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Antiferromagnetic spin fluctuations in the metallic phase of quasi-two-dimensional organic superconductors

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We give a quantitative analysis of the previously published nuclear magnetic resonance (NMR) experiments in the κ-$(ET)_2X$ family of organic charge-transfer salts. The temperature dependence of the nuclear-spin relaxation rate $1/T_1$, the Knight shift K_s, and the Korringa ratio $\mathcal{K}$ is compared to the predictions of the phenomenological spin-fluctuation model of Moriya and Millis, Monien, and Pines (M-MMP), that has been used extensively to quantify antiferromagnetic spin fluctuations in the cuprates. For temperatures above $T_{\mathrm{NMR}} \simeq 50$ K, the model gives a good quantitative description of the data in the metallic phases of several κ-$(ET)_2X$ materials. These materials display antiferromagnetic correlation lengths which increase with decreasing temperature and grow to several lattice constants by T_{NMR}. It is shown that the fact that the dimensionless Korringa ratio is much larger than unity is inconsistent with a broad class of theoretical models (such as dynamical mean-field theory) which neglects spatial correlations and/or vertex corrections. For materials close to the Mott insulating phase the nuclear-spin relaxation rate, the Knight shift, and the Korringa ratio all decrease significantly with decreasing temperature below T_{NMR}. This cannot be described by the M-MMP model and the most natural explanation is that a pseudogap, similar to that observed in the underdoped cuprate superconductors, opens up in the density of states below T_{NMR}. Such a pseudogap has recently been predicted to occur in the dimerized organic charge-transfer salts materials by the resonating valence bond (RVB) theory. We propose specific experiments on organic superconductors to elucidate these issues. For example, measurements to see if high magnetic fields or high pressures can be used to close the pseudogap would be extremely valuable.

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I. INTRODUCTION

In the past twenty years a diverse range of new strongly correlated electron materials with exotic electronic and magnetic properties have been synthesized. Examples include high-temperature cuprate superconductors,[1] manganites with colossal magnetoresistance,[2] cerium oxide catalysts,[3] sodium cobaltates,[4] ruthenates,[5,6] heavy fermion materials,[7] and superconducting organic charge-transfer salts.[8] Many of these materials exhibit a subtle competition between diverse phases: paramagnetic, superconducting, insulating, and the different types of order associated with charge, spin, orbital, and lattice degrees of freedom. These different phases can be explored by varying experimental control parameters such as temperature, pressure, magnetic field, and chemical composition. Although chemically and structurally diverse, the properties of these materials are determined by some common features; such as strong interactions between the electrons, reduced dimensionality associated with a layered crystal structure, large quantum fluctuations, and competing interactions. Many of these materials are characterized by large antiferromagnetic spin fluctuations. Nuclear magnetic resonance (NMR) spectroscopy has proven to be a powerful probe of local spin dynamics in many strongly correlated electron materials.[9–12] The focus of this paper is on understanding what information about spin fluctuations can be extracted from NMR experiments on the organic charge-transfer salts.

The systems which are the subject of the current study are the organic charge-transfer salts based on electron donor molecules BEDT-TTF (ET), in particular the family κ-$(ET)_2X$ (where κ indicates a particular polymorph[13]). Similar physics occurs in the other dimerized polymorphs, such as the β, β', and λ phases.[8] These materials display a wide variety of unconventional behaviors[8] including antiferromagnetic and spin liquid insulating states, unconventional superconductivity, and the metallic phase which we focus on in this paper. They also share highly anisotropic crystal and band structures. However, for various sociological and historical reasons, the κ salts have been far more extensively studied, and because we intend, in this paper, to make detailed comparisons with experimental data, we limit our study to κ phase salts. This begs the question, do similar phenomena to those described below occur in the β, β', or λ salts? We would suggest that the answer is probably *yes* but this remains an inviting experimental question.

The metallic phase of κ-$(ET)_2X$ is very different from a conventional metallic phase. Many features of the metallic phase agree well with the predictions of dynamical mean-field theory (DMFT)[14] which describes the crossover from a "bad metal" at high temperatures to a Fermi liquid as the temperature is lowered.[15–17] This crossover from incoherent to coherent intralayer[18] transport has been observed in a number of experiments such as resistivity,[17] thermopower,[15,19] and ultrasonic attenuation.[20,21] The existence of coherent quasiparticles is also apparent from the observed magnetic quantum oscillations at low temperatures in κ-$(ET)_2X$.[22–24] However, NMR experiments (see Figs. 1 and 2) on the metallic phase on κ-$(ET)_2X$ are not consistent with a Fermi-liquid description. The nuclear-spin relaxation rate per unit temperature, $1/T_1T$, is larger than the Korringa form predicted from Fermi-liquid theory. As the temperature

