The effect of irradiation-induced disorder on the conductivity and critical temperature of the organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$

James G. Analytis,1 Arzhang Ardavan,1 Stephen J. Blundell,1 Robin L. Owen2, Elspeth F. Garman,1,2 Chris Jeynes3 and Ben J. Powell1

1University of Oxford, Department of Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK
2University of Oxford, Department of Biochemistry, South Parks Road, Oxford OX1 3QU, UK
3University of Surrey Ion Beam Centre, Guildford GU2 7XH, UK and
4Department of Physics, University of Queensland, Brisbane, Queensland 4072, Australia

(Dated: September 9, 2018)

We have introduced defects into clean samples of the organic superconductor $\kappa$-(BEDT-TTF)$_2$-Cu(SCN)$_2$ in order to determine their effect on the temperature dependence of the conductivity and the critical temperature $T_c$. We find a violation of Matthiessen’s rule that can be explained by a model of the conductivity involving a defect-assisted interlayer channel which acts in parallel with the band-like conductivity. We observe an unusual dependence of $T_c$ on residual resistivity which is not consistent with the generalised Abrikosov-Gor'kov theory for an order parameter with a single component, providing an important constraint on models of the superconductivity in this material.

PACS numbers: 74.70.Kn, 74.62.Dh, 74.25.Fy

Quasi-two-dimensional organic conductors based on the donor molecule bisethylenedithiotetrathiafulvalene (BEDT-TTF or ET, see inset to Fig. 1) have attracted sustained interest [1]. These materials consist of layers of ET separated by inorganic anions and can be prepared with exceptional purity, so that magnetic oscillations in the resistivity can be observed at relatively low fields [2]. Many experiments have been conducted to elucidate the symmetry of the superconducting order parameter but despite growing evidence of unconventional superconductivity [3], the matter has remained unresolved [4].

The normal state of these materials is unusual with the temperature dependence of the electrical transport and the optical conductivity deviating significantly from what would be expected for a conventional metal [2, 6], showing a crossover from insulating-like conductivity at high temperature to metallic-like behaviour at lower temperature (see Fig. 1). This effect has been successfully described within the framework of dynamical mean-field theory (DMFT) as a crossover from an incoherent “bad-metal” state at high temperatures to a coherent Fermi liquid below $\sim$30 K [6, 7]. The usual effect of disorder is to change only the temperature independent component of the resistivity; this is known as Matthiessen’s rule. However, several strongly correlated materials violate Matthiessen’s rule including various cuprate [7] and organic [8] superconductors. Violations of Matthiessen’s rule have previously been taken as evidence for non-Fermi liquid behaviour. In particular, Strack et al. [8] have argued that the violations of Matthiessen’s rule in the salt $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br indicate that the description of the conductivity in terms of a crossover from an incoherent metal to a Fermi liquid is incorrect.

The behaviour of the superconducting transition temperature $T_c$ as a function of non-magnetic disorder [4] [9, 10] also provides a crucial test of the symmetry of the order parameter. Anderson’s theorem [11] states that for s-wave pairing non-magnetic impurities do not affect $T_c$. For magnetic impurities $T_c$ is strongly reduced for singlet states in a manner described by the Abrikosov-Gor’kov (AG) formula [12]. For non-s-wave (including extended-s) order parameters, scattering due to non-magnetic impurities reduces $T_c$ in a manner again described using the AG formula [4, 8, 10].

In order to investigate these effects experimentally for the ET superconductors, we have selected $\kappa$-(ET)$_2$Cu(SCN)$_2$, which has one of the highest transition temperatures ($T_c \approx 10$ K) in this family and whose electronic properties have been the subject of detailed study [2]. It is possible to introduce disorder into these samples by adjusting the cooling rate [13, 14], an effect which is probably due to the freezing of terminal ethylene group disorder which occurs at around 70–80 K [15, 16]. However, we find that we have more control in our experiment by introducing disorder via irradiation by either x-rays or protons. X-rays and protons give similar effects, but we have been able to perform more detailed experiments using the former and hence we concentrate mainly on the x-ray damaged samples in our discussion.

In this Letter we report the violation of Matthiessen’s rule in $\kappa$-(ET)$_2$Cu(SCN)$_2$. However, we find that a simple theory which includes the effect of interlayer scattering from impurities is able to explain this effect. Further we have confirmed quantitative predictions of this model relating the low temperature resistivity to the high temperature conductivity. Thus we find that the violation of Matthiessen’s rule is consistent with the DMFT description of the crossover in transport behaviour [6]. We also observe a disorder-induced suppression of $T_c$ which is consistent with a non-s-wave gap.

