Confinement in Bechgaard Salts: Anomalous Magnetoresistance and Nuclear Relaxation

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We present and analyze the normal phase temperature dependence of resistivity and nuclear spin-lattice relaxation of $(TMTSF)_2ClO_4$ under strong transverse magnetic fields. From a field-dependent scaling theory we show that the singular enhancement of the one-dimensional electron-electron umklapp scattering and antiferromagnetic spin correlations under field play a fundamental role in the large enhancement of magnetoresistance and nuclear relaxation of Bechgaard salts.

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Following the discovery of superconductivity in the $(TMTSF)_2X$ series of quasi-one-dimensional organic conductors [1], the observation of anomalously large and anisotropic magnetoresistance over a broad low temperature domain has soon been recognized as a fundamental feature of the normal phase of this series (TMTSF stands for tetramethyl-tetraselenafulvalene) [2]. It was also quickly realized that the classical magnetotransport theory fails to account for such a large effect in the presence of open orbits [3]. It is along these lines that different authors call upon either the existence of superconducting correlations [4] or the possibility of field-induced weak localization [5] in order to explain the origin of this anomalous phenomenon. So far, however, these proposals did not receive any sound experimental support so that the whole issue still remained unresolved. Not less puzzling is the apparent inability of the so-called "standard model" [6,7] to include in its description of the cascade of field-induced spin-density-wave transitions $[T_N(H)]$ the two important *noncritical precursors*, namely, the large magnetoresistance effects and the concomitant gradual freeze-up of charge degrees of freedom below the resistivity minimum temperature $T_\rho(H) \gg T_N(H)$ [8,9].

In this paper we reconsider this problem for the $(TMTSF)_2ClO_4$ compound from both an experimental and a theoretical point of view. We first show that the amplitude of the magnetoresistance and the existence of $T_\rho(H)$ naturally comes out if one joins high-energy many-body effects due to longitudinal umklapp scattering to those resulting from the progressive *unidimensionalization* of low-energy electronic states under field [2]. The properties of the normal phase are then found to present striking similarities with the closely related but more one dimensional sulfur series $(TMTTF)_2X$ at low pressure and field [10,11]. These undergo a $4k_F$ type of localization with a charge degrees of freedom gap and strong antiferromagnetic correlations below a temperature scale $T_\rho \gg T_N$ [11–13]. As a remarkable confirmation of the 1D origin of anomalous magnetoresistance in $(TMTSF)_2ClO_4$, we present ^{77}Se nuclear relaxation rate data at 15 T which show the predicted enhancement of 1D $2k_F$ spin correlations near $T_\rho(H)$ [11].

Resistivity data were obtained on slowly cooled $(TMTSF)_2ClO_4$ single crystals in magnetic field H up to 27 T. For magnetic fields higher than 12 T the experiments were performed, at ambient pressure, using the hybrid magnet at the Laboratoire des Champs Magnétiques Intenses at Grenoble. Samples, with evaporated gold pads, were mounted in the conventional four-probe configuration for longitudinal measurements. Clamped contacts were used for both current and voltage leads and two configurations of fields (along c^* and b') were used. The temperature was regulated in the range from 4.2 to 45.7 K, using a precalibrated capacitance thermometer during the magnetic field sweeps. The low magnetic fields measurements were carried out at Orsay using a conventional 12 T superconducting solenoid. The samples were mounted in the same configuration as described above, with the magnetic field along the c^* direction. Temperature sweeps in the range 1.4 to 18 K were performed at fixed values of magnetic field, using a carbon-glass thermometer. Each sample was cooled at 50 mK/min between 26 and 22 K to insure relaxation for the anion ordering transition at 24 K.

^{77}Se NMR spectra were obtained from the Fourier transform of half of the echo signal after a $\pi/2$-τ-π pulse sequence, while nuclear spin-lattice relaxation rates T_1^{-1} were estimated from the decay of the echo amplitude after an inversion recovery pulse sequence. The shift of NMR lines was measured using ^{77}Se NMR line in H_2SeO_3 as a reference. The reduced size of the coil, i.e., of the single

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crystal (~2 mm^3), allowed the use of moderate RF power, thus providing a thermal stability within ±0.1 K over all the temperature range (1.2–300 K). The orientation of the single crystal was inferred from the position of the four NMR lines corresponding to the four inequivalent Se sites [14]. The accuracy of the alignment was estimated to be within 10°.