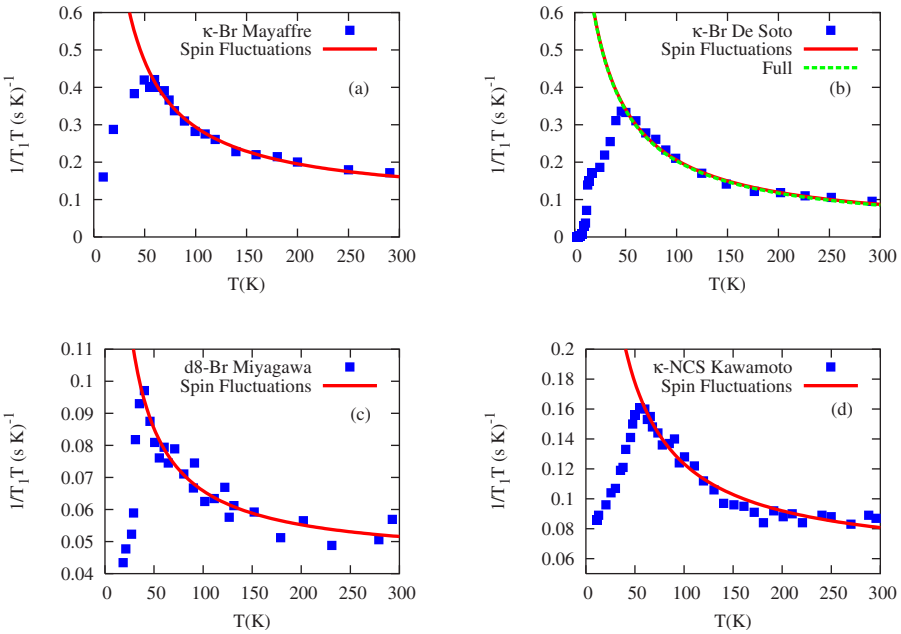

FIG. 1. (Color online) Comparison of the measured nuclear-spin relaxation rate per unit temperature, $1/T_1T$, with the predictions of the spin-fluctuation model for various organic charge-transfer salts. Panel (a) shows data for κ-$(ET)_2Cu[N(CN)_2]Br$ measured by Mayaffre *et al.* (Ref. 25). Panel (b) shows data for κ-$(ET)_2Cu[N(CN)_2]Br$ measured by De Soto *et al.* (Ref. 26). Panel (c) shows data for $\kappa(d8)$-$(ET)_2Cu[N(CN)_2]Br$ measured by Miyagawa *et al.* (Ref. 48). Panel (d) shows data for a κ-$(ET)_2Cu(NCS)_2$ powder sample measured by Kawamoto *et al.* (Ref. 49). The $1/T_1T$ data are weakly temperature dependent at high temperatures, have a maximum at $T_{NMR}\sim 50$ K, and drop abruptly below $T_{NMR}\sim 50$ K, contrary to what one would expect for a Fermi liquid in which $1/T_1T$ is constant. The remarkable similarities of these data result from the quantitative and qualitative similarity of the antiferromagnetic spin fluctuations in the metallic phases of these materials. The parameters that produce the best fits (solid lines) to Eq. (11c) are tabulated in Table I. The spin-fluctuation model gives a good fit to the experimental data between $T_{NMR}\sim 50$ and room temperature which suggests strong spin fluctuations in the metallic states of κ-$(ET)_2Cu[N(CN)_2]Br$, $\kappa(d8)$-$(ET)_2Cu[N(CN)_2]Br$, and κ-$(ET)_2Cu(NCS)_2$. However, below T_{NMR} the spin-fluctuation model does not describe the data well, indicating that some other physics dominates over the spin-fluctuation physics. In each figure the solid line is obtained from the approximate form for $1/T_1T$ given by Eq. (13). To check that this approximation is reasonable, we also plot $1/T_1T$ without any approximation, given by Eq. (11a), as a dashed line in panel (b). The full and dashed lines cannot be distinguished until well below T_{NMR} and so we concluded that the approximation is excellent in the relevant regime. Note that the analysis on $1/T_1T$ cannot differentiate between antiferromagnetic and ferromagnetic spin fluctuations (see Sec. II A 2), but the Korringa ratio strongly differentiates between these two cases and indicates that the fluctuations are antiferromagnetic (see Fig. 2). The nomenclature κ-Br, $d8$–Br, and κ-NCS is used as shorthand for κ-$(ET)_2Cu[N(CN)_2]Br$, $\kappa(d8)$-$(ET)_2Cu[N(CN)_2]Br$, and κ-$(ET)_2Cu(NCS)_2$, respectively, in the figure keys.

is lowered $1/T_1T$ reaches a maximum; we label this temperature T_{NMR} (the exact value of T_{NMR} varies with the anion X, but typically, $T_{NMR}\sim 50$ K, see Fig. 1). $1/T_1T$ decreases rapidly as the temperature is lowered below T_{NMR} (see Fig. 1).[12,25,26] The Knight shift also drops rapidly around T_{NMR}.[26] This is clearly in contrast to the Korringa-like behavior one would expect for a Fermi liquid in which $1/T_1T$ and K_s are constant for $T\ll T_F$, the Fermi temperature. A similar non-Fermi-liquid temperature dependence of $1/T_1T$ and K_s is observed in the cuprates.[27,28] It has been argued that the large enhancement of the measured $1/T_1T$ in cuprates is associated with the growth of antiferromagnetic spin fluctuation within the CuO_2 planes as the temperature is lowered.[29,30] The large decrease observed in $1/T_1T$ and K_s measurements for underdoped cuprates[27] at temperatures well above T_c is suggestive of a depletion of the density of states (DOS) at the Fermi level which might be expected if a pseudogap opens at T_{NMR}.

A quantitative description of spin fluctuations in the metallic phase of κ-$(ET)_2X$ has not been given previously. However, the importance of spin fluctuations for the superconducting κ-$(ET)_2X$ has been pointed out by several groups.[8,31–36] Since superconductivity arises from an instability of the metallic phase, it is important to understand the strength of the spin fluctuations in the metallic phase.

We use the phenomenological antiferromagnetic spin fluctuation model which was first introduced by Moriya in his self-consistent renormalization (SCR) theory[29] and then applied by Millis, Monien, and Pines (MMP)[30] to cuprates, to examine the role of spin fluctuations in the metallic phase of κ-$(ET)_2X$. We fit the spin-fluctuation model to the nuclear-spin relaxation rate per unit temperature $1/T_1T$, Knight shift K_s, and Korringa ratio $\mathcal{K}$ data. We find that the large enhancements measured in $1/T_1T$ and $\mathcal{K}$ above T_{NMR} are the result of large antiferromagnetic spin fluctuations (see Figs. 1 and 2). The antiferromagnetic correlation length increases as temperature decreases and the relevant correlation length is found to be 2.8 ± 1.8 lattice spacings at $T=T_{NMR}=50$ K. The model produces a reasonable agreement with experimental data down to $T\sim 50$ K. The spin-fluctuation model predicts a monotonically increasing $1/T_1T$ with decreasing temperature while the measured $1/T_1T$ below 50 K is suppressed but

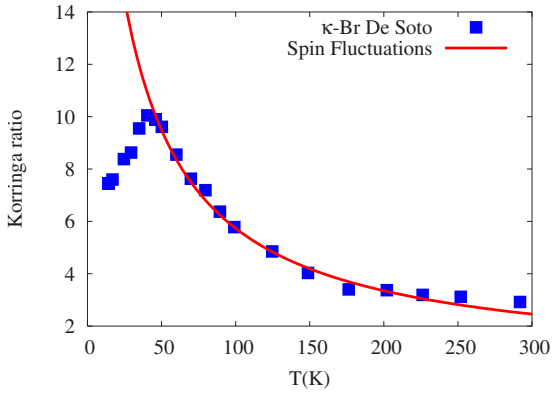

FIG. 2. (Color online) Comparison of the Korringa ratio $\mathcal{K} \propto 1/T_1TK_s^2$ of κ-$(ET)_2Cu[N(CN)_2]Br$ measured by De Soto *et al.* (Ref. 26) with the prediction of the antiferromagnetic spin-fluctuation model. The best fit to Eq. (15) is indicated by the solid line. The Korringa ratio is larger than 1 which indicates that the spin fluctuations are antiferromagnetic ($\mathcal{K}<1$ for ferromagnetic fluctuations; see Sec. II A 2). The antiferromagnetic correlation length is found to be 2.8 ± 1.8 lattice spacings at $T=50$ K. Below $T=50$ K the Korringa ratio is suppressed, and the spin-fluctuation model does not explain this behavior. This is a clear indication that different physics is at play below 50 K.

never saturates to a constant value. This is contrary to what is expected for a Fermi liquid where $1/T_1T$ is constant. This indicates that the metallic phase of κ-$(ET)_2X$ is richer than a renormalized Fermi liquid as has been previously thought to describe the low-temperature metallic state.

The structure of the paper is as follows. In Sec. II we introduce the temperature dependence of the nuclear-spin relaxation rate, Knight shift, and Korringa ratio and describe how they probe the dynamic susceptibility. We calculate these properties in a number of approximations and contrast the results. In Sec. III we demonstrate that the spin-fluctuation model provides reasonable fits to the existing experimental results for κ-$(ET)_2X$ above T_{NMR} and discuss its limitations when applied to those materials. In Sec. IV we discuss the unresolved issues and suggest different experiments to understand those issues. Finally, we give our conclusions in Sec. V.

