Restoring Force and Displacement of the Pinned Spin Density Wave Condensate in $(TMTSF)_2PF_6$

W. H. Wong, M. E. Hanson, W. G. Clark, B. Alavi, and G. Grüner

Department of Physics and Solid State Science Center, University of California at Los Angeles, Los Angeles, California 90024-1547

(Received 29 January 1993; revised manuscript received 13 April 1993)

We report NMR spin echo measurements of the average spin density wave condensate displacement at 4.2 K in $(TMTSF)_2PF_6$ when it is driven by an electric field below the depinning threshold over time scales of 10–25 μs. The displacement, which corresponds to internal deformations, varies linearly as a function of the electric field and has a restoring force constant per electronic charge $k=(1.3\pm0.3)\times10^{-9}$ N/m. At the depinning threshold the average condensate displacement is 0.46 ± 0.06 Å. The corresponding low frequency dielectric constant is $(3.4\pm0.7)\times10^9$, which is close to that obtained from electrical transport measurements.

PACS numbers: 75.30.Fv, 72.15.Nj, 76.60.Lz

The dynamical response of spin density wave (SDW) condensates in the so-called Bechgaard salts has been firmly established by a variety of experiments conducted in both dc and ac electric fields [1]. The conductivity was found to be nonlinear above a well-defined threshold field E_T [2] which is small (typically 3–5 mV/cm) in nominally pure specimens and increases rapidly with the impurity concentration [3]. The observation of current oscillations [4] and elastic anomalies [5] together with changes in the NMR spectrum [6–8] give clear evidence for the translational motion of the condensate under the influence of the applied electric field. In addition, a strongly frequency dependent response has been found in the spectral range well below the single particle gap [9,10].

These experimental results have been interpreted in terms of a collective mode which is pinned to the underlying lattice by impurities, with depinning occurring only above a threshold field E_T. The results are similar to those observed in several systems with a charge density wave (CDW) ground state [11]. While many of the essential features of the two broken symmetry ground states are similar, there are important differences. The most significant among these is that the CDW ground state arises as a consequence of electron-phonon interactions, while the SDW state is due to electron-electron interactions. This difference significantly affects the collective mode dynamics.

In this Letter we report direct NMR spin echo measurements of the static displacement of the SDW in response to the force applied by an electric field below E_T and present a model for its interpretation. The response of the collective mode in the frequency (ω) range that applies for our experimental conditions, $\omega/2\pi<3\times10^4$ Hz, is dominated by internal deformations of the SDW. From this displacement, we obtain the corresponding force constant k and the low frequency dielectric constant ε.

Our samples were grown using standard electrochemical methods and procedures to provide high quality materials. A laboratory built NMR spectrometer and cryostats were used for the measurements. All of the spin echo measurements reported here were made on protons in a single crystal sample of approximate dimensions $0.15\times0.15\times5$ mm^3 (~250 μg) at 4.2 K in an external field of 0.35 T, which is below the spin-flop transition field $H_{SF}\geq0.48$ T [12]. Electrical contacts to the sample were made by silver plating the ends of the sample and applying 50 μm diam gold wires under tension. In this way, cracking of the sample was minimized [13].

The model for SDW's used to interpret our experimental results involves the following elements: The total magnetic field at a nucleus located at $\mathbf{r}_j$ is

$$\mathbf{B}(\mathbf{r}_j)=\mathbf{B}_0+\mathbf{B}_d+\mathbf{B}_S\cos(\mathbf{q}\cdot\mathbf{r}_j+\phi)\,, \tag{1}$$

