Anomalous nuclear spin-lattice relaxation rate and superconductivity in the Bechgaard salts

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Abstract. The problem of interdependence of antiferromagnetism and superconductivity in the Bechgaard salts series of organic conductors is examined in the light of the temperature dependence of nuclear spin-lattice relaxation rate in the metallic phase of these materials. We show how the emergence of unconventional superconductivity close to antiferromagnetism can be linked to the nuclear relaxation within the framework of the scaling theory of the quasi-one-dimensional electron gas model.

1. Introduction
The Bechgaard salts, the (TMTSF)$_2$X series of organic molecular superconductors, stand out as a remarkable and early example of materials showing a spin-density-wave (SDW) state bordering on superconductivity (SC) in a phase diagram [1, 2]. This proximity found as one moves along the pressure axis gave a clear sign that both phases are not mutually exclusive and that the mechanisms responsible for both types of long-range order might be actually closely related. The role of spin correlations in the development of superconductivity has been further implied from the properties of the high temperature metallic phase. The temperature dependence of the spin-lattice relaxation rate $T^{-1}$ of the compounds studied so far by the NMR technique, revealed the existence of an anomalously large enhancement of $T^{-1}$ above the superconducting critical temperature $T_c$. This feature spreads relatively deeply in the metallic phase and its amplitude, like $T_c$, rapidly decreases when one progressively reaches the high pressure domain [3, 4, 5, 6].

From the theoretical side, a number of works based on the renormalization group (RG) method have been recently devoted to the interplay between the SDW and SC phases in a quasi-one-dimensional (quasi-1D) metal with weak electron-electron repulsion [7, 8, 9, 10, 11]. In the framework of the quasi-1D electron gas model, RG calculations at the one-loop level have shown that an unconventional ‘d-wave’ SC (SC$^d$) or ‘f-wave’ SC$^f$ state can be dynamically generated next to SDW when alterations of nesting are sufficiently large. For a wide range of reasonable parameters, the model proved to be rather generic of the pattern of phases that is actually found in the Bechgaard salts, especially for the relative temperature scale associated to the instabilities and their evolution with nesting frustration which simulates the effect of pressure. A question then arises whether the same approach can also give a satisfactory description of spin fluctuations of the normal phase, namely those at the origin of the anomalous temperature dependence of $T^{-1}$ in the metallic region.
In this short report, our attention will be directed to this question. We re-examine the problem of the NMR relaxation rate of the Bechgaard salts in the light of the recently developed scaling theory. We will show how the RG results for the quasi-1D electron gas model that was used to construct the phase diagram, apply equally well to the description of the temperature and pressure profiles of the observed $T_\perp^\dagger$.

2. Renormalization group results

2.1. The phase diagram

Let us consider the quasi-1D electron gas model which consists of a non interacting part defined by the free electron spectrum

$$E_p(\mathbf{k}) = v_F(pk - k_F) - 2t_{\perp b} \cos k_b - 2t'_{\perp b} \cos 2k_b - 2t_{\perp c} \cos k_c,$$  

where $p = \pm$ stands for right (left) moving electrons for the linearized 1D part of the spectrum; $v_F$ and $k_F$ are the longitudinal Fermi velocity and wave vector, respectively. As for the transverse directions, $t_{\perp b}$ is the hopping integral along $b$ direction, and $t_{\perp c}$ along $c$. The range of band parameters used in the following for the Bechgaard salts obeys to the narrowness which take the form $E_p(\mathbf{k} + \mathbf{q}_0) = -E_{-p}(\mathbf{k}) + 4t'_{\perp b} \cos 2k_b$ at $\mathbf{q}_0 = (2k_F, \pi, \pi)$. We define the interacting part of the model by the coupling constants for $g_1$, $g_2$ and $g_3$, corresponding to backward, forward, and Umklapp scattering amplitudes, respectively [12].