II. SPIN LATTICE RELAXATION RATE, KNIGHT SHIFT, AND KORRINGA RATIO

In this section we discuss the temperature dependence of the nuclear-spin lattice relaxation rate $1/T_1$, Knight shift K_s, Korringa ratio $\mathcal{K}$, and their dependence on the dynamic susceptibility $\chi(\mathbf{q},\omega)=\chi'(\mathbf{q},\omega)+i\chi''(\mathbf{q},\omega)$. The general expressions for $1/T_1$, K_s, and $\mathcal{K}$ are given by[37]

$$\frac{1}{T_1} = \lim_{\omega\to 0}\frac{2k_BT}{\gamma_e^2\hbar^4}\sum_{\mathbf{q}}|A(\mathbf{q})|^2\frac{\chi''(\mathbf{q},\omega)}{\omega}, \tag{1a}$$

$$K_s = \frac{|A(\mathbf{0})|\chi'(\mathbf{0},0)}{\gamma_e\gamma_N\hbar^2}, \tag{1b}$$

and

$$\mathcal{K} = \frac{\hbar}{4\pi k_B}\left(\frac{\gamma_e}{\gamma_N}\right)^2\frac{1}{T_1TK_s^2}, \tag{1c}$$

where $A(\mathbf{q})$ is the hyperfine coupling between the nuclear and electron spins, and γ_N (γ_e) is the nuclear (electronic) gyromagnetic ratio. For simplicity we will consider a momentum independent hyperfine coupling $|A|$ in what follows. Note that Eqs. (1a)–(1c) show that this is an approximation for T_1 but that it is not an approximation at all for K_s. This is because K_s only probes the long-wavelength physics and hence only depends on $A(\mathbf{0})$, the hyperfine coupling at $\mathbf{q}=\mathbf{0}$.

The calculation of the quantities in Eqs. (1a)–(1c) boils down to determining the appropriate form of the dynamic susceptibility. Below we discuss, in some detail, the dynamic susceptibility within the spin-fluctuation model and calculate $1/T_1T$, K_s, and $\mathcal{K}$. The results from dynamical mean-field DMFT will also be discussed for comparison.

A. Spin-fluctuation model

The dynamic susceptibility in this model is given by[29,30]

$$\chi(\mathbf{q},\omega) = \chi_{LW}(\omega) + \chi_{AF}(\mathbf{q},\omega), \tag{2}$$

where $\chi_{LW}(\omega)$ is the dynamic susceptibility in the long wavelength regime and $\chi_{AF}(\mathbf{q},\omega)$ is a contribution to the dynamic susceptibility which is peaked at some wave vector $\mathbf{Q}$. These susceptibilities take the form

$$\chi_{LW}(\omega) = \frac{\bar{\chi}_0(T)}{1-i\omega/\Gamma(T)},$$

$$\chi_{AF}(\mathbf{q},\omega) = \frac{\chi_Q(T)}{1+\xi(T)^2|\mathbf{q}-\mathbf{Q}|^2-i\omega/\omega_{SF}(T)}, \tag{3}$$

where $\bar{\chi}_0(T)$ [$\chi_Q(T)$] is the static spin susceptibility at $\mathbf{q}=\mathbf{0}$ [$\mathbf{Q}$], $\Gamma(T)$ [$\omega_{SF}(T)$] is the characteristic spin fluctuation energy which represents damping in the system near $\mathbf{q}=\mathbf{0}$ [$\mathbf{Q}$], and $\xi(T)$ is the temperature-dependent correlation length. Hence the real and imaginary parts of the dynamic susceptibility can then be written as

$$\chi'(\mathbf{q},0) = \bar{\chi}_0(T)\left[1+\frac{\chi_Q(T)}{\bar{\chi}_0(T)}\frac{1}{(1+\xi(T)^2|\mathbf{q}-\mathbf{Q}|^2)^2}\right],$$

$$\chi''(\mathbf{q},\omega) = \frac{\omega\bar{\chi}_0(T)}{\Gamma}\left[1+\frac{\chi_Q(T)\Gamma}{\bar{\chi}_0(T)\omega_{SF}(T)}\frac{1}{(1+\xi(T)^2|\mathbf{q}-\mathbf{Q}|^2)^2}\right]. \tag{4}$$

Note that the above form of $\chi_{LW}(\omega)$ is the appropriate form for a Fermi liquid. Therefore if the system under discussion is not a Fermi liquid then the validity of this expression for $\chi_{LW}(\omega)$ cannot be guaranteed. For example, the marginal Fermi-liquid theory predicts a different frequency dependence.[38] If the dynamic susceptibility has a large peak at $\mathbf{Q}\neq\mathbf{0}$ then $1/T_1$ will not be strongly dependent on the long-wavelength physics [because $1/T_1$ measures the susceptibility over the entire Brillouin zone, cf. Eq. (1a), and there-

fore will be dominated by the physics at $\mathbf{q}=\mathbf{Q}$]. On the other hand, the Knight shift is a measure of the long-wavelength properties [cf. Eq. (1b)] and therefore may be sensitive to the details of $\chi_{\mathrm{LW}}(\omega)$. Below we follow MMP,[30] and explicitly assume that the uniform susceptibility ($\overline{\chi}_0$) and the spin-fluctuation energy near $\mathbf{q}=\mathbf{0}$ (Γ) are temperature independent. One justification for this approximation in organics is that the Knight shift is not strongly temperature dependent.[26] However, this approximation breaks down in systems where the uniform susceptibility is strongly temperature dependent such as $YBa_2Cu_3O_{6.63}$ (Ref. 39) and $La_{1.8}Sr_{0.15}CuO_4$.[40]

In the critical region $\xi(T) \gg a$, where a is the lattice constant, one has[30]

$$\chi_Q(T) = \left(\frac{\xi(T)}{\xi_0}\right)^{2-\eta} \overline{\chi}_0,$$

$$\omega_{\mathrm{SF}}(T) = \left(\frac{\xi_0}{\xi(T)}\right)^{z} \Gamma, \tag{5}$$

where η is the critical exponent which governs the power-law decay of the spin-correlation function at the critical point, z is the dynamical critical exponent, and ξ_0 is a temperature-independent length scale. The simplest assumptions are relaxation dynamics for the spin fluctuations (characterized by $z=2$) and mean-field scaling of the spin correlations ($\eta=0$). Within these approximations the real and imaginary parts of the dynamic susceptibility are given by

$$\chi'(\mathbf{q},0) = \overline{\chi}_0 \left[1 + \sqrt{\beta}\frac{[\xi(T)/a]^2}{[1+\xi(T)^2|\mathbf{q}-\mathbf{Q}|^2]^2}\right],$$

$$\chi''(\mathbf{q},\omega) = \frac{\omega\overline{\chi}_0}{\Gamma}\left[1 + \beta\frac{[\xi(T)/a]^4}{[1+\xi(T)^2|\mathbf{q}-\mathbf{Q}|^2]^2}\right], \tag{6}$$

where $\beta=(a/\xi_0)^4$. The temperature-independent, dimensionless parameter β can also be expressed in terms of the original variables appearing in the dynamic susceptibility in Eq. (3) as

$$\beta = \frac{\chi_Q(T)\Gamma}{\overline{\chi}_0\omega_{\mathrm{SF}}(T)}\left(\frac{a}{\xi(T)}\right)^4. \tag{7}$$

Written in this form, β has a clear interpretation: it represents the strength of the spin fluctuations at the wave vector $\mathbf{Q}$ relative to those at $\mathbf{q}=\mathbf{0}$. We will now consider two cases: antiferromagnetic and ferromagnetic spin fluctuations.

