Dependence of the superconducting transition temperature of organic molecular crystals on intrinsically nonmagnetic disorder: A signature of either unconventional superconductivity or the atypical formation of magnetic moments

B. J. Powell* and Ross H. McKenzie
Department of Physics, University of Queensland, Brisbane, Queensland 4072, Australia
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We give a theoretical analysis of published experimental studies of the effects of impurities and disorder on the superconducting transition temperature T_c of the organic molecular crystals κ-(BEDT-TTF)$_2X$ (where $X=$Cu[N(CN)$_2$]Br and Cu(NCS)$_2$ and BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene) and β-(BEDT-TTF)$_2X$ (for $X=I_3$ and IBr$_2$). The Abrikosov-Gorkov (AG) formula describes the suppression of T_c both by magnetic impurities in singlet superconductors, including *s*-wave superconductors and by nonmagnetic impurities in a non-*s*-wave superconductor. We show that various sources of disorder (alloying anions, fast electron irradiation, disorder accidentally produced during fabrication, and cooling rate induced disorder) lead to the suppression of T_c as described by the AG formula. This is confirmed by the excellent fit to the data, the fact that these materials are in the clean limit and the excellent agreement between the value of the interlayer hopping integral $t_\perp$ calculated from this fit and the value of $t_\perp$ found from angular-dependent magnetoresistance and quantum oscillation experiments. There are only two scenarios consistent with the current state of experimental knowledge. If the disorder induced by all of the four methods considered in this paper is, as seems most likely, nonmagnetic then the pairing state cannot be *s* wave. We show that published measurements of the cooling rate dependence of the magnetization are inconsistent with paramagnetic impurities. Triplet pairing is ruled out by NMR and upper critical field experiments. Thus if the disorder is nonmagnetic then this implies that $l \geqslant 2$, in which case Occam's razor suggests that *d*-wave pairing is realized in both β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$. However, particularly given the proximity of these materials to an antiferromagnetic Mott transition, it is possible that the disorder leads to the formation of local magnetic moments via some atypical mechanism. Thus we conclude that either β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$ are *d*-wave superconductors or else they display an atypical mechanism for the formation of localized moments, possibly related to the competition between the antiferromagnetic and superconducting grounds states. We suggest systematic experiments to differentiate between these two scenarios.

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I. INTRODUCTION

Superconductivity is often found near magnetic ordering. This may be antiferromagnetic (AFM) order such as in the cuprates[1] and the heavy fermion superconductors[2] or ferromagnetic order as in the $ZrZn_2$ or UGe_2 (see Refs. 3 and 4, respectively). In each of these cases it is believed that the superconductivity is unconventional,[5–8] that is to say that the Cooper pairs have a nonzero angular momentum. The issue of unconventional superconductivity near magnetic ordering is of general interest because it may lead to insights into both nonphononic pairing mechanisms[9] and the theory of quantum critical points.[10]

Despite the fact that it is now twenty years since superconductivity was discovered[11,12] in the layered organic compounds (BEDT-TTF)$_2X$ (where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and X is an anion, e.g., Cu[N(CN)$_2$]Br or I_3) the pairing symmetry remains a matter of debate.[13] BEDT-TTF salts form a number of crystal structures which are denoted by greek letters. All of the crystal structures consist of alternating layers of BEDT-TTF and an anion.[14] In β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$, which we consider here, the BEDT-TTF molecules form a dimerized structure where the anion removes one electron per dimer. Thus we have alternating conducting (BEDT-TTF) and insulating (anion) layers. A particularly interesting feature of these materials is that they can be driven from an AFM insulating state to a superconducting state by the application of hydrostatic pressure or by changing the anion.[15,16]

In principle, the simplest way to identify the pairing symmetry, or at least the nodal structure, of a superconductor is to measure the low-temperature behavior of thermodynamic or transport properties. For example, the specific heat follows an exponentially activated temperature dependence for a nodeless gap ($C_V \propto \exp[-|\Delta(0)|/k_BT]$, where $\Delta(0)$ is the superconducting gap at zero temperature) and a power-law dependence for a gap with nodes ($C_V \propto T^2$ for line nodes and $C_V \propto T^3$ for point nodes on a three-dimensional Fermi surface).[17] In practice, however, there are difficulties associated with this method of identifying the pairing symmetry, not the least of which is the need to make measurements at extremely low temperatures. (Typically a wide temperature range is required in the region $T/T_c \lesssim 0.2$, so in the case of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br ($T_c \sim 10$ K) one requires measurements taken over a wide range of temperatures below ~ 2 K.) The apparently strong coupling[18,19] nature of the superconductivity in theses charge-transfer salts means that the behavior of thermodynamic and transport functions near T_c is unable to differentiate between pairing states on

symmetry grounds alone and so we must wait for calculations based on a specific theory of superconductivity to use this data to examine the pairing symmetry.

Regardless of the reasons one fact is clear,[13] low-temperature behaviors have been, to date, unable to settle the debate on the pairing symmetry in the layered organic superconductors. In particular, two pairing symmetries have been widely discussed: strong coupling *s*-wave superconductivity and *d*-wave pairing.

In κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br the ^{13}C NMR spin lattice relaxation rate[20–22] $(T_1)^{-1}$ shows no Hebel-Slichter peak and a power-law cutoff $(T_1)^{-1} \propto T^n$, where $n \simeq 3$. A Hebel-Slichter peak is expected for *s*-wave pairing while $(T_1)^{-1} \propto T^3$ is expected for line nodes.[23]

Much controversy has surrounded the London penetration depth with some groups reporting *s*-wave pairing[24–28] and others finding line nodes consistent with *d*-wave pairing[29–34] in both κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Refs. 24–26 and 29–32) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Refs. 25–28, 31, 30, 33, and 34). However, the most recent measurements[31] have two advantages over older experiments. First, very low magnetic fields were used. The use of fields less than the lower critical field is important in penetration measurements because vortex dynamics are a serious impediment to accurately measuring the penetration depth. Second, Carrington *et al.*[31] made measurements down to 0.4 K and therefore made a large range of measurements below $T \sim 0.2T_c$. This is the lowest temperature range considered in any of the thermodynamic or transport experiments, making the conclusions of Carrington *et al.* the most reliable drawn from experiments of this type. Carrington *et al.* found that the temperature dependence of the penetration depth of both κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is inconsistent with a nodeless gap.

Initial measurements of the specific heat of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br showed a T^2 dependence[35] but the interpretation of these results has been questioned.[13] More recent measurements of the specific heat have found an exponentially activated temperature dependence for both κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 18) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Ref. 19).

Several groups have considered probes which do not rely on the low-temperature behavior of the measurement. Brando *et al.*[36] and Arai *et al.*[37,38] attempted to observe the local density of states (LDOS) of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by measuring the differential conductance using a scanning tunneling microscope. Each of these experiments found a LDOS that is consistent with *d*-wave pairing, however, none of the experiments observed the coherence peaks which are a characteristic feature of the superconducting state and have been observed[39–41] in similar experiments on $Bi_2Sr_2CaCu_2O_{8+x}$. Also one should note that Bando *et al.*[36] observed a LDOS in the layered *s*-wave superconductor NbN which has the same form as that which is interpreted as *d*-wave in experiments on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

Schrama *et al.*[42] attempted to determine the anisotropy in the superconducting order parameter by measuring the magneto-optical properties of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and found results indicative of *d*-wave pairing. However, in light of the debate over the interpretation of these results[43–45] one cannot consider these measurements to have determined the pairing symmetry.

Izawa *et al.*[46] measured the thermal-conductivity tensor of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in a magnetic field. They observed a fourfold anisotropy at low temperatures which they interpreted as evidence for *d*-wave pairing. However, it is possible that the vortices produced in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are actually Josephson vortices. Therefore it remains to be shown whether or not the theory[47–49] on which Izawa *et al.* base their analysis is valid for this material.

The ^{13}C NMR Knight shift has been measured[20,21] for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. With a magnetic field, **H** parallel to the conducting planes, as $T \to 0$ so does the Knight shift.[178] This does not actually rule out triplet pairing, although it does make triplet pairing extremely unlikely. This experiment is compatible with a triplet state in which $\mathbf{d}(\mathbf{k}) \times \mathbf{H} = 0$ where $\mathbf{d}(\mathbf{k})$ is the usual Balian-Werthamer order parameter for triplet superconductivity.[50,51] An example of a triplet phase compatible[52,53] with this experiment is an *A* phase with $\mathbf{d}(\mathbf{k})$ pinned to the *c* axis,[54] which is not an impossibility given the highly anisotropic nature of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. However, Zuo *et al.*[55] measured the critical field as a function of temperature with **H** parallel to the conducting planes. In this configuration no orbital currents flow so the critical field is due to Clogston-Chandrasekhar (or Pauli) limit.[53,56,57] There is no Clogston-Chandrasekhar limit for $\mathbf{H} \perp c$ for triplet states compatible with measured Knight shift. Thus for such states there would be no critical field with $\mathbf{H} \| b$ (in fact for such states one would increase T_c by applying a field parallel to the *b* axis[53]). Experimentally[58] it is found that superconductivity is destroyed by a magnetic field parallel to the *b* axis. Therefore only when considered together do the three experiments discussed above[20,55,58] strictly rule out triplet pairing.[59] Further evidence for Clogston-Chandrasekhar limiting comes from the observation that the in plane upper critical field is independent of the field direction.[63] Given the anisotropic nature of the Fermi surface of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br it is extremely unlikely that orbital mechanisms for the destruction of superconductivity would be so isotropic.

