NMR Investigation of Spin Density Wave Motion and Fluctuations in $(TMTSF)_2PF_6$

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We report low field proton NMR measurements in the spin density wave (SDW) state of $(TMTSF)_2PF_6$ that show a narrowing of the linewidth when the SDW is depinned by an electric field. The NMR absorption amplitude affirms that sample heating is negligible. A shortening of the spin-phase memory time corresponding to the line narrowing is also observed. Low field measurements of the spin-lattice relaxation rate show a fluctuation enhancement just below the spin density wave transition and a rapid drop below 3 K that lack a quantitative understanding.

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One of the most active areas of current investigation in solid state physics is the formation and properties of broken-symmetry ground states in highly anisotropic materials. These states include superconductivity, charge density waves (CDW), and spin density waves (SDW). They are particularly prevalent in organic conductors.

In this paper we present an NMR investigation that shows direct, microscopic evidence of sliding SDW in $(TMTSF)_2PF_6$ (TMTSF denotes tetramethyltetraselenafulvalene). There is a long history of using NMR as a local probe of the SDW state in low-dimensional materials. Indeed, the original confirmation of the SDW state in $(TMTSF)_2PF_6$ [1] was based upon the increase in the NMR linewidth ($\Delta\nu$) and spin-phase memory time (T_2) when the sample was cooled below the transition temperature ($T_{SDW}=12$ K). The effect on $\Delta\nu$ was due to the additonal, incommensurate magnetization of the SDW and the increase in T_2 was caused by inhibition of mutual spin flips because of their "detuning" in the presence of the corresponding *microscopic* spatial variation of the magnetic field. More recently, careful NMR measurements have confirmed that the SDW in $(TMTSF)_2PF_6$ is incommensurate and established many characteristics of the order parameter [2,3]. Recent measurements in $(TMTSF)_2ClO_4$ by Delrieu and Kinoshita [4] have reported a narrowing of the NMR line with the application of a dc current (I), analogous to the effect seen earlier for CDW [5], and they attributed their result to sliding SDW. There are, however, ambiguities in their work with regard to sample heating that are not present in the experiments reported here.

In this paper we report preliminary proton pulsed NMR observations of the motion of sliding SDW in $(TMTSF)_2PF_6$. Direct evidence is presented to show that there is an NMR line narrowing that coincides with the depinning of the SDW and that heating of the sample is negligible. In addition to this narrowing, changes in the spin echoes are observed that we attribute to the effect of the sliding SDW which, we believe, can be developed into a useful tool for investigating SDW dynamics with a microscopic probe. We also report and discuss single-crystal measurements of the proton spin-lattice relaxation rate ($1/T_1$).

The samples used in this work were prepared using standard electrochemical methods. Electrical measurements indicate that they are of high quality. Pulsed NMR measurements were done with a laboratory-built spectrometer of conventional design. In-phase and quadrature-phase free induction decay (FID) and spin-echo signals were recorded using a digital oscilloscope and then transferred to a computer for further analysis. The sample was a single crystal with approximate dimensions $0.25\times0.25\times6$ mm^3 (mass $\simeq850$ μg). It was placed in a small NMR coil with approximately 40 turns, an inside diameter of about 0.5 mm, and length of about 3 mm. Current (I) and voltage (V) leads were attached to the sample using silver paste. The coil axis was horizontal in the field of an electromagnet so that the applied static field ($\mathbf{H}_0$) was approximately perpendicular to the chain (a) axis, but it could not be oriented in the plane perpendicular to it. Measurements were made at $H_0=4.44$ and 3.50 kOe; i.e., below the reported minimum H_{SF} of 4.8 kOe at 4.2 K [6]. The operating temperature (T) was obtained by either direct immersion in liquid He or with a He gas flow cryostat. Primary temperature measurements were made with a calibrated carbon resistance thermometer or the vapor pressure of pumped liquid He. We estimate the uncertainty in T is $\pm2\%$ or less. The sample current and voltage were measured with an accuracy of better than $\pm1\%$. Because the sample coil is so small, the rf magnetic field (H_1) is large even with substantial attenuation of the power output from the transmitter. The duration of a $\pi/2$ pulse was about 1 μs (rotating $H_1\simeq60$ G). Such pulses were used to generate the FID signal. Our largest echo signal was obtained with a $\pi/2$-$\pi/4$ sequence, presumably because the dominant spin-phase relaxation is caused by the dipolar interaction among rapidly tunneling methyl protons [7]. The typical dead time recovery of the system after an rf pulse was about 3–4 μs. This rapid recovery time permit-

ted reasonably accurate recordings of the FID signal for subsequent Fourier transform analysis.

One of the most important aspects of our experiment was that through NMR measurement of the amplitude of the nuclear magnetization (M_0) as a function of I we measured directly the temperature of the sample while the current was applied. In this way we verified that our observed effects were not due to heating of the sample. We estimate the relative accuracy of this measurement was $\pm 5\%$.