1. Antiferromagnetic spin fluctuations

If we have antiferromagnetic spin fluctuations then the dynamic susceptibility $\chi(\mathbf{q},\omega)$ is peaked at a finite wave vector $\mathbf{q}=\mathbf{Q}$; for example, on a square lattice with nearest-neighbor exchange only, $\mathbf{Q}=(\pi,\pi)$. The NMR relaxation rate, Knight shift, and Korringa ratio can be calculated straightforwardly from the real and imaginary parts of the dynamic susceptibility given in Eq. (4). The results are

$$\frac{1}{T_1T} = \frac{2\pi k_B|A|^2\overline{\chi}_0}{\gamma_e^2\hbar^4\Gamma}\left[1 + \beta\frac{[\xi(T)/a]^4}{1+[\tilde{Q}\xi(T)]^2}\right], \tag{8a}$$

$$K_s = \frac{|A|\overline{\chi}_0}{\gamma_e\gamma_N\hbar^2}\left[1 + \sqrt{\beta}\frac{[\xi(T)/a]^2}{1+[\tilde{Q}\xi(T)]^2}\right], \tag{8b}$$

$$\mathcal{K} = \frac{\hbar\gamma_e^2}{2\Gamma\overline{\chi}_0}\frac{\left[1 + \beta\dfrac{[\xi(T)/a]^4}{1+[\tilde{Q}\xi(T)]^2}\right]}{\left[1 + \sqrt{\beta}\dfrac{[\xi(T)/a]^2}{1+[\tilde{Q}\xi(T)]^2}\right]^2}, \tag{8c}$$

where $\tilde{Q}$ is a cutoff from the momentum integration [cf. Eq. (1a)]. For $\xi(T) \gg a$, $1/T_1T \sim \xi(T)^2$ and ΔK_s which leads to the Korringa ratio $\mathcal{K} \simeq (\hbar\gamma_e^2/2\Gamma\overline{\chi}_0)[\tilde{Q}\xi(T)]^2$. In this model the Korringa ratio can only be equal to unity if the spin fluctuations are completely suppressed ($\beta=0$). Hence one expects $\mathcal{K}>1$ if antiferromagnetic fluctuations are dominant.[41,42] It has been shown[43] that the Korringa ratio is unity when the hyperfine coupling $A(\mathbf{q})$ is momentum independent and the vertex corrections are negligible. The fact that the Korringa ratio is larger than 1 indicates that there are significant vertex corrections when there are large antiferromagnetic fluctuations.

2. Ferromagnetic spin fluctuations

For ferromagnetic spin fluctuations, $\chi(\mathbf{q},\omega)$ is peaked at $\mathbf{q}=\mathbf{0}$. The NMR relaxation rate is exactly the same as that given in Eq. (8a) because $1/T_1T$ comes from summing the contributions from all wave vectors in the first Brillouin zone, which makes the location of the peak in $\chi(\mathbf{q},\omega)$ in the momentum space irrelevant. In contrast, the Knight shift will be different in the ferromagnetic and antiferromagnetic cases because K_s only measures the $\mathbf{q}=\mathbf{0}$ part of the dynamic susceptibility; hence K_s will be enhanced by the ferromagnetic fluctuations. Thus for ferromagnetic spin-fluctuation description the Knight shift K_s is given by

$$K_s = \frac{|A|\overline{\chi}_0}{\gamma_e\gamma_N\hbar^2}[1 + \sqrt{\beta}(\xi/a)^2] \tag{9}$$

and the corresponding Korringa ratio by

$$\mathcal{K} = \frac{\hbar\gamma_e^2}{2\Gamma\overline{\chi}_0}\frac{\left[1 + \beta\dfrac{[\xi(T)/a]^4}{1+[\tilde{Q}\xi(T)]^2}\right]}{[1 + \sqrt{\beta}(\xi/a)^2]^2}. \tag{10}$$

For $\xi(T) \gg a$, $1/T_1T \sim \xi(T)^2$ and $K_s \sim \xi(T)^2$ which leads to $\mathcal{K} \simeq (\hbar\gamma_e^2/2\Gamma\overline{\chi}_0)[\pi\xi(T)/a]^{-2}$. Thus we see that $\mathcal{K}<1$ in the presence of ferromagnetic fluctuations.[41,42] So again vertex corrections are important if the system has strong ferromagnetic fluctuations. Recall that, in contrast, for antiferromagnetic fluctuations the Korringa ratio is larger than 1. Thus evaluating the Korringa ratio allows one to determine whether antiferromagnetic or ferromagnetic spin fluctuations are dominant.

B. Dynamical mean-field theory

DMFT is an approach based on a mapping of the Hubbard model onto a self-consistently embedded Anderson impurity

model.[14,44,45] DMFT predicts that the metallic phase of the Hubbard model has two regimes with a crossover from one to the other at a temperature T_0. For $T<T_0$ the system is a renormalized Fermi liquid characterized by Korringa-like temperature dependence of $1/T_1T$ and coherent intralayer transport. Above T_0, the system exhibits anomalous properties with $1/T_1T \sim a+b(T_0/T)$ (cf. Ref. 45) and incoherent charge transport. This regime is often referred to as the "bad metal".[8,15] Microscopically the bad metal is characterized by quasilocalized electrons and the absence of quasiparticles. This temperature dependence is similar to that for the single impurity Anderson model.[46] Note that this temperature dependence is similar to that found for spin fluctuations [cf. Eq. (13)].

The predictions of DMFT correctly describe the properties of a range of transport and thermodynamic experiments on the organic charge-transfer salts.[8,15–17,47] This suggests that these systems undergo a crossover from a bad metal regime for $T>T_0$ to a renormalized Fermi liquid below T_0. However, we will show below (also see Fig. 1) that the nuclear-spin relaxation rate is suppressed but never saturates below T_{NMR}; this is *not* captured by DMFT. This suggests that the low-temperature regime of κ-$(\mathrm{ET})_2X$ is more complicated than the renormalized Fermi liquid predicted by DMFT which, until now, has been widely believed to be the correct description of the low-temperature metallic state in the organic charge-transfer salts.