In the RG procedure, the electronic degrees of freedom are integrated out from the high Fermi energy cut-off $\frac{1}{2}E_0 = v_Fk_F$ (half the bandwidth $E_0$), down to the energy distance $\frac{1}{2}E_0(\ell) = \frac{1}{2}E_0 e^{-\ell}$ from the quasi-1D Fermi surface. At the one-loop level, the successive outer-shell contributions of the most singular density-wave (Peierls) and electron-electron (Cooper) scattering channels generate a momentum dependence for the scattering amplitudes $g_{1,2,3}(k_{b1}, k_{b2}; k'_{b1}, k'_{b2})$, a dependence parameterized by the in-going ($k_b$) and out-going ($k'_b$) transverse momentum in a three-variables RG scheme [11]. The integration over $\ell$ of the flow equations for the $g_i(\{k_b, k'_b\})$ leads to the effective couplings at a given temperature $T$. Here the influence of the very small $t_{\perp c}$ has been neglected in the computation of the RG flow. A singularity in the couplings is the signature of an instability of the metallic state towards the formation of long-range order at $T$. The nature of the new state is readily obtained from the determination of response functions.

For typical band parameters $E_0 = 6000K$, $t_{\perp b} = 200K$, and repulsive normalized ($g_i/\pi v_F \equiv g_i$) interactions, $g_1 = 0.32$, $g_2 = 0.64$, with weak Umklapp $g_3 = 0.02$ (due to a small dimerization of the organic stacks [13]), a singularity can be found in the SDW and SCd responses as a function of $t'_{\perp b}$ [7, 8, 10, 11]. In the framework of the RG approach, the $\mu = SDW$, SCd dynamic susceptibilities can be expressed as a loop integration

$$\chi^0_\mu(\mathbf{q}, \omega) = \frac{1}{\pi v_F} \int_0^\infty \langle f_\mu(k_b) z^2_\mu(k_b) \rangle dl,$$ 

where $\langle f_\mu(k_b)z_\mu(k_b) \rangle$ is a $k_b$-averaged product of the scaling coefficient $z_\mu$ associated to the susceptibility times a form factor $f_\mu$ [11]. For $\mu = SDW$, $f_{SDW} = 1$, and the dependence on wave vector and (real) frequency of the susceptibility (needed for the calculation of nuclear relaxation), is obtained by fixing the upper bound of integration to the normalized free SDW loop at $\mathbf{q} + \mathbf{q}_0$ and $\omega$,

$$\chi^0_{SDW}(\mathbf{q} + \mathbf{q}_0, \omega) = \ln \frac{E_F}{T} + \psi\left(\frac{1}{2}\right) - \frac{1}{8\pi^2} \int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} dk_b dk_c \left[ \psi\left(\frac{1}{2} - i \frac{\xi_F(k_{\perp b}, q_\perp)}{4\pi T}\right) + c.c. \right].$$
where \( \mathbf{q} = (q, q_\perp), \mathbf{k}_\perp = (k_b, k_c), \mathbf{q}_\perp = (q_b, q_c), \) and \( \psi(x) \) is the digamma function; \( \xi_F \) is defined as
\[
\xi_F(\mathbf{k}_\perp, \mathbf{q}, \omega) \approx v_Fq + (2t_{\perp,b}\cos k_b) q_b - 4t_{\perp,b}^2 \cos 2k_b + (2t_{\perp,c}\sin k_c) \sin q_c + \omega. \quad (4)
\]

For \( \mu = \text{SCd}, f_{\text{SCd}}(k_b) = \cos^2 k_b \) and the susceptibility is evaluated at zero pair momentum \( \mathbf{q} = 0 \) and \( \omega = 0 \), with \( \chi^{0}_{\text{SCd}} = \ln(E_F/T) \).

The one-loop RG results as a function of temperature for both susceptibilities are shown in Fig. 1-a for different \( t_{\perp,b}' \). At small \( t_{\perp,b}' \), \( \chi_{\text{SDW}}(q_0) \) is singular at the temperature scale \( T_{\text{SDW}} \) for an instability of the metallic state against the formation of a SDW phase. When \( t_{\perp,b}' \) is larger, \( T_{\text{SDW}} \) decreases rapidly and in the end, the instability of the metallic state becomes against SCd superconductivity. The corresponding temperature scale \( T_{\text{SCd}} \) is maximum at the junction of the two instability lines and goes down monotonically as \( t_{\perp,b}' \) grows further. The resulting phase diagram near the threshold value of \( t_{\perp,b}' \) for superconductivity is shown in Fig. 1-b. When nesting deviations are in first approximation squared with pressure, all these characteristics depicted by the calculations are key features of the actual phase diagram found in experiments [2].