Magnetoresistance.—From resistivity curves under field $\vec{H} \parallel c^*$ shown in Fig. 1, a distinct and noncritical feature emerging at high field is a minimum at $T = T_\rho(H)$, its amplitude monotonously increasing with H (Fig. 2). At $H = 27$ T, for example, $T_\rho \approx 22$ K, which is more than 20 times the value of $T_N(H) < 1$ K measured at this field for ClO_4 [8]. Below T_ρ, the resistivity curves evidence thermal activation with a localization gap $\Delta_\rho(H)$ increasing with field, in agreement with earlier results [8]. In contrast, when H is oriented along the b' direction the magnetoresistance is weak and the system remains metallic down to low temperature; see the inset of Fig. 1.

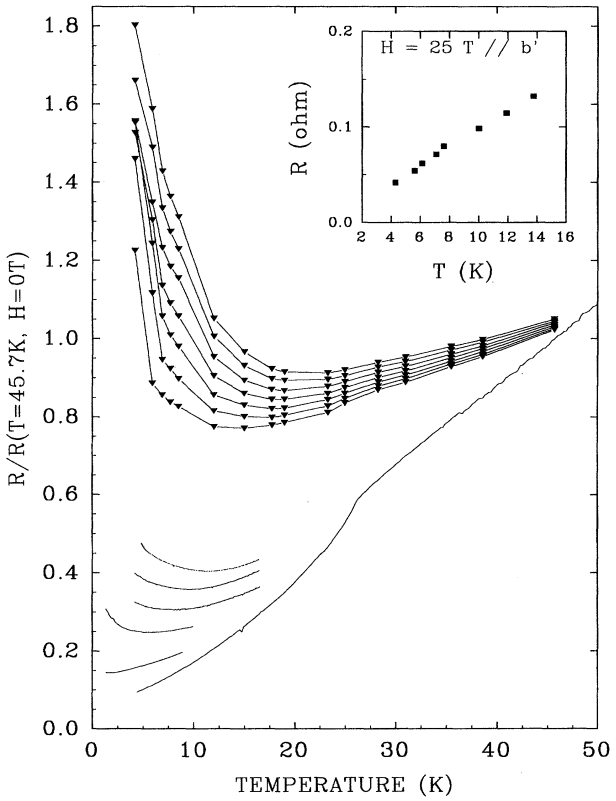

FIG. 1. Resistivity results for two different samples. The continuous lines are the measurements performed at low fields 12.3, 10, 8, 6, 3, and 0 T, respectively. The high field points 27, 25, 22.5, 20, 17.5, 15, and 12.5 T were taken from the field sweeps at fixed temperatures. It clearly shows that resistance minima are shifted towards higher temperatures at higher magnetic fields. Inset: Resistance vs temperature at 25 T along the b' direction. No minimum is observed down to 4.2 K.

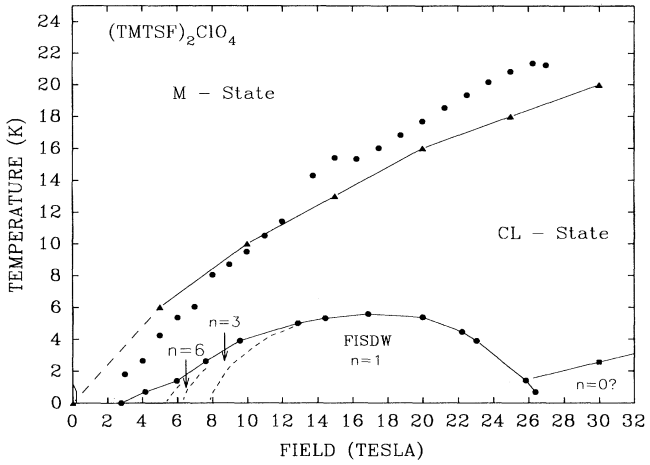

FIG. 2. Temperature vs magnetic field phase diagram of $(TMTSF)_2ClO_4$ displaying the various phases, metallic (M), charge-localized (CL), and the field-induced spin-density-wave phases (FISDW). Triangles show the field dependence of $T_\rho(H)$ from the theory with the set of parameters given in the text.