III. SPIN FLUCTUATIONS IN κ-$(\mathrm{ET})_2X$

The NMR relaxation rate, Knight shift, and Korringa ratio in the antiferromagnetic spin-fluctuations model are given by Eqs. (8a)–(8c). Their temperature dependence comes through the antiferromagnetic correlation length. We adopt the form of $\xi(T)$ from M-MMP:[29,30] $\xi(T)/\xi(T_x)=\sqrt{2T_x/(T+T_x)}$. For this form of the correlation length, T_x represents a characteristic temperature scale of the spin fluctuations and $\xi(T)$ is only weakly temperature dependent for $T \ll T_x$. For this choice of $\xi(T)$ we have

$$\frac{(T_1T)_0}{T_1T} = \left[1 + \frac{\beta C^2}{(T/T_x+1)^2 + 2\pi^2 C(T/T_x+1)}\right], \quad (11a)$$

$$K_s = (K_s)_0\left[1 + \frac{\sqrt{\beta}C}{1+2\pi^2 C + T/T_x}\right], \quad (11b)$$

$$\mathcal{K} = \mathcal{K}_0 \frac{\left[1 + \frac{\beta C^2}{(T/T_x+1)^2 + 2\pi^2 C(T/T_x+1)}\right]}{\left[1 + \frac{\sqrt{\beta}C}{1+2\pi^2 C + T/T_x}\right]^2}, \quad (11c)$$

where we have defined

$$C = 2\left[\frac{\xi(T_x)}{a}\right]^2,$$

$$(1/T_1T)_0 = \frac{2\pi k_B |A|^2 \bar{\chi}_0}{\gamma_e^2 \hbar^4 \Gamma},$$

$$(K_s)_0 = \frac{|A|\bar{\chi}_0}{\gamma_e \gamma_N \hbar^2},$$

$$\mathcal{K}_0 = \frac{\hbar \gamma_e^2}{2\Gamma \bar{\chi}_0}, \quad (12)$$

to simplify the notation.

A. The nuclear-spin relaxation rate

We now analyze the temperature dependence of $1/T_1$. In the discussion to follow, we will assume that the correlation length is sufficiently large compared to the lattice spacing and that the quantity $2\pi^2 C = 4\pi^2[\xi(T_x)/a]^2$ is much larger than T/T_x. These two assumptions imply that $2\pi^2 C(T/T_x+1)$ is more dominant than $(T/T_x+1)^2$ in the denominator of the second term inside the square bracket of Eq. (11a). Keeping only the dominant term, we arrive at the expression for $1/T_1T$,

$$\frac{(T_1T)_0}{T_1T} \simeq 1 + \frac{\beta}{\pi^2}\left(\frac{\xi(T_x)}{a}\right)^2\left(\frac{1}{T/T_x+1}\right). \quad (13)$$

The assumption $2\pi^2 C(T/T_x+1) \gg (T/T_x+1)^2$ can be easily worked out to give a self-consistency condition

$$\left[\frac{\xi(T_x)}{a}\right]^2 \gg \frac{T/T_x+1}{4\pi^2}. \quad (14)$$

We will use this relation later in Sec. III B as one of the tests for the validity of our approximation.

The NMR relaxation rate per unit temperature calculated from the spin-fluctuation model [cf. Eqs. (8a)–(8c)] is a monotonic decreasing function of temperature. Thus one realizes immediately that the data, reproduced in Fig. 1, for temperatures below T_{NMR} are *not* consistent with the predictions of the spin-fluctuation theory. We will return to discuss this regime later. We begin by investigating the high-temperature regime, $T>T_{\mathrm{NMR}}$.

We fit the $1/T_1T$ expression, Eq. (13), to the experimental data of De Soto[26] for κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ between T_{NMR} and 300 K with $(1/T_1T)_0$, $\beta[\xi(T_x)/a]^2$, and T_x as free parameters. It is not possible to obtain β and $\xi(T_x)/a$ independently from fitting to $1/T_1T$ data because the model depends sensitively only on the product $\beta[\xi(T_x)/a]^2$ [see Eq. (13)]. The results are plotted in Fig. 1 and the parameters from the fits are tabulated in Table I. We have checked the validity of our approximation by plotting $1/T_1T$ given by Eq. (11a) for κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ in Fig. 1(b), where there are Korringa ratio data (see Fig. 2) and thus we can determine β and $\xi(T_x)/a$ individually. It can be seen from Fig. 1(b) that the disagreement between $1/T_1T$ plotted from Eqs. (11a) and (13) is smaller than the thickness of the curves. Therefore this approximation is well justified. It will also be shown in Sec. III B that the correlation length is indeed rather large and the self-consistency condition, Eq. (14), is satisfied thus providing further justification for the use of Eq. (13) here.

The model produces a reasonably good fit to the experimental data on κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ (Ref. 26) between

TABLE I. The parameters obtained from the fits which are used to produce Fig. 1. Evidence for strong spin fluctuations come from the large value of $\beta[\xi(T_x)/a]^2$ which are present for all the materials tabulated above. T_{NMR} is determined from the peak of $1/T_1T$ (see Fig. 1). The correlation length shown in the last column in the table was obtained by analyzing the Korringa ratio data available for κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ (see Sec. III B). The correlation length for Mayaffre, κ-Br (Ref. 25), Miyagawa, $d8$-Br (Ref. 48), and Kawamoto's κ-NCS (Ref. 49) cannot be determined from our analysis because there are not sufficient data. This is shown with question marks in the correlation length column. In the table κ-Br, $d8$–Br, and κ-NCS are used as shorthand for κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$, $\kappa(d8)$-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$, and κ-$(\mathrm{ET})_2\mathrm{Cu}(\mathrm{NCS})_2$, respectively.

Material	Ref.	$(1/T_1T)_0$ $(\mathrm{s}^{-1}\ \mathrm{K}^{-1})$	T_x (K)	T_{NMR} (K)	$\beta[\xi(T_x)/a]^2$	$\xi(T_{\mathrm{NMR}})/a$
κ-Br	Mayaffre[25]	0.09±0.01	7±6	60	290±250	?
κ-Br	De Soto[26]	0.02±0.01	20±10	50	680±430	2.8±1.8
$d8$-Br	Miyagawa[48]	0.04±0.01	6±4	40	85±65	?
κ-NCS	Kawamoto[49]	0.06±0.01	11±3	55	110±90	?

T_{NMR}, the temperature at which $1/T_1T$ is maximum, and room temperature. In the high-temperature regime (e.g., around room temperature), $1/T_1T$ has a very weak temperature dependence, indicating weakly correlated spins. The large enhancement of $1/T_1T$ can be understood in terms of the growth of the spin fluctuations: as the system cools down, the spin-spin correlations grow stronger which allows the nuclear spins to relax faster by transferring energy to the rest of the spin degrees of freedom via these spin fluctuations. Strong spin fluctuations, measured by large values of $\beta[\xi(T_x)/a]^2$, are not only present in κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ but also observed in other materials such as fully deuterated κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ {which will be denoted by $\kappa(d8)$-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$} and κ-$(\mathrm{ET})_2\mathrm{Cu}(\mathrm{NCS})_2$. The results of the fits for $\kappa(d8)$-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ and κ-$(\mathrm{ET})_2\mathrm{Cu}(\mathrm{NCS})_2$ are shown in Fig. 1. The parameters that produce the best fits are also tabulated in Table I. In all of the cases studied here, strong spin fluctuations are evident from the large value of $\beta[\xi(T_x)/a]^2$.