The results of quantum chemistry calculations suggest that the simplest theoretical model which can describe these materials is a half-filled Hubbard model on an anisotropic triangular lattice.[16,64] Because of the proximity of the antiferromagnetic insulating phase and the superconducting phase several groups have examined the possibility of spin fluctuation induced superconductivity within the confines of this model using a variety of techniques, including mean-field theory,[64] the fluctuation-exchange approximation,[65–67] third order perturbation theory,[68] weak coupling renormalization-group analysis,[69] the random-phase approximation,[70,71] and quantum Monte Carlo methods.[72] All of these groups concluded that spin fluctuations lead to *d*-wave pairing. These authors found an enhanced dynamical susceptibility at $(\pi, \pm\pi)$ which leads to $d_{x^2-y^2}$ pairing. Alternatively, both

d-wave[73] and *s*-wave[74–76] pairing symmetries have been considered in the context of phononic pairing mechanisms.

So, perhaps the only emerging consensus is that the low-temperature behaviors have not been able to conclusively settle the debate between *s*-wave and *d*-wave pairing symmetries. In the remainder of this paper we will investigate how the effects of disorder can be used to distinguish between these two symmetries.

II. THE ABRIKOSOV-GORKOV FORMULA

Anderson's theorem[77] states that for *s*-wave pairing nonmagnetic impurities do not change T_c. This is because Cooper pairs are formed from time reversed states and although nonmagnetic impurities may change, for example, the phonon spectrum, they do not break time-reversal symmetry (TRS). However, magnetic impurities strongly reduce T_c for all singlet states because they do break TRS.[78] This behavior is described by the Abrikosov-Gorkov (hereafter AG) formula:[79]

$$\ln\left(\frac{T_{c0}}{T_c}\right)=\psi\left(\frac{1}{2}+\frac{\hbar}{4\pi k_B T_c}\frac{1}{\tau_M}\right)-\psi\left(\frac{1}{2}\right), \tag{1}$$

where T_{c0} is the superconducting critical temperature in the pure system and $\psi(x)$ is the digamma function. τ_M is the quasiparticle lifetime due to scattering from magnetic impurities. Assuming *isotropic* scattering τ_M is given by[80]

$$\frac{\hbar}{\tau_M}=N_M\pi J_i(J_i+1)N(0)|u_M|^2, \tag{2}$$

where N_M is the number density of magnetic impurities, $N(0)$ is the density of states per spin at the Fermi level, J_i is the total angular momentum of the paramagnetic atoms, and u_M is the amplitude for scattering from a magnetic impurity.

In the superconducting state the anomalous Green's function $F_{\alpha\beta}(\mathbf{k},\omega_n)$ is finite and therefore there is, in the presence of nonmagnetic impurities, an anomalous self-energy $\Sigma_{2,\alpha\beta}(\omega_n)$, which, in *n* dimensions, is given by[17]

$$\Sigma_{2,\alpha\beta}(\omega_n)=\frac{1}{2\pi N(0)\tau_N}\int\frac{d^n k}{(2\pi)^n}F_{\alpha\beta}(\mathbf{k},\omega_n), \tag{3}$$

where τ_N, the lifetime for scattering from nonmagnetic impurities, is given by[80]

$$\frac{\hbar}{\tau_N}=N_N\pi N(0)|u_N|^2, \tag{4}$$

where N_N is the number density of nonmagnetic impurities and u_N is the amplitude for scattering from a nonmagnetic impurity.

For *s*-wave pairing $\Sigma_{2,\alpha\beta}(\omega_n)$ is clearly finite, and it can be shown that the anomalous self-energy cancels exactly with the normal self-energy $\Sigma_{1,\alpha\beta}(\omega_n)$, when the critical temperature is evaluated. Therefore T_c is unchanged by nonmagnetic impurities for an *s*-wave superconductor, as expected from Anderson's theorem.[77] However, for non-*s*-wave pairing[81] it can be seen, from symmetry grounds alone, that the integral in Eq. (3) vanishes. Thus the anomalous self-energy does not cancel the normal self-energy and T_c is lowered by nonmagnetic impurities in a non-*s*-wave superconductor. Further, it can be shown that for pairing states with non-*s*-wave symmetry nonmagnetic impurities reduce T_c via the Abrikosov-Gorkov formula.[82,17] However, in this case

$$\ln\left(\frac{T_{c0}}{T_c}\right)=\psi\left(\frac{1}{2}+\frac{\hbar}{4\pi k_B T_c}\frac{1}{\tau_N}\right)-\psi\left(\frac{1}{2}\right), \tag{5}$$

where again we have assumed isotropic scattering. The predictions[83] of Anderson's theorem have been confirmed for the alloys of many *s*-wave superconductors.[84–87]

Hasegawa and Fukuyama[88] suggested that weak localization could lead to an alternative mechanism for the suppression of T_c in organic superconductors. Notably this mechanism allows for the suppression of T_c by nonmagnetic disorder in *s*-wave superconductors, in violation of Anderson's theorem. However, the Hasegawa-Fukuyama mechanism has a dramatically different τ_N dependence to the AG formula. We will show in this paper that the observed suppression of T_c in β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$ is described by the AG formula and therefore the predictions of Hasegawa and Fukuyama are not in agreement with experiment. For a multiband superconductor interband scattering processes can also lead to a suppression in T_c (see, for example, Ref. 89). However, of the two polymorphs discussed in this paper only one [κ-(BEDT-TTF)$_2X$] has multiple sheets to its Fermi surface. As it seems reasonable to assume (unless evidence is found to the contrary) that the suppression of T_c in both materials is due to the same mechanism we will not discuss interband scattering effects further. Also note that for moderate amounts of disorder, interband scattering effects and the AG formula give very different predictions for the suppression of T_c.

It can be shown that the digamma function has the property

$$\psi\left(\frac{1}{2}+x\right)=\psi\left(\frac{1}{2}\right)+\frac{\pi^2 x}{2}+O(x^2). \tag{6}$$

Hence for $\hbar/\tau \ll k_B T_c$ (i.e., as the number of impurities tends to zero) the AG equation becomes

$$T_{c0}-T_c\simeq\frac{\pi\hbar}{8k_B}\frac{1}{\tau}. \tag{7}$$

Clearly the above is valid for both magnetic impurities in singlet states ($\tau=\tau_M$) and nonmagnetic impurities in non-*s*-wave pairing states (in which case $\tau=\tau_N$).

A. Mixed order parameters

In addition to *s*-wave pairing and non-*s*-wave pairing, a third logical possibility exists: a state which contains a superposition of both *s*- and non-*s*-wave pairing. For example the $s+id$ and $s+d$ states. In general, such a state can be written as

$$\Delta(\tau)=\Delta_0(\tau)\{\cos[\varphi(\tau)]\hat{\Delta}_s+e^{i\theta}\sin[\varphi(\tau)]\hat{\Delta}_n\}, \tag{8}$$

where τ is the quasiparticle lifetime, $\Delta(\tau)$ is the order parameter of the superconductor, $\Delta_0(\tau)$ gives the magnitude of the order parameter, $\hat{\Delta}_s$ is a function with a magnitude of unity and *s*-wave symmetry, $\hat{\Delta}_n$ is a function with a magnitude of unity and the appropriate non-*s*-wave symmetry, and θ and $\varphi(\tau)$ parametrize the superposition. For clarity we have suppressed all spin and momentum labels. We will describe this state as the $s+n$ state.

Naively, it might appear that the $s+n$ state might explain the low-temperature behavior of the thermodynamic and transport properties. If the states had a large *d*-wave component it would appear to have nodes at high temperatures, but at low temperatures the small fully gapped *s*-wave part of the order parameter would cause an exponential cutoff. However, a more careful analysis of the data shows that this scenario is not what has been observed, indeed the results of the experiments performed to the lowest temperatures suggested nodes in the gap.[31]

To describe the effect of disorder on the $s+n$ state we will begin by studying the two extreme cases of total coherence between the states and zero coherence between the states. It will then be seen that all other possibilities are intermediates of these two extremes.

If there is total coherence between the states, then adding disorder does not change the ratio between the *s*-wave and non-*s*-wave parts of the order parameter, i.e., φ is independent of τ. It is straightforward to show that, subject to this constraint,

$$\ln\left(\frac{T_{c0}}{T_c}\right)=2\pi N(0)VT\sum_{n\geqslant 0}\left(\frac{R}{\omega_n+1/2\tau}-\frac{1}{\omega_n}\right), \qquad (9)$$

where V is the effective pairwise interaction between the electrons. For *s*-wave pairing in the presence of nonmagnetic impurities[90]

$$R=1+\frac{1}{2\tau|\omega_n|} \qquad (10)$$

and one finds that $T_c=T_{c0}$ independent of τ, in confirmation of Anderson's theorem. But, for non-*s*-wave pairing $R=1$ and we arrive at the AG equation (5).

For an $s+n$ superconductor

$$R=1+\frac{\alpha(\varphi)}{2\tau|\omega_n|}. \qquad (11)$$

$\alpha(\varphi)$ is an unknown function, however, it is clear that $\alpha(0)=1$ and $\alpha(\pi)=0$. Thus one finds that

$$\ln\left(\frac{T_{c0}}{T_c}\right)=\psi\left(\frac{1}{2}+\frac{\hbar}{4\pi k_B T_c}\frac{1}{(1-\alpha)\tau}\right)-\psi\left(\frac{1}{2}\right). \qquad (12)$$

Thus we find that rigid coherence in an $s+n$ superconductor simply ''renormalizes'' the quasiparticle lifetime in the AG equation.

