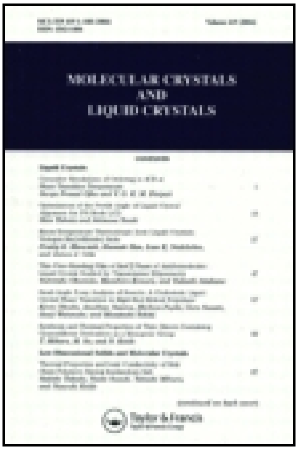

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NMR Studies of $(TMTSF)_2PF_6$

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NMR STUDIES OF $(TMTSF)_2PF_6$

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Pulsed NMR determinations of the relaxation times T_2, T_2^* and T_1, as a function of temperature and field, for the methyl group protons in $(TMTSF)_2PF_6$ are reported. Below the metal-insulator transition (T_{MI}) T_2^* shortens while T_2 increases, indicating a line which is inhomogeneously broadened due to the onset of a SDW. The SDW also contributes to the spin-lattice relaxation rate, T_1^{-1}, in the neighborhood of T_{MI}. A frequency dependent maximum in T_1^{-1} is observed near 20K and is attributed to methyl group rotation. A frequency independent maximum at 58K suggests a structural phase transition involving rearrangement of the methyl and PF_6 groups.

The magnetic nature of the spin-density-wave (SDW) ground state of $(TMTSF)_2PF_6$ makes NMR a particularly useful probe. We have performed proton NMR, using both CW and pulsed techniques, as a function of temperature and frequency. The results reveal the inhomogeneous line broadening expected for the interaction of the SDW with inequivalent protons. Fluctuations in the SDW order parameter near the metal-insulator transition temperature, $T_{MI}=T_{SDW}=12K$, contribute to the spin-lattice relaxation rate, T_1^{-1}.

In a previous publication,[1] it was shown that the proton NMR linewidth, measured CW at 10.5 MHz (2.5 kgauss), increases by approximately 25% on cooling through T_{SDW}. Work by Andrieux et al.[2] at 45 MHz showed a somewhat larger increase in linewidth below T_{SDW}. This paper reports preliminary results at fields between those of the previous measurements.

In Fig. 1, are shown the results of T_2 and T_2^* measurements at 20 MHz (4.7 kgauss). At high temperature ($T \gtrsim T_{SDW}$), T_2^* was determined by examination of the free-induction decay (FID) following a $\pi/2$ pulse and by dipole echo studies. For $T \lesssim T_{SDW}$, T_2^* was obtained from the FID and from the echo width in a spin-echo

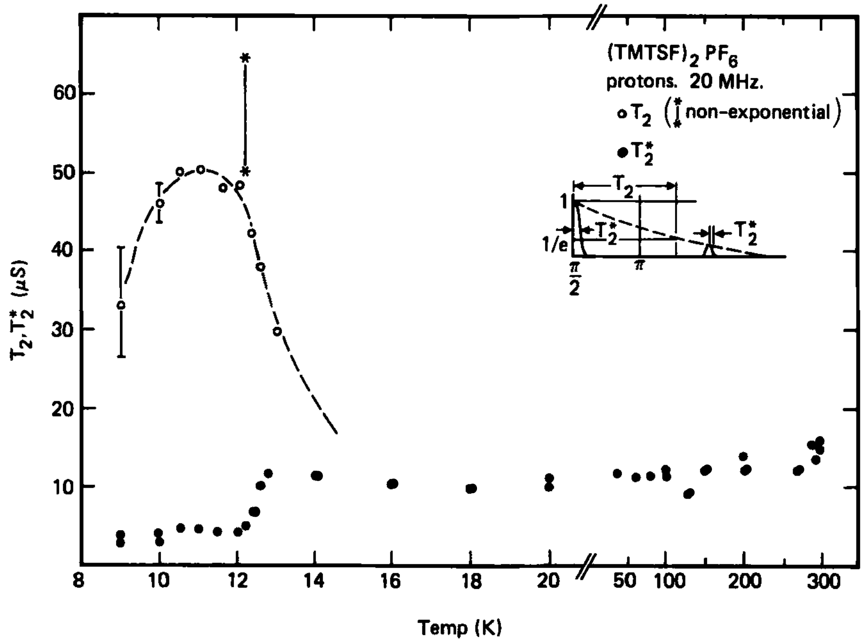

FIGURE 1 Proton T_2 and T_2^* at 20 MHz in $(TMTSF)_2PF_6$.