The nature of the spin fluctuations, i.e., whether they are antiferromagnetic or ferromagnetic, cannot, even in principle, be determined from the analysis on $1/T_1T$. Both cases yield the same $1/T_1T$ [see Eq. (8a) and Sec. II A 2] because the nuclear spin-relaxation rate is obtained by summing all wave-vector contributions in the first Brillouin zone. However, in the next section we will use the Korringa ratio to show that the spin fluctuations are antiferromagnetic.

Below T_{NMR}, the calculated $1/T_1T$ continues to rise while the experimental data show a decrease in the nuclear-spin relaxation rate per unit temperature. However, the data do not reach a constant $1/T_1T$ as expected for a Fermi liquid. This indicates that the physics below T_{NMR} is dominated by some other mechanism not captured by the spin-fluctuation theory, Fermi-liquid theory, or DMFT.

One might argue that the discrepancy between the theory and experiments below T_{NMR} stems from our assumption of a q-independent hyperfine coupling in the $1/T_1T$ expression. However, in Sec. III D we will show that the Knight shift is also inconsistent with the predictions of the spin-fluctuation model below T_{NMR}. While including the appropriate q-dependent hyperfine coupling might change the temperature dependence of $1/T_1T$, it certainly cannot affect the temperature dependence of the Knight shift because K_s only depends on $A(\mathbf{0})$ [as can be seen from Eq. (1b)].

B. Korringa ratio

In the previous section we compared the predictions of the spin-fluctuation model for $1/T_1T$ to the experimental data and obtained good agreement with the data between T_{NMR} and 300 K. However, we were not able to determine β and $\xi(T_x)/a$ independently because $1/T_1T$ is sensitive only to the product $\beta[\xi(T_x)/a]^2$. We were also unable to determine whether antiferromagnetic or ferromagnetic spin fluctuations are dominant. We resolve these questions by studying the Korringa ratio $\mathcal{K}$. It has previously been pointed out that antiferromagnetic (ferromagnetic) fluctuations produce a Korringa ratio that is larger (less) than 1.[41,42] We have also seen in Sec. II that in the limit of large correlation lengths, $\mathcal{K}\sim(\xi/a)^2>1$ for antiferromagnetic spin fluctuations and $\mathcal{K}\sim(a/\xi)^2<1$ for ferromagnetic spin fluctuations. The Korringa ratio data for κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ (see Fig. 2) are significantly larger than 1 at all temperatures which shows that antiferromagnetic fluctuations dominate. With this in mind, we study the antiferromagnetic spin-fluctuation model.

First we note that K_s, given by Eq. (11b), has a weak temperature dependence because of our assumption that $[\xi(T_x)/a]$ is generally larger than unity and $2\pi^2C\gg T/T_x$. Thus the second term inside the square bracket in Eq. (11b) can be approximated by $\sqrt{\beta}C/(1+2\pi^2C+T/T_x)^{-1}\simeq\sqrt{\beta}/(2\pi^2)$ and the Knight shift will be given by $K_s\simeq(K_s)_0[1+\sqrt{\beta}/(2\pi^2)]$ which is temperature independent. We use this temperature-independent Knight shift to calculate the Korringa ratio $\mathcal{K}$,

$$\mathcal{K}=\frac{\hbar}{4\pi k_B}\left(\frac{\gamma_e}{\gamma_N}\right)^2\frac{1}{T_1TK_s^2}\simeq\mathcal{K}_0\left(1+\frac{\beta[\xi(T_x)/a]^2}{\pi^2(T/T_x+1)}\right)\left(\frac{1}{1+\sqrt{\beta}/(2\pi^2)}\right)^2, \quad (15)$$

where the prefactor $\mathcal{K}_0$ is given by Eq. (12).

We fit Eq. (15) to the experimental data for the Korringa for κ-$(ET)_2Cu[N(CN)_2]Br$.[26] The result is plotted in Fig. 2. The Korringa ratio data are well reproduced by the antiferromagnetic spin-fluctuation model when $T > T_{NMR}$. This is again consistent with our earlier conclusion that the spin fluctuations are antiferromagnetic. In this fit we have three free parameters, $\beta[\xi(T_x)/a]^2$, T_x, and $\sqrt{\beta}$, two of which, $\beta[\xi(T_x)/a]^2$ and T_x, have been determined from fitting $1/T_1T$. There is only one remaining free parameter in the model, $\sqrt{\beta}$, which can then be determined unambiguously from the Korringa fit yielding $\beta = 60 \pm 20$. This value of β implies that the antiferromagnetic correlation length $\xi(T) = 2.8 \pm 1.8a$ (a is the unit of one lattice constant) at $T = 50$ K. This value is in the same order of magnitude as the value of the correlation length estimated in the cuprates.[39]

We now return to discuss the validity of our approximation which was stated in the beginning of Sec. III A. The correlation length has been determined to be $\xi(T)/a = 3.7 \pm 2.4$ at $T = T_x = 20$ K from the fit to the Korringa ratio data. This result surely satisfies the requirement that the correlation length is larger than unit lattice spacing. A stronger justification for our approximation comes from the self-consistency relation Eq. (14). With $\xi(T_x)/a = 3.7$ and $T_x = 20$ K, one could easily check that Eq. (14) is indeed satisfied in the relevant regime, i.e., between T_{NMR} and room temperature.

A large Korringa ratio[50,51] has previously been observed in the cuprates indicating similar antiferromagnetic fluctuations in these systems. The Korringa ratio has also been measured in a number of heavy fermion compounds.[52–54] Similar antiferromagnetic fluctuations are also present in $CeCu_2Si_2$; the Korringa ratio of this material has a value of 4.6 at $T = 100$ mK.[53] In contrast, $YbRh_2Si_2$ (Ref. 52) and $CeRu_2Si_2$ (Ref. 54) show strong ferromagnetic spin fluctuations as is evident from the Korringa ratio less than unity. In Sr_2RuO_4 (Ref. 55) the Korringa ratio is approximately 1.5 at $T = 1.4$ K. Upon doping with Ca to form $Sr_{2-x}Ca_{x2}RuO_4$, the Korringa ratio becomes less than 1 which indicates that there is a subtle competition between antiferromagnetic and ferromagnetic fluctuations in these ruthenates.

C. Antiferromagnetic correlation length

It is important to realize that the spin-fluctuation formalism can be used to extract quantitative information about the spin correlations from NMR data. From the fit for κ-$(ET)_2Cu[N(CN)_2]Br$ (Table I) we found that the antiferromagnetic correlation length $\xi(T)/a = 2.8 \pm 1.8$ at $T = 50$ K. In order to understand the physical significance of this value of $\xi(T)$ it is informative to compare this value with the correlation length for the square[56] and triangular[57] lattice antiferromagnetic Heisenberg models with nearest-neighbor interaction only.

