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Spin fluctuations and the pseudogap in organic superconductors

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We show that there are strong similarities in the spin-lattice relaxation of nonmagnetic organic charge-transfer salts and that these similarities can be understood in terms of spin fluctuations. Further, we show that, in all of the κ-phase organic superconductors for which there is nuclear-magnetic-resonance data, the energy scale for the spin fluctuations coincides with the energy scale for the pseudogap. This suggests that the pseudogap is caused by short-range spin correlations. In the weakly frustrated metals κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (under pressure) the pseudogap opens at the same temperature as coherence emerges in the (intralayer) transport. We argue that this is because the spin correlations are cutoff by the loss of intralayer coherence at high temperatures. We discuss what might happen to these two energy scales at high pressures, where the electronic correlations are weaker. In these weakly frustrated materials the data is well described by the chemical pressure hypothesis (that anion substitution is equivalent to hydrostatic pressure). However, we find important differences in the metallic state of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, which is highly frustrated and displays a spin liquid-insulating phase. We also show that the characteristic temperature scale of the spin fluctuations in (TMTSF)$_2$ClO$_4$ is the same as superconducting critical temperature, which may be evidence that spin fluctuations mediate the superconductivity in the Bechgaard salts.

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I. INTRODUCTION

Strongly correlated superconductors such as the cuprates,[1] heavy fermions,[2] and organic charge-transfer salts,[3] share many phenomena not found in weakly correlated metals and superconductors. Examples of such effects include superconductivity in close proximity to the Mott transition,[1,3] metallic states not described by Landau's theory of Fermi liquids,[1,3] small superfluid stiffnesses in the superconducting state,[4,5] and pseudogap phenomena.[1,6–9] Important questions about these materials include: do these phenomena have a common origin and how similar are the phenomena observed in the different families of materials?

One common feature of the materials discussed above is that they display strong antiferromagnetic spin fluctuations.[9–12] This can be seen in the spin-lattice relaxation rate, $1/T_1$, which is very different from those found in weakly correlated materials (where $1/T_1 \propto T$ cf. Ref. 13). In many cuprates, heavy fermion materials, and organic superconductors $1/T_1T$ is strongly temperature dependent: as the temperature is lowered from room temperature $1/T_1T$ increases until it reaches a maximum at a temperature we label T_{NMR}. Below T_{NMR} a suppression of spectral weight is manifest in $1/T_1T$ due to the opening of a superconducting gap or a pseudogap. Throughout this paper, when we refer to the pseudogap regime of the organic superconductors we mean to indicate the temperatures between T_{NMR} and T_c, the superconducting critical temperature, where there is a loss of spectral weight evident in the NMR, but no bulk superconductivity.

It has recently been shown that in the high-temperature regime (i.e., where there is neither a pseudogap nor superconductivity) simple scaling relations, based on a phenomenological two-fluid picture, describe the spin-lattice relaxation rate, $1/T_1$, in a large number of high-temperature superconductors[14,15] and heavy fermion materials.[15–18] Further, it has been shown that this two-fluid model can describe many other experiments on the heavy fermion materials.[18,19] Therefore, given the similarities between these materials and the organic charge-transfer salts,[3,20] it is natural to ask whether similar scaling behaviors describe the behavior of the organic charge-transfer salts. In this paper we focus on this question in the context of the κ-(ET)$_2X$ family of organic charge-transfer salts, however, we also make some comments on (TMTSF)$_2$ClO$_4$.

An important difference between the cuprates and heavy fermion materials, and the κ-(ET)$_2X$ salts is that the κ-phase organics there is a single half-filled band, whereas the other materials are multiband and/or doped. The Mott transition in κ-(ET)$_2X$, where X is a monovalent anion, can be driven by applying a hydrostatic pressure or varying the anion, which is often referred to as chemical pressure. It is believed that this corresponds to increasing the ratio of t/U in the single band Hubbard model description of these systems (cf. Fig. 1).[3,22]

The behavior of the spin degrees of freedom in κ-(ET)$_2$Cu$_2$(CN)$_3$ are particularly interesting. Whereas the insulating phases of other κ-(ET)$_2X$ salts order antiferromagnetically, the insulating phase of κ-(ET)$_2$Cu$_2$(CN)$_3$ shows no signs of magnetic order to the lowest temperatures investigated ($\sim$32 mK).[23] As the exchange energy extracted[23,24] from fits to the high-temperature bulk susceptibility is $\sim$250 K this has been taken as evidence that κ-(ET)$_2$Cu$_2$(CN)$_3$ is a spin liquid.[3,23] κ-(ET)$_2$Cu$_2$(CN)$_3$ suffers from stronger geometrical frustration than other κ-(ET)$_2X$ salts: tight-binding calculations[25] indicate that the band structure of κ-(ET)$_2$Cu$_2$(CN)$_3$ is close to that of an equilateral triangular lattice (i.e., $t \simeq t'$; cf. Fig. 1), whereas other κ-(ET)$_2X$ materials are described by an anisotropic tri-

