Rapid Communications

Proton NMR in the organic conductor tetramethyltetraselenafulvalinium hexafluorophosphate

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Proton NMR measurements have been made on $(TMTSF)_2PF_6$ (di-tetramethyltetraselenafulvalene PF_6) at 10 MHz. The linewidth increases below the metal-insulator transition, T_{MI}, indicating the onset of inhomogeneous local fields associated with the appearance of a spin-density wave. The spin-lattice relaxation time T_1 increases steeply below T_{MI}. Two minima in T_1, at 18 and 60 K, are tentatively associated with changes in the molecular dynamics.

In this Communication we report preliminary cw and pulsed NMR results on the organic conductor $(TMTSF)_2PF_6$, where TMTSF is the donor tetramethyltetraselenafulvalene. The charge-transfer salts of TMTSF are proving to be a remarkable series of materials,[1] exhibiting relatively low metal-insulator transition temperatures (T_{MI}) and superconductivity.[2-7] Electron-spin-resonance measurements[8] on $(TMTSF)_2PF_6$ at ambient pressure revealed that the magnetic properties changed much more abruptly at T_{MI} than expected for a charge-density-wave (CDW) distortion. Further studies[9-13] have been presented as evidence for a spin-density-wave (SDW) instability, and a ground state similar to an antiferromagnet.

In an effort to observe the effects of antiferromagnetic ordering in the low-temperature phase of $(TMTSF)_2PF_6$, we have undertaken cw NMR measurements of the proton linewidth and pulsed measurements of the spin-lattice relaxation time T_1. These experiments were made at 10 MHz, corresponding to a resonance field, H_0, of 2.3 kG. In an independent study, Andrieux et al.[13] made similar measurements at 45 MHz (10.5 kG). Note that the spin-flop field observed by Scott et al.,[10] and by Mortensen et al.[12] at 6–8 kG falls between these two values.

cw measurements on a combination of both polycrystalline samples (80 mg) used in the work of Ref. 10 were made with a bridge circuit based on a hybrid junction and using a PAR 5202 radio-frequency

lock-in as the detector. The signal could be observed directly (i.e., without modulation and lock-in techniques) as the field was swept through resonance. The line shape was found to be Gaussian with a full width (see Fig. 1) of 6.0 ± 0.5 G between 12 K and room temperature. At the metal-insulator transition $T_{MI} = 11.5$ K there is a step in the linewidth and at low temperature the absorption envelope is approximately 25% broader and still Gaussian.

T_1 measurements were made on the same sample using a home-built pulse spectrometer of standard design. Peak transmitter power was such that the duration of a $\pi/2$ pulse was 1.2 μsec. A ($\pi, \tau, \pi/2$) pulse sequence was used, and the major limitation in
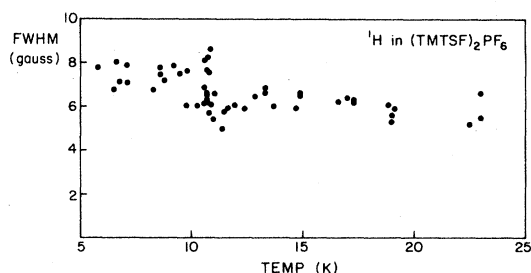

FIG. 1. Full width at half maximum of the proton resonance at 10 MHz in $(TMTSF)_2PF_6$. The 6-G value persists, independent of temperature, up to 300 K.

the signal-to-noise ratio was due to a receiver recovery time of ~ 10 μsec, relatively long compared to the free-induction-decay time. The FID was "captured" using a Biomation 8100 transient recorder and signal averaged (8–32 repetitions, depending on temperature) with a Nicolet 1170. Seven to ten delay times ($\tau = 10$ μsec to 5 sec) were used at each temperature. In all cases the recovery of the FID amplitude was well described by a single exponential. The data T_1 vs T are shown in Fig. 2. Two distinct minima in T_1 are observed at 18 and 60 K, respectively. The metal-insulator transition is seen as the region of steepest slope in the low-temperature behavior.

