Angular and Temperature-Dependent $^{77}$Se NMR in the Metallic, SDW, and Field-Induced Spin Density Wave Phases of (TMTSF)$_2$X

L L Lumata$^1$, J S Brooks$^1$, P L Kuhns$^1$, A P Reyes$^1$, S E Brown$^2$, H B Cui$^1$, R C Haddon$^3$, J-I Yamada$^4$

$^1$Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA
$^2$Department of Physics and Astronomy, University of California at Los Angeles, Los Angeles, CA 90095 USA
$^3$Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521 USA
$^4$Department of Material Science, Graduate School of Science, University of Hyogo, Hyogo 678-1297, Japan

E-mail: brooks@magnet.fsu.edu

Abstract.

We report angular dependent $^{77}$Se NMR measurements on the partially quenched, metallic, and magnetic field-induced spin density wave (FISDW) states of $(TMTSF)\_2ClO_4$. To correlate the NMR data with the FISDW phase diagram, electrical transport was also measured concurrently in some cases. Similar measurements on $(TMTSF)\_2PF_6$ allow comparison of the behavior of the NMR signal of the spin density wave (SDW) transition with that of the FISDW transition. We present details of the experimental findings including the enhancement behavior, and correlations of the angular dependence of the NMR spectra with the spin-lattice relaxation rate $1/T_1$. A possible model to describe the behavior of the NMR signal intensity and $1/T_1$ in terms of a Hebel-Slichter mechanism upon crossing the metal-FISDW transition is presented.

1. Introduction

We have recently reported an investigation of the magnetic field induced spin density wave (FISDW) phase diagram of $(TMTSF)\_2ClO_4$ using angular dependent $^{77}$Se NMR [1], a description of which is presented in Fig. 1. In “relaxed” samples, where the cooling rate is very slow ($\approx 10$ mK/min), through the anion ordering transition $T_{ao} = 24$ K, superconductivity appears below 1.2 K, and in fields above 3.5 T, there is a cascade of FISDW transitions [2] followed by a series of anomalies involving the magnetoresistance [3], rapid oscillations, and Hall oscillations [4, 5]. The boundary between the metallic and FISDW phases is believed to be second-order, and transitions within this boundary first-order. We find that the positions of the peaks in the spin relaxation rate $1/T_1$ do not correspond to second-order line, but appear within this boundary, and that peaks in $1/T_1$ are also observed upon crossing first-order transitions within the FISDW phase. The crossing of phase boundaries is accomplished either by fixed field temperature-dependent sweeps, or angular-dependent measurements at constant temperature.
Figure 1. Top: overview of the T-B phase diagram for (TMTSF)$_2$ClO$_4$ for B/c based on a number of different measurements [3, 6, 7, 8], including a summary of the observed $^{77}$1/T$_1$ peaks (dotted-dashed line and open squares) and the corresponding features in the transport measurements (dark circles) from our recent work [1]. Field labels $B_{th}$, $B^*$, and $B_{re}$ are defined in text.) We note that a number of recent angular dependent studies including this work indicates that $B_{re}$ is at 26 T, and not at higher fields as previously reported in Ref. [3]. Bottom: model for changes in Fermi surface nesting in the metal, FISDW, and re-entrant phases (after Ref. [10]). As discussed in the text, there is a significant change in the $^{77}$Se NMR enhancement factor $\eta$ when the $B_{re}$ phase boundary is crossed at low temperatures.

where the field is also held constant. In the latter case, the orbital nature ($B_\perp = B_0\cos(\theta)$) of the FISDW phases allows a full investigation of field-dependent phase diagram for a constant NMR frequency. In the process of this work, we have explored a number of phenomena involving NMR in these materials, which are discussed in more detail in this report.

2. Experimental methods and the enhancement factor

Single crystals of (TMTSF)$_2$ClO$_4$ with typical dimensions $5 \times 0.6 \times 0.5$ mm$^3$ were inserted microcoils made from # 40 copper wire with filling factors of order 50 to 75% by volume. Four 12 $\mu$m Au wires were attached to the sample ends with carbon paste for concurrent ac 4-terminal electrical transport measurements.