For a superconductor without coherence between the two parts of the order parameter φ varies strongly with τ and the two parts of the order parameter are independent of one another. Thus nonmagnetic disorder does not change the bulk critical temperature because of the *s*-wave part of the wave function. But nonmagnetic disorder would reduce the critical temperature for the non-*s*-wave part of the wave function. This would lead to there being two phase transitions in the presence of nonmagnetic disorder, the first from the nonsuperconducting state to an *s*-wave superconductor and the second from an *s*-wave superconductor to an $s+n$ superconductor. Two such phase transitions would have a clear experimental signature. For example, there would be two anomalies in the specific heat. This has, to the best of our knowledge, never been observed in the layered organic superconductors. Therefore we can rule out the possibility of $s+n$ superconductivity with zero or, indeed, weak coherence between the states on phenomenological grounds.

B. Nonmagnetic disorder in other superconductors

The effects of nonmagnetic disorder have been carefully observed in several other superconductors. The best known case is Sr_2RuO_4. Mackenzie *et al.*[91] measured T_c for several samples with varying residual resistivities. Assuming the Drude model of conductivity they found the variation of T_c with ρ_0 to be in excellent agreement with the AG formula.

Both magnetic (Ni) and intrinsically nonmagnetic (Zn, Pr, fast electron irradiation) defects lead to the suppression of T_c of $YBaCu_3O_{6+x}$ (YBCO) in line with the AG formula.[92,93] However, it is known[94] that the substitution of Zn atoms for Cu atoms in the CuO_2 planes of YBCO can lead to the formation of localized magnetic moments. It is thought that these local moments form on the nearest-neighbor Cu atoms rather than on the Zn site itself.[94] There has been much debate[95,96] as to whether the mechanism for pair breaking in YBCO crystals with Zn impurities is local moment scattering or potential scattering due to the Zn impurity (of course, the two mechanisms are not mutually exclusive[97]). Recent work by Davis *et al.*[40,41] indicates that nonmagnetic scattering is the dominant mechanism by which Zn impurities[41] lower T_c and further that even the magnetic impurities (Ni) act primarily as potential scatterers.[40]

In the heavy fermion superconductor UPt_3 a suppression of T_c has been observed that is consistent with the AG theory.[98,99] Surprisingly both magnetic (Ni) impurities and nonmagnetic (Gd) impurities suppress T_c in the same way.[99] In light of the discovery that Ni impurities act primarily as potential scatterers in YBCO it seems plausible that the same thing may happen in UPt_3. Alternatively some unknown mechanism may be inducing local moments around the Gd atoms. This seems unlikely as for this to be consistent with the observation that Gd and Ni impurities suppress T_c in the same way this scenario would require the moment induced around Gd atoms to be the same as the moment due to Ni atoms.

The Bechgaard salts, $(TMTSF)_2X$ (TMTSF is tetramethylteselanafulvalene and X is an anion, for example, ClO_4 or ReO_4), are also very sensitive to nonmagnetic disorder. It has been suggested that this is because they are quasi-one-dimensional systems.[14,88,100,101] Disorder can be induced by x-ray irradiation, alloying, or by a cooling rate controlled anion disorder transition (which we will discuss further be-

low). All of these sources of disorder can reduce T_c and can even suppress superconductivity altogether and lead to the formation of a spin density wave.[100,102]

III. β-(BEDT-TTF)$_2X$

There are a series of competing ground states in both β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$ including antiferromagnetism and superconductivity. By applying pressure or changing the anion the ground state of these layered organic crystals can be changed, thus it is thought that different anions apply different ''chemical pressures.''[15,16] For superconducting crystals pressure lowers T_c. Thus one might expect that by alloying anions one could observe the same change in T_c due to the change in ''chemical pressure.'' However, if one adds small amounts of a second anion the second anion sites will act as nonmagnetic impurities. Thus, unless the pairing state is *s* wave, alloying anions will suppress T_c. The suppression of T_c should be governed by the AG formula.

Tokumoto *et al.*[103] have produced alloys in the series β-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(IBr$_2$)$_x$. For $x=0$ they found that $T_c=7.4$ K and for $x=1$ they found $T_c=2.4$ K. Based on Anderson's theorem one expects that for *s*-wave pairing T_c will vary monotonically with *x*. However, Tokumoto *et al.* found no indications of superconductivity for $0.2\lesssim x\lesssim 0.7$. A natural explanation of this experiment is that for small, nonzero values of *x* the IBr$_2$ anions act as (intrinsically) nonmagnetic impurities in β-(BEDT-TTF)$_2$I$_3$ and thus quickly reduce T_c to zero. Similarly for $x\lesssim 1$ the I$_3$ anions act as impurities in β-(BEDT-TTF)$_2$IBr$_2$ and reduce T_c to zero for quite small concentrations. This explanation of course requires non-*s*-wave pairing.

In Fig. 1 we plot the data for T_c against ρ_0 for β-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(IBr$_2$)$_x$ with $x\lesssim 1$ from Tokumoto *et al.*[103] on the same graph as data for β-(BEDT-TTF)IBr$_2$ samples[104] which have differing residual resistivities because of impurities accidently induced in the fabrication process. The excellent agreement with the AG formula is strong evidence against the weak localization scenario. In this fit we assume only that $\rho_0\propto 1/\tau_N$. There were not enough data points reported for $x\lesssim 0$ to make a similar comparison for β-(BEDT-TTF)I$_3$. For a more detailed discussion of the role of disorder in β-(BEDT-TTF)I$_3$ see Ref. 105.

It is also interesting to note that the compound β-(BEDT-TTF)$_2$I$_2$Br is not superconducting. For β-(BEDT-TTF)$_2X$, when *X* is a trihalide, the three positions of the halide atoms are crystallographically distinct. In β-(BEDT-TTF)$_2$I$_3$ the three iodine atoms are arranged approximately linearly (which we represent by I-I-I) and are clearly indistinguishable particles. In β-(BEDT-TTF)$_2$IBr$_2$ the atoms are arranged Br-I-Br, that is to say that the iodine atom is always in one particular location. But, in β-(BEDT-TTF)$_2$I$_2$Br, the atoms can either be arranged I-I-Br or Br-I-I. This means that the crystal is intrinsically disordered. β-(BEDT-TTF)$_2$I$_2$Br is found to have a high residual resistivity.[103] Thus we propose that it is the intrinsically nonmagnetic disorder, caused by the two possible arrangements of the anion, that suppresses superconductivity in β-(BEDT-TTF)$_2$I$_2$Br. Further Tokumoto *et al.* observed that no samples with $R(0)/R(295)\gtrsim 0.3$ from any of the alloys β-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(IBr$_2$)$_x$, β-(BEDT-TTF)$_2$(IBr$_2$)$_{1-x}$(I$_2$Br)$_x$ or β-(BEDT-TTF)$_2$(I$_2$Br)$_{1-x}$(I$_3$)$_x$ superconducted. This is exactly what one would expect from the AG formalism (cf. Fig. 1).

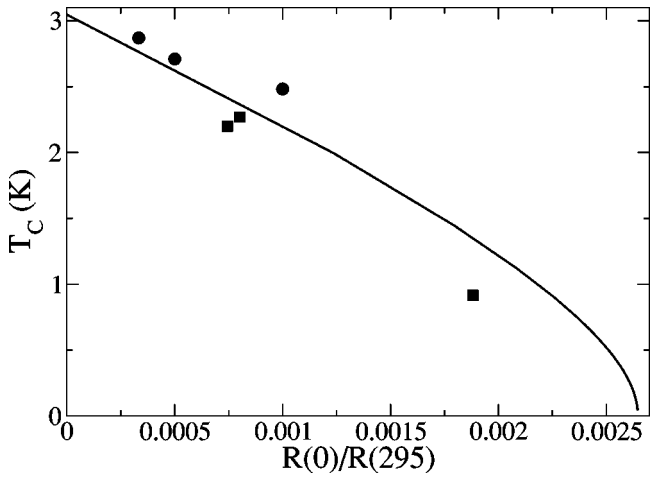

FIG. 1. The variation of the superconducting transition temperature of β-(BEDT-TTF)$_2$IBr$_2$ with the residual resistance ratio $R(0)/R(295)$. The curve is a fit, using the AG formula assuming the residual resistivity, $\rho_0\propto 1/\tau_t$, where τ_t is the quasiparticle lifetime, to the data of Tokumoto *et al.* (Ref. 103) (squares) who induced disorder by substituting I$_3$ anions for IBr$_2$ and Shegolev and Yagubskii (Ref. 104) (circles) who reported resistivity measurements for several samples. This indicates that either both types of impurities induce magnetic moments or else the pairing symmetry is non-*s*-wave. Note that although we have written $R(0)$ Tokumoto *et al.* did not actually report $R(0)/R(295)$, but $R(T_c)/R(295)$ thus their data (squares) should be shifted slightly to the left. As Shegolev and Yagubskii reported $R(T)/R(295)$ for a range of temperatures near T_c we were able to fit to their data to the form $R(T)/R(295)=R(0)/R(295)+AT^2$ and thus determine both $R(0)/R(295)$ and T_c accurately.

At this stage it may appear that the arguments presented above are in contradiction to what is known about the cuprate superconductors. These materials have *d*-wave order parameters and yet nonstoichiometric compounds often have far higher transition temperatures than the (stoichiometric) parent compounds (indeed in many cases the parent compound is nonsuperconducting). An excellent example of this is La$_{2-x}$Sr$_x$CuO$_4$ for which optimal doping is $x\sim 0.15$. It was suggested[106] that *d*-wave superconductivity is observed in nonstoichiometric compounds because the Born approximation is not valid for the cuprates. However, it has been shown[107] that even in the unitary (or resonant) scattering limit which is appropriate for the cuprates nonmagnetic disorder still destroys *d*-wave pairing in line with the predictions of the AG formula and leaves *s*-wave pairing unaffected. Further unitary scattering is the appropriate limit[108] for the unconventional superconductor[109] UPt$_3$ and in this material T_c is suppressed by nonmagnetic impurities in a manner consistent with the AG formula[99] as discussed in Sec. II B.