The 6-G FWHM corresponds to a second moment $M_2^{expt} = 9$ G^2, which is intermediate between the rigid-lattice value $M_2^{RL} \sim 23$ G^2 and the motionally (methyl-rotation) narrowed value $M_2^{MN} \sim 5$ G^2 calculated on the basis of the structure of Bechgaard et al.[1] and Jacobsen et al.[14] (the major contribution, $\sim 85\%$, to each of these is due to intramethyl proton-proton interactions). This is particularly puzzling in view of the fact that the width is independent of temperature over such a wide range. A possible explanation for the intermediate linewidth value is that half of the methyl groups are rotating while the other half are not. The structure[1,14] of $(TMTSF)_2PF_6$ is such that there are two types of methyl, one of which may be hindered in its rotation by close interaction with a selenium atom on the neighboring molecule.

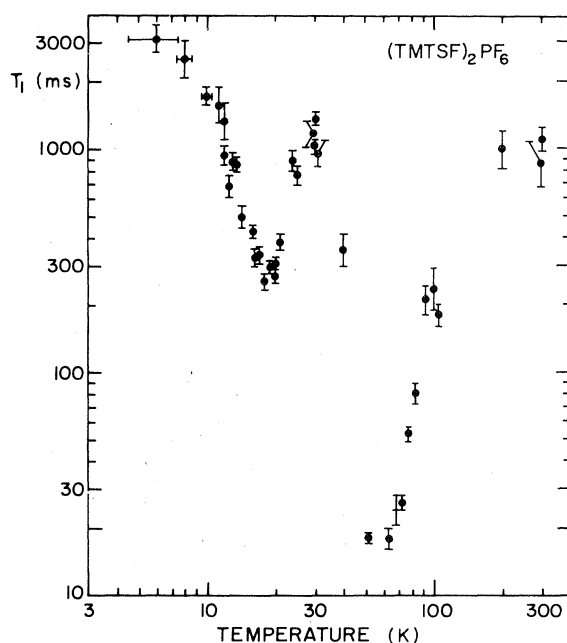In spite of the difficulty of interpreting the absolute magnitude of the linewidth in the metallic phase, it is clear that the increase below 11.5 K is due to an additional broadening mechanism in the semiconducting state. Such a phenomenon arises naturally within the SDW picture of the metal-insulator transition: the development of static electronic moments associated with the pinned SDW creates an inhomogeneous local field at the inequivalent proton sites. As the electronic moments lock into the SDW state their contribution to relaxation processes decreases and the proton T_1 lengthens, as seen in the steep slope of $T_1(T)$ near 11 K. (Our data hint at a weak, narrow T_1 minimum at T_{MI}, but the signal-to-noise ratio makes it impossible to resolve it fully.)

From the magnitude of the increase in linewidth ($\Delta M_2^{expt} \simeq 5$ G^2) and assuming dipolar interaction with electronic moments localized near the center of the TMTSF molecule, it is possible to estimate the effective moment per site: $\mu/\mu_B \sim (10^{-1}-10^{-2})$ (the wide range reflects the uncertainty in spin density within the molecule and in the orientation of the sublattice magnetization).

The T_1 data show a much richer temperature dependence. Consider first the T_1 minimum at 60 K. It is in this temperature range that Nevald[15] observed a change in the linewidth of the ^{19}F NMR absorption corresponding to the cessation of PF_6 rotation upon cooling. We therefore attribute the enhanced proton relaxation rate to dipolar ^1H-^{19}F interaction, and analyzed the data according to

$$T_1^{-1} = \frac{\gamma_H^2 H_{HF}^2 \tau}{1 + \omega_0^2 \tau^2} \quad ,$$

where H_{HF} is the amplitude of the fluctuating dipole field at the proton due to fluorine, γ_H and ω_0 are the proton gyromagnetic ratio and Larmor frequency, and $\tau = \tau_0 e^{\Delta/T}$ is the fluorine correlation time with activation energy Δ. The results are $\Delta = 450 \pm 100$ K, $\tau_0^{-1} = [1.5(+7, -1.2)] \times 10^{11}$ sec^{-1}, and $H_{HF} = 3.5 \pm 0.5$ G, values which are not unreasonable for the motion of the PF_6^- anion. (If the 60-K T_1 minimum were due to methyl motion these parameters predict an increase in proton linewidth by a factor of at least 4 centered at 25–30 K. No such increase is observed.)

