^{13}C NMR Measurements of the High-Magnetic-Field, Low-Temperature Phases of $(TMTTF)_2PF_6$

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We report NMR spectroscopy of ^{13}C-labeled TMTTF molecules in high-magnetic fields that established the field-temperature phase diagram for $(TMTTF)_2PF_6$. The dimerized spin-Peierls (D) ground state is driven to an incommensurate (I) phase for fields $B > B_c = 19.1 \pm 0.1$ T. In the I phase, the staggered component of the magnetization is much larger for $(TMTTF)_2PF_6$ than it is for $CuGeO_3$. On approaching the transition to the D phase from higher temperatures, we observe an unusual broadening of the NMR spectrum which is probably from extrinsic sources and related to pinning of solitonlike excitations in individual chains. [S0031-9007(98)06225-5]

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Spin-Peierls (SP) ground states are observed in materials with half-filled bands which might be quasi-one-dimensional antiferromagnetic insulators except that, in addition to nearest-neighbor coupling, either a spin-phonon coupling or a competing exchange interaction leads to the formation of a nonmagnetic phase at low temperatures [1,2]. Until now, this SP ground state has been identified in a handful of charge-transfer salts with donors based on the TTF molecule [3–5], and more recently the inorganic material $CuGeO_3$ [6]. At high-magnetic fields, the dimerized (D) SP phase is unstable because of the Zeeman energy. The predicted spin structure of the high-field (I) phase is incommensurate with the lattice, with the change in wave vector attributed to periodic solitonlike domain walls within which the paramagnetic spin excitations are localized.

$(TMTTF)_2PF_6$ is an important example of the molecular materials undergoing SP transitions because it is a representative of a family of charge-transfer salts based on either the TMTSF or TMTTF molecules which exhibit a remarkable variety of electronic ground states and normal state behavior and that are "tunable" by changing the anion, or by applying high pressure or a magnetic field [7]. The systematics are well documented, and are believed to be a manifestation of manipulating the dimensionality in the presence of electronic correlations. The different behaviors are linked by a "generic" phase diagram [8], and the measurements reported here extend the parameter space to include the effects of high-magnetic fields on the charge-localized portion of this phase diagram. In addition to the establishment of the D-I phase boundary at $B_c \sim 19$ T, we observe a substantial broadening of the NMR line in the high-temperature uniform (U) phase that we attribute to extrinsic pinning of one-dimensional (solitonlike) magnetic excitations. The line narrowing seen below the transition $T_{SP}(B)$ is interpreted as a consequence of the binding of soliton-antisoliton pairs.

Various authors [8,9] have attributed the semiconductinglike resistivity of $(TMTTF)_2PF_6$ to a Mott-Hubbard charge gap $\Delta_\rho = 500$–600 K, in part because the spin susceptibility is Pauli-like down to low temperatures, but with distinct 1D-like characteristics. Below about 40 K, strong SP fluctuations are apparent in the spin susceptibility [4] and x-ray scattering studies [5], and below about 20 K a gap Δ_s opens in the magnetic spectrum.

The $(TMTTF)_2PF_6$ single crystals used in this study were prepared at UCLA using standard electrolysis methods from 1, 1′-$^{13}C_2$-tetramethyltetrathiafulvalene material. The synthesis was carried out by the methods of Ferraris and co-workers [10] using ^{13}C-labeled carbon disulfide as the initial source and a final dimerization using the procedure of Le Coustumer and Mollier [11]. Measurements of the crystal structure were in good agreement with the report of Ref. [12]. The spectrometer and probes for the experiments were designed and constructed at UCLA. High-field NMR data were obtained at the National High Magnetic Field Laboratory (NHMFL) 24.5 T Solid State NMR facility, and data at 9 T were recorded on the same sample and another at UCLA. Resolution of the spectra from the NHMFL magnet is limited to about 10–20 ppm, and was sufficient for our experiments. The magnetic field was applied in the b-c plane.