However, so far we have neglected the major difference

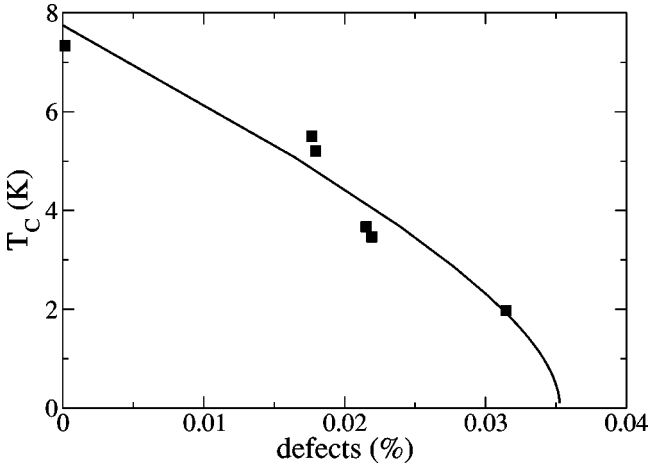

FIG. 2. The variation of the superconducting transition temperature of β-(BEDT-TTF)$_2$I$_3$ with the number of impurities. The data are taken from Forro *et al.* (Ref. 112) who induced defects by irradiating samples with fast electrons. The curve is a fit to the AG formula and Eq. (4). This indicates that either the radiation induces magnetic moments or else the pairing symmetry is non-*s*-wave.

between nonstoichiometric compounds in the organics and the cuprates. In the cuprates the change in stoichiometry introduces a change in the current carrier concentration. This dramatically alters the ground state of the cuprates. This effect is absent in the organics[179] because all of the anions have the same electronegativity. It should be noted however that, both the cuprates and the organics are similarly two dimensional as is attested by the ratio of the zero-temperature interlayer coherence length $\xi_\perp(0)$ to the interlayer spacing a. For example, in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 14) $\xi_\perp(0)/a = 5.8/30.016 = 0.19$ and in the cuprates[110] $\xi_\perp(0)/a \sim 0.06$–0.45. Therefore, as both compounds are quasi-two-dimensional and alloying anions suppresses T_c in β-(BEDT-TTF)$_2X$, it cannot be merely the two dimensional nature of the cuprates which is responsible for observation of superconductivity in nonstoichiometric compounds.

It has been shown[103] that by alloying anions one can introduce enough disorder into the system to suppress superconductivity. Assuming that this disorder is nonmagnetic this rules out $s+n$ superconductivity with anything other than completely rigid coherence between the two states [that is to say that α is independent of φ in the language of Eq. (11)]. Any other type of coherence would leave a small residual *s*-wave component even in the presence of very large amounts of disorder.

Defects can also be induced in materials by irradiating them with fast electrons.[93,111] Such experiments were performed on β-(BEDT-TTF)$_2$I$_3$ by Forro *et al.*[112] who noted a marked drop in T_c as the number of defects increased. From Fig. 2 it can be seen that the fit to the AG formula and Eq. (4) is excellent. Unfortunately Forro *et al.* did not report the residual resistivity of their irradiated samples so a comparison with transport theory cannot be made. Again the excellent fit of the data to the AG theory is strong evidence against the weak localization theory.

We have therefore shown that impurities in β-(BEDT-TTF)$_2X$ suppress T_c via the AG mechanism for three sources of impurities: alloying anions, fast electron irradiation, and accidentally created defects from the fabrication process. There is no obvious mechanism for any of these methods to form magnetic scattering centers. Thus the most natural interpretation is that there is non-*s*-wave pairing in β-(BEDT-TTF)$_2X$ and the reduction in T_c is due to potential scattering. However, there is a strong similarity between the layered organic superconductors and the cuprates,[15,16,64,113] in particular, both are close to an antiferromagnetic phase. As we have already noted, the substitution of Zn for Cu in the CuO_2 planes of YBCO leads to the unexplained formation of local moments on the Cu atoms neighboring the Zn impurity. Therefore one must consider the possibility that an atypical mechanism is creating local moments in all three of experiments discussed above. This may seem unlikely, but until further experimental evidence on the nature of the impurities formed in these experiments becomes available we cannot use disorder to unambiguously determine whether or not there is *s*-wave pairing in β-(BEDT-TTF)$_2X$.

IV. κ-(BEDT-TTF)$_2X$

One of the most unusual features of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is that T_c is dependent on the rate at which the sample is cooled from $T \gtrsim 80$ K (Ref. 114 and 115). The residual resistivity along the c axis, ρ_0, is also dependent on the cooling rate. It would appear then that if one cools κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br quickly one can ''freeze in'' disorder, whereas if the cooling is slower then the disorder can relax out. The observation that this disorder suppresses T_c implies that if the pairing state has *s*-wave symmetry then the disorder must arise from magnetic impurities, but if another pairing symmetry is realized then this disorder may arise from nonmagnetic impurities.

There is always a certain amount of intrinsically nonmagnetic impurities in any given crystal. These ''structural'' impurities will also contribute to the residual resistivity, but they only affect T_c in the non-*s*-wave case. We denote the quasiparticle lifetime caused by this structural disorder by τ_s. Similarly we will denote the quasiparticle lifetime caused by the cooling rate induced disorder by τ_c.

As nonmagnetic impurities do not affect T_c for *s*-wave pairing, T_c is given by Eq. (1) with $\tau_M = \tau_c$. On the other hand, both scattering from magnetic and nonmagnetic impurities contribute to the residual resistivity so we might expect

$$\rho_0 \propto \frac{1}{\tau_t} \equiv \frac{1}{\tau_s} + \frac{1}{\tau_c} \tag{13}$$

where τ_t is the appropriate quasiparticle lifetime for transport experiments.

The fabrication of different samples will lead to different values of τ_s. For *s*-wave pairing this will cause a variation in ρ_0 but not T_c, thus one reaches the conclusion that different samples cooled at the same rate will have different residual resistivities, but the same maximum critical temperature. In Fig. 3 we fit the linearized AG equation (7) to the data of Su *et al.*[114] We also show the effect of varying τ_s for the *s*-wave

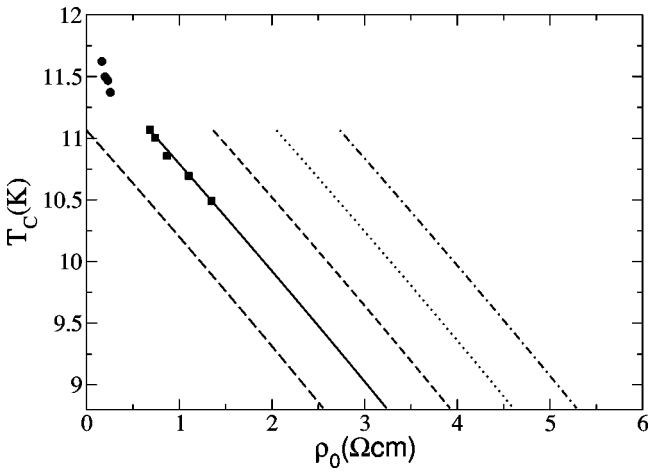

FIG. 3. Variation of the superconducting transition temperature T_c of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with the interlayer residual resistivity ρ_0. The solid line is a fit to the data of Su *et al.* (Ref. 114) (squares). The other lines are predictions of the *s*-wave theory for other samples with different amounts of structural disorder and thus a different τ_s. This structural disorder is assumed to be nonmagnetic. Thus for *s*-wave pairing the structural disorder changes ρ_0 but does not affect T_c. The data of Stalcup *et al.* (Ref. 115) then represent a test of the theory. It can clearly be seen that the theory does not describe the data as both T_c and ρ_0 are changed for all cooling rates. This indicates that the τ_s is different for both samples and therefore that either the assumption of nonmagnetic structural disorder is incorrect or the assumption of *s*-wave pairing is incorrect. Note that we have reanalyzed the experimental data and used a consistent definition of both T_c [based on when the resistivity falls to half of its normal state value) and ρ_0 (based on a fit to the form $\rho(T)=\rho_0+AT^2$; Matthiessen's rule (Ref. 116) was found to be obeyed].