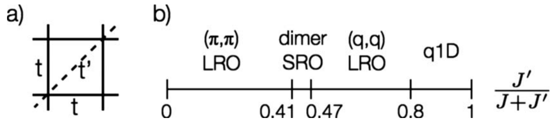

FIG. 1. (a) The anisotropic triangular lattice is believed to provide the basic description of the electronic structure of the κ-(ET)$_2X$ salts. This model has a tight-binding structure where each site represents a dimer, (ET)$_2$. There is a hopping integral, t, along the sides of a square and another, t', along one diagonal. Further, there is a strong Coulomb repulsion, U, if two electrons are placed on the same site. For a review see Ref. 3. For X=Cu$_2$(CN)$_3$ $t' \simeq t$ and hence, in the Mott insulating phase, $J \simeq J'$, as $J \simeq 4t^2/U$ and $J' \simeq 4t'^2/U$. For the other X discussed in this paper $t > t'$ and thus the geometrical frustration is significantly reduced. (b) Phase diagram of the Heisenberg model of the anisotropic triangular lattice from series-expansion calculations (Ref. 21), which shows the sensitivity of this model to variations in J'/J. The following abbreviations are used in the figure: long-range order (LRO), short-range order (SRO), and qausi-one dimensional (q1D). (π,π) is the wave vector associated with Néel order and (q,q) is the wave vector for spiral ordering, which varies continuously from $q=\pi$ to $q=\pi/2$ as J'/J increases.

angular lattice $(t > t')$.[3] More importantly, fits of high-temperature series expansions to the bulk susceptibility show that $J \simeq J'$ in κ-(ET)$_2$Cu$_2$(CN)$_3$ but that $J > J'$ in κ-(ET)$_2$Cu[N(CN)$_2$]Cl.[23,24] A pressure of greater than ~0.3 GPa drives the ground state of κ-(ET)$_2$Cu$_2$(CN)$_3$ from a spin liquid to a superconductor. To date very little is known experimentally about this superconducting state. It has recently been argued[26,27] that the frustration will drive changes in the spin fluctuations which will lead to a superconducting state with broken time-reversal symmetry, i.e., a $d+id$ (or more strictly A_1+iA_2) state. Therefore it is important to understand the nature of the spin fluctuations in κ-(ET)$_2$Cu$_2$(CN)$_3$ in both the insulating and the metallic phases.

In order to investigate the spin fluctuations we present, below, a theoretical analysis of previously published NMR experiments. In Sec. II we show that although NMR experiments on the organic charge-transfer salts are rather similar to those on the cuprates and heavy fermion materials there are some important differences. A detailed analysis shows that, in the κ-phase organics, the pseudogap energy scale is set by the spin fluctuations and in (TMTSF)$_2$ClO$_4$ the superconducting gap is the same size as the characteristic spin fluctuations. In Sec. III we compare the pseudogap energy scale with the temperature at which coherence emerges in the intralayer transport. We find that they are the same to within experimental error and propose a phenomenological interpretation of this. In Sec. IV we discuss the behavior of the organic charge-transfer salts under hydrostatic pressures and raise some important issues about the pseudogap that have not yet been addressed experimentally. Finally, we draw our conclusions in Sec. V.

II. HIGH-TEMPERATURE SPIN-LATTICE RELAXATION

A. Scaling and the two-fluid model

In the two-fluid model proposed by Pines *et al.*[14–18] the spin-lattice relaxation rate is given by

$$\frac{T_1T}{(T_1T)_{\mathrm{NMR}}} = \phi + \kappa T_{\mathrm{NMR}} \frac{T}{T_{\mathrm{NMR}}}, \tag{1}$$

where κ and ϕ are material dependent constants, the latter measuring the proximity to a putative quantum critical point, and T_{NMR} is the temperature where there is a maximum in $1/T_1T$. The two fluids are proposed to be a Fermi-liquid component and a spin-liquid component.

