Effect of Irradiation-Induced Disorder on the Conductivity and Critical Temperature of the Organic Superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$

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We have introduced defects into clean samples of the organic superconductor κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ in order to determine their effect on the temperature dependence of the interlayer conductivity σ and the critical temperature T_c. We find a violation of Matthiessen's rule that can be explained by a model of σ involving a defect-assisted interlayer channel which acts in parallel with the bandlike conductivity. We observe an unusual dependence of T_c on residual resistivity, inconsistent with the generalized Abrikosov-Gor'kov theory for an order parameter with a single component, providing an important constraint on models of the superconductivity in this material.

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Quasi-two-dimensional organic conductors based on the donor molecule bisethylenedithiotetrathiafulvalene (BEDT-TTF or ET, see inset of 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 [5,6], showing a crossover from insulatinglike conductivity at high temperature to metalliclike behavior 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$30 K [5,6]. The usual effect of disorder is to change only the temperature independent component of the resistivity; this is known as Matthiessen's rule. However, several strongly correlated materials violate Matthiessen's rule, including various cuprate [7] and organic [8] superconductors. Violations of Matthiessen's rule have previously been taken as evidence for non-Fermi-liquid behavior. In particular, Strack *et al.* [8] have argued that the violations of Matthiessen's rule in the salt κ-(ET)$_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 behavior of the superconducting transition temperature T_c as a function of *nonmagnetic* disorder [4,9] also provides a crucial test of the symmetry of the order parameter. Anderson's theorem [10] states that for s-wave pairing nonmagnetic 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 [11]. For non-s-wave (including extended-s) order parameters, scattering due to nonmagnetic impurities reduces T_c in a manner again described using the AG formula [4,9].

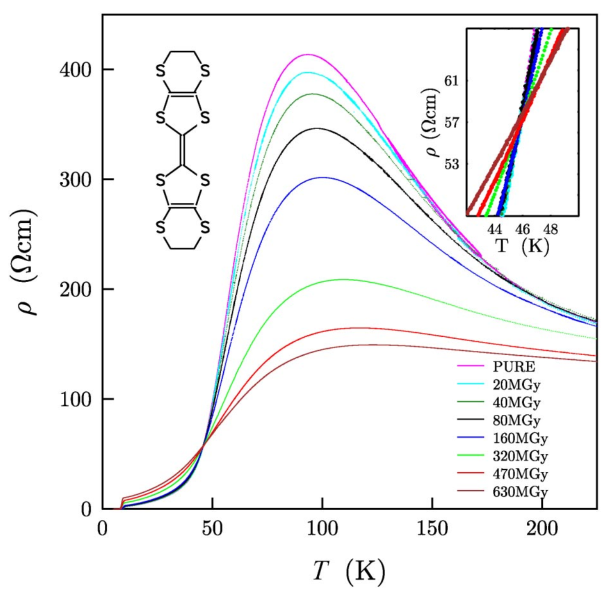

FIG. 1 (color online). Interlayer resistivity of an x-ray damaged sample as a function of temperature for a range of irradiation doses, showing the violation of Matthiessen's rule. Data from the proton-irradiated samples are qualitatively the same. Insets show the ET molecule and a magnified view of the region near T_{cross} (defined in the text).