It has been shown[56] that, on the square lattice, the antiferromagnetic Heisenberg model with nearest-neighbor interaction only has a correlation length of order $\xi(T)/a \sim 1$ for $T = J$ and of order $\xi(T)/a \sim 30$ for $T = 0.3J$. On the other hand, for the antiferromagnetic Heisenberg model with nearest-neighbor interaction only on the isotropic triangular lattice, the correlation length is only of order a lattice constant at $T = 0.3J$.[57] Thus the correlation length, $\xi(T)/a = 2.8 \pm 1.8$ at $T = 50$ K, obtained from the analysis of the data for κ-$(ET)_2Cu[N(CN)_2]Br$ is reasonable and places the materials between the square and isotropic triangular lattice antiferromagnetic Heisenberg model as has been argued on the basis of electronic structure calculations.[8,32,58]

One of the best ways to measure antiferromagnetic correlation length is by inelastic neutron-scattering experiments. To perform this experiment, one needs high quality single crystals. Unfortunately, it is difficult to grow sufficiently large single crystals for κ-$(ET)_2X$; however, recently some significant progress has been made in this direction.[59] Another way to probe the correlation length is through the spin-echo experiment. The spin-echo decay rate $1/T_2$ is proportional to the temperature-dependence correlation length. To the authors' knowledge there is no spin-echo decay rate measurement on the metallic phase of the layered organic materials at the present time. Thus it is very desirable to have such experimental data to compare with the value of $\xi(T)$ we have extracted above.

D. Knight shift

As we pointed out in Sec. II the Knight shift K_s will generally have a weak temperature dependence throughout the whole temperature range and so, thus far, we have neglected its temperature dependence. However, it is apparent from Eq. (11c) that for any choice of parameter values $[\beta, \xi(T_x)/a$ and $T_x]$, K_s will always increase monotically as the temperature decreases. Therefore the temperature dependence of the Knight shift potentially provides an important check on the validity of the spin-fluctuation model. However, in the following discussion one should recall the caveats (discussed in Sec. II A) on the validity of the calculation of the Knight shift stemming from the assumption that the dynamics of the long wavelength part of dynamical susceptibility relax in the same manner as a Fermi liquid does.

In contrast to the prediction of the spin-fluctuation model, the experimental data[26] for κ-$(ET)_2Cu[N(CN)_2]Br$ show that K_s decreases slowly with decreasing temperature which then undergoes a large suppression around $T_{K_s} \sim 50$ K. It should be emphasized here that T_{K_s} is approximately the same as T_{NMR}, the temperature at which $1/T_1T$ is maximum.

Since it is not possible to explain any of the NMR data below T_{NMR} in terms of the spin-fluctuation model within the approximations discussed thus far, we focus on the temperature range between 50 and 300 K just as we did for the analysis of $1/T_1T$. Even in this temperature range, there is a puzzling discrepancy between theory and experiment: the experimental data decrease slowly with decreasing temperature while the theoretical calculation predicts the opposite. We will argue below that this discrepancy arises because the data are obtained at constant pressure while the theoretical prediction assumes constant volume. Since the organic charge-transfer salts are particularly soft, thermal expansion of the unit cell may produce a sizeable effect to the Knight shift and may not be neglected. In principle, an estimate of the

size of this effect could be made following Wzietek *et al.*,[60] as

$$\Delta K_s = K_s^p - K_s^v = \int_0^T dT' \left(\frac{\partial K_s^p}{\partial P}\right)_{T'} \left(\frac{V\,\partial P}{\partial V}\right)_{T'} \left(\frac{\partial V}{V\,\partial T'}\right)_P, \tag{16}$$

where K_s^p is the (experimentally obtained) isobaric Knight shift, K_s^v is the (calculated) constant volume Knight shift, $(V\partial P/\partial V)_T$ is the isothermal compressibility, and $\frac{1}{V}(\partial V/\partial T)_P$ is the linear thermal expansion. However, it is not possible to obtain an accurate estimate for ΔK_s at this time because there are no complete data sets for K_s^p, isothermal compressibility, and thermal expansion as a function of temperature and pressure for the κ-$(ET)_2$-X family. However, a rough estimate for ΔK_s may be made using the available experimental data.[43] This suggests that the experimental data are consistent with the spin-fluctuation theory. Clearly, further experiments are required to test this claim conclusively. Therefore we raise this issue predominately to stress the importance of systematic measurements of the parameters in Eq. (16).

Given the large uncertainty in ΔK_s we take K_s to be constant for temperatures above 50 K in the rest of this paper. This is clearly the simplest assumption, it is not (yet) contradicted by experimental data, and, perhaps most important, any temperature dependence in the Knight shift is significantly smaller than the temperature dependence of $1/T_1T$.

Regardless of the size of ΔK_s, the Knight shift calculated from the spin-fluctuation model is inconsistent with the experimental data below $T_{K_s} \sim 50$ K (see Fig. 4 in Ref. 43). The calculated K_s shows a weakly increasing K_s with decreasing temperature, while the measured K_s is heavily suppressed below 50 K. One important point to emphasize here is that the temperature dependence of K_s will not change even if one uses the fully q-dependent $A(\mathbf{q})$ since K_s only probes the $\mathbf{q}=\mathbf{0}$ component of the hyperfine coupling and susceptibility [see Eq. (1b)]. Thus putting an appropriate q-dependent hyperfine coupling will not change the result for K_s (although it might give a better description for $1/T_1T$). This provides a compelling clue that some nontrivial mechanism is responsible for the suppression of $1/T_1T$, K_s, and $\mathcal{K}$ below 50 K.

We have not addressed how the nuclear-spin relaxation rate is modified by the thermal expansion of the lattice. Since the organic compound is soft, it is interesting to ask if there is a sizeable effect to $1/T_1T$. Wzietek *et al.*[60] have performed this analysis on quasi-1D organic compounds whose relaxation rate is found to scale like χ_s^2. One can straightforwardly derive the effect of volume changes from the Hubbard model. If one uses the relation $1/T_1T \sim \chi_s^2$ and assumes fixed U and t, then $1/T_1T \sim 1/V^2$ will follow. However, it is clear from the phase diagram of the organic charge-transfer salts (see Ref. 8) that there is a rather large change in U and t for even small pressure variations. Therefore there is no obvious relationship between $1/T_1T$ and χ_s for the quasi-2D organics and it is not clear how the imaginary part of the susceptibility $\chi''(\mathbf{q},\omega)$, which enters $1/T_1T$, is affected by thermal expansion and lattice isothermal compressibility. Again, this stresses the importance of the detailed experiments needed to determine the effect of thermal expansion of the lattice on the measured relaxation rate.