where $\mathbf{B}_0$ is the externally applied field, $\mathbf{B}_d$ is the dipolar field of the other nuclear moments, $\mathbf{B}_S\cos(\mathbf{q}\cdot\mathbf{r}_j+\phi)$ is the field of the SDW, $\mathbf{q}$ is the SDW wave vector, and ϕ is the phase of the SDW [11]. When an electric field $E<E_T$ is applied along the chain direction (a direction) of the sample, an average force per electron $F=-eE$ is applied to the SDW along the same direction as in the classical particle model for a CDW [14]. Because of the internal modes of the SDW and the presumed random distribution of pinning centers, there will be a local displacement of the SDW phase (x_j). This situation corresponds to a reversible displacement of the SDW by an average distance $\bar{x}$, which is related to F by $F=-eE=-k\bar{x}$; k is the corresponding restoring force constant. Furthermore, we treat the displacement as instantaneous on the 10^{-4}–10^{-5} s time scale of the spin echo measurement. Support for this latter assumption is presented later in the paper.

In our spin echo experiments an external current $I(t)$ is applied as a function of time t along the chain direction (a axis). It is related to the electric field by $E=RI/l$, where R is the electrical resistance of the sample and l is its length between electrical contacts along the a axis. The corresponding change in $\phi(\mathbf{r}_j)$ ($\delta\phi_j$) is

$$\delta\phi_j=\frac{\partial\phi}{\partial x}x_j=\frac{2\pi x_j}{\lambda_a}\,, \tag{2}$$

where $\lambda_a=14.6$ Å [14] is the SDW wavelength along the

0031-9007/94/72(16)/2640(4)$06.00

a axis.

For the condition $B_S \ll B_0$ that corresponds to our experiments [15], there is a change in the NMR frequency (ω_S) caused by the component of $\mathbf{B}_S$ parallel to $\mathbf{B}_0$ ($B_\parallel$) given by

$$\omega_S = \gamma B_\parallel \cos(\mathbf{q}\cdot\mathbf{r}_j + \phi) = \gamma B_\parallel(\mathbf{r}_j)\,, \tag{3}$$

where γ is the nuclear gyromagnetic ratio (proton $\gamma = 2\pi \times 4.257\times 10^3$ rad/sG). The change in the NMR precession frequency ($\delta\omega_S$) caused by a small ($x_j \ll \lambda_a$) static displacement of the SDW is

$$\delta\omega_S = \frac{\partial \omega_S}{\partial \phi}\frac{\partial \phi}{\partial x}x_j = -\frac{2\pi\gamma B_\parallel x_j}{\lambda_a}\sin(\mathbf{q}\cdot\mathbf{r}_j + \phi)$$
$$= \pm\frac{2\pi\gamma B_\parallel x_j}{\lambda_a}\left[1 - \left(\frac{B_\parallel(\mathbf{r}_j)}{B_\parallel}\right)^2\right]^{1/2}. \tag{4}$$

For the spin echo measurements we apply a $\pi/2$ rf pulse at the NMR frequency to the proton spins at time $t = 0$, wait a time τ ($\sim\frac{1}{2}$ the spin echo decay time), apply a second pulse (empirically adjusted to provide the largest spin echo signal), and record the complex spin echo signal $S(t)$ with height $h(2\tau) = \mathrm{Re}[S(2\tau)]$ at the time 2τ after the first pulse [16]. The sequence is shown on the upper right of Fig. 1. It is first done with $I = 0$ and generates an echo height we label $h_0(2\tau)$. The additional effect of the SDW displacement is measured by applying a pulsed current wave form during the time period 0–2τ and recording the modified $h(2\tau)$. During this period each spin will develop an additional precession phase whose rate is given by Eq. (4). The quantity we use to evaluate the corresponding effect on the echo amplitude is the total phase accumulated by each spin (Φ_j) over the time interval $0 < t < 2\tau$:

$$\Phi_j(2\tau) = -\int_0^\tau \delta\omega_S(t')dt' + \int_\tau^{2\tau}\delta\omega_S(t')dt'\,. \tag{5}$$

Equation (5) is based upon the assumption, discussed later, that the effect of the second pulse is to reverse the additional phase accumulated because of the SDW displacement. This kind of experiment is similar to that done by Ross, Wang, and Slichter on a CDW system [17].