In the TMTSF donor, the selenium sites are situated close to the molecular orbitals, with a natural $^{77}$Se abundance of 7.5% and $\gamma = 8.13$ MHz/T. A standard spin-echo method was used, where pulse optimization was done using $\pi/2-\pi/2$ pulse trains ranging from 50 ns to 10 $\mu$s in duration to obtain the maximum NMR intensity. Typically, in the metallic state the optimum $\pi/2$ pulse width was $\tau_M = 1$ $\mu$s. However, upon entering the FISDW phase, we found that for certain sample-coil configurations, the signal would quickly vanish. As others have observed [14], the signal in a SDW state can be recovered by reducing the pulse duration $\tau_{sdw}$ (and therefore integrated power) to between 50 ns and 500 ns. Since the same pulse power level (12 W) was used for all measurements, the RF enhancement factor was defined as the ratio $\eta \equiv \tau_M/\tau_{sdw}$. The effect is associated with rf-induced displacement or depinning of the SDW phase by the electric fields. There is no enhancement ($\eta=1$) in the metallic phase, and in the FISDW phase...
\( \eta \) will increase according to the ability of the electric field to modulate the condensate [11]. The electric fields associated with de-pinning are typically of order 5 mV/cm or less [12, 13], and in the present case we estimate that the ac electric field in the NMR coil is of similar magnitude (≈ 4 mV/cm) (in the b’-c* plane) (see also Ref. [14]). The spin-lattice relaxation rate \( T_1^{-1} \) was defined using a single-exponential form for the magnetization recovery, and varied by less than 10% over the spectrum in all cases. Long recycle times (0.5 to 1 s) were used to avoid sample heating. The spectra were typically taken in two modes. In the frequency mode, the spectrum was derived from the fourier transform of the echo signal, and in the field-sweep mode, the amplitude of the echo was recorded as a function of magnetic field.

![Figure 2. Evolution of \(^{77}\text{Se}\) NMR spectra with temperature (a) High-temperature spectra of \((\text{TMTSF})_2\text{ClO}_4\) at 12.11 T. The splitting above 40 K is due to chemically inequivalent Se sites in the TMTSF molecule. The split peaks begins to merge into a single broad peak around 35 K as the anion ordering temperature \( T_{so} \) is approached. (b) Low-temperature field-sweep spectra from the metallic to FISDW state at 98.2 MHz. The single-peak metallic lineshapes broaden and split into double-horned spectra below the FISDW transition. Note that the frequency/field (0.1 MHz/0.012 T) linewidths for \( T = 14 \) K in (a) and 12 K in (b) are similar.](example-image.png)

![Figure 3. (a) Power dependence of the \(^{77}\text{Se}\) (field-sweep) spectrum for constant \((\tau_{\text{SDW}})\) pulse widths at 98.2 MHz and 1.8 K in the FISDW phase. The optimum pulse parameters are near 38 dB, which corresponds to 12 W. (b) Dependence of the spin-echo intensity on power attenuation at the central peak and shoulder regions of the spectra.](example-image.png)

In Fig. 2 the temperature dependence of the \(^{77}\text{Se}\) spectrum is shown for \((\text{TMTSF})_2\text{ClO}_4\). Above 4 K, a metallic pulse width was used \((\tau_{M} = 2 \mu s)\), and below 4 K, in the FISDW phase, the pulse width was reduced \((\tau_{\text{sdw}} = 100 \, \text{ns})\) due to the enhancement factor. The power dependence has also been studied in the FISDW phase for fixed \(\tau_{\text{sdw}}\) in the range 450 to 900 ns shown in Fig. 3. For high power (26 dB), the spectrum is saturated. For a reduced, optimum power near 38 dB, the amplitude is greatest, and for decreasing power the amplitude drops. The changes in the spectral shape with power are not presently understood.
3. Angular-dependent $^{77}$Se NMR at constant field and frequency

Orbital effects are primarily responsible for driving the FISDW transitions in Fig. 1. Hence by fixing the field and frequency at, for instance $B_0 = 30 \, T$, the entire $(TMTSF)_2\text{ClO}_4$ phase diagram can be probed by rotating the sample since the NMR frequency depends only on $B_0$, and the FISDW transitions depend on $B_0 \cos(\theta)$. In all cases reported herein, the rotation was in the b-c plane. We show first in Fig. 4 the $^{77}$Se NMR spectra vs. a rotation in the b-c plane in the metallic state above the FISDW transition, which gives an estimate of the size of the Knight shift effect, which is of order 120 ppm between the B//b and B//c orientations.