The conductance of the sample after its first cooldown to 4.2 K is shown in Fig. 1(a) at $H=0$ and $H=0.35$ T. There, the threshold for depinning is clearly seen at $I\simeq 0.6$ mA. We attribute the H dependence of I below the threshold as the magnetoresistance of the background current. Each time the sample was cooled there was evidence of minor cracking and a progressive rounding of dI/dV near the transition. In our experience, such changes did not affect the NMR observations described below, presumably because they involved only a small part of the sample volume.

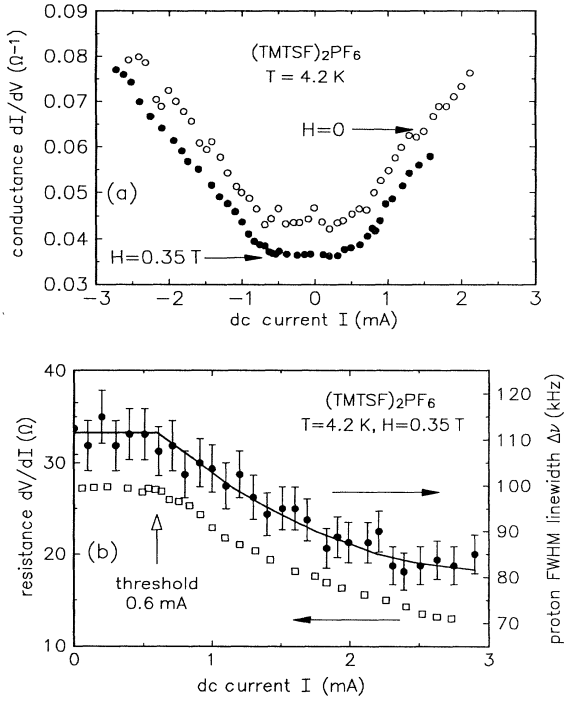

FIG. 1. (a) Electrical conductance of the $(TMTSF)_2PF_6$ sample as a function of the dc current at $H=0$ (open circles) and $H=0.35$ T (solid circles) oriented perpendicular to the chain (a) axis at 4.2 K. The threshold at 0.6 mA signals the onset of SDW conduction and the difference in the conductance below threshold reflects the magnetoresistance of the uncondensed carriers in the sample. (b) Proton NMR linewidth (solid circles) and sample resistance (open squares) as a function of electrical current at 0.35 T and 4.2 K. The solid line is a guide to the eye. The reduction in the linewidth for I above the 0.6 mA threshold is attributed to narrowing of the field distribution of the SDW when they become depinned.

Plots of the proton full width at half maximum (FWHM) linewidth ($\Delta\nu$) and the differential resistance (dV/dI) are shown in Fig. 1(b) as a function of I at 4.2 K and 0.35 T (note the offset axes). There is a clear narrowing of $\Delta\nu$ for increasing I and, within experimental error, the onset of the NMR line narrowing coincides with the threshold for SDW depinning at $I\simeq 0.6$ mA and the changes in the two curves track reasonably closely. These are the effects expected of sliding SDW in the volume of the sample and are a key part of our evidence in support of this picture. We also point out that since the proton has spin $\frac{1}{2}$, it has no quadrupole moment; hence, the effect on the linewidth must be purely magnetic. This is further evidence that it is a sliding SDW that is observed. A sliding CDW should have no corresponding effect on the proton NMR.

The other key piece of evidence is shown in Fig. 2, where M_0 and $\Delta\nu$ are plotted as a function of I up to 9 mA at 4.2 K and 0.35 T. There, it is seen that the change in $\Delta\nu$ we attribute to sliding SDW is *not* accompanied by a change in M_0. Since the paramagnetic M_0 follows a Curie law ($T\propto 1/M_0$), it serves as an *in situ* thermometer for the sample. Figure 2 shows that the current does not heat the sample to any significant degree up to $I=9$ mA. In these measurements, the sample was in direct contact with liquid He.

It should be repeated here that in these preliminary results the direction of $\mathbf{H}_0$ in the $\mathbf{b}'$-$\mathbf{c}^*$ plane is not known and that H_0 is below the minimum value of H_{SF} at 4.2 K. It is possible that other values of H_0 and its orientation will give quantitatively different results.

In measurements of the spin-echo signal with a current above the 0.6 mA threshold (not shown here), we observed that the amplitude of the echo at a long, fixed delay time (~ 130 μs) decreased as the current was in-

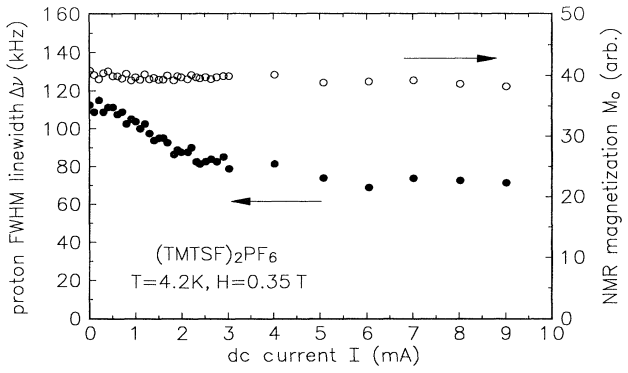

FIG. 2. Proton linewidth and nuclear magnetization as a function of current in $(TMTSF)_2PF_6$ for $H=0.35$ T (below the spin-flop transition) oriented perpendicular to the chain at 4.2 K. The small variation of the magnetization shows that heating of the sample by the current is negligible.