The monotonous increase of T_ρ versus field is *at variance* with the characteristic reentrance of T_N observed above 14 T in ClO_4 [8]. The comparison between both phenomena shows first that the upturn of the resistivity below T_ρ is not ascribable to incipient critical fluctuations in the vicinity of 3D ordering.

In order to assess the importance of electron-electron umklapp scattering as a source of strong longitudinal magnetoresistance, it is essential to take into account the influence of 1D high-energy scales. This is provided by the lowest order scaling theory of the quasi-one-dimensional electron gas model [12,13]. In this scheme, one looks at the flow of the repulsive dimensionless ($\tilde{g}_i \equiv g_i/\pi v_F$) backward ($\tilde{g}_1 > 0$), forward ($\tilde{g}_2 > 0$), and umklapp ($\tilde{g}_3 > 0$) scattering amplitudes when one successively integrates an outer energy shell of electronic states of thickness $E_F e^{-\ell} d\ell$ on either side of the 1D Fermi level. Here $E_F e^{-\ell}$ is the energy distance at $\ell \in [0, \ln(E_F/T)]$ from the 1D Fermi points $\pm k_F$, with $E_F = v_F k_F$ the Fermi energy of an isolated chain. The one-loop (parquet) scaling theory gives the flow equations

$$\begin{aligned} \frac{d\tilde{g}_1}{d\ell} &= -\tilde{g}_1^2 K(2k_F, t'_\perp, H, \ell), \\ \frac{d(2\tilde{g}_2 - \tilde{g}_1)}{d\ell} &= \tilde{g}_3^2 K(2k_F, t'_\perp, H, \ell), \\ \frac{d\tilde{g}_3}{d\ell} &= \tilde{g}_3(2\tilde{g}_2 - \tilde{g}_1) K(2k_F, t'_\perp, H, \ell), \end{aligned} \tag{1}$$

where $K(2k_F, t'_\perp, H, \ell) \equiv d\chi^0(2k_F)/d\ell > 0$ is the derivative of the bare electron-hole (Peierls) susceptibility with respect to ℓ at the longitudinal nesting vector $(2k_F, 0)$,

evaluated in the presence of an effective interchain single-particle hopping $t'_\perp$ and of an orbital effect due to the magnetic field. The adequacy of these flow equations to describe the normal phase of the Bechgaard salts can be readily established by first looking at their zero field application on the sulfur analog compound $(TMTTF)_2Br$ which stands only a few kilobars in pressure apart from $(TMTSF)_2X$ in the general phase diagram of both series [11–13]. Thanks to the detailed analysis of NMR data for uniform spin fluctuations (here governed by $\tilde{g}_1$), the $\ell = 0$ bare value $\tilde{g}_1 \approx 1$ is found to fit well the temperature dependence of constant volume susceptibility data [11]. This value was obtained using $E_F \approx 2000$ K, in accordance with band calculations [15] and considering $t'_\perp$ as irrelevant, that is $K(2k_F, t'_\perp, \ell) \approx 1$ for this more 1D compound. As for the charge degrees of freedom which are governed by the combination $(2\tilde{g}_2 - \tilde{g}_1, \tilde{g}_3)$, one first assumes a Hubbard type of local interaction by putting, for simplicity, $\tilde{g}_1 = \tilde{g}_2$ at $\ell = 0$. One then adjusts the bare amplitude of umklapp scattering to the small value $\tilde{g}_3 \approx 0.09$ so that the well known strong coupling condition $\tilde{g}_3(\ell_\rho) \approx 1$ [indicating the presence of an insulating charge degrees of freedom gap [16] at $\ell_\rho = \ln(E_F/T_\rho)$] coincides with the observed temperature $T_\rho \approx 100$ K for the location of the resistivity minimum at 1 bar [13]. This small value of $\tilde{g}_3$ is consistent with the relatively weak half-filled character of the longitudinal band [12,13].