IV. OPEN PROBLEMS AND FUTURE EXPERIMENTS

Open problems. The large suppression of $1/T_1T$ and K_s below T_{NMR} observed in all the κ salts studied here cannot be explained by the M-MMP spin-fluctuation model. One plausible mechanism to account for this feature is the appearance of a pseudogap which causes the suppression of the density of states at the Fermi energy. This is because at low temperature $1/T_1T$ and K_s are proportional to $\tilde{\rho}^2(E_F)$ and $\tilde{\rho}(E_F)$, where $\tilde{\rho}(E_F)$ is the full interacting density of states at the Fermi energy.[43] Independent evidence for the suppression of density of states at the Fermi level comes from the linear coefficient of the specific heat γ.[27] The electronic specific heat probes the density of excitations within k_BT of the Fermi energy. Any gap will suppress the density of states near the Fermi surface which results in the depression of the specific-heat coefficient γ. Kanoda[61] compared γ for several κ-$(ET)_2X$ salts and found that in the region close to the Mott transition, γ is indeed reduced. One possible interpretation of this behavior is a pseudogap which becomes bigger as one approaches the Mott transition. However, other interpretations are also possible. In particular one needs to take care to account for the possible coexistence of metallic and insulating phases; this is expected as the Mott transition is first order in the organic charge-transfer salts.[62,63] The existence of a pseudogap has also been suggested in λ–$(BEDT–TSF)_2GaCl_4$ (Ref. 64) from microwave conductivity measurements. The reduction of the real part of the conductivity σ_1 from the Drude conductivity σ_{dc} and the steep upturn in the imaginary part of the conductivity σ_2 may be interpreted in terms of preformed pairs leading to a pseudogap in this material. A pseudogap is predicted by the RVB theory of organic superconductivity.[34,36]

The experimental evidence from measurements of $1/T_1T$, K_s, and heat capacity all seem to point to the existence of a pseudogap below T_{NMR} in κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$. Thus a phenomenological description which takes into account both the spin fluctuations which are important above T_{NMR} and a pseudogap which dominates the physics below T_{NMR} would seem to be a reasonable starting point to explain the NMR data for the entire temperature range (clearly superconductivity must also be included for $T<T_c$). We will pursue this approach in our future work. In particular, if there is a pseudogap then important questions to answer include (i) How big is the pseudogap and what symmetry does it have? (ii) How similar is the pseudogap in κ-$(ET)_2X$ to the pseudogaps in the cuprates and in other strongly correlated materials such as manganites and heavy fermions? (iii) Is there any relationship between the pseudogap and the superconducting gap in κ-$(ET)_2X$? The answer to these questions may help put constraints on the microscopic theories.

Future experiments. There are a number of key experiments required to resolve the issue of whether or not a pseudogap is present in the low-temperature metallic phase of κ-$(ET)_2X$. The pressure and magnetic-field dependence of

the nuclear-spin relaxation rate and Knight shift will be valuable in determining the pseudogap phase boundary, estimating the order of magnitude of the pseudogap, and addressing the issue how the pseudogap is related to superconductivity. In the cuprates, there have been several investigations of the magnetic-field dependence of the pseudogap seen in NMR experiments. For $Bi_2Sr_{1.6}La_{0.4}CuO_6$ the nuclear-spin relaxation rate does not change with field up to 43 T.[65] However, since $T^* \sim 200$ K, one may require a larger field to reduce the pseudogap. Similar results were found in $YBa_2Cu_4O_8$.[66] However, in $YBa_2Cu_3O_{7-\delta}$ (see especially Fig. 6 of Ref. 67) a field of order 10 T is enough to start to close the pseudogap.

The interlayer magnetoresistance of the cuprates has proven to be a sensitive probe of the pseudogap.[68–71] Moreover, it is found that for the field parallel to the layers (which means that Zeeman effects will dominate orbital magnetoresistance effects) the pseudogap is closed at a field given by

$$H_{PG} \simeq \frac{k_B T^*}{\hbar \gamma_e}, \tag{17}$$

where T^* is the pseudogap temperature. For the hole-doped cuprates this field is of the order 100 T. In contrast, for the electron-doped cuprates this field is of the order 30 T (and $T^* \sim 30-40$ K), and so this is much more experimentally accessible.[70] The field and temperature dependence of the interlayer resistance for several superconducting organic charge-transfer salts[72] is qualitatively similar to that for the cuprates. In particular, for temperatures less than the zero-field transition temperature and fields larger than the upper critical field, negative magnetoresistance is observed for fields perpendicular to the layers. A possible explanation is that, as in the cuprates, there is a suppression of the density of states near the Fermi energy, and the associated pseudogap decreases with increasing magnetic field.

A Nernst experiment can be used to probe whether there are superconducting fluctuations in the pseudogap phase, as has been done in the cuprates.[73] This experiment is particularly important in understanding the relation between the pseudogap and superconductivity.

One could also study the pressure dependence of the linear coefficient of heat capacity γ. Since γ is proportional to the density of states at the Fermi energy, a detailed mapping of $\gamma(P)$ would be an important probe for studying the pseudogap. Finally, measurements of the Hall effect have also led to important insights into the pseudogap of the cuprates[27] and so perhaps the time is ripe to revisit these experiments in the organic charge-transfer salts.

V. CONCLUSIONS

We have applied a spin-fluctuation model to study the temperature dependences of the nuclear-spin relaxation rate, Knight shift, and Korringa ratio in the metallic phase of several quasi-two-dimensional organic charge-transfer salts. This model was based on Moriya's self-consistent renormalization theory[29] which was then applied by Millis, Monien, and Pines[30] to cuprates. The large enhancement of $1/T_1T$ between T_{NMR} $\{\sim 50$ K in κ-$(ET)_2Cu[N(CN)_2]Br\}$ and room temperature has been shown to be the result of strong antiferromagnetic spin fluctuations.

The antiferromagnetic correlation length is estimated to be 2.8 ± 1.8 lattice spacings in κ-$(ET)_2Cu[N(CN)_2]Br$ at $T=50$ K. This value falls between those for the Heisenberg model on the isotropic triangular lattice and the square lattice.

The spin fluctuations in κ-$(ET)_2Cu[N(CN)_2]Cl$, κ-$(ET)_2Cu[N(CN)_2]Br$, $\kappa(d8)$-$(ET)_2Cu[N(CN)_2]Br$, and κ-$(ET)_2Cu(NCS)_2$ are found to be similar both qualitatively and quantitatively. Strong spin fluctuations seem to be manifested in materials close to Mott transition. Recent NMR experiments[74] on κ-$(ET)_2Ag(CN)_2 \cdot H_2O$, which is situated further away from the Mott transition, suggests that the spin fluctuations in this material are not as strong as those in the other κ salts studied here.

The temperature dependence of $1/T_1T$ for $T > T_{\mathrm{NMR}}$ from the spin-fluctuation model is qualitatively similar to the predictions of DMFT. Below T_{NMR}, the spin-fluctuation model predicts a monotically increasing $1/T_1T$ with decreasing temperature while DMFT produces a constant $1/T_1T$. Neither of these models can account for the large suppression of $1/T_1$, K_s, and $\mathcal{K}$ below $T_{\mathrm{NMR}} \sim 50$ K observed in all the κsalts studied here. This suggests two things. First, the low-temperature regime is more complicated than the renormalized Fermi liquid previously thought to be the correct description of the low-temperature metallic phase in these materials. Second, a pseudogap exists at low temperatures near the Mott insulating phase of the organic charge-transfer salts.

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