We plot previously published[28–34] NMR data for both insulating and metallic phases of organic charge-transfer salts in this "scaling" form in Fig. 2. For the metallic salts it can be seen that, while there is a broad trend in the data, the data

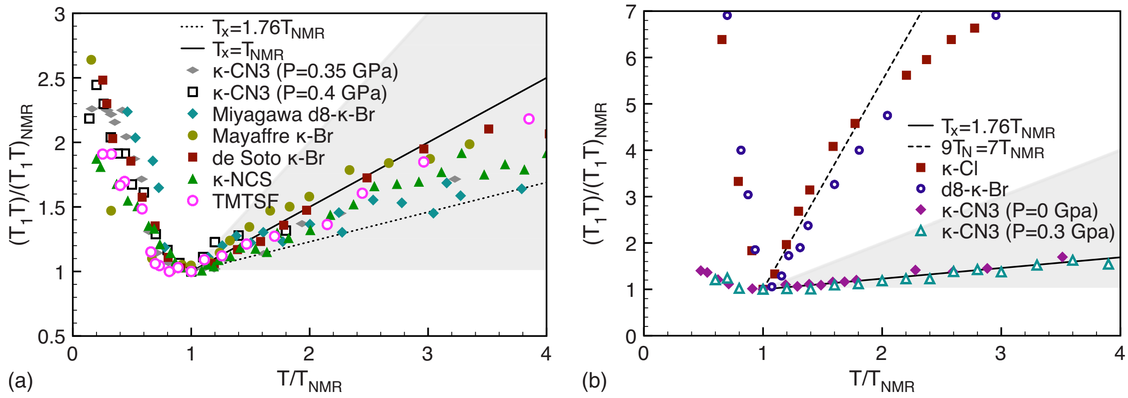

FIG. 2. (Color online) Rescaled plots of the temperature dependence of $1/T_1T$ for (a) metallic and (b) insulating organic charge-transfer salts. While there is a clear trend in the data of the nonmagnetic materials, they do not collapse onto a single curve as the data for the cuprates and heavy fermion materials do (Refs. 14–18) This suggests that a two-fluid description is not required for the organic superconductors. However, this data is in good agreement with the prediction of the spin-fluctuation model [Eqs. (5) and (7)]. Equation (5) predicts that the data will lie in the gray shaded regions, which represent the extrema of possible values of T_x/T_{NMR}. The lines show the predictions for particular values of T_x/T_{NMR} in Eq. (5) or T_N/T_{NMR} in Eq. (7) as marked. The abbreviations used in the figure and the sources of the data are, κ-CN3 is κ-(ET)$_2$Cu$_2$(CN)$_3$ (Ref. 28), κ-Br is κ-(ET)$_2$Cu[N(CN)$_2$]Br (Refs. 29 and 30), d8-κ-Br is κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br (Ref. 31), κ-NCS is κ-(ET)$_2$Cu(NCS)$_2$ (Ref. 32), TMTSF is (TMTSF)$_2$ClO$_4$ (Ref. 33), and κ-Cl is κ-(ET)$_2$Cu[N(CN)$_2$]Cl (Ref. 34).

do not collapse onto a single curve as they do in the cuprates and the heavy fermion materials.[14–18] This suggests that two-fluid model may not be relevant to the organic charge-transfer salts but also that there is something to be learnt from Fig. 2. For the insulating states the spin-lattice relaxation is very different for those compounds that order magnetically, κ-(ET)$_2$Cu[N(CN)$_2$]Cl and fully dueterated κ-(ET)$_2$Cu[N(CN)$_2$]Br {henceforth κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br}, from that in the spin liquid κ-(ET)$_2$Cu$_2$(CN)$_3$. Indeed the data for κ-(ET)$_2$Cu$_2$(CN)$_3$ is remarkably similar to the data for the metallic salts.

Important evidence that a two-fluid model is required in the heavy fermion materials comes from comparing the Knight shift, K_s, to the bulk susceptibility χ. According to the two-fluid model

$$\chi = f(T)\chi_{FL} + [1 - f(T)]\chi_{SL}, \tag{2}$$

where $f(T)$ is the fraction of electrons in the Fermi liquid, χ_{FL} is the susceptibility of the Fermi liquid, which is basically independent of temperature, and χ_{SL} is the susceptibility of the spin liquid. Further, the two-fluid model predicts that