sequence ($\pi/2$-τ-π). T_2 was measured by the usual spin-echo method. Above T_{SDW}, the values of T_2^* are in agreement with the earlier CW linewidth measurements: $T_2^* = 1/\gamma\Delta H$. However, at low temperature T_2^* decreases by a factor of three, in contrast to the 25% increase in linewidth reported earlier.[1] This apparent discrepancy is attributed to the field difference in the two experiments, the pulsed measurement being performed in the range where the susceptibility is becoming non-linear in association with the spin-flop behavior.[3,4]

The difference between T_2 and T_2^* in the SDW state confirms that the observed linebroadening is indeed of inhomogeneous origin. An estimate[5] of the dipole field at each proton site due to moments aligned antiferromagnetically on the same and neighboring molecules gives values ranging up to 80 gauss for a SDW amplitude of one Bohr magneton. The observed broadening is only a few gauss; therefore we conclude that the SDW amplitude is only a few percent. This magnitude is in agreement with the prediction of mean field theory.[6]

The increase in T_2 below T_{SDW} reflects a reduction in the spin-spin interaction because of the different resonant frequencies of

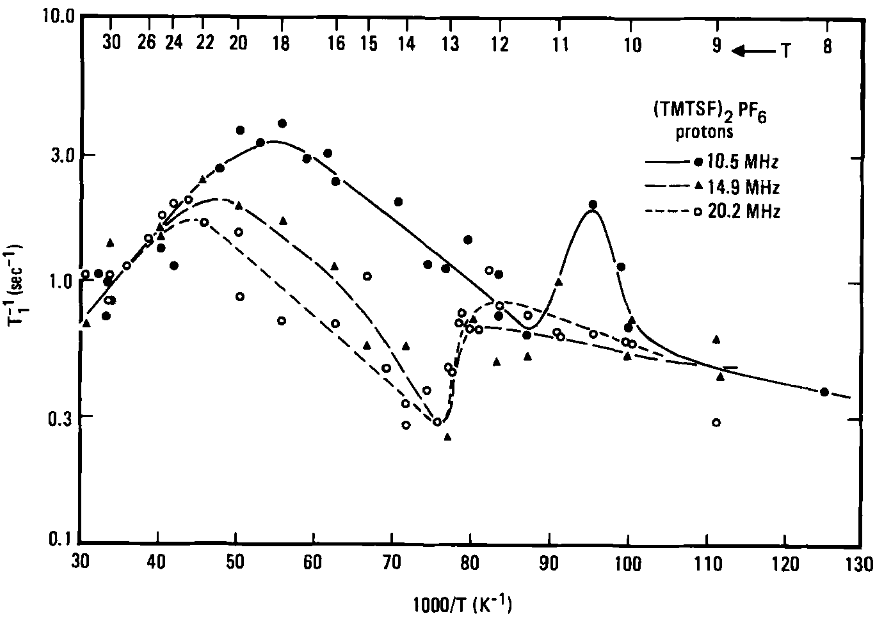

FIGURE 2 Proton spin-lattice relaxation rate in the vicinity of the SDW transition. The 10 MHz data were obtained on a different spectrometer, and therefore the apparent temperature shift should be ignored.

the individual protons. Mutual spin-flips, due to the dipole-dipole interaction, can no longer conserve Zeeman energy.

