considerable advantage that its intralayer band-structure may be represented to good accuracy by the *effective dimer model* [4, 19, 20]:

$$E(\boldsymbol{k}) = \pm 2\cos\left(\frac{k_b b}{2}\right)\sqrt{t_{c1}^2 + t_{c2}^2 + 2t_{c1}t_{c2}\cos(k_c c)} + 2t_b\cos(k_b b). \tag{7}$$

Here k_b and k_c are the intralayer components of $\boldsymbol{k}$ and t_b, t_{c1} and t_{c2} are interdimer transfer integrals [19, 20]; the + and − signs result in the quasi-one-dimensional (Q1D) sheets and Q2D pocket of the Fermi surface respectively [1]. Moreover, the Fermi-surface warping in the interlayer direction is rather small [4], so it may be ignored for the current purposes. Accurate de Haas–van Alphen and magnetic breakdown data constrain the parameters in equation (7) rather tightly, leading to the values $t_b = 15.6$ meV, $t_{c1} = 24.2$ meV and $t_{c2} = 20.3$ meV [4].

Figure 2 shows N_s, the areal quasiparticle density per layer, as a function of quasiparticle energy E for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$; the curve has been derived using the parameters listed in the previous paragraph and equation (7). The position of the Fermi energy and the value of N_s corresponding to the well-known magnetic breakdown β-frequency [1], which encompasses the entire Fermi surface, are indicated by dotted lines. Whereas for many purposes [4] the bands of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are rather parabolic close to E_F, some curvature of N_s versus E is visible in figure 2, resulting in a $g(E_F)$ which varies with energy (figure 2, inset). Using the results shown in figure 2, we obtain $g'(E_F)/g(E_F) \approx 1.45$.

Whilst it is unlikely that κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is a weak-coupling BCS superconductor [1, 8, 20–22], equation (1) is known to describe the *functional dependence* of T_c on $g(E_F)$ very well, as shown in the pressure-dependent experiments of Caulfield *et al* [19]. Using $g(E_F)V \approx 0.3$ [19] and $10^{-4} \lesssim \bar{x} \lesssim 10^{-2}$ we obtain $0.015 \lesssim \Delta T_c/T_c \lesssim 0.15$, encompassing all known experimental data.

In order to find a suitable value of $\bar{x}$ for the sample used in figure 1, we turn to reference [13], which shows that spatial variations in the potential experienced by the quasiparticles leads to

[8] The anisotropy is $\sim$100–350 [8, 16, 17], and the in-plane coherence lengths are estimated to be $\approx$76 Å [7, 18].

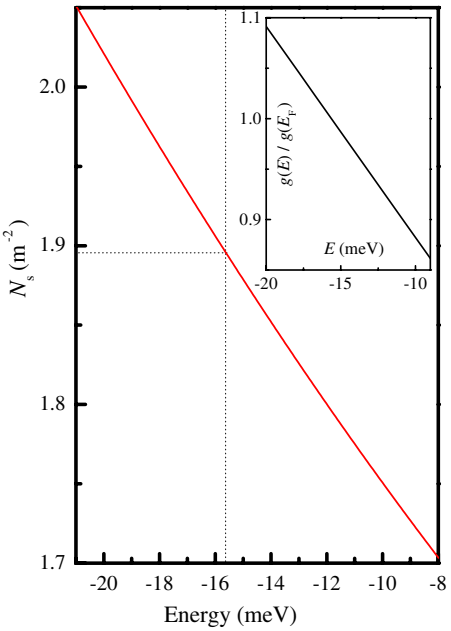

Figure 2. N_s, the areal quasiparticle density per layer, as a function of quasiparticle energy E for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$; the curve has been derived using the parameters listed in the text and equation (7). The position of the Fermi energy and the value of N_s corresponding to the well-known magnetic breakdown β-frequency [1] are indicated by dotted lines. The inset shows the variation of the quasiparticle density of states $g(E)$, normalized to its value at $E = E_F$, as a function of the quasiparticle energy.

broadening of Landau levels and hence damping of Shubnikov–de Haas and de Haas–van Alphen oscillations. This damping is parametrized by an effective Dingle temperature

$$T_D = \frac{\bar{x}[1-\bar{x}]F'(\bar{x})^2 a}{\pi k_B m^*}\sqrt{\frac{\hbar e^3}{2F}}. \tag{8}$$

In the current context, F is the quantum oscillation frequency of the breakdown β-orbit and $F' = dF/dx$; it is simple to show that $F' \equiv F \approx 3920$ T [1]. The sample used in figure 1 had $T_{D\alpha} \approx 0.42$ K [4] for the α-orbit Shubnikov–de Haas oscillations, which translates into a Dingle temperature of $T_D \approx 0.76$ K for the magnetic breakdown β-orbit [1]. Substituting this value of T_D into equation (8) yields $\bar{x} \approx 0.0017$, which can be used in equation (6) to give $\Delta T_c \approx 0.6$ K. This value is in good agreement with $\Delta T_c^{\text{Gauss}} \approx 0.7$ K extracted from the MHz experiments (see figure 1, inset) and close to the value $\Delta T_c^{\text{linear}} \approx 0.9$ K found using the alternative linear extrapolation method.

One possible interpretation of the value of $\bar{x} \approx 0.0017$ is that ∼0.1–0.2% of the molecular sites in our crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are in some way defective, functioning as 'impurities' or 'vacancies'; possible mechanisms might include neutral BEDT-TTF molecules, anions which are missing or in which the Cu ion possesses the wrong charge, or the incorporation of other molecular species from the growth process. The detection of such defects by other means is very difficult; all that can be noted at present is that such concentrations of defects are thought to be not unlikely [23].

In summary, using a statistical model, we are able to account for the broadened superconducting-to-normal transitions observed in organic superconductors. Our model consistently

explains the superconducting transition width and the Landau-level broadening in κ-(BEDT-TTF)$_2$Cu(NCS)$_4$ using one parameter, $\bar{x}$. Given the precise knowledge of the Fermi-surface topologies of many organic superconductors, and the availability of many samples of differing quality and effective dimensionality [9], our model may be useful in obtaining a more detailed understanding of the factors which influence the formation of the superconducting state.

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