$$K_s = Af(T)\chi_{FL} + B[1 - f(T)]\chi_{SL}, \tag{3}$$

where A is the hyperfine coupling constant between the itinerant electrons and the probe nuclei and B is hyperfine coupling of the spin liquid to the nuclei. Hence, if $A \neq B$ then K_s will not be proportional to χ. Systematic differences between temperature dependence of K_s and that of χ are indeed found in the heavy fermion materials.[18] In the high-temperature ($T > T_{\mathrm{NMR}}$) regime $K_s \propto \chi$ in κ-(ET)$_2$Cu[N(CN)$_2$]Br (Refs. 29 and 32), κ-(ET)$_2$Cu(NCS)$_2$ (Ref. 35), and κ-(ET)$_2$Cu$_2$(CN)$_3$ (Refs. 28 and 36). We are not aware of any reports of K_s in either κ-(ET)$_2$Cu[N(CN)$_2$]Cl or κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br, or data for K_s at high temperatures in (TMTSF)$_2$ClO$_4$. There is only a single band that plays an important role in the organics, so one might reasonably argue that $A = B$. Nevertheless the comparison of K_s and χ does not force one to consider a two-fluid model and we now move on to discuss another possible explanation of the data in Fig. 2.

B. Spin fluctuations

Moriya's[10] theory of spin fluctuations in nearly antiferromagnetic metals, particularly in the phenomenological form pioneered by Millis *et al.*,[11] has been shown to give good agreement with NMR experiments in the cuprates,[10,11] heavy fermion materials,[10,15] and the organics.[9] Therefore, it is natural to ask whether this can explain the similarities between the rescaled data for the various materials in Fig. 2. The simplest assumption[10,11] for the temperature dependence of the spin-correlation length is $\xi(T)/\xi(T_x) = \sqrt{2T_x/(T+T_x)}$. Here the temperature dependence of the spin fluctuations is controlled by a single parameter, T_x, thus one finds[10,11] that, in the limit of strong spin fluctuations,

$$\frac{1}{T_1T} = \frac{C^2/(T_1T)_0}{(T/T_x+1)^2 + 4\pi^2 C(T/T_x+1)}, \tag{4}$$

where $C = 2[\xi(T_x)/a]^2$, a is the lattice spacing and $1/(T_1T)_0$ is a material specific constant. For $C \gg (T/T_x)+1$, i.e., if the magnetic correlation length is large and the temperature is low, one can "rescale" this to T_{NMR} so that material specific part cancels and we find that

$$\frac{T_1T}{(T_1T)_{\mathrm{NMR}}} = \frac{T_{\mathrm{NMR}}}{T_{\mathrm{NMR}}+T_x}\left(\frac{T}{T_{\mathrm{NMR}}}\right) + \frac{T_x}{T_{\mathrm{NMR}}+T_x}. \tag{5}$$

Thus the spin-fluctuation model predicts that, for nearly antiferromagnetic metals, $T_1T/(T_1T)_{\mathrm{NMR}}$ is linear in T/T_{NMR}. This is in good agreement with the data for the metallic materials in Fig. 2(a). Further, the spin-fluctuation theory for a nearly antiferromagnetic metal constrains the gradient of the data to lie between 0 ($T_{\mathrm{NMR}}=0$, for a material with neither a pseudogap nor superconductivity) and 1 ($T_x=0$, for material with no spin fluctuations), cf. Eq. (5). Indeed, we find that $T_{\mathrm{NMR}} \sim T_x$ for all of the metallic organic charge-transfer salts. This last result is an important conclusion, as it suggests that the pseudogap energy scale is set by that of the spin fluctuations.

Note that in (TMTSF)$_2$ClO$_4$ the maximum in the $1/T_1T$ occurs at the superconducting critical temperature, i.e., $T_c = T_{\mathrm{NMR}} \approx T_x$. This suggests that spin fluctuations may determine the superconducting critical temperature and thus the spin fluctuations may mediate the superconductivity in (TMTSF)$_2$ClO$_4$. This is consistent with the unconventional superconducting state observed in this material.[37]

For materials that order antiferromagnetically, one expects, within mean-field theory (whence the correlation length critical exponent $\nu = 1/2$), that $\xi(T)/\xi_0 = \sqrt{2T_N/(T-T_N)}$, where T_N is the Néel temperature. Thus

$$\frac{1}{T_1T} = \frac{C_0^2/(T_1T)_0}{(T/T_N-1)^2 + 4\pi^2 C_0(T/T_N-1)}, \tag{6}$$

where $C_0 = 2[\xi_0/a]^2$ and a is the lattice spacing. Rescaling we find that

$$\frac{T_1T}{(T_1T)_{\mathrm{NMR}}} = \frac{T_{\mathrm{NMR}}}{T_{\mathrm{NMR}}-T_N}\left(\frac{T}{T_{\mathrm{NMR}}}\right) - \frac{T_N}{T_{\mathrm{NMR}}-T_N}. \tag{7}$$