Our measurements have been performed on single crystals of $\kappa$-(ET)$_2$Cu(SCN)$_2$ grown electrochemically. Gold
wire of thickness 12.5 µm was attached to the samples (typical dimensions 0.3×0.3×0.1 mm³) with graphite paste in the four-probe configuration. Samples were cooled from 120 K to 10 K at a rate of 20 K/hr, below the slowest rate used in Ref. 14, in order to avoid introducing disorder from fast-cooling. Defects in our samples were created at room temperature by filtered Cu Kα radiation (E = 8 keV, λ = 1.54 Å) from a Cu x-ray rotating anode (typically 55 kV, 50 mA) at a flux of ≈ 2.5 × 10⁸ photons s⁻¹. The computer program RADDOSE [16] allowed this to be converted into a dose rate of ≈ 10⁵ Gy s⁻¹. Using tabulated absorption coefficients and assuming that the mass absorption coefficient of κ-(ET)₂Cu(SCN)₂ can be calculated as the sum of the mass absorption coefficients of the constituent atoms [17], we estimate the x-ray attenuation length to be 90 µm, approximately the thickness of the samples. In order to attain uniform damage we irradiated both sides of the sample. X-ray doses up to 630 MGy were used. Proton irradiation experiments took place at Surrey Ion Beam Centre. Protons were accelerated to 4 MeV and could be implanted to a mean depth of 150 µm, providing an approximately uniform damage profile for samples ≤100 µm. For each incremental radiation dose, we make a measurement of the transport properties; the contact configurations stay the same throughout the experiment. For each type of irradiation, the resistivity was found to be reproducible over multiple thermal cycles, so that we can be confident that the observed changes are due to irradiation and not to thermal cycling.

It is immediately apparent from Fig. 1 that the effect of increasing irradiation dose is to decrease the resistivity over most of the temperature range, and in particular to reduce the magnitude of the broad peak centred around T_p ∼ 90 K. Well into the Fermi-liquid regime however, the behaviour recovers a traditional metallic character; below ∼ 46 K, the resistivity increases with increasing irradiation dose (see inset to Fig. 1 and Fig. 2). This violation of Matthiessen’s rule is not predicted by DMFT alone for the low defect densities produced in our experiments and therefore appears at first sight to be at odds with the DMFT description of electronic transport in layered organic charge transfer salts.

The low-temperature region of Fig. 1 is presented in detail in Fig. 2, more clearly showing the superconducting transition for the same range of x-ray irradiation doses. For each trace, the resistivity follows a Fermi-liquid like T² dependence at temperatures above the superconducting transition and a sharp drop at the onset of superconductivity. The residual resistivity ρ₀ is extracted by fitting data to ρ = ρ₀ + AT² in the temperature range from just above T_c to 20 K. The upper inset to Fig. 2 presents the change in residual resistivity Δρ₀ with respect to an undamaged sample as a function of dosage, showing an approximately linear dependence.

The observation that increasing defect density in-
creases the interlayer conductivity over a wide temperature range leads us to hypothesize that defects affect the conductivity in two ways: (i) the resistivity associated with band-like transport due to the overlap of the molecular orbitals increases linearly with defect density as prescribed by Matthiessen’s rule; (ii) there is a parallel defect-assisted interlayer channel, whose conductivity is proportional to the defect density [18]. This model suggests that the interlayer conductivity $\sigma(x,T)$ depends on a dimensionless quantity $x$, which is proportional to the defect density, and temperature $T$ as

$$\sigma(x,T) = \frac{1}{\rho(0) + x\rho_{\text{imp}} + \rho_{\text{intrinsic}}(T)} + x\sigma_{\perp},$$

where $\rho(0)$ is the residual resistivity of the undamaged sample, $x\rho_{\text{imp}}$ is the contribution to the resistivity from defect scattering in the transport due to molecular orbital overlap, $\rho_{\text{intrinsic}}(T)$ is the intrinsic temperature-dependent scattering contribution (due to electron-electron interactions, phonon scattering, etc.) and $x\sigma_{\perp}$ is the defect-assisted interlayer conductivity.