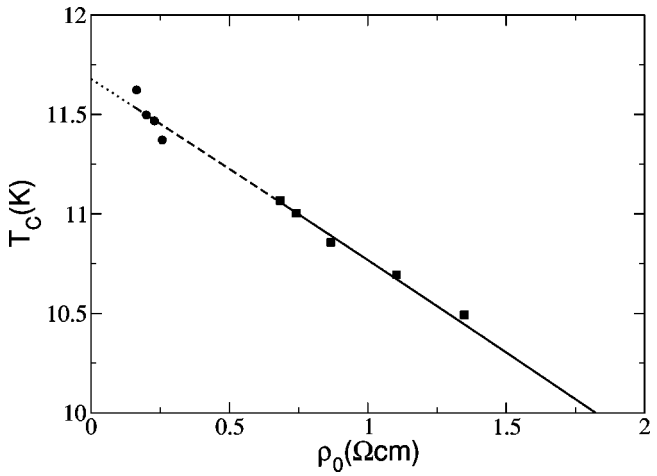

FIG. 4. Variation of the superconducting transition temperature T_c of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with the interlayer residual resistivity ρ_0. The solid line is a fit to the data of Su *et al.* (Ref. 114) (squares). For non-*s*-wave pairing the structural disorder changes both ρ_0 and T_c. The data of Stalcup *et al.* (Ref. 115) then represent a test of the theory. The broken lines are a prediction of the non-*s*-wave theory for other samples with different levels of structural disorder and thus a different τ_s. It can clearly be seen that the theory describes the data as both T_c and ρ_0 are changed for all cooling rates in line with the predictions of the AG formula and Eq. (22). The dashed portion of the line describes the data of Stalcup *et al.*, the dotted line is the prediction for a crystal with even less structural disorder. The experimental data and the solid line are identical to those shown in Fig. 3. Note, however, that this figure also represents the prediction for *s*-wave pairing assuming that the structural impurities are solely magnetic scatterers.

pairing/nonmagnetic structural impurity scenario, which is that from sample to sample the minimum ρ_0 as a function of cooling rate changes, but the maximum T_c does not change. The broken lines then show the expected behavior for different samples based on the data of Su *et al.*assuming *s*-wave pairing and nonmagnetic structural impurities. Also shown are equivalent data from experiments performed by Stalcup *et al.*[115] It is clear that the data from Stalcup *et al.* do not fit with the expectations for *s*-wave pairing and nonmagnetic structural impurities. For non-*s*-wave pairing and/or magnetic structural impurities both structural disorder and cooling rate induced disorder reduce T_c. Thus T_c is given by Eq. (5) with $\tau_N=\tau_t$. While the residual resistivity is still determined by Eq. (13).

The solid line in Fig. 4 represents a fit to the data of Su *et al.* The fabrication of different samples will lead to different values of τ_s. This will cause a variation from sample to sample in both the minimum value of ρ_0 and the maximum value of T_c obtainable by varying the cooling rate. However, as T_c and ρ_0 are both functions of only one variable (τ_t) the data for all samples will lie on a single line. Thus the broken lines in Fig. 4 represent the prediction of the behavior of different samples based on the data of Su *et al.* assuming non-*s*-wave pairing and/or magnetic structural impurities. It is clear that the data of Stalcup *et al.* are in excellent agreement with the expectations for non-*s*-wave pairing.

We stress that this result is based on experiments on only two samples. To be conclusive one would require the study of many more samples. Further it has been argued[117] that some measurements of the critical temperature and residual resistivity in the literature[118] are more consistent with the *s*-wave pairing scenario (Fig. 3). Clearly, a detailed, systematic study is required to settle this debate.

The above work is based on the (reasonable) assumption that the structural impurities are nonmagnetic. As we speculated in the case of β-(BEDT-TTF)$_2X$, it may be that some atypical mechanism of local moment formation exists in the layered organic superconductors. Applying a hydrostatic pressure or changing the anion (X) in κ-(BEDT-TTF)$_2X$ has a dramatic effect on the ground state. For example, at ambient pressure and low-temperature κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl is a Mott-Hubbard antiferromagnetic insulator. Applying a small pressure ($\sim$200 bar, Ref. 119) moves κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl into a superconducting state with properties very similar to those of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Thus it is thought that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is close (in anion/pressure space) to an antiferromagnetic phase transition.[16] A possible mechanism for the formation of local moments in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is that nonmagnetic impurities change the local electronic structure by a small amount.

This small local perturbation could cause the formation of a local moment similar to those found in the antiferromagnetic phase. A similar suggestion was made by Kohno *et al.*,[120] who considered the competition of antiferromagnetic and superconducting ground states in $Ce_xCu_2Si_2$ with $x \lesssim 1$. In their scenario Ce vacancies act as intrinsically nonmagnetic impurities, but lead to the formation of local moments. At low enough densities such magnetic impurities will act as independent, paramagnetic spins. As such the impurities' behavior in a magnetic field is governed by the Brillouin function:[116]

$$M = N_M g \mu_B J_i \left\{ \left(1 + \frac{1}{2J_i} \right) \coth\left[\left(1 + \frac{1}{2J_i} \right) \frac{g\mu_B H J_i}{k_B T} \right] - \frac{1}{2J_i} \coth\left(\frac{g\mu_B H J_i}{2k_B T} \right) \right\}, \tag{14}$$

where N_M is the total number of magnetic impurities, J_i is the total angular momentum of the impurity, and g is the usual g factor. For localized, noninteracting electrons it is appropriate to take $J_i = \frac{1}{2}$ and $g \simeq 2$. In which case

$$M = N_M \mu_B \tanh\left(\frac{\mu_B H}{k_B T} \right). \tag{15}$$

From Eq. (2) we have

$$N_M = \frac{4}{3\pi N(0) |u_M|^2} \frac{1}{\tau_c}. \tag{16}$$

$N(0)$ is known[121] because for a quasi-two-dimensional metal the density of states at the Fermi level is given by

$$N(0) = \frac{m_c}{2\pi\hbar^2}, \tag{17}$$

where m_c is the cyclotron mass. In the presence of interactions Luttinger's theorem[122] for a Fermi liquid ensures that[121]

$$N(0) = \frac{m^*}{2\pi\hbar^2}, \tag{18}$$

where m^* is the effective mass, regardless of the details of the band structure. It is known from Shubnikov–de Haas experiments[123] that, for the β or magnetic breakdown orbit $m^*/m_e = 6.4$ and so $N(0) = 14.9$ eV^{-1} unit cell^{-1}spin^{-1}.

A more difficult problem is estimating u_M. We can make an estimate because of our knowledge of the Mott-Hubbard state which is nearby in pressure/anion space. We estimate that u_M will be of the same order as JV where J is the exchange coupling in the Mott-Hubbard state and V is the volume occupied by a dimer and an anion. This is dimensionally correct and we know that in the Mott antiferromagnetic state there is one spin per dimer. It is estimated that $J \sim 40$ K (Ref. 124) and hence $|u_M| = 0.026$ eV Å^3. A less theory-laden estimate of J can be made from the fact that the Kondo effect is not observed in these materials. In the Kondo effect a minimum in the resistivity occurs at the Kondo temperature T_K, which is given by[126]

$$T_K = \frac{W}{k_B} \exp\left(-\frac{1}{2JN(0)} \right), \tag{19}$$

where W is the bandwidth. For κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, $W = 2(t_1 + t_2) \simeq 0.23$ eV, where t_1 and t_2 are the nearest-neighbor and next-nearest-neighbor hopping integrals, respectively,[121] and $N(0)$ is given by Eq. (18) with $m^*/m_e = 6.4$. That the Kondo effect is not observed implies that $T_K < T_c < T_{c0} < 12$ K from the fit in Figs. 3 and 4. This implies that $J < 155$ K and thus that $|u_m| < 0.4$ eV Å^3. However, while the Kondo temperature is defined for a single impurity, the Kondo minimum will not be observable unless there are a sufficiently large number of impurities (typically a few percent[126]).

Substituting Eq. (7) into Eq. (16) we find that

$$N_M = \frac{32 k_B}{3\pi^2 \hbar N(0) |u_M|^2} (T_{c0} - T_c). \tag{20}$$

For example, Su *et al.*[114] report a maximum variation in the critical temperature of $T_{c0} - T_c = 0.58$ K, which leads to, as a lower bound (based on $J \sim 155$ K), $N_M \gtrsim 0.03$ impurities per unit cell. For our best guess ($J \sim 40$ K) we find $N_M \gtrsim 0.50$ impurities per unit cell. This should be sufficient to observe a Kondo minimum and thus the Kondo effect places a limit on the number of impurities.

Substituting Eq. (20) into Eq. (15) we find that

$$\frac{M}{\mu_B} = \frac{32 k_B}{3\pi^2 \hbar N(0) |u_M|^2} (T_{c0} - T_c) \tanh\left(\frac{\mu_B H}{k_B T} \right). \tag{21}$$

Two studies of the variation in magnetization with cooling rate in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br have been conducted.[127,128] Both studies were primarily concerned with the weak field limit, but surprisingly even these results may tell us something about the presence of magnetic impurities. Taniguchi and Kanoda[128] measured $M(H)$ at $T = 7$ K. They found an interesting weak field dependence (presumably this is due to vortex dynamics as it disappears when the irreversibility line is reached, but we will not discuss this here). Above the irreversibility line they found that the change in M with cooling rate is only weakly dependant on H. (Results were reported up to $H = 1200$ Oe.) Based on the observed cooling rate dependence of T_c in this sample[129] we estimate that the variation in T_c between when the sample is cooled at 10 K/min and when the sample is cooled at 0.5 K/min is 0.25 K. This leads to the conclusion that the difference in the magnetization of the two samples due to the magnetic impurities (required in the *s*-wave scenario) would be 1.3×10^{-4} emu at $H = 1200$ Oe and $T = 7$ K (based on our lower bound from the Kondo effect, $J = 155$ K). This is well within the resolution of the experiment (in fact this contribution would dominate the observed magnetization) and *is not observed* (see Fig. 5). Thus the experiments of Taniguchi and Kanoda are inconsistent with the hypothesis that cooling rate induced disorder creates paramagnetic impurities. (However, it is possible that paramagnetic impurities are present in the sample and that there presence is screened by the superconducting state.) We therefore suggest that there is non-*s*-wave