Note that the maximum in $1/T_1T$ does not occur at T_N due to short-range correlations. Rather, $1/T_1T$ has a infinite tangent at T_N, as does the bulk susceptibility.[38] Therefore on very general grounds[38] one expects $T_N < T_{\mathrm{NMR}}$. A sharp decline in $1/T_1T$ below T_{NMR} is observed in the data for κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br (Ref. 29) and κ-(ET)$_2$Cu[N(CN)$_2$]Cl (Ref. 34), consistent with these expectations. Thus Eq. (7) provides an excellent description of the data for κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br and κ-(ET)$_2$Cu[N(CN)$_2$]Cl [shown in Fig. 2(b)]. Note, in particular, that Eq. (7), correctly, predicts a steep gradient and a negative intercept in agreement with the data and in contrast to Eq. (5) and the data for the nonmagnetic salts.

The rescaled NMR relaxation rate in metallic κ-(ET)$_2$Cu$_2$(CN)$_3$ (data at 0.35 and 0.4 GPa) is remarkable similar to that in κ-(ET)$_2$Cu[N(CN)$_2$]Br and

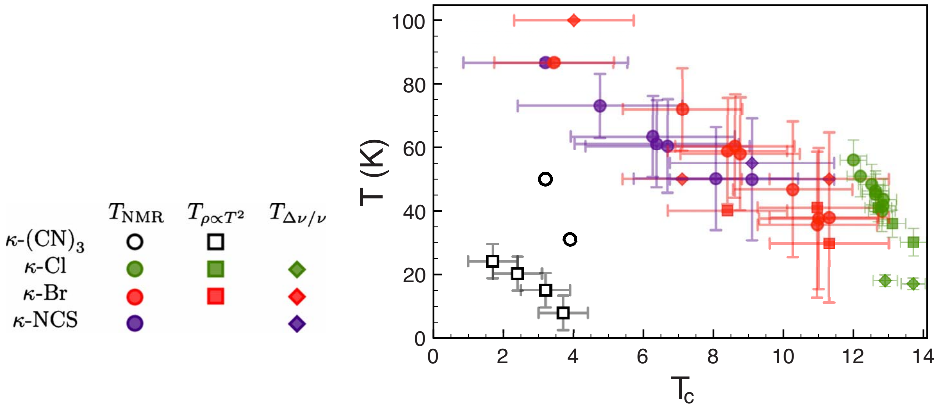

FIG. 3. (Color online) Variation in experimental energy scales in κ-(ET)$_2X$ with hydrostatic pressure. As, in each material, the superconducting transition temperature decreases monotonically with the applied pressure the superconducting transition temperature serves to parameterize the proximity to the Mott transition (high T_cs closest to the Mott transition). The fact that T_{NMR}, $T_{\rho\propto T^2}$, and $T_{\Delta v/v}$ show such similar behaviors in κ-(ET)$_2$Cu[N(CN)$_2$]Cl, κ-(ET)$_2$Cu[N(CN)$_2$]Br, and κ-(ET)$_2$Cu(NCS)$_2$ is a success for the chemical pressure hypothesis. The chemical pressure hypothesis is seen to fail dramatically in the case of κ-(ET)$_2$Cu$_2$(CN)$_3$, which shows a markedly different behavior to the other salts. Further in κ-(ET)$_2$Cu$_2$(CN)$_3$ T_{NMR} does not coincide with $T_{\rho\propto T^2}$. We stress that the large error bars in the figure result predominately from the errors measuring the hydrostatic pressure which appears parametrically when comparing multiple different experiments. Data is taken from Refs. 28, 29, 32, and 39–46.

κ-(ET)$_2$Cu(NCS)$_2$, which are much more weakly frustrated. This can be understood because $1/T_1T$ depends only the integral over the Brillouin zone of the dynamic susceptibility. The spin-fluctuation theory, which gives a good description of all of the data, only assumes that the dynamic susceptibility has a peak *somewhere* in the Brillouin zone and that the peak is away from the origin. The predicted scaled T_1T is independent of the location of the peak. Thus this data does not indicate which $\mathbf{q}$ has the strongest magnetic fluctuations but does show that the magnetic fluctuations are just as strong in metallic κ-(ET)$_2$Cu$_2$(CN)$_3$ as they are in the more weakly frustrated κ-(ET)$_2X$ salts.