Spin-lattice relaxation rate (T_1^{-1}) measurements were made at frequencies up to 20 MHz. The low temperature results are shown in Fig. 2. Near T_{SDW}, there is an enhancement of T_1^{-1} by about a factor of three due to the critical fluctuations of the order parameter. A theoretical discussion of this effect is given separately.[5]

A second maximum in the relaxation rate, at 18K for 10 MHz moving to 24K at 20 MHz, is attributed to the effects of methyl group rotation. The data are semiquantitatively consistent with the usual theory of molecular dynamics, but differ in detail. The discrepancies are attributed to the quantum mechanical nature of methyl rotation,[7] and the absence of proton-proton dipolar linebroadening as the motion

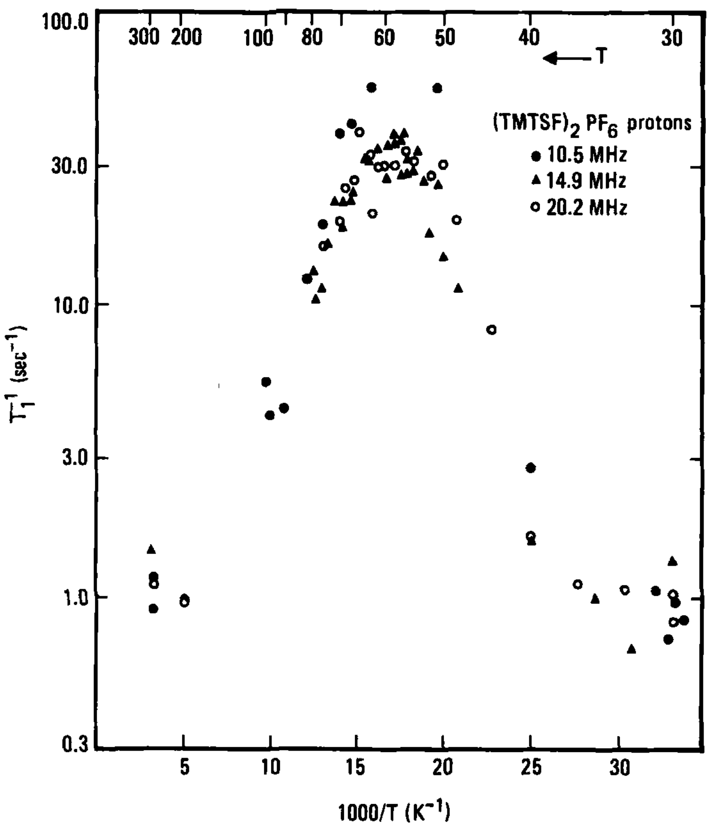

FIGURE 3 Proton spin-lattice relaxation rate around 60K.

decreases implies that the tunnelling frequency is greater than the nuclear Larmor frequency.

A third maximum in T_1^{-1} is observed at 60K (see Fig. 3). This was previously[1] associated with the interaction of the methyl protons with fluorine-19 moments on the PF_6^- species. However, the frequency independence of the peak position makes it obvious that the dynamics are not the simple classical behavior associated with PF_6^- rotation. It may be that there is some sort of structural transition involving cooperative locking of the anions, with relatively strong coupling to the methyl protons.

Nowhere do we observe any Korringa-like ($T_1^{-1} \propto T$) relaxation behavior. Indeed, if such a conduction electron contribution were dominant at room temperature, ($T_1^{-1} \simeq 1$ sec $^{-1}$) then, over the remainder of the temperature range covered, it is at least two orders of magnitude smaller than the processes which we have described. The assumption of dipolar coupling between SDW and protons below 12K is therefore justified.

In summary, we have observed the effects of the SDW transition on the proton NMR linewidth, spin-spin interaction and spin-lattice relaxation rate. The magnitude of the inhomogeneous broadening implies a SDW amplitude of order a few percent of a Bohr magneton.

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