In a second angular dependent study, the angular dependent NMR spectrum of a partially quenched sample (the cooling rate was of order 1 K/s or greater through the $T_{ao}$ range) was measured just below the FISDW phase boundary (Fig. 5a). The double peaked spectrum due to the SDW order is visible below the threshold field region for the FISDW (in the range 60 to 120 degrees), but then grows dramatically when the FISDW state is entered. We believe the additional pinning of the coexisting SDW and FISDW phases leads to and enhanced double peaked spectra, based on comparisons with well-ordered samples to be discussed below. (For a sample rapidly quenched from room temperature, $(TMTSF)_2\text{ClO}_4$ will exhibit a zero field SDW ground state below about 5 K.)

**Figure 4.** Anisotropic relative Knight shift at 10.6 T, 2.47 K in the metallic phase above the FISDW transition.

**Figure 5.** a) Angular evolution of spectra at 109 MHz and 2K for a partially quenched sample, where the zero field SDW order competes with metallic and FISDW components. Here the threshold field ($B_{th} \approx 6.4 \, T$) for FISDW corresponds to $\theta = 60$ and 120 degrees, where 0 and 90 degrees correspond to B//c and B//b respectively. The same pulse was used for all the field-swept spectra. The changes in line width are significantly larger (4,700 ppm) than the Knight shift in Fig. 4. b) Angular dependent field-swept spectra for a relaxed sample at 1.8 K in the range of the two threshold field angles $\pm 60$ degrees. The field is aligned along the TMTSF axis at position X.

In Fig. 5b the angular dependence of field-sweep spectra for a relaxed sample are shown for angles between the threshold field angles of $\pm 60$ degrees. The linewidth narrows in the metallic
state corresponding to $\pm 65$ degrees, and we note that near $+25$ degrees (marked X) there is a narrowing of the spectrum, which is associated with the alignment of the field along the donor axis.

**Figure 6.** Angular-dependent NMR and electrical transport at 7.84 T, 4.28 K for a partially-quenched ClO$_4$ above the FISDW phase boundary. The orientation $B//b$ corresponds to $\pm 90$ deg. (a) ADMR and the metal spectra peak center fitted to $|B \cos(\theta)|^{3/2}$. There is a systematic difference between the positions in angle of the extrema of the two curves: The NMR c*-axis is $+\sim 25$ degrees away from the transport c*-axis. We note that the minima in $R_{zz}$ were used to identify the exact positions for $B//b$ to calibrate the rotation stage. (b) $1/T_1$ (solid squares) and spectral FWHM (solid dots) fitted to $|B \cos(\theta)|$.

4. Concurrent electrical transport, enhancement, and spin relaxation measurements.

The sample resistance was measured concurrently with spectra and the spin-lattice relaxation rate $1/T_1$ to correlate previously known features of the FISDW phase diagram with the new $^{77}$Se NMR behavior. An example is shown first for the metallic state in Fig. 6a where the resistance and relative Knight shift of a partially quenched sample are plotted vs. angle, and in Fig. 6b where the corresponding full width - half maximum (FWHM) of the spectra and $1/T_1$ are shown. (The temperature is too high to see the “magic angle” effects in $R_{zz}$, but in general find no evidence for magic angle effects in the NMR signal in accord with previous investigations [9].) The relative changes in $1/T_1$ with angle in the metallic state are comparatively smaller than the changes observed in the FISDW phases. Many of the details of Fig. 6b, including the dips in $1/T_1$ and the systematic departure of the FWHM from the $|B \cos(\theta)|$ behavior remain unexplained at present.