2.2. Nuclear relaxation rate

We now turn to the derivation of the nuclear relaxation rate in the RG scheme. The \( T_1^{-1} \) calculation starts from the general Moriya expression

\[
T_1^{-1} = 2\gamma_N^2 T \int |A_{\mathbf{q}}|^2 \frac{\chi''(\mathbf{q}, \omega)}{\omega} d^3q,
\]

which connects \( T_1^{-1} \) to the imaginary part of the retarded spin susceptibility at \( \mathbf{q} \) and \( \omega \). Here \( A_{\mathbf{q}} \) is proportional to the hyperfine matrix element and \( \gamma_N \) is the gyromagnetic ratio of the nucleus. The integral over all \( \mathbf{q} \) indicates that \( T_1^{-1} \) is sensitive to uniform and staggered electronic spin correlations. We then consider the following decomposition

\[
T_1^{-1} = 2\gamma_N^2 T \left( \int_{\mathbf{q} \sim 0} + \int_{\mathbf{q} \sim \mathbf{q}_0} \right) |A_{\mathbf{q}}|^2 \frac{\chi''(\mathbf{q}, \omega)}{\omega} d^3q,
\]


\[ T^{-1}_1(q \sim 0) = T^{-1}_1(q_0) \].

Let us first examine the staggered component, \( T^{-1}_1(q_0) \). Using (2), the expansion of \( \chi''(q + q_0,\omega) \) at small \( q \) and \( \omega \), gives the expression

\[
\chi''(q + q_0,\omega) \approx \frac{\chi_{\text{SDW}} \Gamma \omega}{1 + \xi^2 q^2 + \xi^2_0 q^2 + \xi^2_c (\sin q e_c)^2 + (\Gamma \omega)^2},
\]

where \( \xi^2 = \xi^2_{0,a}(\xi^2_{\text{SDW}}(k_b))/\chi_{\text{SDW}} \), is the squared of the correlation length along \( i = a, b, \) and \( c \) directions; \( \xi_{0,a} \propto v_F / T^0 \) and \( \xi_{0,b,c} \propto t_{\perp,b,c}/T^0 \) are the corresponding coherence lengths evaluated at the SDW temperature \( T^0 \approx 12 \text{K} \) obtained for small \( t'_{1,b} \); \( \Gamma = \Gamma_0 \xi^2_{\text{SDW}}(k_b)/\chi_{\text{SDW}} \) is the relaxation time for SDW fluctuations and \( \Gamma_0 \propto 1/T^0 \) is a characteristic short-range time scale. The integration over \( q \) leads to

\[
T^{-1}_1(q_0) = C_1 T[N(E_F)]^2 \frac{v F_0}{\xi_{0,a} \xi_{0,b} \sqrt{1 + \xi^2_c}} \chi_{\text{SDW}},
\]

where \( N(E_F) = 1/\pi v_F \) is the density of states at the Fermi level and \( C_1 = 4\pi^2 |A_{q_0}|^2 \gamma_\chi^2/N \). The enhancement of the staggered component as the temperature is lowered is thus connected to \( \xi_c \) and the static SDW response, both obtained by the RG method.

If we now look at the uniform component, the imaginary part of the dynamic susceptibility at small \( \omega \) and \( q \) is known to be weakly enhanced by interactions at low temperature [14, 15]. Its expression will be then approximated to the imaginary part of the free electron response, which reads

\[
\chi''(q,\omega)|_{\omega,q=0} = \frac{1}{4\pi^2} \sum_p \int dk dk_0 dk_c [n(E_p(k + q)) - n(E_p(k))] \delta(\omega - E_p(k + q) + E_p(k)),
\]

\[
= \frac{\omega}{4\pi^2} \sum_p \int \frac{dS_F}{|\nabla E_p(k_F)|} \delta(E_p(k_F + q) - E_p(k_F)).
\]