For the experiments reported here, two particularly simple current wave forms were used: (1) a constant current of amplitude I_0 (constant local displacement x_{0j}) and duration t_0 during the period 0–τ, ("single I pulse," first dashed line, Fig. 1), and (2) an identical pair of such pulses divided between the intervals 0–τ and τ–2τ ("double I pulse," both dashed lines, Fig. 1). For the double I pulse, $\Phi_j(2\tau) = 0$; i.e., Eq. (5) predicts that the extra dephasing by the SDW during the first current pulse is canceled by the effect of the second current pulse, so that there should be no change in $h(2\tau)$. This condition occurs if the SDW displacement is reversible and independent of the placement of each current pulse within its respective time window. We have tested the latter requirement and find that it is satisfied. We have also tested Eq. (5) with a variety of current pulse configurations. The results, which are not discussed in detail here, support the assumption upon which it is based.

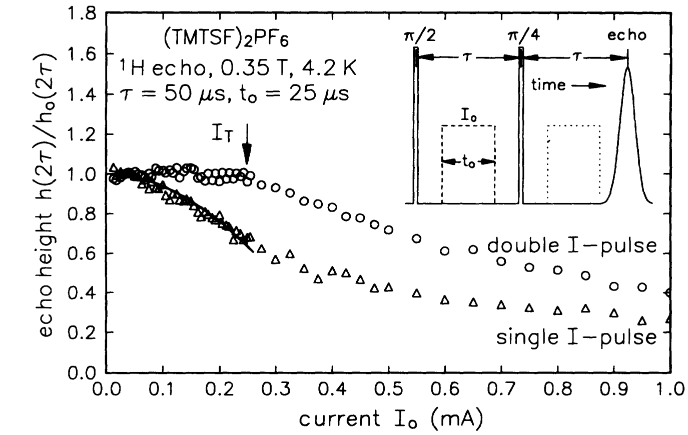

FIG. 1. Normalized spin echo height for protons in $(TMTSF)_2PF_6$ as a function of total pulsed current at 4.2 K and 0.35 T. The constant value below the depinning threshold $I_T = 0.25$ mA for the double I-pulse sequence (circles) shows that the displacements induced for the two current pulses are identical. The drop above I_T is caused by the sliding motion of the depinned SDW. The drop in echo height for the single I pulse below I_T is due to the lack of echo refocusing when the second current pulse is absent. The solid line shows the fit by the model developed in the text.

For the single I pulse, $h(2\tau)$ is obtained by summing the spin echo signal for all $\mathbf{r}_j$. There are two important variations to be taken into account: (1) The four different values of $B_\parallel$ for the inequivalent methyl group protons [15], and (2) the different values of x_{0j} caused by internal distortions of the SDW. For a subset of protons with the same values for x_{0j} and $B_\parallel$, the height of the spin echo is given by

$$\frac{h_B(2\tau, B_\parallel, x_{0j})}{h_0(2\tau)} = \frac{2}{\pi B_\parallel}\int_0^{B_\parallel}\frac{dB}{\sqrt{1-(B/B_\parallel)^2}}\cos\left\{\frac{2\pi\gamma B_\parallel t_0 x_{0j}}{\lambda_a}\left[1-\left(\frac{B}{B_\parallel}\right)^2\right]^{1/2}\right\} = J_0(u)\,, \tag{6}$$

where

$$u = 2\pi\gamma B_\parallel t_0 x_{0j}/\lambda_a \tag{7}$$

and J_0 is the Bessel function of order zero. Up to $u = 1.7$, $J_0(u) \simeq 1 - \frac{1}{4}u^2 + \frac{1}{64}u^4$ is an excellent approximation (justified later). When the distribution of u, $P(u)$, is taken into account,

$$\frac{h_B(2\tau)}{h_0(2\tau)} = \int P(u) J_0(u) du$$
$$\simeq \int P(u)[1 - \tfrac{1}{4}u^2 + \tfrac{1}{64}u^4] du \, . \qquad (8)$$