For angular dependent NMR data, the angle was set, and the field swept up from the metallic state to the field of interest ($B_0$) and the MR was recorded. In Fig. 7 an example of the correspondence between the resistance ($R_{zz}$), $1/T_1$ and the spin-spin relaxation rate $1/T_2$ are shown, starting well within the FISDW phase at 1.5 K and $B_0 = 14$ T for $\theta = 0$ (or 180) degrees ($c-b-c$ axis rotation). It is evident how the features in the magnetoresistance, which define the FISDW phases, correlate with the NMR data. Specifically, for $B//b$, the system is in the metallic state, but as $B_1 = B_0 \cos(\theta)$ increases, the threshold field is approached at $1/T_1$ is observed to increase. However, the peak in $1/T_1$ occurs not at the second order threshold field $B_{th}$, but at a
FISDW subphase transition \( B_1 \). It is interesting to note that the magnetoresistance at 14 T, at the critical angle where \( B_{th} = B_0 \cos(\theta) \), exhibits a sharp dip that indicates the position of the second order phase boundary. Hence the peak in \( 1/T_1 \) clearly occurs within the FISDW phase in a subphase transition (i.e. \( B_1 \); see Fig. 1). Angular dependent \( 1/T_1 \) results are shown in Fig. 8a,b for two different temperatures (\( b - c - b \) axis rotation). The enhancement factor in Fig. 8c also shows a significant change with angle, exhibiting a metallic value \( \eta = 1 \) for \( B_{\perp} < B_1 \), a peak at \( B_1 \), and then a decrease (\( \eta \approx 5 \)) for \( B_{\perp} > B_1 \). Also prominent is a dip in \( 1/T_1 \) for \( \theta = 25 \) degrees which occurs when the field is parallel to the long axis of the donor molecule, where a narrowing of the NMR spectral line also occurs (see “X” in Fig. 5b.) This feature does not show up in the electrical transport.

**Figure 7.** \( c - b - c \) axis rotation: simultaneous (a) resistance, (b) \( ^{77}\text{Se} \) \( 1/T_1 \) where the “dip” effect in \( 1/T_1 \) (marked “X”) is evident below 30 degrees where the field is aligned along the main donor axis, and (c) \( 1/T_2 \) measurements vs. angle for 1.5 K and 14 T.

**Figure 8.** \( b - c - b \) axis rotation: \( 1/T_1 \) vs. \( \theta \) for (a) 3.87 K and (b) 1.8 K at 12.86 T. c) The enhancement factor \( \eta \) corresponding to the data for (b) at 1.8 K. The “dip” effect in \( 1/T_1 \) is evident below 30 degrees.

5. High field NMR results

To explore the subphase transitions in the FISDW phase, high field \( (B_0 = 30 \) T) experiments were carried out in a resistive magnet, and the main results are shown in Fig. 9. The trends are similar to Fig. 7 for rotation away from \( B//b \) where there is a slow increase in \( 1/T_1 \) as the threshold field is approached, followed by a peak in \( 1/T_1 \) at the first order \( B_1 \) transition. At higher effective \( B_{\perp} \) fields, a significant peak, termed \( B^* \), appears in the range 15 to 17 T, and another feature appears near 26 T which corresponds to the so-called re-entrant phase boundary \( B_{re} \) (see Fig. 1). The enhancement parameter \( \eta \) also has a significant change as \( B_{re} \) is crossed, going from \( \eta = 5 \) to \( \eta = 1 \). However, the corresponding spectra above \( B_{re} \) are
still representative of the presence of antiferromagnetic order [1]. The data upon crossing $B_{re}$ are consistent with a model [10] (see also Fig. 1) where both Fermi surfaces are nested at lower fields, (e.g. in the ”dome” region between $B^*$ and $B_{re}$) but above $B_{re}$ only one of the Fermi surfaces is nested. The un-nested Fermi surface could, for instance “short out” the enhancement mechanism, but the nested Fermi surface would still provide antiferromagnetic order.

In order to complement the variable $B_{\perp}$ data at lower temperatures, we carried out several temperature dependent investigations at 23 T (Fig. 10) which passes through the “dome” phase (see Fig. 1) and at 29 T (Fig. 11) which is above the $B_{re}$ phase boundary. A general observation of these results, similar to those reported in our previous work[1] is that the peak in $1/T_1$ occurs below the onset ($B_{th}$) of semimetallic behavior. To check this effect in a SDW system, we have done a similar simultaneous transport and $^{77}$Se NMR experiment on $(TMTSF)_2PF_6$ as shown in Fig. 12. Here we find that the peak in $1/T_1$ is closer in temperature to the onset of semimetallic behavior. Also shown in Fig. 13 is a summary of temperature dependent $1/T_1$ measurements for different fields where we note that in no case did the peak in $1/T_1$ fall on the second order phase boundary.