In Fig. 1, we show four spectra which demonstrate some of the effects of the SP transition. The top trace (a) is a spectrum recorded at $T = 35$ K and 21.5 T. Two distinct lines are seen, corresponding to the inequivalent paramagnetic shifts of the two ^{13}C nuclei in each molecule. The dipolar coupling of the same nuclei gives a

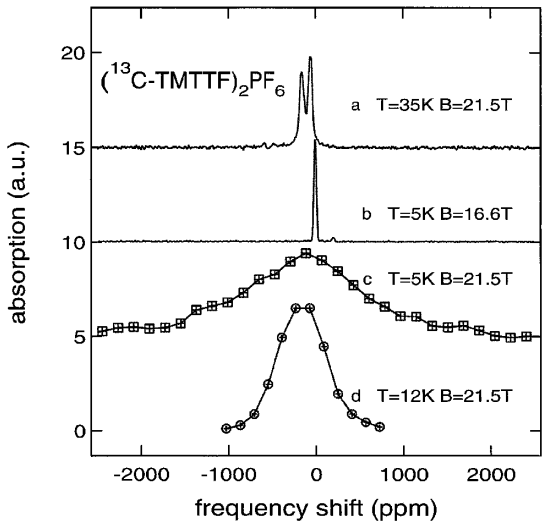

FIG. 1. ^{13}C spectra in $(TMTTF)_2PF_6$ taken at different fields and temperatures. The relative shift from zero in parts per million arises from the hyperfine coupling.

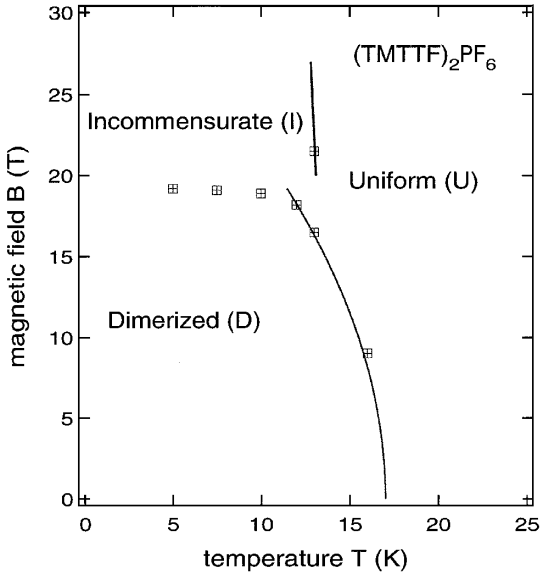

FIG. 2. Magnetic field B-temperature T phase diagram of $(TMTTF)_2PF_6$. Each of the three regions is labeled according to the text. The data points were established by measuring the NMR linewidths. The thin solid line is the expected low-field variation, $T_{SP}(B) = T_{SP}(B = 0) - \alpha B^2$.

splitting ($\sim$7 kHz) at the resolution limit of the magnetic field at the NHMFL. As for the other sulfur-based Bechgaard salts [13], we found the two frequency shifts to be only weakly anisotropic in the b'-c^* plane, negative, and about 50–60 ppm for one site and 150–160 ppm for the second [14].

The second spectrum (b) was taken at 16.5 T, well below B_c, and shows a single resolution-limited line. The change from 35 K is a result of the phase transition and the associated vanishing paramagnetic shift. Finally, the traces (c) and (d) are broad spectra recorded at $T = 5$ and 12 K, respectively, with the field centered near $B = 21.5$ T. These data were obtained by time integration of the real part of the spin echo and stepping the field. We were far enough above the identified critical field ($B_c \sim$ 19.1 T) that stepping in frequency at fixed field led to similar results. The spectra are consistent with an incommensurate phase (I) with a linewidth of order 500 kHz–1 MHz, corresponding to an internal field *variation* of order 1000 G at the ^{13}C nuclei for $T = 5$ K. The onset of the strong temperature dependence to the linewidth appears to be at 12.5–13 K, which we identify as the transition temperature to the I phase.

From spectra like these, we constructed the phase diagram shown in Fig. 2. The solid line is $T_c(B) = T_{c0} - \alpha B^2$ and the square symbols were determined by our NMR measurements. The variation with B^2 is seen for other SP systems such as $CuGeO_3$ [15], and is the predicted low-field behavior [16,17]. Although we have not measured for fields less than 9 T, the intercept T_{c0} is consistent with the reported value of Creuzet *et al.* [4], based upon low-field proton spin-lattice relaxation measurements. The incommensurate-dimerized phase boundary is seen when T_{SP} is reduced by the field by about (30–35)%, also consistent with the models [16,17].