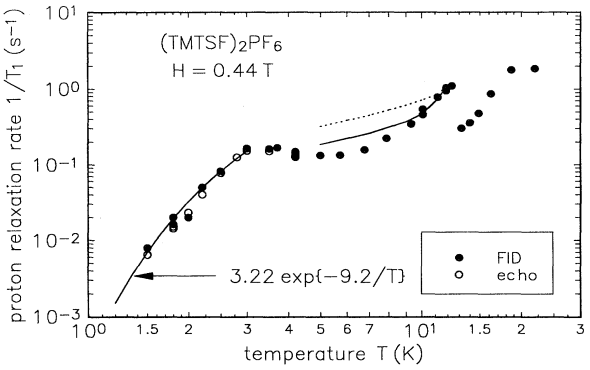

FIG. 3. Proton spin-lattice relaxation rate as a function of temperature in $(TMTSF)_2PF_6$ for $H=0.44$ T oriented perpendicular to the chain (a) axis. The rapid variation below the spin density wave transition near 12 K is evidence of critical fluctuations. Fits to the model of a weak antiferromagnet using different parameters are shown by the solid and dotted lines that end at 12 K. The rapid drop below 3 K can be fit to a temperature-independent gap model (solid line; gap $=9.2$ K) or to a power law (T^5).

creased, even though the intensity of the FID was unchanged (Fig. 2). This phenomenon is also consistent with the interpretation of the narrowing being caused by sliding SDW. Upon formation of the SDW, $1/T_2$ decreases because mutual spin flips are inhibited by their reduced ability to conserve energy in the presence of the microscopically inhomogeneous magnetic field [1,8]. When the SDW condensate slides fast enough, this inhomogeneity is averaged out and $1/T_2$ returns to a correspondingly larger value.

In Fig. 3 we report measurements of the spin-lattice relaxation rate ($1/T_1$) of the protons in our sample over the temperature range $1.5\ \text{K} < T < 22$ K. They were made using both the FID and spin-echo signals at $H=0.44$ T (below the minimum $H_{SF}=0.48$ T [6] at 4.2 K). Where they overlap, both types of signals give the same value for $1/T_1$. Above 3 K a single exponential recovery of the magnetization is observed. In this range we estimate the error in the measurements to be the size of the plotted points. Below 3 K the recovery does not follow a single exponential, in agreement with an earlier report by Takahashi *et al.* [9]. This deviation from a single exponential becomes more prominent the lower the temperature. In Fig. 3 we have plotted representative values of $1/T_1$ obtained from fitting the recovery curve with a single exponential.

The main features seen in Fig. 3 are the jump in $1/T_1$ at $T_{SDW}=12$ K, the decrease to a plateau down to 3 K, and the rapid drop below 3 K. Although these characteristics are in qualitative agreement with earlier measurements [9,10], there are important quantitative differences between both the measurements and the theory of weak antiferromagnetism [11]. Here we discuss these differences and comment on them briefly. Our data show a peak in $1/T_1$ at T_{SDW} that rises above the 3–7 K plateau 2 times higher than that reported by Takahashi *et al.* [9]. The weak antiferromagnet analysis gives $1/T_1 \propto T/M_{AF}$, where M_{AF} is the antiferromagnetic order parameter. The dotted and solid curves near the transition show the fit using values reported from muon spin rotation at zero field [12] and NMR at 11.2 kOe [9], respectively. It is not clear at present whether the discrepancy is due to the different samples, to the different fields used, or that the theoretical model does not apply. The temperature dependence of $1/T_1$ in the plateau region shows a slight peak near 3 K that is absent in the results of Takahashi *et al.* This difference may be associated with our traversing H_{SF} as T is decreased.

As indicated by the solid line below 3 K, the data can be fitted to a model of excitations across a temperature-independent gap of energy 9.2 K, which is close to the value of 10–11 K quoted by Takahashi *et al.* [9]. Alternatively, an even better fit can be made to a simple power law with $1/T_1 \propto T^5$. On the basis of the presently available data, it is not clear whether this behavior reflects a new phase and the opening of a gap or simply the temperature dependence of relaxation by low-energy excitations such as magnons, single electrons, etc. We plan measurements to lower temperatures with careful attention paid to the nonexponential recovery to help clarify this situation.

In conclusion, we have presented data that show a motional narrowing of the proton NMR absorption in $(TMTSF)_2PF_6$ by SDW below the spin-flop field. A corresponding reduction in $1/T_2$ is also observed. Simultaneous measurement of the nuclear magnetization shows that heating of the sample by the electrical current is negligible in our experiments. Low field measurements of the spin-lattice relaxation rate show an enhanced relaxation rate just below the SDW transition (~ 12 K) and a substantial drop below 3 K whose detailed origin is not understood.

After this work was performed we learned that D. Jerome and co-workers [13] have also observed sliding SDW in $(TMTSF)_2PF_6$ by NMR of ^{13}C at high magnetic fields.

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