LETTER TO THE EDITOR

Nuclear magnetic resonance in the organic conductor (TMTSF)$_2$ClO$_4$ under pressure: field-induced magnetic state and spin–lattice relaxation rate

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Abstract. We report $^{77}$Se NMR data on (TMTSF)$_2$ClO$_4$ showing that the field-induced spin density wave state is pushed to higher fields under pressure. The pressure dependence of the FISDW state suggests a common phase diagram for all (TMTSF)$_2$X systems.

The change of the $1/T_1$ temperature dependence occurring under pressure can be understood as a sizeable growth of longitudinal and transverse bandwidths which decreases the effects of Coulomb correlations.

It has been shown (Takahashi et al 1982, 1984), that the application of a large magnetic field (above 40 kG) along the $c^*$ axis on a slowly cooled (relaxed) sample of (TMTSF)$_2$ClO$_4$ can stabilise a spin density wave (SDW) state at low temperature and induce a sequence of phases in which the Hall resistance is quantised (Ribault et al 1983, 1984). In the present work we have been interested in the pressure dependence of the phase transition between the non-magnetic one-dimensional (1D) conductor and the magnetic semi-metal. This study has been performed by observing the temperature dependence of the $^{77}$Se NMR properties. The salient result is a rapid suppression of the SDW temperature under pressure at a rate similar to the pressure dependence of the superconducting state (Mailly 1983). In the conducting regime at low fields, the dimensionality cross-over temperature $T_X$ (1D to 3D) studied by Bourbonnais et al (1984) appears also to be pressure dependent. For a pressure of 10 kbar it shifts from 8 K to 25 K. Finally, based on the present high-pressure study, we shall propose a general phase diagram ($T$, $P$, $H$) for the organic superconductors of the (TMTSF)$_2$X series.

Details concerning the preparation and the structure of (TMTSF)$_2$X compounds can be found elsewhere (Bechgaard et al 1981). In spite of slightly different NMR experimental conditions for the determination of field-induced magnetic state and cross-over temperature, all data collected in this work have been obtained with the same single-crystal sample.

$^{77}$Se NMR measurements were performed on a single crystal with the magnetic field aligned along the $c^*$ direction. Hydrostatic pressure was obtained with pressurised argon and was measured with an external manometer just above the freezing temperature, in agreement with the phase diagram of argon given by Bridgman (1934). The temperature was measured with the vapour pressure above the $^4$He bath. A pulsed NMR spectrometer was operated at a frequency of 60 MHz, corresponding to a resonance field of 73.9 kG
for $^{77}$Se nuclei. All measurements were performed with the single-coil geometry, the coil being wound around the $a$ axis. The free induction decay following a 90° pulse was accumulated and the absorption signal was recorded by an analogue box-car integrator while sweeping the magnetic field through resonance. The signal intensity is defined, in arbitrary units, by the product of the signal height and its width at half maximum. The linewidth of 38 G is a little larger than at the ambient pressure value.

![Figure 1](image)

Figure 1. (TMTSF)$_2$ClO$_4$ R state; $H_0 = 73.9$ kG parallel to $c^*$. (a) $^{77}$Se NMR signal intensity versus temperature showing the magnetic transition at various pressures (○ 200 bar, □ 750 bar, △ 1000 bar); the full curve indicates the Curie law behaviour. (b) $^{77}$Se relaxation rate versus temperature at 750 bar. The dashed line is a guide to the eye, the mixed line corresponds to the data at ambient pressure (Takahashi et al 1982, 1984).

The most striking effect is shown in figure 1(a). At high temperature, the linewidth is almost constant and the signal intensity follows a Curie law. While decreasing the temperature, the $^{77}$Se signal suddenly disappears, as observed at ambient pressure (Takahashi et al 1982, 1984). The vanishing of the NMR signal can be related to the onset of a local magnetisation in the field-induced spin density wave (FISDW) phase. According to figure 2, the transition temperature, as defined by the lowest temperature at which the Curie law is still fairly well obeyed, decreases rapidly under pressure. The width of the transition (0.3 K) was found to be a little larger than at ambient pressure, probably due to stresses on the sample in the solidified pressure medium at low temperature.