The applicability of this model can be demonstrated by examining low and high temperature limits. At low temperature $\rho_{\text{intrinsic}}(T)$ is small so that

$$\rho(x,T) \approx \rho(0) + x\rho_{\text{imp}} + \rho_{\text{intrinsic}}(T),$$

and hence the resistivity increases linearly with defect density, $x$. At high temperature $\rho_{\text{intrinsic}}(T) \gg \rho(0) + x\rho_{\text{imp}}$ and Eqn (1) becomes

$$\rho(x,T) \approx (x\sigma_{\perp} + \rho_{\text{intrinsic}}^{-1}(T))^{-1}$$

hence the conductivity $\rho(x,T)^{-1}$ linearly increases with $x$, as observed. The inset to Fig. 1 shows that there is a temperature, $T_{\text{cross}}$, at which the resistivity is independent of defect density. In our model, this can be found by evaluating $d\sigma(x,T)/dx = 0$. We find that a $T$-independent crossing point occurs when the conditions (i) $x\rho_{\text{imp}} \ll \rho(0) + \rho_{\text{intrinsic}}$ and (ii) $\rho(0,T_{\text{cross}}) = (\rho_{\text{imp}}/\rho_{\text{intrinsic}})^{1/2}$ are satisfied. For our x-ray damaged samples, this yields an estimate of $\rho_{\text{imp}}/\rho_{\text{intrinsic}} = 3 \times 10^3 \Omega^2 \text{cm}^2$. We can obtain an independent estimate of this parameter by plotting $\Delta\sigma_p = \sigma(x,T_p) - \sigma(0,T_p)$ against $\Delta\rho_0 = \rho_0(x) - \rho_0(0)$, as shown in Fig. 3. The former quantity can be evaluated in the high temperature limit (Eqn. 2) to be $\Delta\sigma_p \approx x\sigma_{\perp}$, while the latter quantity can be evaluated in the low-temperature limit to be $\Delta\rho_0 \approx x\rho_{\text{imp}}$. The approximate straight-line dependence (which breaks down when $\Delta\rho_0$ and $\Delta\sigma_p$ are large) observed in Fig. 3 shows that both quantities are parameterised by $x$ in the same way, and the gradient of the line yields $\rho_{\text{imp}}/\sigma_{\perp} = 1.5 \times 10^3 \Omega^2 \text{cm}^2$, in order of magnitude agreement with our previous estimate [19]. We note that for proton irradiation, both the gradient of the line in Fig. 3 and the temperature $T_{\text{cross}}$ are increased, demonstrating that the nature of the irradiation affects the ratio $\rho_{\text{imp}}/\sigma_{\perp}$, suggesting that x-rays and protons produce different types of damage (protons producing a more effective interplane transport channel than x-rays).

The value of $T_c$, corresponding to the maximum of $d\rho/dT$ in Fig. 2, is plotted as a function of $\rho_0$ in Fig. 4. We find that $T_c$ falls with defect density (in agreement with measurements of defects induced by cooling-rate disorder [13]), but the dependence exhibits a sharp change in gradient when $\rho_0$ reaches a threshold value $\rho_0^{\ast} \approx 2 \Omega \text{cm}$. However, even at the highest defect densities studied, the samples exhibit a superconducting ground state. We also find that the width $\Delta T = T_{c2} - T_{c1}$ (see Fig. 2) of the superconducting transition decreases with increasing defect density, as shown in the inset to Fig. 4. This is consistent with $T_c$ exhibiting a change of gradient with damage; at high damage, local variations in damage have a smaller effect on the broadening of the transition because $dT_c/d\rho_0$ is lower.

The theory of AG [9, 12] for non-magnetic defects in a non-s-wave superconductor implies that the suppression of $T_c$ follows the AG formula given by

$$\ln \frac{T_c}{T_{c0}} = \psi \left( \frac{1}{2} \right) - \psi \left( \frac{1}{2} + \frac{h}{4\pi k_B T_c \tau} \right)$$

where $\psi$ is a digamma function and $\tau$ is the scattering time. In the low-defect density limit ($\rho_0 < \rho_0^{\ast}$), this
yields $T_{c0} - T_c \simeq \pi \hbar / 8 k_B \tau$. This linear sector should have a slope consistent with interlayer transport theory \([4]\), i.e. $dT_c/\rho_0 = -e^2 m^* d_\perp t_\perp^2 / (4k_B \hbar^3)$, where $m^*$ is the effective mass, $d_\perp$ is the interlayer spacing and $t_\perp$ is the interlayer transfer integral. Using the value of $m^*$ from transport measurements, our measured slope of the suppression of $T_c$ for $\rho_0 = 2 \Omega \mathrm{cm}$ yields $T_{c0} - T_c \approx 0.03 \pm 0.01 \text{meV}$, in good agreement with the value from angle-dependent magnetotransport \([20]\). Thus the suppression of $T_c$ for $\rho_0 < \rho^*_0$ is consistent with a non-s-wave gap. However, the departure from the AG formula for $\rho_0 > \rho^*_0$ casts doubt on this interpretation.