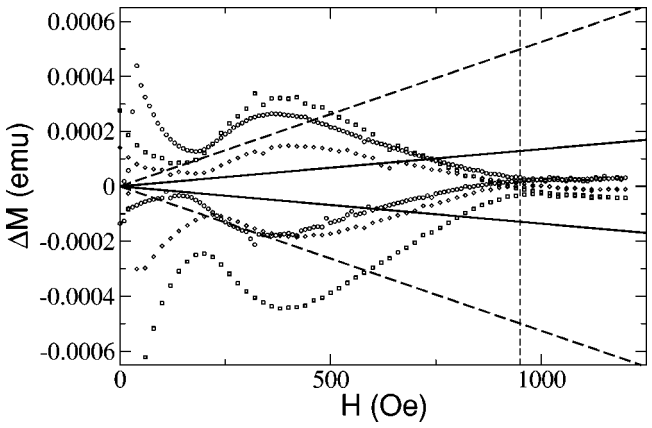

FIG. 5. The cooling rate dependence of the magnetization of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. We plot the difference in the magnetization of the same sample when it is cooled at 10 K/min and when it is cooled at 0.5 K/min (circles) measured by Taniguchi and Kanoda (Ref. 128). Also shown is the difference in the magnetization for the same sample when it had been annealed at 70 K for 12 h and when it was cooled at 0.5 K/min (diamonds) and the difference in magnetization between when the sample was annealed and when it was cooled at 10 K/min (squares). All sets of data were taken at $T=7$ K$<T_c$. The solid lines are the calculated lower bound on the change in the magnetization at $T=7$ K due to paramagnetic impurities which produce a 0.25 K change in T_c which is the estimated change in T_c between the sample cooled at 10 K/min and the sample cooled at 0.5 K/min based on the observed cooling rate dependence of this sample (Ref. 129). This lower bound is required to ensure the Kondo temperature $T_K<T_c$ and thus to be consistent with the fact that the Kondo effect is not observed in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The long dashed lines represent the predicted magnetization assuming that the interaction energy of the magnetic impurities is the same as the observed antiferromagnetic exchange interaction in the insulating phase of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (i.e., $J\sim 40$ K). The vertical dashed line indicates the irreversibility line at 7 K, $H_{\rm ir}(T=7{\rm K})$, as measured by Taniguchi and Kanoda (Ref. 128) in the same experiment. Thus we see that for $H<H_{\rm ir}(T=7$ K) (left of the dashed line) the nontrivial vortex dynamics of the system cause a complicated variation in the magnetization, which we do not discuss here. However, for $H>H_{\rm ir}(T=7$ K) (right of the dashed line) the measured difference in the magnetization is less than that required by the Brillouin function. Therefore these measurements suggest that no paramagnetic impurities are induced by varying the cooling rate of this sample. But this conclusion requires that the moments are not screened by supercurrents.

pairing in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and that varying the cooling rate induces nonmagnetic disorder which causes the variation in both T_c and ρ_0. Again we stress that because there are little data above the irreversibility line, $H_{\rm ir}$, and no data outside the superconducting state, further careful systematic experiments are required preferably in the normal state.

Two groups have investigated anomalies in heat capacity[130,131] and thermal expansion[132] at $T\sim 80$ K in κ-(BEDT-TTF)$_2X$ for $X=$Cu[N(CN)$_2$]Cl, (Refs. 131 and 132) Cu[N(CN)$_2$]Br (Refs. 130, 131, and 132) and Cu(NCS)$_2$ (Ref. 132). Both groups concluded that the anomalies are due to a transition in which disorder becomes frozen into the orientational degrees of freedom in the terminal ethylene groups of the BEDT-TTF molecules. This ethylene ordering transition provides a natural explanation for the observed cooling rate dependence of the residual resistivity of κ-(BEDT-TTF)$_2X$. However, one should note that such an ethylene ordering transition would result in intrinsically nonmagnetic impurities and is therefore strong evidence in support of our suggestion that the cooling rate induced disorder is nonmagnetic in nature.

Terminal ethylene group disorder in κ-(BEDT-TTF)$_2X$ is rather similar to the anion disorder observed in the Bechgaard salts. In both (TMTSF)$_2$ClO$_4$ and (TMTSF)$_2$RuO$_4$ the anions can occupy two inequivalent orientations. Fast cooling leads to partially disordered domains, the size of the domains has been shown to be proportional to the cooling rate.[133] As mentioned in Sec. II B, varying the cooling rate can lead to a reduction in T_c and even the complete suppression of superconductivity in favor of a spin density wave. Also note that the anion ordering temperature T_{AO} is highly dependent on which anion is considered. For $X=$ClO$_4$, $T_{AO}\sim 24$ K; for $X=$ReO$_4$, $T_{AO}\sim 170$ K; and for $X=$PF$_6$ no anion ordering transition is observed.[100] The nature of the anion order also differs for $X=$ClO$_4$ and $X=$ReO$_4$ (Ref. 100). A similar disordering transition is observed[134] in the organic conductors (DMET)$_2$BF$_4$ and (DMET)$_2$ClO$_4$.

Of the salts considered here, a variation in T_c with cooling rate had only been observed in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br to date. If our hypothesis that the variation in T_c with cooling rate is due to cooling rate induced disorder which in turn is due to the ethylene ordering transition in the terminal ethylene groups is correct then one would also expect a variation in T_c with cooling rate in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as the ethylene ordering transition has been observed in this compound.[132,135] An ethylene ordering transition has also been observed in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (Ref. 132). However, this compound only becomes superconducting under pressure and it is not known what effect pressure has on the disordered ethylene state. Clearly the dependence of T_c on cooling rate is in need of further investigation. It may be of interest to investigate the effect of pressure on the ethylene ordering transition, particularly with reference to κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and cooling rate dependence of the Néel temperature.

In light of the variation of T_c with cooling rate it is important that in experiments on the κ-(BEDT-TTF)$_2X$ salts the cooling rate is reported regardless of whether or not it is varied. Results for $T\lesssim 80$ K lose much of their significance if the cooling rate is not known.

Work by Taniguchi *et al.*[138,139] has raised the possibility of inhomogeneous phase coexistence between antiferromagnetism and superconductivity in deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. There is no evidence of phase coexistence in fully hydrogenated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br so phase coexistence can be ruled out as the cause of the suppression of T_c in the hydrogenated compound, which we consider here. Further varying the cooling rate

of deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl offers the possibility of studying the Mott transition in the presence of disorder with fine experimental control over the level of disorder in the sample and of varying the level of disorder within a single sample.

V. INTERLAYER TRANSPORT THEORY

The residual resistivity for interlayer transport in a layered Fermi liquid is given by (see, for example, Ref. 140)

$$\rho_0 = \frac{\pi\hbar^4}{2e^2 m^* c t_\perp^2}\frac{1}{\tau_t}, \tag{22}$$

where c is the interlayer spacing, m^* is the effective quasiparticle mass, and $t_\perp$ is the interlayer hopping integral. Thus the assumption that $\rho_0 \propto 1/\tau_t$ (13) is justified.

Substituting Eq. (22) into Eq. (7) we find that

$$T_c = T_{c0} - \frac{e^2 m^* c t_\perp^2}{4k_B\hbar^3}\rho_0. \tag{23}$$

Thus from our fit to the data of Su *et al.*[114] (shown in Fig. 4) we have, for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br,

$$T_{c0} = 11.7 \text{ K} \tag{24}$$

and

$$\frac{e^2 m^* c t_\perp^2}{4k_B\hbar^3} = 0.9 \ \Omega \text{ cm}. \tag{25}$$

Taking $m^* = 6.4m_e$ (Refs. 141 and 121) and $c = 30.016$ Å (Ref. 14) we have $t_\perp = 0.022$ meV. However, we note that m^* was determined for the β sheet (which is the magnetic breakdown orbit) only whereas here we are considering an effective one band model. Nevertheless, this value is in excellent agreement with an independent determination of $t_\perp$ from angular-dependent magnetoresistance (AMRO) experiments. Although $t_\perp$ has not been measured experimentally in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, for κ-(BEDT-TTF)$_2$I$_3$ $t_\perp \approx 0.016$ meV (Ref. 142) and for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ $t_\perp \approx 0.04$ meV (Ref. 143).

For β-(BEDT-TTF)$_2$IBr$_2$ (see Fig. 1) we find that $T_{c0} = 3.0$ K. Tokumoto *et al.*[103] reported that the room-temperature resistivity of their samples was $\rho(295) = (5.0 \pm 2.5) \times 10^{-2}$ Ω cm. Therefore

$$\frac{e^2 m^* c t_\perp^2}{4k_B\hbar^3} = 40 \pm 20 \ \Omega \text{ cm}. \tag{26}$$

Taking $m^* = 4.2m_e$ (Ref. 14) and $c = 15.291$ Å (Ref. 14) we have $t_\perp = 0.26 \pm 0.07$ meV. Note that this is an order of magnitude larger than for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. However, this value is also in agreement with previous estimates from de Haas–van Alphen experiments. Wosnitza *et al.*[144] showed that for β-(BEDT-TTF)$_2$IBr$_2$, $t_\perp/E_F \approx 1/280$ they also found that $k_F \sim 3.46 \times 10^9$ m^{-1}. Therefore taking $m^* = 4.2m_e$ (Ref. 14) again and assuming a cylindrical Fermi surface

$$E_F \cong \frac{\hbar^2 k_F^2}{2m^*} \tag{27}$$

one finds that $t_\perp \approx 0.35$ meV in excellent agreement with our result.

The agreement between $t_\perp$ calculated from our fits via Eq. (22) and the values found from AMRO experiments for both β-(BEDT-TTF)$_2$IBr$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is further evidence that in these compounds T_c is suppressed by the AG mechanism and not by weak localization.

It has recently been shown[105] that the observed variation of T_c and ρ_0 for alloy β-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(IBr$_2$)$_x$ for small x predicted by Eq. (23) is consistent with the observations of Tokumoto *et al.*[103] Note that this theory has no free parameters once the T_{c0} (this work and Forro *et al.*[112]) and $t_\perp$ (AMRO experiments[142]) have been determined.