In (TMTSF)$_2$X compounds, it is well known that the disappearance of the $^{77}$Se NMR signal which is the signature of a transition towards a magnetic state is accompanied by an enhancement of the spin–lattice relaxation rate. This feature is also observed here, for example at 750 bar (figure 1(b)). At this pressure the transition temperature has already decreased by 20\% below the ambient pressure value. Therefore, we might expect the 3D critical region to be restricted to a temperature domain lower than at ambient pressure. But, on the other hand, the spin–lattice relaxation rate increases more rapidly below 4.2 K, and reaches 200 s$^{-1}$ just above the transition, a value twice that at
ambient pressure. This unexpected phenomenon seems to be unusual and will require more experimental investigations in the future.

At ambient pressure, the work of Bourbonnais et al (1984) has revealed strong deviations from the Korringa law in the metallic regime (low magnetic field) of \((\text{TMTSF})_2\text{ClO}_4\) even in the absence of any transition. This unusual behaviour has been interpreted by the existence of cooperative phenomena in the 1D regime and according to the proposed model it was possible to define a dimensionality cross-over temperature \(T_X\) as the temperature at which the Korringa regime appears to be restored.

\(^{77}\text{Se}\) spin–lattice relaxation rate measurements were performed on the same single crystal with the magnetic field of 31.9 kG along the \(b^*\) direction. For measurements at high temperature we used a powder sample of total weight 70 mg and no detectable difference was observed with the single crystal behaviour.

We have plotted in figure 3 the results obtained at 5 and 10 kbar together with previous ambient pressure data. The application of a high pressure increases significantly the characteristic energy or temperature \(E_0\) at which deviations from the Korringa behaviour are clearly observed. The temperature domain at low temperature in which \(1/T_1\) is proportional to \(T\) is also widened by pressure. As the amplitude of the \(T^{-1}_1\) enhancement is lowered under pressure, the high-pressure data appear to be more Fermi liquid-like.

Two complementary theoretical approaches have been proposed to explain the existence of FISDW states in \((\text{TMTSF})_2\text{ClO}_4\) at high magnetic fields (Gor'kov and Lebed 1984) and the quantisation of the Hall constant within each sDW state (Heritier et al 1984). The interpretation was based on the orbital effect of the magnetic field reducing the effective three dimensionality of the quasi-1D (Q1D) electron gas, hence improving the nesting of the warped Q1D Fermi surface.

In zero magnetic field, the simplified model of Q1D sinusoidal Fermi surfaces characterised by overlap integrals \(t_s\) and \(t_b\) along the \(a\) and \(b\) axes respectively do exhibit perfect nesting conditions for the transverse nesting vector, \(Q_T = (2k_F, \pi/b)\), neglecting the much smaller overlap integral along the \(c\) direction, provided the energy dispersion law

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**Figure 2.** Pressure dependence of the field-induced spin density wave transition temperature in \((\text{TMTSF})_2\text{ClO}_4\) at a field of 73.9 kG along the \(c^*\) axis. The broken curve is a guide to the eye and indicates the rapid suppression of the transition (see text).
at the Fermi level for wave-vectors parallel to the chain is linear in $k$ vector. The deviation from perfect nesting comes from second-order corrections to the linear dispersion law. However, it was shown that an equivalent model for the theory consists of keeping a linear dispersion law for the longitudinal dispersion but introducing a coupling $t'_b$ between second-nearest-neighbour chains in the transverse direction (Heritier et al 1984). The transverse coupling $t'_b$ is actually related to $t_b$ and $t_a$ via the following relation.

$$t'_b \sim t_b/t_a.$$  

(1)