The rescaled NMR relaxation rate in insulating κ-(ET)$_2$Cu$_2$(CN)$_3$ (data at 0 and 0.3 GPa) is very different from that in the insulating phases of κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br and κ-(ET)$_2$Cu[N(CN)$_2$]Cl. Instead the data for the insulating phase of κ-(ET)$_2$Cu$_2$(CN)$_3$ is well described by Eq. (5), which describes the data in the metallic materials considered above. Thus it appears that the central difference between the scaled NMR relaxation rates is not whether the material is insulating or metallic but whether the material orders magnetically or not. We note that both data sets fit remarkably well to the prediction of Eq. (5) for $T_x=1.76T_{\mathrm{NMR}}$ in the insulating phases of κ-(ET)$_2$Cu$_2$(CN)$_3$. This brings to mind the weak-coupling BCS form formula for the pairing temperature in a superconductor. However, at this stage we have no evidence that this is any more than a numerical coincidence.

III. PSEUDOGAP AND COHERENCE

We now turn our attention to how the pseudogap energy scale, T_{NMR}, is related to the other energy scales in the κ-phase organic charge-transfer salts. Figure 3 shows that, for the weakly frustrated salts {κ-(ET)$_2$Cu[N(CN)$_2$]Cl, κ-(ET)$_2$Cu[N(CN)$_2$]Br, and κ-(ET)$_2$Cu(NCS)$_2$} T_{NMR} coincides with the temperature below which the resistivity varies quadratically, $T_{\rho\propto T^2}$, and the temperature at which a broad, deep minimum is observed in the ultrasonic velocity, $T_{\Delta v/v}$. Further, when these quantities are plotted against the superconducting transition temperature, T_c, all three materials show the same trend.

Figure 3 represents a significant quantitative success for the chemical pressure hypothesis, which holds that the major effect of changing the anions is to alter the size of the unit cell, and therefore, control the strength of the electronic correlations, which underpins a great deal of the thinking on the organic charge-transfer salts. However, the chemical pressure hypothesis clearly fails for κ-(ET)$_2$Cu$_2$(CN)$_3$, which does not share the same scaling of temperature scales as the other salts investigated. Further, T_{NMR} is clearly rather different from $T_{\rho\propto T^2}$ in κ-(ET)$_2$Cu$_2$(CN)$_3$. This suggests that the metallic state of κ-(ET)$_2$Cu$_2$(CN)$_3$ is rather different from the metallic states of the more weakly frustrated κ-phase organic charge-transfer salts, consistent with the idea that the spin fluctuations in this material differ from those in its less frustrated cousins in important ways.[26,27] Nevertheless the observation of a quadratic temperature dependence of the resistivity at temperatures slightly above T_c shows that charge transport is coherent in the metallic state of κ-(ET)$_2$Cu$_2$(CN)$_3$ under pressure.

The observation that the crossover to a quadratic temperature dependence of the resistivity approximately coincides with the minimum in the ultrasonic attenuation has been understood[39,47] in terms of dynamical mean-field theory (DMFT). DMFT predicts a crossover from a Fermi liquid at low temperatures to a "bad metal" (characterized by the absence of quasiparticles and the Drude peak, and a resistivity that exceeds the Mott-Ioffe-Regal limit) as the temperature is increased above a coherence temperature, T_{coh}. Thus it is believed that $T_{\mathrm{coh}}\simeq T_{\rho\propto T^2}\simeq T_{\Delta v/v}$. However, while DMFT gives an adequate description of the nuclear-spin-relaxation rate above $T_{\mathrm{coh}}\simeq T_{\mathrm{NMR}}$, below T_{coh} DMFT predicts a Fermi liquid and thus a constant $1/T_1T$; this is clearly *not* what is observed.[9] This shows that DMFT does not capture all of the relevant physics below T_{coh}.[13] It is also interesting to note that DMFT does describe the observed behavior of probes of charge degrees of freedom, such as the resistivity, and only fails for probes of the spin degrees of freedom, such as $1/T_1T$. As DMFT is a purely local theory a reasonable hypothesis is that the relevant physics, not described by DMFT, involves short-range spin correlations. Further, the enhanced Korringa ratios observed[9] at temperatures slightly above T_c suggest that antiferromagnetic correlations remain important in the coherent transport regime.[13,48]