If $P(u)$ is very narrow, the experimental measurement of $h_B(2\tau)$ as a function of I_0 can be fitted with

$$h_b(2\tau) = h_0(2\tau)\left[1 - \beta\left(\frac{\bar{u}}{I_0}\right)^2 I_0^2 + \frac{1}{64}\left(\frac{\bar{u}}{I_0}\right)^4 I_0^4\right], \qquad (9)$$

where $\beta = \frac{1}{4}$ and $\bar{u}$ is the volume average of u. If, on the other hand, $P(u)$ is broad, the numerical coefficients in Eq. (9) are changed accordingly. We have carried out this calculation for the case of a uniform distribution in u from zero to twice the mean value, which is very broad indeed. In that case, the only significant effect on Eq. (9) is that β changes from $\frac{1}{4}$ to $\frac{1}{3}$. This means that the echo height is not very sensitive to the width of the distribution for u.

For the alignment of $\mathbf{B}_0$ used in this experiment (54° from the b' axis) $B_\parallel$ has a rather broad distribution, with a mean value $\bar{B}_\parallel = 8.4$ G (examination of the line shape recorded in our experiments indicates $\bar{B}_\parallel = 7.6$ G). Since this width will be augmented by variations in x_{0j}, we apply the "broad" limit ($\beta = \frac{1}{3}$) and analyze the data treating $\bar{u}/I_0$ as a single parameter that is varied to fit the data. It will also be assumed that $B_\parallel$ and x_{0j} are uncorrelated, so that $\bar{u} = (2\pi\gamma t_0/\lambda_a)\bar{B}_\parallel \bar{x}_0$ ($\bar{x}_0$ is the volume average).

An example of measurements using these two current wave forms is shown in Fig. 1, where the normalized echo height $h(2\tau)/h_0(2\tau)$ is plotted as a function of I_0 for protons in $(TMTSF)_2PF_6$ at 4.2 K and $B_0 = 0.35$ T using the single and double current pulse wave forms indicated in the figure. For the double I-pulse measurement (open circles) there is no change in echo height up to the threshold current $I_T = 0.25 \pm 0.02$ mA ($E_T = 3.5 \pm 0.9$ mV/cm determined from a two-probe electrical measurement). This result indicates that there is a reversible displacement of the SDW condensate for $I_0 < I_T$ in agreement with Eq. (5). For $I_0 > I_T$, there is a reduction in the echo height that is caused by SDW depinning; the phase accumulation of the nuclear spins during the two current pulse periods no longer cancels. The same depinning threshold is seen in the dc current-voltage characteristics of this sample, which is independent confirmation that the onset of the change in echo height is caused by depinning of the SDW. The fact that the change in slope is so abrupt is evidence for a single depinning threshold value throughout the volume of the sample.

The behavior of the echo for the single I-pulse measurement (open triangles) drops monotonically throughout the region where the double I-pulse behavior shows that the SDW displacement is the same for both pulses. We ascribe this behavior to the static displacement described by Eqs. (6)–(9). The solid line shows the fit of Eq. (9) to the data using $\bar{u}/I_0 = 4.3$ mA^{-1} and $\beta = \frac{1}{3}$. From $I_{0T} = 0.25 \pm 0.03$ mA (subscript T indicates at threshold) we obtain the threshold value for $\bar{u}$; $\bar{u}_T = 1.08 \pm 0.12$. This value for $\bar{u}_T$ justifies using the series approximation used in Eq. (9). Equation (7) and the values $\bar{B}_\parallel = 8.4$ G [15], $t_0 = 25$ μs then give $\bar{x}_{0T} = 0.46 \pm 0.06$ Å ($\delta\phi = 0.19 \pm 0.03$ rad) for the average condensate displacement at the depinning threshold.