This is the existence of a significant value for $t'_b$ which prevents the stability of an SDW state at low temperature. But, under high magnetic fields, an SDW state is restored when the magnetic field becomes larger than a ‘threshold field’ $H_T$, determined qualitatively by $H_T = t'_b$. It is thus natural to observe an increase of the threshold field under pressure (here about 10 kG per kbar) as $t'_b$ is expected to be enhanced by pressure according to equation (1). The calculation of Heritier et al (1984) shows that the transition temperature depends exponentially on $t'_b$. According to a recent calculation (Montambaux et al 1985), variations in $t'_b$ and $T_{SDW}$ are related by the following equation:

$$\frac{dT_{SDW}}{T_{SDW}} = -\frac{2}{(\text{Max } J_n(z))^2} \left( \frac{dt'_b}{t'_b} \right)$$

(2)

where $J_n(z)$ is the $n$th-order Bessel function associated with the label of the phase $n$. For the SDW phase we are looking at, the maximum of the Bessel function amounts to 0.4,
so that the enhancement prefactor in the right-hand side of equation (2) is of the order of 10. Close to ambient pressure, figure 2 shows that $dT_{\text{SDW}}/T_{\text{SDW}}$ is about $-30\%$ per kbar. A $3\%$ per kbar increase of $t_b$ would thus be large enough to account qualitatively for the experimental data. An estimate for the pressure dependence of $t_b$ can be derived from the study of the conductivity anisotropy under pressure at room temperature together with equation (1). Both $\sigma_a$ and $\sigma_b$ increase linearly with pressure in the low-pressure region ($P < 5$ kbar) with respective rates of $23\%$ kbar$^{-1}$ (Cooper et al 1985, Greene et al 1982) and $21.6\%$ kbar$^{-1}$ (Mailly 1983). It is thus reasonable to consider the ratio $\sigma_a/\sigma_b$ as pressure independent at room temperature in the pressure domain under consideration. Since the transverse motion of the electrons is diffusive at room temperature as shown by the absence of a well defined transverse plasma edge in the optical reflectance data (Jacobsen et al 1981), the conductivity and overlap integral anisotropy are related by the equation (Soda et al 1977)

$$\frac{\sigma_a}{\sigma_b} = \left(\frac{a}{b t_b}\right)^2.$$  

Consequently, the pressure coefficient of $t_a/t_b$ cannot be reasonably larger than, say $1\%$ kbar$^{-1}$. The shift of $t_a$ under pressure has not yet been measured in (TMTSF)$_2$X materials as it was in TTF-TCNQ or TSF-TCNQ by high-pressure optical techniques (Welber et al 1978). However, we feel there cannot be too large a difference between pressure dependences of plasma edges in similar organic conductors such as TTF-TCNQ and

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Figure 4. Proposed generalised phase diagram (temperature-pressure-magnetic field) for the Bechgaard salts (TMTSF)$_2$X.
Axial compressibility (Filhol et al. 1981) and optical reflectance data of TTF-TCNQ under pressure lead to $\delta \ln t''/\delta P \approx 3\%\text{ kbar}^{-1}$. We see by taking $\delta \ln t_b/\delta P \approx 3\%\text{ kbar}^{-1}$ following equation (1) and TTF-TCNQ data that the nesting mechanism can account fairly well for the pressure dependence of the FISDW state in (TMTSF)$_2$ClO$_4$.

We come now to the discussion of the relaxation rate under pressure. It is important to distinguish two different temperature domains. First, below the apparent microscopic energy $E_0$ (25 K) strong deviations to Korringa law are observed at ambient pressure (Bourbonnais et al. 1984) and have been ascribed to the development of the 1D power law divergence of sdw correlations. Secondly, for the high-temperature region, the sdw enhancement is weak and a somewhat more classical Korringa-like behaviour for $1/T_1$ is recovered. In the latter regime, figure 3 shows that the slope of $1/T_1$ decreases by a factor $\kappa^2$ of the order of 1.5 between 1 bar and 10 kbar. Such a pressure dependence for $1/T_1$ would correspond to an increase of the longitudinal bandwidth (or Fermi energy) by a factor $\kappa \approx 1.2$ if we assume $1/T_1 \approx \chi^2$. Such an enhancement for the bandwidth (namely $4t_g$ in a tight-binding model) is reasonable for (TMTSF)$_2$ClO$_4$ between 1 bar and 10 kbar taking into consideration the following two points:

(i) The thermopower of (TMTSF)$_2$ClO$_4$ ($S \sim T/E_F$) drops by 15% under 10 kbar at ambient temperature (Weyl 1985).