We now turn to the minimum in T_1 at 18 K. It is intriguing that this temperature corresponds to the transition temperature reported in the earliest transport[1,14,16] and ESR[8,9] experiments. However, it is considerably above more recent determinations[5,10,12,17,18] of the transition temperature (~ 12 K) and above the step in linewidth discussed earlier in this paper. Thus, although we cannot yet rule out fluctuation effects in the electronic spin density, we shall consider the methyl dynamics as a source of relaxation. The quantum-mechanical nature of the methyl group can yield a type of motion which produces a T_1 minimum, without accompanying increase in linewidth. As discussed by Allen[19] a tunneling-in-

FIG. 2. Spin-lattice relaxation time T_1 of protons in $(TMTSF)_2PF_6$ measured at 10 MHz.

duced splitting of the threefold rotor ground state larger than the dipolar broadening interaction yields a linewidth narrowed to one-quarter of the rigid-lattice value. Thus, a slowing from a hindered rotation rate, $\omega_{rot} \propto \exp(-E_a/T)$ to a tunneling rate ω_{tun}, where $\gamma^2 \hbar / r_{HH}^3 < \omega_{tun} < \omega_0$ will produce a T_1 minimum when $\omega_{rot} \simeq \omega_0$, but negligible change in linewidth. In order to check these ideas it will be necessary to study the behavior of the T_1 minimum as a function of resonance frequency.

In contrast to our data (at 10 MHz), Andrieux *et al.*[13] report Korringa-like behavior ($T_1^{-1} \propto T$) between 13 and 30 K (at 45 MHz) and a broad minimum in T_1 around 8 K. It seems that at low frequency the methyl dynamics mask relaxation through the conduction electrons, but we note that if Korringa behavior persists to room temperature the relaxation rate would be 10 times more rapid than we observed. Hence, we believe that the proton-electron relaxation in the metallic phase is not a simple frequency-independent Korringa process. The difference in behavior of T_1 below T_{MI} at 10 and 45 MHz

may result from spin-flopped magnetic alignment at the higher field.

To summarize: Proton NMR linewidth and T_1 measurements have confirmed the magnetic nature of the metal-insulator transition in $(TMTSF)_2PF_6$. At a Larmor frequency of 10 MHz molecule dynamics apparently mask the proton-electron relaxation processes in the metallic state. The frequency dependence of T_1 must be determined in order to decide conclusively whether the 18-K T_1 minimum is due to methyl motion or to electronic fluctuations. Such studies will also elucidate the effects upon relaxation rate of the spin-flop transition which has been observed at 8 kG.

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[1]K. Bechgaard, C. S. Jacobson, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Commun. **33**, 1119 (1980).

[2]D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L-95 (1980).

[3]M. Ribault, G. Benedek, D. Jerome, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L-397 (1980).

[4]K. Andres, F. Wudl, D. B. McWhan, G. A. Thomas, D. Nalewajek, and A. L. Stevens, Phys. Rev. Lett. **45**, 1449 (1980).

[5]R. L. Greene and E. M. Engler, Phys. Rev. Lett. **45**, 1587 (1980).

[6]M. Ribault, J. P. Pouget, D. Jerome, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L-607 (1980).

[7]K. Bechgaard, K. Carniero, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen, and J. C. Scott, J. Am. Chem. Soc. **103**, 2442 (1981).

[8]H. J. Pedersen, J. C. Scott, and K. Bechgaard, Solid State Commun. **35**, 207 (1980).

[9]W. M. Walsh, F. Wudl, G. A. Thomas, D. Nalewajek, J. J. Hauser, P. A. Lee, and T. Poehler, Phys. Rev. Lett. **45**, 829 (1980).

[10]J. C. Scott, H. J. Pedersen, and K. Bechgaard, Phys. Rev. Lett. **45**, 2125 (1980).

[11]J. C. Scott, H. J. Pedersen, and K. Bechgaard, Chem. Scr. (in press).

[12]K. Mortensen, Y. Tomkiewicz, T. D. Schultz, and E. M. Engler, Phys. Rev. Lett. **46**, 1238 (1981).

[13]A. Andrieux, D. Jerome, and K. Bechgaard, J. Phys. (Paris) Lett. **42**, L-87 (1981).

[14]C. S. Jacobsen, K. Mortensen, N. Thorup, D. B. Tanner, M. Weger, and K. Bechgaard, Chem. Scr. (in press).

[15]R. Nevald (private communication).

[16]C. S. Jacobsen, K. Mortensen, M. Weger, and K. Bechgaard, Solid State Commun. (in press).

[17]P. M. Chaikin, G. Gruner, E. M. Engler, and R. L. Greene, Phys. Rev. Lett. **45**, 1874 (1980).

[18]W. M. Walsh (private communication).

[19]P. S. Allen, J. Chem. Phys. **48**, 3031 (1968).