In order to investigate these effects experimentally for the ET superconductors, we have selected κ-$(ET)_2Cu(SCN)_2$, 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 [12,13], an effect which is probably due to the freezing of terminal ethylene group disorder which occurs at around 70–80 K [4,14]. 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 κ-$(ET)_2Cu(SCN)_2$. However, we find that a simple theory which includes the effect of interlayer scattering from impurities is able to explain this effect phenomenologically. 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 behavior [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 κ-$(ET)_2Cu(SCN)_2$ grown electrochemically. Gold wires of thickness 12.5 μm were attached to the samples (typical dimensions $0.3 \times 0.3 \times 0.1$ mm^3) with graphite paste in the four-probe configuration in order to extract the interlayer resistivity. Samples were cooled from 120 to 10 K at a rate of 20 K/h, below the slowest rate used in Ref. [13], in order to avoid introducing disorder from fast cooling. Defects in our samples were created at room temperature by filtered Cu K_α radiation ($E = 8$ keV, $\lambda = 1.54$ Å) from a Cu x-ray rotating anode (typically 55 kV, 50 mA) at a flux of $\approx 2.5 \times 10^8$ photons s^{-1}. The computer program RADDOSE [15] 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 [16], 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 $\leq$100 μm. Over the whole temperature range, the conductivity is highly anisotropic (the ratio of the in-plane to the interplane conductivity exceeds 10^3), ensuring that our measurement is always dominated by the interlayer resistivity. 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 the irradiation dose is to *decrease* the resistivity over most of the temperature range, and, in particular, to reduce the magnitude of the broad peak centered at $T_p \sim 90$ K. Well into the Fermi-liquid regime, however, the behavior recovers a traditional metallic character; below $\sim$46 K, the resistivity *increases* with increasing irradiation dose (see inset of Figs. 1 and 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 T^2 dependence at temperatures above the superconducting transition and a sharp drop at the onset of superconductivity. The residual resistivity ρ_0 is extracted by fitting data to $\rho = \rho_0 + AT^2$ in the temperature range from just above T_c to 20 K. The upper inset of Fig. 2 presents the change in residual resistivity $\Delta\rho_0$ with respect to an undamaged

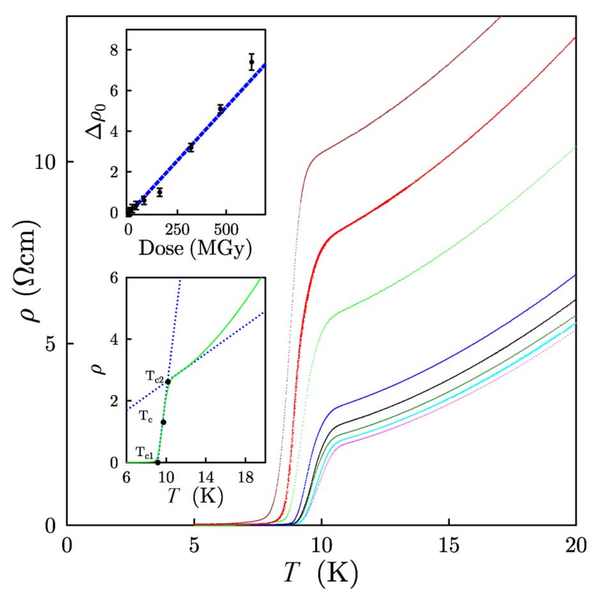

FIG. 2 (color online). The low-temperature region of Fig. 1. The upper inset shows that $\Delta\rho_0$ increases with x-ray dose in an approximately linear fashion. Data from proton-irradiated samples show a similar pattern as a function of disorder. The lower inset shows three methods of defining the critical temperature: a lower T_{c1}, an upper T_{c2}, and T_c, the maximum of the first derivative, which is the definition used in this Letter.

sample as a function of dosage, showing an approximately linear dependence.

The observation that increasing defect density increases 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 bandlike 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 [17]. We note that a complete justification of the latter hypothesis would require a determination of the evolution of the in-plane to interplane conductivity ratio in the damaged samples over a wide range of temperature, which has not yet been measured. 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

$$\sigma(x, T) = \frac{1}{\rho_0(0) + x\rho_{\rm imp} + \rho_{\rm intrinsic}(T)} + x\sigma_\perp, \qquad (1)$$