(ii) The calculated bandwidth of TSF-TCNQ (Herman 1977) versus lattice parameter along the stacking direction reveals also an increase of the TSF bandwidth by about 15% under 10 kbar.

The previous analysis relies on the assumption of Coulombic repulsions being small compared to the bandwidth.

At low temperature, the situation for $1/T_1$ under pressure is much more intricate. Several coexisting phenomena must be considered.

(i) The cross-over temperature (a quantity which becomes ill defined at high pressures) shows a tendency to move towards higher temperatures under pressure. It can be located approximately at 13 K and 25 K under 5 and 10 kbar respectively.

(ii) The enhancement of the Korringa constant with respect to the high-temperature regime, namely the ratio of high to low temperature slopes of $1/T_1$ versus temperature, exhibits an important decrease under pressure.

(iii) The microscopic energy $E_0$ for $T_1^{-1}$ enhancement has increased up to 50 K at 10 kbar.

The first two effects can be qualitatively understood within the framework of the model proposed by Bourbonnais et al (1984). The cross-over temperature is given by

$$T_x = T_x^0 \left( \frac{t_b}{E_F} \right)^{\alpha/(1 - \alpha)}$$

where $T_x^0 = t_b/\pi$ is the cross-over temperature for the free Q1D electron gas. In the presence of weak Coulomb correlations ($0 < \alpha < 1$ for positive backward scattering) the actual cross-over temperature $T_x$ can therefore be significantly depressed below its bare value $T_x^0$. The ambient pressure analysis strongly supports $T_x \approx 8$ K with $\alpha$ lying between 0.25 and 0.5 ($T_x^0 = 30$–80 K and $t_b/E_F = 0.05$–0.15 for the actual band parameters of (TMTSF)$_2$ClO$_4$) (Bourbonnais et al. 1984). The first non-zero contribution to $\alpha$ is proportional to the square of the Coulomb interactions (Prigodin and Firsov 1979) so that we can write in a good approximation $\alpha(P) \approx \alpha/k^2(P)$. Here $k(P)$ is the factor by which the longitudinal bandwidth is increased at a pressure $P$. In the present context,
\( k^2(P) \) is precisely the ratio of the slopes of 1/T \(_1\) at high temperature between 1 bar and P kbar. As \( t_b/E_F \) is almost constant under pressure, this gives the following relation:

\[
T_X(P) = k(P) T_X^0 \left( \frac{t_b}{E_F} \right)^{\alpha(P)/(1 - \alpha(P))}
\]

(5)

for the cross-over temperature as a function of pressure. For \( P = 10 \) kbar, \( k^2 \) (10 kbar) = 1.5 and with the ambient pressure value of \( T_X^0 \), \( t_b/E_F \) and \( \alpha \) we get \( T_X \) (10 kbar = 25 K). On figure 3 this temperature is located in a region which corresponds precisely to a change of regime for \( T_1^{-1} \). At 5 kbar equation (5) gives \( T_X \) (5 kbar) = 13 K.

The ratio between high- and low-temperature slopes of 1/T \(_1\) versus T is given approximately by \( (T_X/E_0)^{-\eta} \). Here, \( \eta \) is the power law exponent for the SDW response function in the 1D regime at low temperature (0 < \( \eta < 2 \). As the first contribution to \( \eta \) is always linear in the amplitude of the electron–electron interaction constant we can write \( \eta(P) = \eta/k(P) \). At ambient pressure (Bourbonnais et al 1984) we had \( \eta = 1 \) and \( (T_X/E_0)^{-1} \approx 3 \). So at 10 kbar we have \( (25/50)^{-0.8} = 1.7 \) by taking \( T_X = 25 \) K and \( E_0 = 50 \) K. Such an enhancement is compatible with data in figure 3. As far as the SDW characteristic energy \( E_0 \) is concerned, whose microscopic origin remains to be determined, an increase under pressure (as observed) is not inconsistent with a pressure increase of the bandwidth, since it only marks the onset of the microscopic mechanism for strong SDW correlations.