The spin degrees of freedom in the pseudogap regime of the κ-phase organics behave in much the same way as the spin degrees of freedom in the pseudogap regime of the underdoped cuprates. There has been significant debate as to whether, and if so how, the pseudogap in the cuprates is related to the other exotic phenomena seen in the normal state, such as the linear temperature dependence of the resistivity. In this context it is interesting to note that in the region of the phase diagram of the organics where the pseudogap is found, the resistivity varies quadratically with temperature[39] and the magnitude of the coefficient of the quadratic term in the resistivity is as expected from Fermi-liquid theory given the observed effective mass.[49] Further, clear evidence of quasiparticles is seen via quantum oscillation experiments.[50] Therefore, in κ-(ET)$_2$Cu[N(CN)$_2$]Br, κ-(d8)-(ET)$_2$Cu[N(CN)$_2$]Br, and κ-(ET)$_2$Cu(NCS)$_2$ the loss of spectral weight in the pseudogap is not associated with non-Fermi-liquid behavior.

An important difference between the cuprates and the organics is that the organics are half filled whereas the cuprates are more strongly correlated, doped systems. In this context it is worth noting that a linear resistivity has recently been reported in an organic charge-transfer salt with an anion layer that has a lattice constant that is incommensurate with the lattice constant of the organic layer.[51] The authors argued that this nonstoichiometric organic charge-transfer salt is effectively doped away from half filling.

IV. HIGH PRESSURES

An important question in understanding the phenomenology of the κ-(ET)$_2X$ salts is: do the two energy scales, T_{coh} and T_{NMR} remain equal as pressure is increased and we move further from the Mott transition? This question is difficult to answer at present because there is little experimental data for high pressures (including high chemical pressure, i.e., materials with low T_c's). There is however tantalizing evidence that something rather interesting happens to the superconducting state at high pressures.[5] In particular, while the materials near the Mott transition have a superfluid stiffness, n_s, within a factor of 2 or so of the prediction of BCS theory, at high pressures the superfluid penetration depth, λ, increases as $T_c \propto 1/\lambda^3$ (Ref. 52). With some materials having superfluid stiffnesses ($n_s \propto 1/\lambda^2$) that are an order of magnitude smaller than the prediction of BCS theory.[5,52]

We are only aware of one NMR experiment at high pressures in these materials. Reference 29 reports data for κ-(ET)$_2$Cu[N(CN)$_2$]Br at 3 kbar (which leads to $T_c \simeq 3.8$ K) (Ref. 40) and 4 kbar ($T_c \simeq 1.4$ K). At these pressures strong spin fluctuations are not observed and the $1/T_1T$ looks quite conventional. Yet for the 3 kbar data there is small but noticeable decrease in $1/T_1T$ below ~ 20 K. Is this the last vestige of the pseudogap? If so, it suggests that at high pressures the pseudogap and the coherent intralayer transport energy scales are different. Either way more experiments are clearly required to understand where the pseudogap vanishes.

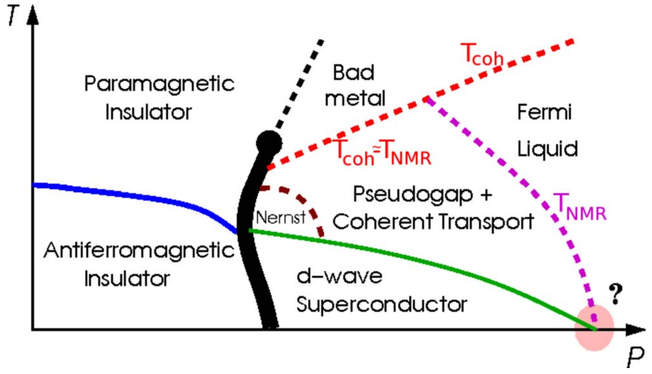

FIG. 4. (Color online) Schematic phase diagram for weakly frustrated κ-(ET)$_2X$ as a function of temperature and pressure. Thin solid lines represent second-order phase transitions, the thick solid line is the first-order transition line which ends at a critical point shown as a filled circle and dashed lines indicate crossovers. The pseudogap regime is much more complicated than a renormalized Fermi liquid that has been previously thought to characterize the paramagnetic metallic phase at low temperatures. It shows a coherent transport character with long-lived quasiparticles, marked by T^2 resistivity behavior (Ref. 39) with the coefficient of the quadratic term as expected from Fermi-liquid theory given the observed effective mass (Ref. 49), and magnetic quantum oscillations (Ref. 50). But, a loss of spectral weight is clearly observed in the NMR data. There are not sufficient data at this moment to determine what happens to the pseudogap regime at high pressures; this uncertainty is represented by the shaded area with the question mark.