The first point we discuss here is the linewidth of the I phase [Figs. 1(c) and 1(d)], for which domain wall formation is expected to play a dominant role as in other SP systems [18,19]. The physics is associated with the energetics of solitons in dimerized chains such as polyacetylene. In one-dimensional models of these systems, there is a doubly degenerate ground state which can be parametrized according to the distortion of the lattice $u_i = u_0 \cos[2k_F x + \theta(x)]$, with $2k_F = 2\pi/a$, $x = ia$ for $i = 1, 2, 3, \ldots$, and $\theta = 0, \pi$. Soliton solutions are found for varying the phase 0 to π or π to 0, which are the phase-antiphase domain walls separating the two phases [20,21]. Except for finite length chains with odd-numbered sites, the creation of domain walls is topologically constrained to occur in pairs. For a SP system in the I phase, there is an average spin density S_0, which when summed over sites within each soliton yields a total spin of $\frac{1}{2}$. It is accounted for over a characteristic wall width of order $2\xi \sim \pi J a/\Delta_s$, where J is the exchange interaction. There is also a staggered component of the magnetization S_1, which ought to be influenced by the intersite antiferromagnetic coupling [21,22]. From the characteristic width, it follows that S_0 must vary as ξ^{-1} [21]. For the maximum staggered part S_1, Nakano and Fukuyama [20] and Inagaki and Fukuyama [21] point out that, for classical spins, nearly the entire moment would be observed. Quantum fluctuations evaluated in a Gaussian approximation lead to a reduction $S_1 \sim \xi^{-1/2}$ for $\xi/a \gg 1$. The relation follows from an analysis of the spin-wave spectrum when the excitations are confined to regions of order the soliton width rather than infinite chains.

A comparable magnitude for S_1 was found for TTF-AuBDT and described in Ref. [18].

Several semiquantitative features of the low-temperature line shapes can be pointed out. The frequency shift from zero of the various spectra in Fig. 1 reflects the coupling to the electronic paramagnetism. Thus, the broad line shapes of (c) and (d) arise from the wide variation of the local spin density at the nuclear sites. At both extrema of the spectra appear distinct "ledges," where the absorption is actually increasing as the field is stepped away from the center of the spectrum. The natural interpretation is that the ledges are made up of those nuclei at the center of the domain wall where the staggered component is a maximum, and it is larger than the average component. Note that there are nuclei from two inequivalent sites contributing and their paramagnetic shifts are very different in magnitude [see Figs. 1(a) and 1(b)]. Presumably the ^{13}C nuclei with the larger shift are contributing to the observed ledges at the extrema of the spectra, and the smaller shifts associated with the other nucleus are broadening somewhat the stronger central feature.

Our expected broadening is evaluated as follows. The soliton creation energy E_{s0} in zero field is believed to be of order $\Delta_s/2$ [16], and this is reduced in field by the Zeeman energy $E_s(B) = E_{s0} - g\mu_B B/2$. From $B_c = 19.1$ T, we obtain $\Delta_s \sim 50$ K. With $J \sim 500$ K [4], then $S_1 \sim 0.1$, or about 20% of the full spin value. To compare this number with our result, the Knight shift tensor and uniform magnetic susceptibility χ from the normal state are combined to evaluate the maximum staggered moment. However, because absolute values of χ are not yet available, we use 3×10^{-4} emu/mol obtained from low-temperature measurements of $(TMTTF)_2Br$ [23]. By combining χ with the normal state shift, we estimate the maximum staggered moment S_1 per electron to be $0.2\mu_B$, in reasonable agreement. S_0 is evaluated from the shift of the midpoint between the extrema of the lines away from zero; it is about 7 times smaller than S_1.

The presence of two ledges at nearly equivalent positive and negative shifts is a distinction from the NMR results of Fagot-Revurat *et al.* on $CuGeO_3$ [19]. Their observations were interpreted very successfully in terms of the model described in Ref. [24], which is based on a phonon-coupled Heisenberg model transformed to a Peierls-Frohlich Hamiltonian with interactions and then solved in a Hartree-Fock approximation [1]. The soliton solutions are similar to those of the noninteracting Su-Schrieffer-Heeger [25] model which give a staggered amplitude the same size as the average of the spin density for isolated neutral solitons; namely, $\langle S_i^z \rangle \sim \mathrm{sech}^2(i/\xi)\cos^2(\pi i/2)$ for the total spin density at sites i.