Another remarkable observation is the large pressure coefficient of the superconducting transition in \((TMTSF)_2X\) superconductors (Jerome and Schulz 1982) and in other organic superconductors (Laukhin et al 1985). As far as \((TMTSF)_2\)ClO\(_4\) is concerned, superconductivity is no longer observed above 3 kbar (i.e. when \( N(E_F) \) has dropped by an amount which can be estimated to 6% below its ambient pressure value).

If we look at \( T_c \), within a weak coupling picture for Q1D superconductors, it is given by the equation (Bourbonnais 1985)

\[
T_c = T_X \exp\left(-1/N(E_F)\hat{g}\right)
\]

(6)

where \( \hat{g} \) describes the effective attractive interaction in the 3D regime renormalised by the interplay between Cooper and Peierls channels in the 1D regime. As \( T_c \) decreases under pressure, the dominant factor in equation (6) must come from the exponential and not from the prefactor \( T_X \). A band broadening of 3% kbar\(^{-1}\) is thus insufficient to account for the initial pressure coefficient of \( T_c \), i.e. \(-30\% \) kbar\(^{-1}\) (Mailly 1983). Considering the very similar pressure dependences for \( T_c \) and \( T_{SDW} \), we may infer that nesting properties could be related to the still unknown mechanism which governs the superconducting attractive coupling.

Summarising, we can say that the behaviour of the NMR relaxation and \( T_{SDW} \) both support an increase of band parameters under pressure. The pressure dependence of the ‘threshold field’ as determined for the first time in the present work leads to the generalised \((P, T, H)\) phase diagram of \((TMTSF)_2X\) compounds which is illustrated in figure 4.

The salient result of the present high-pressure NMR study is the strong pressure dependence of the FISDW state in \((TMTSF)_2\)ClO\(_4\), which is consistent with the already known fast pressure dependence of \( T_{SDW} \) in systems such as \((TMTSF)_2PF_6\) or \((TMTSF)_2AsF_6\) under no applied magnetic field (Jerome and Schulz 1982). Furthermore, we have been led to propose a generalised phase diagram for the Bechgaard salts (figure 4). Such a diagram indicates a continuity between the SDW state of \((TMTSF)_2PF_6\)
like systems at ambient pressure and the SDW state which is stabilised by a large magnetic field in (TMTSF)$_2$ClO$_4$. However, the wave-vector of the magnetic distortion may not be the same in both situations.

The temperature dependence of the relaxation rate under pressure indicates a pressure-induced decrease of Coulomb correlations.

The diagram in figure 4 does not take into account the effects of anion ordering which can be considered as 'extrinsic' effects, loosely related to 'intrinsic' instabilities pertaining to the organic stacks. Anion orderings are important, however, for compounds with non-centrosymmetric ions such as ReO$_4$, FSO$_4$ etc. . . . Whenever ordering with doubling of the unit cell along the $a$ direction arises, it gives rise to a non-magnetic insulating state. Anion ordering is superimposed to the intrinsic behaviour of the organic stacks. In this respect (TMTSF)$_2$PF$_6$-like compounds seem to be better suited for the study of the organic stack's behaviour.

The present work has emphasised once more the strong links existing between magnetism and superconductivity in Bechgaard salts. Several crucial questions remain open and will require an appropriate answer in the future, for example:

(i) the nature of the superconducting state: singlet or triplet coupling and its connection to the nesting properties of the Fermi surface;

(ii) the interplay between different wave-vectors in the various SDW states of the (TMTSF)$_2$X compounds.

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