On the basis of the above discussion we propose that a number of new features should be included in the phase diagram of these materials, which we sketch in Fig. 4. We stress that this phase diagram is relevant to the weakly frustrated materials for which the chemical pressure hypothesis holds and therefore does not include κ-(ET)$_2$Cu$_2$(CN)$_3$ which would necessitate an additional axis to include the effects of frustration. We have included the Nernst region where Nam *et al.*[7] have observed a large Nernst effect above T_c in κ-(ET)$_2$Cu[N(CN)$_2$]Br at ambient pressure, which they find to be absent in κ-(ET)$_2$Cu(NCS)$_2$ at ambient pressure. Note that we have drawn the T_{NMR} and the T_c lines both suppressed to zero at the same pressure. This is deliberately provocative. As we have stressed above there is insufficient experimental data to determine the relative order in which the superconductivity and the pseudogap disappear as pressure is increased.

The issue of where the superconductivity and pseudogap vanish is related to an ongoing debate in the cuprates. A recent review of a wide range of experimental data in a wide variety of cuprates suggested that the pseudogap and superconductivity both vanish at the same critical doping.[53] Similarly, more detailed experimental and theoretical studies of the organics in the vicinity of the pressure above which superconductivity vanishes might give important insights into how the pseudogap is related to superconductivity. The possibility of a quantum critical point somewhere in the vicinity of the pressure where the superconducting critical temperature goes to zero may have important consequences for the observation that the materials with the lowest superconducting critical temperatures have extremely small superfluid stiffnesses and are very different from BCS superconductors.[5,52]

Finally, we sketch an explanation of the observed phase diagram (Fig. 4). We have noted above that DMFT describes the competition between the insulating, bad metal, and Fermi-liquid phases.[39,47] But DMFT fails to predict either the pseudogap or the unconventional superconductivity, which suggests that these effects involve nonlocal physics. However, it has recently been argued that the resonating valence-bond (RVB) theory can describe the superconducting state of the quasi-two-dimensional organic charge-transfer salts,[27,54] this theory also predicts a pseudogap with approximately the right energy scale. Therefore, we propose that DMFT captures the crossover from incoherent to coherent charge transport but is insufficient to describe the behavior in the coherent regime because short-range spin correlations play a significant role here. The simplest theory that can capture the low-temperature physics of is the RVB theory. However, the RVB theory does not capture the loss of coherence as the temperature is raised, which we argue leads to a cutoff of the pseudogap phenomena. If this speculation is correct, the challenge is then to produce a single theory capable of describing all of the physics, including the large Nernst effect above T_c in κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ (Ref. 7), which neither the DMFT nor the RVB theory predicts. Therefore cellular DMFT calculations, which can describe both short-range spin fluctuations and the loss of intralayer coherence, may have an important role to play in understanding the organic superconductors.

V. CONCLUSIONS

We have argued that a two-fluid description is not required for the organic charge-transfer salts. It is interesting to speculate why this is. One possibility is that the difference between the organic salts discussed above and many other strongly correlated superconductors is that the organics are stoichiometric while, for example, the metallic cuprates are doped systems and the heavy fermions show a subtle hybridization between almost localized states and conduction electrons. Therefore it would be interesting to measure the nuclear-relaxation rate in the recently discovered nonstoichometric organic superconductors.

We have seen that there are strong similarities in the rescaled spin-lattice relaxation across the nonmagnetic organic charge-transfer salts. These similarities can be understood in terms of spin fluctuations. Further, our analysis suggests that the energy scale for the spin fluctuations may set the energy scale for the pseudogap in the organic charge-transfer salts.

In the weakly frustrated metals [all the metals studied bar κ-$(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$] the pseudogap opens at the same temperature as coherence emerges in the (intralayer) transport. We argued that this is because spin correlations, which are responsible for the pseudogap, are cutoff by the loss of intralayer coherence at high temperatures. In these weakly frustrated materials the data can be compared across materials quite reliably, consistent with the chemical pressure hypothesis. In contrast the metallic state of κ-$(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$, which is highly frustrated, was shown to be rather different from those of the other materials.

Finally, we have also shown that in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ the characteristic temperature scale of the spin fluctuations is the same as T_c. This suggests that spin fluctuations may mediate the superconductivity in the Bechgaard salts.

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