where $\rho_0(0)$ is the residual resistivity of the undamaged sample, $x\rho_{\rm imp}$ is the contribution to the resistivity from defect scattering in the transport due to molecular orbital overlap, $\rho_{\rm intrinsic}(T)$ 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 $\rho_{\rm intrinsic}(T)$ is small so that $\rho(x, T) \approx \rho_0(0) + x\rho_{\rm imp} + \rho_{\rm intrinsic}(T)$, and hence the *resistivity* increases linearly with defect density, x. At high temperature $\rho_{\rm intrinsic}(T) \gg \rho_0(0) + x\rho_{\rm imp}$ and Eq. (1) becomes $\rho(x, T) \approx [x\sigma_\perp + \rho_{\rm intrinsic}^{-1}(T)]^{-1}$, hence the *conductivity* $\rho(x, T)^{-1}$ linearly increases with x, as observed. The inset of Fig. 1 shows that there is a temperature, $T_{\rm cross}$, 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) $x\rho_{\rm imp} \ll \rho_0(0) + \rho_{\rm intrinsic}$ and (ii) $\rho(0, T_{\rm cross}) = (\rho_{\rm imp}/\sigma_\perp)^{1/2}$ are satisfied. For our x-ray damaged samples, this yields an estimate of $\rho_{\rm imp}/\sigma_\perp = 3 \times 10^3\ \Omega^2\,{\rm cm}^2$. We can obtain an independent estimate of this parameter by plotting $\Delta\sigma_{\rm p} = \sigma(x, T_{\rm p}) - \sigma(0, T_{\rm p})$ 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 to be $\Delta\sigma_{\rm p} \approx x\sigma_\perp$, while the latter quantity can be evaluated in the low-temperature limit to be $\Delta\rho_0 \approx x\rho_{\rm imp}$. The approximate straight-line dependence (which breaks down when $\Delta\rho_0$ and $\Delta\sigma_0$ are large) observed in Fig. 3 shows that both quantities are parametrized by x in the same way, and the gradient of the line yields $\rho_{\rm imp}/\sigma_\perp = 1.5 \times 10^3\ \Omega^2\,{\rm cm}^2$, in order of magnitude agreement with our previous estimate [18]. We note

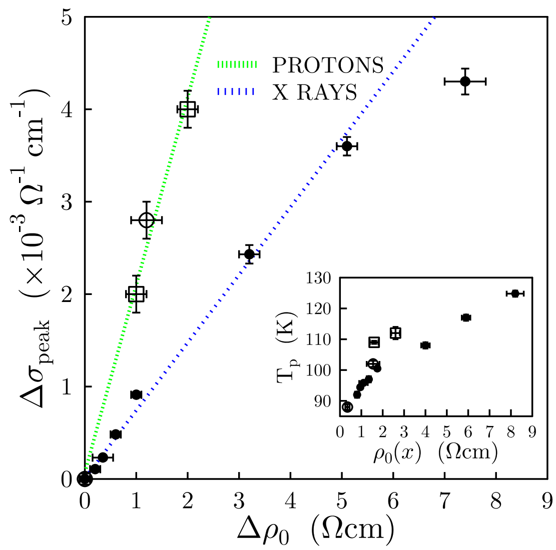

FIG. 3 (color online). The dependence of the change in interlayer conductivity at the peak, $\Delta\sigma_{\rm p}$, on the change in residual resistivity, $\Delta\rho_0$, which is approximately linear, except for at large $\Delta\rho_0$. Because of the different nature of the defects, the slope of proton (two different samples shown with open circles and squares) and x-ray (one sample indicated by solid circles) data differ, though the effect remains qualitatively the same. Inset: the position $T_{\rm p}$ of the resistivity peak shifts slightly to higher temperature with increasing $\rho_0(x)$.