In the limit of small temperature, it reduces to an integral over the quasi-1D Fermi surface \( n(x) \) is the Fermi distribution). Substituting in (6) and carrying out the remaining integrals leads to the ‘Korringa’ component

\[
T^{-1}_1(q \sim 0) = C_0 T[N(E_F)]^2,
\]

where \( C_0 = \pi |A_0|^2 \gamma_\chi^2/N \). While the uniform contribution is nonsingular, its amplitude becomes ultimately larger than the staggered component at high enough temperature [14]. To compare the RG prediction to the experimental findings obtained for \( T^{-1}_1 \) of \( ^{77}\text{Se} \) [5], we fix the constant \( C_0 \) so that \( T^{-1}_1 \) coincides with the observed value at 50K (Fig. 2-a), which is known to be dominated by the uniform contribution [16]. The other constant \( C_1 \) is adjusted to get the observed magnitude of \( T^{-1}_1 \) at 20K. The total expression of \( T^{-1}_1 \) is plotted in Fig. 2-b for various values of the nesting frustration parameter \( t'_{1,b} \), namely below and above the threshold for superconductivity in the phase diagram of Fig. 1-b.

Below the threshold, the singularity in \( \chi_{\text{SDW}} \) induces, according to Eq. (8), the square root divergence for \( T^{-1}_1 \sim (T - T_{\text{SDW}})^{-1/2} \) as \( \xi_c \rightarrow \infty \) close to \( T_{\text{SDW}} \). This is the expected 3D classical critical behavior [14]. This critical profile has been found experimentally when \( T \) is not too close to \( T_{\text{SDW}} \) [16]. Above the threshold, the singularities in \( \chi_{\text{SDW}} \) and \( T^{-1}_1 \) are suppressed by nesting deviations. However, the amplitude of correlations remains large (Fig. 1-a) and continues to affect the temperature dependence of \( T^{-1}_1 \). An important temperature dependent enhancement of \( T^{-1}_1 \) then takes place in the metallic phase, which qualitatively reproduces the
Figure 2. (a) : Temperature dependence of the $^{77}$Se nuclear spin-lattice relaxation rate of (TMTSF)$_2$PF$_6$ at $P = 1$ bar ($\triangle$), 5.5 kbar ($\Box$), 8 kbar ($\times$), and 11 kbar ($\circ$) (after Ref. [5]). (b) : Calculated $T_1^{-1}$ vs $T$ for different values of $t'_{\perp b}$ below and above the threshold for superconductivity.

one of experiments as shown in Fig. 2-a. The amplitude of the effect, as well as the temperature range where it takes place above $T_{SC,d}$ are consonant with observation. Another remarkable feature of the results of Fig. 2-b, is the relatively rapid reduction of the enhancement as $t'_{\perp b}$ further increases in size. This reduction, which is correlated to the one of $T_{SC,d}$ (Fig. 1-b), simulates well the one found under pressure (Fig. 2-a).

Recently Brown et al. [6, 17, 18], re-examined the temperature dependence of the relaxation rate in greater experimental details. They note that the $T_1^{-1}$ enhancement above $P_c$ is actually well fitted by a Curie-Weiss behavior of the form \((T_1T)^{-1} \sim (T + \Theta)^{-1}\). This behavior, which is reminiscent of nearly antiferromagnetic two-dimensional systems [19], covers a rather large temperature interval. The present one-loop RG calculations shown in Fig. 3 indicates that a linear regime for $T_1T$, with a finite intercept as $T \to 0$, does indeed take place below about 10K. This temperature scale marks the scale for the suppression of the SDW singularity by nesting frustration (Fig. 1-a). The predicted scale, however, is noticeably smaller that the one found experimentally [6]. In the framework of the present model, the surviving growth of SDW correlations in the altered, but not completely suppressed, nesting region in the presence of Umklapp scattering is responsible for the Curie-Weiss behavior. The temperature range where it takes place is likely to be affected by non universal factors like the model used for nesting frustration as well as the evolution of the best nesting vector with $t'_{\perp b}$.

3. Conclusion

In conclusion we have computed by the renormalization group method the temperature dependence of the nuclear spin-lattice relaxation rate for the quasi-1D electron gas model. This approach that was used previously for the determination of the phase diagram of systems like the Bechgaard salts, gives a rather reasonable description of the peculiar enhancement of the relaxation rate found in the metallic state of these organic compounds. It thus follows that the temperature dependence of spin fluctuations needed to build up the superconducting pairing interaction in the metallic phase can be logically linked to the description of the anomalous
Figure 3. Calculated $T_1T$ vs $T$ for different values of $t_{lb}'$ above the threshold for superconductivity. A linear (Curie-Weiss) becomes visible below 10K or so.

relaxation rate in the Bechgaard salts.

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