We note that our value of $\rho^*_0$ corresponds to a ratio of the in-plane coherence length to the mean free path $\xi/\ell \approx 0.2$. If all scattering events contributing to $\ell$ were pair-breaking, it would be expected that superconductivity should be suppressed by this degree of scattering. Crucially, the observed change of gradient is not expected for a model involving an order parameter with a single component within the AG theory. Even a generalised AG equation describing multicomponent order parameters \([21]\) does not quantitatively agree with our data, though this approach assumes that disorder does not affect the symmetry of the order parameter; it is probably necessary to examine specific candidate pairing interactions in detail. An explanation for this behaviour might involve a mixed order parameter with both s-wave and unconventional components or interband scattering.

In conclusion, we have investigated the effect of radiation-induced disorder in $\kappa-(ET)_2\text{Cu(SCN)}_2$. We find that a dramatic departure from Matthiessen’s rule can be straightforwardly explained in terms of defect-assisted interlayer tunnelling. Although $T_c$ initially follows a dependence on $\rho_0$ consistent with pair-breaking scattering, the superconducting state proves to be robust into the dirty limit. This unusual dependence of $T_c$ on $\rho_0$ is not consistent with an order parameter with a single component, providing an important constraint on models of the superconductivity in this material.

We acknowledge funding from EPSRC, the Royal Society (A.A.), BBSCR (R.L.O.) and the ARC (B.J.P.). We thank Ross McKenzie, Nigel Hussey and Paul Goddard for useful discussions and H. Mori for providing samples.

\[1\] For a recent review see T. Ishiguro et al., Organic Superconductors (Springer Verlag, Heidelberg, 1998).
\[2\] P.A. Goddard et al., Phys. Rev. B 69, 174509 (2004).
\[3\] A. Carrington et al., Phys. Rev. Lett. 83, 4172 (1999); K. Izawa et al., ibid. 88, 027002 (2002); H. Mayaffre et al., ibid. 75, 4122 (1995).
\[4\] B.J. Powell and R.H. McKenzie, Phys. Rev. B 69, 024519 (2004).
\[5\] R.H. McKenzie, Science 278, 820 (1997).
\[6\] J. Merino and R.H. McKenzie, Phys. Rev. B 62, 2416 (2000); P. Limelette et al., Phys. Rev. Lett. 91, 16401 (2003).
\[7\] D.J.C. Walker et al., Phys. Rev. B 51, 15653 (1995).
\[8\] Ch. Strack et al., Phys. Rev. B 72, 54511 (2005).
\[9\] R.J. Radtke et al., Phys. Rev. B 48, 653 (1993).
\[10\] A.P. Mackenzie et al., Phys. Rev. Lett. 80, 161 (1998); M.Y. Choi et al., Phys. Rev. B 25, 6208 (1982); N. Joo et al., Eur. Phys. J. B 40, 43 (2004).
\[11\] P.W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).
\[12\] A.A. Abrikosov and L.P. Gorkov, Sov. Phys. JETP 12, 1243 (1961); A.I. Larkin, JETP Lett. 2, 130 (1965).
\[13\] T.F. Stalcup et al., Phys. Rev. B 60, 9309 (1999).
\[14\] X. Su et al., Phys. Rev. B 57, 14056 (1998).
\[15\] M.A. Natanar et al., Phys. Rev. B 59, 3841 (1999).
\[16\] J. W. Murray et al. J. Appl. Cryst., 37, 513 (2004).
\[17\] G. Mihaly and L. Zuppiroli, Phil. Mag. A, 45, 549 (1982).
\[18\] A.G. Rojo et al., Phys. Rev. B 48, 1861 (1993); R. J. Radtke et al, Physica C 250, 282 (1995); M.J. Graf et al., Phys. Rev. B 47, 12096 (1993).
\[19\] Strack et al. \[8\] observed the violation of Matthiessen’s rule in two crystals of $\kappa-(ET)_2\text{Cu[N(CN)_2]Br}$ prepared by different synthetic routes. However, this data is consistent with our model if one postulates that the crystal labelled HR in Ref. \[8\] has a larger $\rho_{\text{mfp}}/\sigma_z$ than the crystal labelled LR. This hypothesis is consistent with our observation that x-ray and proton irradiation lead to different $\rho_{\text{mfp}}/\sigma_z$. Our model also explains the very different temperature dependences of the in-plane and out-of-plane resistivities reported for the LR crystal.
\[20\] J. Singleton et al., Phys. Rev. Lett. 88, 037001, (2002).
\[21\] L.A. Openov, Phys. Rev. B, 58, 9468 (1998); A.A. Golubov and I.I. Mazin, ibid. 55, 15146 (1997).