The agreement between our calculated values of $t_\perp$ and those measured in AMRO experiments indicates that if there is an $s+n$ state then the s-wave component $[\cos(\varphi))\Delta_s]$ is small (see Sec. II). [Or more strictly that α is small, cf. Eq. (12).] It therefore appears unlikely that the layered organics are $s+n$ superconductors.

VI. DISCUSSION

This study of the effects of disorder on the layered organic crystals β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$ has shown that disorder has the potential to differentiate between s-wave and non-s-wave pairing states. But, more experiments are needed. This is largely because none of the experiments that we have discussed in this paper were designed to study the pairing symmetry. In this section we will explore what the unresolved issues are and how they could be resolved.

A. Sample variation

Perhaps the simplest test for unconventional superconductivity is to study the variations in the superconducting critical temperature reported in the literature. Crystal growers go to great lengths to avoid the inclusion of magnetic impurities, but the inclusion of nonmagnetic impurities[145] is harder to avoid. For example, the first reports of superconductivity in Sr_2RuO_4, which is widely considered to have an unconventional (triplet) pairing symmetry, indicated that $T_c = 0.93$ K (Ref. 146). However, sample quality was rapidly improved and it is now believed that the maximum critical temperature $T_{c0} = 1.5$ K (Ref. 91) has been achieved. Thus, for Sr_2RuO_4, T_c has increased by over 50% since the first report of superconductivity. In contrast, consider MgB_2. The first report[147] of superconductivity quoted $T_c = 39$ K. No significant increase in T_c has been reported thus far. This is evidence for s-wave pairing in MgB_2. Further, doping MgB_2 with U does not significantly alter T_c (doping with 1 wt% U reduces T_c by $<0.5\%$, Ref. 148). This is in agreement with the emerg-

ing consensus that MgB_2 is a strong coupling *s*-wave superconductor.[149] (For a fuller discussion of the effects of disorder in MgB_2 see Ref. 150.)

The initial reports of superconductivity in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br quote $T_c = 10.8$ K (Ref. 151). While we have shown that $T_{c0} = 11.7$ K. κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ also shows wide variation in T_c from sample to sample. Some authors have reported T_c as low as 8.7 K (Ref. 152), while other studies have found that $T_c = 9.3$ K (Ref. 118). One complication arises from the variety of definitions used to determine T_c. Taking a resistivity measurement as an example, the T_c can be defined in a variety of ways: (i) the temperature at which ρ first begins to deviate from the Fermi liquid form [$\rho(T) = \rho_0 + AT^2$], (ii) the highest temperature at which $\rho(T) = 0$, or (iii) the midpoint of the transition, i.e., the temperature at which the $\rho(T)$ is 50% of the Fermi liquid value. For example, definitions (i) and (ii) give a difference of ~ 1 K for the data reported by Stalcup *et al.*[115] about the value $T_c = 11.6$ K [defined by method (iii), which we use throughout this paper]. The large variations in T_c noted above (8% for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and 7% for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$) are probably too large to be explained by subtle variations in the definition of T_c and are therefore unlikely to occur for *s*-wave pairing although this is far from conclusive.

β-(BEDT-TTF)$_2$I$_3$ shows a strong variation in T_c. In the β_H phase[14] Kahlich *et al.*[153] reported that T_c varied between 4.5 K and 7 K depending on which sample they measured. This represents a 36% variation in T_c. This is also suggestive of non-*s*-wave pairing.

The wide variation in T_c from sample to sample is something that great care should be taken over in experiments designed to study the isotope effect. In particular, any such experiments need to demonstrate that crystals that are nominally identical do indeed have a highly reproducible T_c. If this is not possible then the T_c variation within nominally identical samples needs to be carefully accounted for. For example, by studying the sample dependence of the residual resistivity across a range of nominally identical samples and using this to calibrate the impurity dependence of the various isotopes.

B. Measurement of the scattering time

Disorder would be a much more powerful probe if there existed a method by which the scattering time could be measured directly. The most obvious techniques for this are Shubnikov-de Haas and de Haas-van Alphen experiments. These quantum oscillation experiments measure the quasiparticle lifetime via the Dingle temperature T_D. However, the lifetime determined by quantum oscillation experiments, τ_q, is not the same as the transport lifetime τ_t (Refs. 154 and 155). Even in the best experiments on elemental metals, it is not at all unusual for τ_t to be 10 or even 100 times larger than τ_q (Ref. 156). In particular, T_D and hence τ_q are known to be very sensitive to the mechanical state of the sample. A slight deformation caused by, for example, handling the sample can lead to dramatic increase in T_D (decrease in τ_q), whilst hardly affecting the electrical resistivity ($\rho_0 \propto 1/\tau_t$). Given the large compressibility of the layered organic superconductors τ_q is unlikely to be the same as τ_t.

In its immediate location a dislocation acts just like a line of point defects and thus contributes equally to both transport and quantum oscillation experiments. However, the long-range strain field produced by a dislocation only produces very small angle scattering (as the electron wavelength is smaller than the characteristic length scale of the dislocations). Therefore the long-range strain field contributes negligibly to the transport lifetime but can strongly suppress τ_q even at relatively low dislocation densities.

A sample which is nominally a single crystal is in fact made up of a large number of grains. One can think of this mosaic structure of grains as a certain pattern of dislocations. In this way it is clear that mosaic structure causes highly anisotropic scattering and thus leads to the suppression of τ_q.

Many previous authors have pointed out the difference in the transport and quantum lifetimes. However, Hill[157] noted a similar difference between the lifetime observed in cyclotron resonance experiments, τ_{cr}, and the quantum lifetime. It is therefore interesting to compare the lifetimes from cyclotron resonance and quantum oscillation experiments with the transport lifetime determined from the linearized AG equation (7) and the value of T_{c0} found from the fit to experiment, τ_t^{AG} (see Table I).

We see that $\tau_t^{AG} \sim \tau_{cr}$ across a broad range of (BEDT-TTF)$_2X$ salts, while τ_q is consistently an order of magnitude smaller. This suggests that scattering events are not the dominant contribution to T_D (cf., Singleton *et al.*[170]). It presents the intriguing possibility that cyclotron resonance experiments could be used to probe the quasiparticle lifetime and thus directly compare the experimental T_c with the predictions of the AG equation. Indeed cyclotron resonances have already been observed[166,168] in Sr_2RuO_4. The observed cyclotron resonance lifetime is larger than the observed lifetime in de Haas–van Alphen experiments, but this may be partly explained by the much higher T_c of the sample used for the cyclotron resonance experiments. Excellent agreement is found between the measured cyclotron lifetime and the lifetime calculated from the AG formula. Clearly, a systematic study of how the cyclotron resonance lifetime (and indeed the quantum oscillation lifetime) varies with T_c is needed. Sr_2RuO_4 would be an ideal material for such experiments as the AG formula is seen to be obeyed,[91] and good quality quantum oscillation[167] and cyclotron resonance experiments[166] can be performed. Alternatively the AG behavior of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br would make it an excellent material for such an experiment. This is particularly elegant as the cooling rate can be used to vary the disorder and hence the scattering lifetime, so the experiment could be performed on a single sample. Measurements of the variation of the Dingle temperature with cooling rate have already been made.[115]

Kartsovnik, Grigoriev, and co-workers[158,171] have also investigated the relationship between the quasiparticle lifetimes caused by solely microscopic scattering events, and the lifetime extracted from the Dingle temperature which also

TABLE I. Comparison of the transport/Abrikosov-Gorkov, cyclotron resonance and quantum oscillation quasiparticle lifetimes (τ_t^{AG}, τ_{cr}, and τ_q, respectively). As τ is clearly a highly sample dependent property this table is not intended to report universal results but is indicative of general trends. NS indicates a non-superconducting compound for which τ_t^{AG} cannot be determined. The reported τ_t^{AG} is based on the samples used for the experiments discussed in this paper (or in Ref. 155 in the case of $ZrZn_2$). We have abbreviated BEDT-TTF to ET in this table.

Material	τ_t^{AG} (ps)	τ_{cr} (ps)	τ_q (ps)
κ-$(ET)_2Cu[N(CN)_2]Br$	2.5–20	?	0.5–0.6 (Ref. 115)
β-$(ET)_2IBr_2$	0.6–1.8	?	1.5 (Ref. 158)
β-$(ET)_2I_3$	?	?	2.4 (Ref. 159)
θ-$(ET)_2I_3$	?	15–36 (Ref. 160)	0.6–1.5 (Ref. 161)
α-$(ET)_2KHg(NCS)_4$	?[a]	15 (Ref. 163)	0.3–0.5 (Ref. 164)
α-$(ET)_2NH_4Hg(NCS)_4$	?	40 (Ref. 157)	2 (Ref. 165)
$(ET)_2Br(DIA)$	NS	4.6–5.5 (Ref. 160)	1.7 (Ref. 160)
$(ET)_3Cl(DFBIB)$	NS	5.6 (Ref. 160)	1.7 (Ref. 160)
Sr_2RuO_4	6–38[b]	10–40 (Ref. 168)	1.8 (Ref. 167)
$ZrZn_2$	~6 (Ref. 155)	?	0.3 (Ref. 169)

[a] α-$(ET)_2KHg(NCS)_4$ is only superconducting under pressure (Ref. 162).

[b] The sample measured by Hill *et al.* (Ref. 166) had $T_c = 1.44$ K [for which the AG formula gives $\tau_t^{AG} = 37.9$ ps based on $T_{c0} = 1.52$ K, the value found from fitting the AG formula to the data of Mackenzie *et al.* (Ref. 91)]. $\tau_t^{AG} = 6.25$ ps based on $T_c = 1$ K, the value reported in the de Haas–van Alphen experiments (Ref. 167).

contains the effects of macroscopic inhomogeneities. They have shown that the slow oscillations observed in quantum oscillation experiments on quasi-two-dimensional metals are damped by a modified Dingle temperature T_D^*, which is not affected by macroscopic inhomogeneities. For experiments performed on β-$(BEDT\text{-}TTF)_2IBr_2$ they found an order of magnitude difference between τ_q (1.5 ps) and the lifetime derived from T_D^*, τ_q^* (8.1 ps).