From the value for $\bar{x}_{0T}$, $l = 4$ mm, the sample resistance $R = 5.7$ Ω at 4.2 K, and the relation $k = eI_{0T}R/l\bar{x}_{0T}$ we obtain $k = (1.3 \pm 0.3) \times 10^{-9}$ N/m for the low frequency restoring force constant of the condensate.

Our measured value for $\bar{x}_{0T}$ can be compared with measurements of the low frequency dielectric constant,

$$\varepsilon = 1 + ne\bar{x}_{0T}/\varepsilon_0 E_T \qquad (10)$$

(SI units), on similar materials. In Eq. (10), $n = 1.4 \times 10^{27}$ m^{-3} is the density of the condensate [18]. In another paper, we have determined that the entire condensate slides above threshold in this sample [19]. Two transport measurements of ε that are useful for comparison with our value of $\bar{x}_{0T}$ have been reported, one for $(TMTSF)_2PF_6$ at 2 K [20] and another for $(TMTSF)_2AsF_6$ over the temperature range 1.5–5 K [3]. Comparison of the two results at 2 K shows that the dielectric behavior of both materials is nearly the same, as expected on the basis of all the other similarities shared by these materials [18]. A prominent feature of the behavior of the latter material is that the dielectric constant as a function of frequency has about the same shape at different temperatures, but it is rapidly scaled to higher frequency as T is increased [3]. We therefore compare our results at 4.2 K with those of Traetteberg *et al.* [3] at the same T. The first point for the comparison is that the rolloff from the dc value occurs at around 10^5 Hz. Since Fourier analysis of our 10–25 μs current pulses shows that almost all of the components are below 3×10^4 Hz, our experimental conditions correspond to the dc value of ε. Substitution of the experimental values into Eq. (10) then gives for our NMR result $\varepsilon = (3.4 \pm 0.7) \times 10^9$, which is close to the value 1.8×10^9 obtained from transport measurements on $(TMTSF)_2AsF_6$ at the same temperature [3]. Thus, both methods give values that are in reasonable agreement.

One of the results of this work is that the 0.46 Å average displacement of the SDW at the pinning threshold is only about 3.1% of λ_a. It corresponds to a small fraction of the pinning potential wavelength before the depinning threshold is reached. (It is argued elsewhere that the pinning potential period is $\lambda_a/2$ [19] or λ_a [7].) This small value suggests that depinning is initiated in a small part of the sample and proceeds by an avalanche process.

There are several comments to be made about our results and the method used to obtain them. The first is that the SDW displacement measurement is independent of assumptions made about the transport properties of the material. Also, it can be made in the presence of a relatively large background current from the normal carriers. It is a rather sensitive measurement: The displacement in this case is measured to an accuracy of about 0.06 Å. For nuclei with a longer spin echo decay time, it should be possible to measure correspondingly smaller displacements of the local magnetic field structure. From measurements of the amplitude of the NMR signal as a function of a steady current, we find that heating by I_0 is negligible in this experiment. Also, we have varied t_0 over the range 5–25 μs. For the range 10–25 μs we get the same values for I_T, $\bar{x}_{0T}$, and k within our experimental error. However, for $t_0=5$ μs, we find a somewhat smaller k and a 40% larger value of I_T. It is not yet clear whether these effects are intrinsic to the SDW or artifacts of our electronic instrumentation. Two additional measurements indicate that memory effects do not play a significant role in the results reported here. The first is that the same value of k is obtained when the direction of I_0 is *reversed* for the second pulse (the analysis is modified accordingly). The second is that at 4.2 K we observe significant SDW condensate memory effects in the transport response [21] and the spin echo behavior only when long duration ($\gg 25$ μs) current pulses above the depinning threshold are used.

Other measurements made during the same run (not discussed in detail here) show that almost all of the spins in the sample experience a reversible displacement of the SDW for $I < I_T$ and a broad distribution of velocities when the SDW is depinned by $I > I_T$. The first observation indicates that the displacement is not associated with domain walls between commensurate regions. These conditions also indicate that the SDW displacement obtained in this measurement represents a bulk property of the sample.