Hydrostatic pressure decreases the dimerization gap, carrying with it a drop of T_ρ, which is observed to either merge in the critical domain or simply become irrelevant in the low temperature metallic phase due to the wrapping of the Fermi surface via $t'_\perp$ [17]. In the latter case K takes the form

$$K(2k_F, t'_\perp, \ell) = N_\perp^{-1} \sum_{k_\perp} n[-E_F e^{-\ell} - t'_\perp(k_\perp)] - n[E_F e^{-\ell} - t'_\perp(k_\perp)], \quad (2)$$

where $t'_\perp = 2t_\perp \cos k_\perp d_\perp$ and $n(x) = (e^{x/T} + 1)^{-1}$. Therefore deviations to longitudinal nesting at $T \ll t'_\perp$ ($K \ll 1$) levels off the growth of $\tilde{g}_3(\ell)$ in (1) at low energy or temperature, a characteristic of the metallic phase of the $(TMTSF)_2X$ series. Thus, consistently with band calculations, the Fermi energy in this case falls in the range $E_F \approx 2500$–2700 K [15]. Accordingly, this would imply a reduction of the bare couplings (via v_F), namely, $\tilde{g}_1 = \tilde{g}_2 \approx 0.75$–$0.85$ [13]. As for $\tilde{g}_3$ an extrapolation of T_ρ under pressure from the observed values for $(TMTTF)_2Br$ would lead to $T_\rho \approx 10$–25 K for the selenides (if $t'_\perp$ were absent), corresponding to $\tilde{g}_3 \approx 0.02$–0.04.

However, the presence of a transverse magnetic field H along c^* favoring the unidimensionalization of electronic motion will improve nesting conditions along $(2k_F, 0)$ [6]. Actually, the Peierls kernel for $H \neq 0$ can be put in the form $K(2k_F, t'_\perp, H, \ell) = K(2k_F, t'_\perp, \ell) + \delta K(2k_F, t'_\perp, H, \ell)$, where

$$\delta K(2k_F, t'_\perp, H, \ell) = J_0\left[\frac{8t'_\perp}{\omega_c} \sin\left(\frac{\omega_c}{E_F} e^{\ell}\right)\right] - J_0\left[\frac{8t'_\perp}{E_F} e^{\ell}\right] \quad (3)$$

is the field-dependent correction to longitudinal nesting which increases with H. Here J_0 is the zeroth order Bessel function and $\omega_c = e v_F H d_\perp / c$.

Combining (3) and (2) in the scaling equations (1), a transverse magnetic field is found to restore progressively the flow of $\tilde{g}_3(\ell)$ towards the strong coupling sector and an insulating-like behavior at low temperature. This is nicely displayed in Fig. 2 [$T_\rho(H)$ in the phase diagram] where the calculated profile of $T_\rho(H)$ vs H is compared to the observed temperature scale for strong magnetoresistance. The theoretical curve has been obtained for a set of parameters consistent with the above one-loop scaling analysis for the normal phase of the general phase diagram [13], namely, $\tilde{g}_1 = \tilde{g}_2 \approx 0.77$, $\tilde{g}_3 \approx 0.035$, $E_F = 2650$ K, $t'_\perp \approx 48$ K, with $k_F = \pi/2a$, $a = 7.3$ Å, and $d_\perp = 2 \times 7.7$ Å (for the anion-ordered perchlorate compound).

Nuclear relaxation.—The field-induced insulating behavior of the above model has important consequences on $2k_F$ spin correlations, especially those resulting from the undimensionalization. As one approaches $T_\rho(H)$ from above, a power law enhancement of the $2k_F$ spin response function $\chi(2k_F, T, H) \sim T^{-\gamma}$ occurs, the index $\gamma = 1$ being an *exact* constraint fixed by the strong umklapp conditions [16]. This leads, as in several members of the $(TMTTF)_2X$ series [11], to a characteristic *temperature-independent* contribution $T_1^{-1}[q \sim 2k_F] \sim C_1 T^{1-\gamma} \sim C_1 > 0$ for the normal phase nuclear relaxation rate which reads