The Fermi velocity v_F for both the β and κ polymorphs is typically $v_F \sim 10^5$ ms^{-1} (see Sec. V and Ref. 172). And we have shown here that a quasiparticle lifetime of the order $\tau_t^{AG} \sim 0.1$ ps is required to completely suppress superconductivity. Thus the mean free path, $l = v_F \tau_t$, is typically $l \gtrsim 10$ nm (cf. Ref. 26). The interlayer coherence length $\xi_\parallel$ is typically a few nm (cf. Ref. 14). Thus these materials are in the clean limit even when superconductivity is completely suppressed by disorder. This is further confirmation that the AG mechanism is responsible for the suppression of superconductivity in these materials.

We will conclude this section by outlining a series of experiments that could determine if the disorder in the layered organic superconductors is due to scattering from localized moments or potential scattering. These experiments therefore have the potential to rule out *s*-wave pairing.

C. Identification of the pairing symmetry

Comparatively little attention has been focused on the pairing symmetry of β-$(BEDT\text{-}TTF)_2X$ so we will start by considering this crystal structure. All of the methods of creating disorder considered in this paper (namely, fast electron irradiation, alloying anions and accidental disorder from the fabrication process) should be revisited and studied in more depth. Both Figs. 1 and 2 need more data points. Therefore it is most important that the entire AG is mapped out. In particular, it is important to observe the complete suppression of superconductivity by very small amounts of disorder that is a unique feature of the AG formalism. Careful observation of the entire AG curve is required to rule out other mechanisms for the suppression of T_c such as weak localization, interband scattering, changes in the pairing interaction, or the macroscopic coexistence of superconducting and nonsuperconducting phases. All of these mechanisms for the suppression of T_c produce markedly different relationships between T_c and ρ_0 and thus would be ruled out by the observation of the entire AG curve and in particular the complete suppression of T_c by moderate amounts of disorder which is not caused by any of the other mechanisms for T_c suppression. Forro *et al.*[112] did not measure the resistivity of their irradiated samples. It is important to know the resistivity for several reasons: (i) it allows for easy comparison with other techniques, in particular it allows a consistent definition of T_c to be used, (ii) it provides a check on the estimation of the number of defects produced, and (iii) it allows for the calculation of $t_\perp$ and thus for a further check that AG theory is indeed relevant. All of these methods should also be applied to κ-$(BEDT\text{-}TTF)_2X$.

The next step is to discover whether any of the methods for producing impurities create magnetic scatterers. One way to do this is to measure the magnetization as Taniguchi and Kanoda[128] have for cooling rate induced disorder in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$. However, this experiment should be repeated in the metallic state. This suggests that paramagnetic impurities are not induced by varying the cooling rate of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$. Here we will consider alternative experiments which could be used to search for magnetic impurities. We will describe these ex-

periments in the context of cooling rate induced disorder in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. However, the generalization of these experiments to the other methods of producing disorder is straightforward. Cooling rate induced disorder experiments are particularly elegant as the level of disorder can be controlled within a single sample. This reduces systematic errors, for example, by far the largest source of error in measuring ρ_0 comes from measuring the samples dimensions, such errors cancel in cooling rate induced disorder experiments.

Muon spin relaxation experiments are capable of detecting localized magnetic moments.[173] If local moments are produced, then the muon spin relaxation rate would vary as a function of cooling rate. Clearly the muon spin relaxation rate is changed by the superconducting state. As T_c and presumably H_{c2} are changed by the cooling rate it is important that these experiments be done in the nonsuperconducting state, either above T_c or above H_{c2}. As the ethylene ordering transition occurs at $T \sim 80$ K and $T_c \sim 10$ K any local moments should be well formed several kelvin above T_c.

Nuclear quadrupole resonance experiments have been used to observe the formation of local moments in $La_{2-x}Sr_xCuO_4$ for $x=0.06$ (Ref. 174). As perviously discussed, NMR measurements have observed localized moments induced by Zn impurities in YBCO.[94] Therefore studying the change in $1/T_1$ with cooling rate in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br could determine whether or not local moments are formed. The change in $1/T_1$ as a function of cooling rate has been measured in 98% deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. No change in $1/T_1$ was observed until below 30 K, in particular, $1/T_1$ is independent of cooling rate near 80 K where the ethylene ordering transition occurs.[175] However, fast cooling of deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br drives the ground state from superconductivity to an antiferromagnetic Mott insulator[138,139] (which causes the observed difference in $1/T_1$ below 30 K). Therefore this observation does not rule out the possibility of local moments in hydrogenated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Wang *et al.*[176] carried out an electron spin resonance (ESR) experiment on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Wang *et al.* saw no signal attributable to Cu(II) species at any temperature although they do not comment on other sources of magnetic impurities. Therefore it is reasonable to hope that further ESR studies may shed some light on the issue of magnetic impurities.

The techniques, outlined here, for using intrinsically nonmagnetic disorder to probe the superconducting state are clearly more general than the context of β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$ that we have examined here. Disorder has already been used to study Sr_2RuO_4 (Ref. 91) (although we should note that no experiments have been performed to rule out magnetic impurity formation in this material). Similar results for UPt_3 (Refs. 98 and 99) appear to have gone largely unnoticed. Clearly more careful analysis of this work is required. These methods could also be extended to other heavy fermion superconductors. There are several other quasi-two-dimensional organic superconductors [such as λ-(BETS)$_2X$, θ-(BEDT-TTF)$_2X$, and β''-(BEDT-TTF)$_2X$] which may be unconventional superconductors. Disorder would appear to be a powerful tool for the investigation of the superconducting state in these materials.

But, the study of disorder, perhaps, is most powerful when used to identify *s*-wave pairing. An excellent example from the recent past is the high-temperature superconductor MgB_2, which appears to be a phonon mediated *s*-wave superconductor.[149] This could be confirmed by careful study of the effects of disorder and showing that disorder can be introduced with only a small change in T_c (cf. Ref. 150). This could also be applied to other superconductors which are suspected of being *s* wave, in particular, superconductors suspected of having anisotropic *s*-wave order parameters, such as the borocarbides.[177]

VII. CONCLUSIONS

We have considered the effect of impurities and disorder on the superconducting critical temperature in β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$. We have shown that various sources of disorder (alloying anions,[103] fast electron irradiation,[112] disorder accidentally produced during fabrication,[104] and cooling rate induced disorder[114,115]) lead to a suppression of T_c that is well described by the Abrikosov-Gorkov formula. This is confirmed not only by the excellent fit to a theory with only two free parameters, but also by the excellent agreement between the value of the interlayer hopping integral $t_\perp$, calculated from this fit and the value of $t_\perp$ found from AMRO experiments. This makes a pairing state with a superposition of *s*-wave and non-*s*-wave components extremely unlikely. Although such an $s+n$ state cannot be strictly ruled out, the *s*-wave part of the wave function must be very small and the coherence between the *s*-wave and non-*s*-wave parts of the wave function must be completely rigid [$\alpha(\varphi(\tau))=\alpha \ll 1$]. The agreement between the measured and calculated values of $t_\perp$ effectively leaves T_{c0} as the only free parameter in the theory. In practice, one has very little choice over the value of T_{c0}, so the agreement with experiment is found from an essentially parameter free theory. The AG formula describes the suppression of T_c by magnetic impurities in singlet superconductors, including *s*-wave superconductors. However, T_c is suppressed in exactly the same way by nonmagnetic impurities in a non-*s*-wave superconductor. We therefore have shown that there are only two scenarios consistent with the current state of experimental knowledge. We summarize these scenarios below. The task is now to discover whether the impurities are magnetic or nonmagnetic.

Scenario 1: d-wave pairing. If the disorder induced by all of the four methods considered in this paper is, as seems most likely, nonmagnetic, then the pairing state cannot be *s* wave. Triplet pairing is ruled out by the combination of the three experiments discussed in Sec. I.[20,55,58] Therefore we know that the angular momentum, *l*, of the Cooper pairs is even. If the disorder does turn out to be nonmagnetic then this implies that $l \geqslant 2$. In which case Occam's razor suggests that *d*-wave pairing is realized in both β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$.

Scenario 2: an atypical mechanism for the formation of

local magnetic moments. Given the proximity of β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$, to the Mott-Hubbard antiferromagnetic state in anion/pressure space, it is possible that disorder induces local magnetic moments. Further Taniguchi *et al.*[138,139] have suggested that varying the cooling rate can lead to the macroscopic coexistence of superconductivity in deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Although there is no evidence for anything but a spatially uniform superconducting state in the hydrogenated compound,[138,139] which we have considered here, these experiments would not detect isolated magnetic impurities. On the other hand, we have shown here that the work of Taniguchi and Kanoda[128] is inconsistent with the theory that disorder modulates the local electronic structure and thus moves single sites or small clusters of sites into a state, analogous to the Mott-Hubbard insulating state with localized electrons, which can act as magnetic point scatterers. However, only a little data were reported in the relevant magnetic field range so further work is needed to rigourously test this scenario.

We have suggested experiments to differentiate between these scenarios. Such experiments would either discover an atypical mechanism for the production of localized magnetic moments or determine that the superconducting order parameter is *d* wave in β-(BEDT-TTF)$_2X$ and κ-(BEDT-TTF)$_2X$.

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*Electronic address: powell@physics.uq.edu.au

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