In conclusion, we have presented a proton spin echo measurement of the displacement of the SDW in a high purity sample of $(TMTSF)_2PF_6$ at 4.2 K when an electric field below the depinning threshold is applied. A model to obtain the value of the displacement is described. It is observed that the displacement below depinning, which is due to internal modes, is reversible. An average displacement of 0.46 ± 0.06 Å is found at the depinning threshold. It corresponds to a restoring force constant of $(1.3 \pm 0.3) \times 10^{-9}$ N/m and a dc dielectric constant of $(3.4 \pm 0.7) \times 10^9$.

We acknowledge valuable discussions of this work with S. A. Brown, S. Donovan, and G. Mihály. We especially thank G. Kriza for bringing to our attention the importance of internal modes for the interpretation and for pointing out the use of J_0 in Eq. (6). This project was supported in part by a grant from the UCLA Academic Senate Research Committee (W.G.C.) and in part by NSF Grant No. DMR-9012946 (G.G.).

[1] G. Grüner and K. Maki, Comments Condens. Matter Phys. **15**, 145 (1991).
[2] S. Tomić, J. R. Cooper, D. Jérome, and K. Bechgaard, Phys. Rev. Lett. **62**, 462 (1989).
[3] O. Traetteberg, G. Kriza, C. Lenoir, Y. S. Huang, P. Batail, and D. Jérome, Synth. Met. **56**, 2785 (1993).
[4] G. Kriza, G. Quirion, O. Traetteberg, W. Kang, and D. Jérome, Phys. Rev. Lett. **66**, 1922 (1991).
[5] S. E. Brown, B. Alavi, G. Grüner, and K. Bartholomew, Phys. Rev. B **46**, 10483 (1992).
[6] J. M. Delrieu and N. Kinoshita, Synth. Met. **41-43**, 3947 (1991).
[7] E. Barthel, G. Kriza, G. Quiron, P. Wzietek, and D. Jérome, Phys. Rev. Lett. **71**, 2825 (1993).
[8] W. H. Wong, M. E. Hanson, B. Alavi, W. G. Clark, and W. A. Hines, Phys. Rev. Lett. **70**, 1882 (1993).
[9] D. Quinliven *et al.*, Phys. Rev. Lett. **65**, 1816 (1990).
[10] S. Donovan, Y. Kim, L. DeGiorgi, and G. Grüner, J. Phys. (France) I **3**, 1493 (1993).
[11] G. Grüner, Rev. Mod. Phys. **60**, 1129 (1988).
[12] M. Miljak, J. R. Cooper, and K. Bechgaard, J. Phys. (Paris), Colloq. **44**, C3-893 (1983).
[13] W. Kang, S. Tomić, J. R. Cooper, and D. Jérome, Phys. Rev. B **41**, 4862 (1990).
[14] G. Grüner, A. Zawadowski, and P. M. Chaikin, Phys. Rev. Lett. **46**, 511 (1981).
[15] J. M. Delrieu, M. Roger, Z. Toffano, E. Wope Mbogue, R. Saint James, and K. Bechgaard, Synth. Met. **19**, 283 (1987).
[16] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1989), 3rd ed., Sec. 2.9, 2.10, and 5.6.
[17] J. H. Ross, Jr., Z. Wang, and C. P. Slichter, Phys. Rev. B **41**, 2722 (1990).
[18] See the review by G. Grüner, Rev. Mod. Phys. (to be published).
[19] W. G. Clark, M. E. Hanson, W. H. Wong, and B. Alavi, Phys. Rev. B (to be published).
[20] G. Mihály, Y. Kim, and G. Grüner, Phys. Rev. Lett. **66**, 2806 (1991).
[21] A. Beleznay, R. Gaal, and G. Mihály, J. Phys. IV (France) **3**, 357 (1993).