$$T_1^{-1} = C_0 T \chi_s^2(T) + C_1 \quad (4)$$

for $T_N(H) \ll T \sim T_\rho(H)$ [11]. The first term is the contribution of uniform ($q \sim 0$) spin fluctuations. It is expressed in terms of the field-independent spin susceptibility $\chi_s(T) \propto K_s$ (NMR Knight shift), a quantity which can be independently measured. While the uniform part of the relaxation dominates at high temperature the deviations emerging at low temperature are due to $T_1^{-1}[q \sim 2k_F]$ and in turn to $\chi(2k_F, T, H)$. According to the present model, these deviations must grow with H and be spread out in temperature on the scale of $T_\rho(H)$. A straightforward analysis of the ^{77}Se T_1^{-1} vs T data of Fig. 3 obtained at 15 T when H is oriented along c^* ($T_\rho \approx 15$ K, $T_N \approx 4.4$ K) goes precisely along these lines. One observes at first glance that in the normal phase at low temperature [$T \gg T_N(H = 15\ \mathrm{T})$], the T_1^{-1} profile shows an unambiguous enhancement with respect to the uniform part, quite evident when H is along c^*. From the plot of T_1^{-1} vs $T\chi_s^2(T)$ (inset in Fig. 3) one observes that while at high temperature ($T \geq 150$ K) the $q \sim 0$ component entirely dominates T_1^{-1}; at lower temperature another linear regime takes place which does not

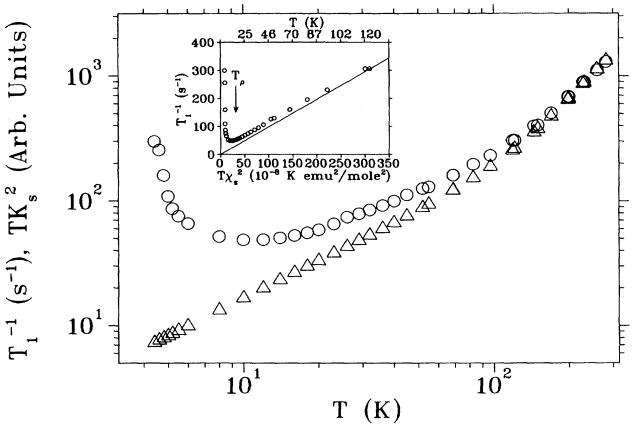

FIG. 3. Temperature dependence of ^{77}Se T_1^{-1} for $H = 15$ T along c^*. TK_s^2 is scaled in order to fit the T_1^{-1} value at high temperature where the uniform contribution dominates. In the inset T_1^{-1} vs $T\chi_s^2$ is reported (the solid line passing through the origin shows the extrapolation of the high temperature regime).

extrapolate to zero (as for the $q \sim 0$ term) but to a finite value C_1 as $T \to 0$, in agreement with our model. Furthermore, the spin susceptibility $\chi(2k_F, T, H)$, estimated from the difference of T_1^{-1} and $T\chi_s^2$ data reported in Fig. 3, follows indeed a power law $\chi(2k_F, T, H) \sim T^{-1}$ as predicted (see Fig. 4). Here it is worthwhile to recall that a similar temperature dependence has been observed for the sulfur compounds $(TMTTF)_2PF_6(T_\rho = 220$ K) and $(TMTTF)_2Br(T_\rho = 100$ K) salts [11] and the sulfur-selenide compound $(TMDTDSF)_2PF_6$ [18].

In conclusion, we have shown that the progressive undimensionalization of low-energy states under field is at the origin of a singular growth of longitudinal umklapp scattering and antiferromagnetic correlations in the normal phase of the Bechgaard salts. This gives a consistent interpretation of the anomalous temperature dependence of the magnetoresistance and of the nuclear relaxation in these systems. Ultimately, this reemphasizes the fact that selenium salts and their sulfur analogs are very closely related series, and besides the existence of superconductivity in both families [19], the history of 1D energy scales appears to play a key role in the understanding of their normal phase.

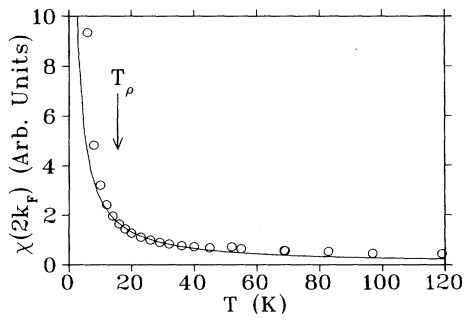

FIG. 4. Temperature dependence of $\chi(2k_F, T, H)$ for $H = 15$ T along c^* derived from the data in Fig. 3. The solid line designates the power law T^{-1}.

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