that for proton irradiation, both the gradient of the line in Fig. 3 and the temperature $T_{\rm cross}$ are increased, demonstrating that the nature of the irradiation affects the ratio $\rho_{\rm imp}/\sigma_\perp$, 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 $T_{\rm c}$, corresponding to the maximum of $d\rho/dT$ in Fig. 2, is plotted as a function of ρ_0 in Fig. 4. We find that $T_{\rm c}$ falls with defect density (in agreement with measurements of defects induced by cooling-rate disorder [12]), but the dependence exhibits a sharp change in gradient when ρ_0 reaches a threshold value $\rho_0^* \approx 2\ \Omega\,{\rm cm}$. However, even at the highest defect densities studied, the samples exhibit a superconducting ground state. We also find that the *width* $\Delta T = T_{\rm c2} - T_{\rm c1}$ (see Fig. 2) of the superconducting transition decreases with increasing defect density, as shown in the inset to Fig. 4. This is consistent with $T_{\rm c}$ 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 $dT_{\rm c}/d\rho_0$ is lower.

The theory of AG [11] for nonmagnetic defects in a non-s-wave superconductor implies that the suppression of $T_{\rm c}$ follows $\ln\frac{T_{\rm c}}{T_{\rm c0}} = \psi(\frac{1}{2}) - \psi(\frac{1}{2} + \frac{\hbar}{4\pi k_B T_{\rm c}\tau})$, where ψ is a digamma function and τ is the scattering time. In the low-defect density limit ($\rho_0 < \rho_0^*$), this yields $T_{\rm c0} - T_{\rm c} \simeq \pi\hbar/8k_B\tau$. This linear sector should have a slope consistent with interlayer transport theory [4], i.e., $dT_{\rm c}/d\rho_0 = -e^2 m^* d_\perp t_\perp^2/(4k_B\hbar^3)$, where m^* is the effective mass, $d_\perp$

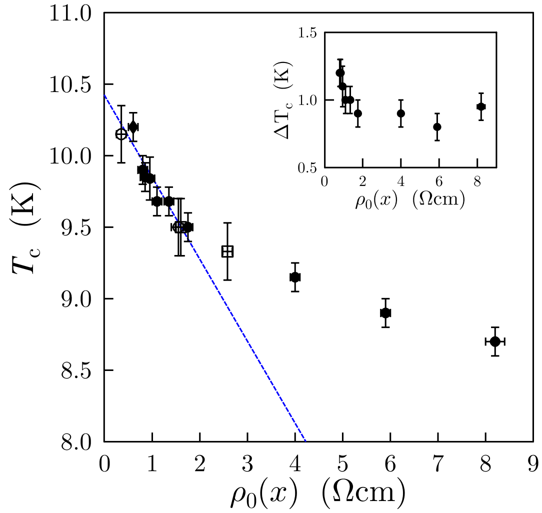

FIG. 4 (color online). The suppression of T_c compared to the interlayer residual resistivity $\rho_0(x)$. The suppression is approximately linear for low damage $\rho_0(x) < \rho_0^* = 2\ \Omega$ cm, but there is a change in gradient for $\rho_0 > \rho_0^*$. The inset shows the dependence of the width ΔT_c of the superconducting transition on $\rho_0(x)$. Symbols correspond to those in Fig. 3 and data for an additional undamaged sample are shown by a solid diamond.

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 $\rho_0 < \rho_0^*$ yields (the line in Fig. 4) a value of $t_\perp = 0.03 \pm 0.01$ meV, in good agreement with the value from angle-dependent magnetotransport [19]. 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 ρ_0^* corresponds to a ratio of the in-plane coherence length to the in-plane mean free path $\xi/l \approx 0.2$ [20]. If all scattering events contributing to l 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 generalized AG equation describing multicomponent order parameters [22] 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 behavior 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 κ-$(ET)_2Cu(SCN)_2$. We find that a dramatic departure from Matthiessen's rule can be straightforwardly explained in terms of defect-assisted interlayer tunneling. Although T_c initially follows a dependence on ρ_0 consistent with pair-breaking scattering, the superconducting state proves to be robust into the dirty limit. This unusual dependence of T_c on ρ_0 is not consistent with an order parameter with a single component, providing an important constraint on models of the superconductivity in this material.

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