6. Discussion and Summary
An important finding in this investigation for the FISDW behavior in $(TMTSF)_2ClO_4$ is that, when approaching the FISDW phase from the metallic phase, either with increasing field or decreasing temperature, the peak in $1/T_1$ does not occur at the second order phase boundary,
but within it. In comparison, for a SDW transition (i.e. not field induced as in (TMTSF)$_2$PF$_6$), the peak in $1/T_1$ is nearly coincident with the onset of the semimetallic transition.

To understand the origin of the peak in $1/T_1$ and its relationship to the opening of the FISDW gap, we have considered a simple model based on the Hebel-Slichter effect for a BCS superconductor[15]. Here the ratio of the relaxation rate in the superconductor to the normal metal is given by

$$\frac{T_n}{T_s} = 2 \int_0^\infty \rho^2(x, T) \left[1 + \eta_0^2(T)/x^2\right] * f(x, t) [1 - f(x, T)] dx$$

(1)

where $x = (E - E_F)/kT$, $\eta_0(T) = \epsilon_0(T)/kT$, and $f(E, T)$ is the Fermi distribution function. The density of states $\rho_s$ is weighted by the BCS density of states, taking into account the width of the energy levels, according to
Fermi surface below main SDW phase transition \([17]\). The 3 K anomaly has also been attributed to an improved nesting of the characteristic relaxation rate of the system, which in the case of \((TMTSF)_2PF_6\) may involve phason fluctuations. We note that “dynamic” effects have been used \([16]\) to describe some features in \(1/T_1\).

\begin{align}
\rho_s(x, T) &= (2\delta)^{-1} \int_{-\delta}^{x+\delta} \rho_{BCS}(y, T) dy \\
\delta &= \Delta/kT \quad \text{and} \quad \Delta \text{ is the BCS gap. This description leads to the “Hebel-Slichter” peak in } 1/T_1 \text{ which appears below } T_c \text{ due to the relative contributions of the temperature dependence terms in Eq. 1. An example of the behavior of } 1/T_1 \text{ based on Eqs. 1 & 2 is shown in Fig. 14 using a simple Ginzburg-Landau gap model. Although the computed peak in } 1/T_1 \text{ appears below } T_c, \text{ we expect that in the case of the FISDW in } (TMTSF)_2\text{ClO}_4, \text{ due to imperfect nesting and the presence of two Fermi surface sheets, only part of the Fermi surface becomes gapped at the FISDW threshold, and we speculate that only below the “dome” region do both FS sheets become nested (see Fig. 1. Hence the parameters and functions in Eqs. 1 & 2 must be modified to account for the more complex FISDW behavior. The peaks in } 1/T_1 \text{ that appear at the first order subphase FISDW transitions can also be modelled, in principle, by including the changes in } \Delta \text{ at } B_1, B^*, \text{ and } B_{re}.\)

We note that “dynamic” effects have been used \([16]\) to describe some features in \(1/T_1\) such as the 3 K anomaly that appears in \((TMTSF)_2PF_6\), as shown in Fig. 12. The mechanism is essentially that which arises when the Larmor frequency coincides with the inverse of the characteristic relaxation rate of the system, which in the case of \((TMTSF)_2PF_6\) may involve phason fluctuations. The 3 K anomaly has also been attributed to an improved nesting of the Fermi surface below main SDW phase transition\([17]\).
Figure 14. $1/T_1$ vs. $T/T_c$ computed from the Hebel-Slichter model [15]. Here a Ginzburg-Landau gap $\Delta = 1.76(1-t)^{1/2}$, with $t = T/T_c$ the reduced temperature was used. An empirical broadening function similar to Eq. 2 gave uncertainties that may reduce the peak position from $t = 0.8$ to 0.7.

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