Possible explanations for the difference between the two systems can be categorized according to whether they originate from static or dynamic sources. For example, the strength of the J^z part of the spin coupling quantitatively alters the staggered part. With $J^z = 0$, the transformation of the spin Hamiltonian to the noninteracting model is exact. However, neutron scattering measurements of the magnetic excitations indicate that the Heisenberg spin Hamiltonian is appropriate to $CuGeO_3$ [26]. Another unlikely source of stabilization for the staggered component could come from 3D couplings; the transverse exchange coupling of $CuGeO_3$ is relatively large [26]. On the other hand, Uhrig and co-workers [27] and Foerster *et al.* [28] have suggested recently that in the case of $CuGeO_3$ there is a dynamic averaging between neighboring sites on the time scale of NMR experiments, and only the average spin density S_0 is measured.

The last issue we address is the broadening of the NMR line shape as T_{SP} is approached from above. In Fig. 3, we show the linewidth at 25% of the maximum peak height as a function of temperature for $B = 9$ and 18 T. The transition is shifted downward in temperature at 18 T from $T_{SP}(9\ \mathrm{T})$, and the broadening is evidently much larger. The inset contrasts spectra below and above T_{SP} at 18 T. Our observations indicate there is broadening over a temperature range ($T < 40$ K), where EPR [4] and x-ray scattering studies [5] give evidence for SP fluctuations. Further, at fields close to B_c, there is a substantial increase in the temperature dependence of the linewidth below about 18 K.

To be seen in the NMR spectra, the line broadening must result from static or at least very slow field variations. A candidate would be pinning by lattice defects of solitons on single chains. What is difficult to understand in this scenario is how *all* of the nuclei seem to be affected, at least close to T_{SP}; we do not see evidence

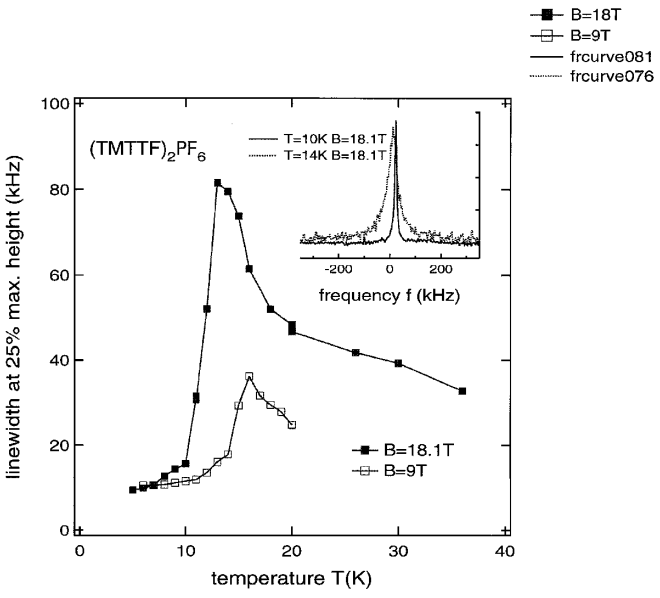

FIG. 3. Broadening of the NMR spectra at two fields below the critical field B_c which designates the onset of the incommensurate (I) phase. The solid lines are a guide to the eye. The inset shows two spectra recorded at $B = 18.1$ T just above and just below the critical temperature T_{SP}.

for a minority set of nuclei near lattice defects and another set in a "clean" phase where the fluctuations are fast and the line is narrow. To be consistent with the data, there has to be static or very slowly fluctuating solitonlike objects which are confined over large length scales in the paramagnetic phase $T > T_{SP}$, such as between the ends of broken chains. The density of the magnetic excitations increases with field strength, accounting for the strong field dependence of the broadening. Further, we propose the sudden drop in linewidth below T_{SP} is evidence for bound-state confinement of the magnetic excitations as the chains become coupled in the low-temperature phase [29].

In conclusion, we have reported ^{13}C NMR experiments in a range of fields on $(TMTTF)_2PF_6$. We find the high-field incommensurate phase above $B = 19.1$ T at $T \ll T_{SP}$ and find evidence for a staggered component to the magnetization which is much larger than the average component. Such a large staggered component is not found for $CuGeO_3$. Although details in either intrastack J^z or interstack spin couplings can lead to this difference, these explanations are unlikely. The uniform (U) phase is associated with a substantial broadening of the spectra in the same temperature regime where SP fluctuations are observable in EPR and x-ray scattering experiments. The fact that we observe broadening at all is somewhat unusual and probably is associated with the presence of pinned solitonlike objects within a single chain which become confined in the low-temperature dimerized phase.

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