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Charge-density-wave dynamics in the molecular conductor $(\text{perylene})_2\text{Pt}(\text{mnt})_2$ (mnt=maleonitriledithiolate)

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We report the observation of nonlinear voltage response both to dc current and to unipolar current pulses in the commensurate charge-density-wave (CDW) state of the molecular conductor $(\text{perylene})_2\text{Pt}(\text{mnt})_2$ (mnt =maleonitriledithiolate). At $T=4.2$ K, two nonlinearities in the I-V curves are observed at $E_{t1}=8.9$ V cm^{-1} and $E_{t2}\sim 30$ V cm^{-1}. Above the threshold field E_{t1}, quasiperiodic asymmetric voltage spikes with large amplitude superimposed on the transient voltage response have been observed. The onset of the spikes shows a delay with respect to the leading edge of the pulse. The Fourier analysis of the voltage at constant current reveals one fundamental frequency, proportional to the CDW current density, accompanied by a large number of harmonics. The results are discussed in relation to the current models for CDW nonlinear transport.

I. INTRODUCTION

During the past 15 years, the phenomenon of depinning of a charge-density wave (CDW) in a quasi-one-dimensional conductor has been studied extensively both experimentally and theoretically.[1] Below a small finite threshold electric field E_t the CDW is pinned to randomly placed impurities or lattice defects or by eventual commensurability effects. Above E_t, the CDW overcomes the impurity pinning force, or, in the case of a commensurate CDW, the commensurability potential, and a remarkable nonlinear conductivity due to the motion of the CDW with respect to the lattice is observed. The onset of CDW sliding motion is marked by the presence of a nonlinearity in the I-V characteristics, and, at constant current, by periodic voltage oscillations commonly referred to as narrow-band noise. The frequency of these oscillations is proportional to the current density carried by the CDW. The onset of nonlinearity is also accompanied by the so-called broad-band noise. A number of theoretical explanations have been proposed for the depinning process. In the classical model,[1] the pinning energy of the CDW is periodic in displacements of the space-averaged phase by 2π and a threshold field E_t is necessary to overcome the pinning force. In the Fukuyama-Lee-Rice (FLR) model,[2,3] the CDW is viewed as an elastic medium, and the pinning results from the competition between the elastic energy of the CDW and the preferred CDW phase at impurity sites. Other models involve structural CDW defects, such as phase dislocations neglected in the FLR model.[4,5] The analogy between the depinning of a CDW and the onset of plastic deformation of a crystal has also been considered.[6]

While in the case of inorganic conductors, such as NbSe_3, TaS_3, $(\text{NbSe}_4)_{10/3}\text{I}$, $(\text{TaSe}_4)_2\text{I}$,[1] and the blue bronze $\text{K}_{0.30}\text{MoO}_3$,[7] all the features mentioned above have been clearly observed, the search for nonlinear transport in the organic conductors has been more difficult. In the case of the intensively studied CDW organic material tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), the narrow-band noise was hardly detected by Fourier-transform analysis of the nonlinear response to rectangular current pulses.[8,9] In the fluoranthene salt $(\text{FA})_2\text{PF}_6$, only the broad-band noise was detected above threshold.[10] Experimental evidence for collective nonlinear transport in organic conductors has been limited for a long time to spin-density-wave systems based on the tetramethyltetraselenafulvalene (TMTSF) molecule.[11]

We have reported recently an observation of CDW nonlinear conductivity and associated narrow-band noise in the molecular conductor $(\text{perylene})_2\text{Au}(\text{mnt})_2$ (mnt =maleonitriledithiolate).[12] In the present work, we report the observation of CDW nonlinear conductivity and periodic voltage oscillations in the isostructural compound $(\text{perylene})_2\text{Pt}(\text{mnt})_2$. Two threshold fields E_{t1} and E_{t2} for the onset of nonlinearity in the I-V characteristics are observed. Periodic asymmetric voltage oscillations in the time domain are clearly observed above the low threshold field E_{t1}. The fundamental frequency of these oscillations is found to increase linearly with the CDW current density in good agreement with Fourier analysis of the noise observed when the sample is submitted to a dc current.

The compounds $(\text{Per})_2M(\text{mnt})_2$ are quasi-one-dimensional conductors that undergo metal-to-semiconductor transitions towards a commensurate CDW state in the temperature range 8–73 K, depending on the metal M.[13–17] The lowest transition temperatures are 8 and 12 K for $M=\text{Pt}$ and Au, respectively.[15] The metallic properties are associated with the existence of regularly spaced stacks along the b axis of partially oxidized perylene molecules $(\text{Per})_2{}^+$ leading to a $\frac{3}{4}$-filled band.[16] The counterions $M(\text{mnt})_2{}^-$ also form stacks along the b axis and their number is one-half of those of the $(\text{Per})_2{}^+$ stacks. However, the interplanar distance between $M(\text{mnt})_2$ units is larger than that of the corresponding perylene molecules,[13,16] and, therefore, these units do not contribute to the electrical conductivity but have a key role in the magnetic properties. For some metals, like M=Pt, Pd, and Ni, the $M(\mathrm{mnt})_2$ units are open-shell systems forming chains of localized $S=\frac{1}{2}$ spins, while in other cases, like M=Au, Cu these units are diamagnetic. The comparison of the different members of this series[16] reveals that the metal-to-semiconductor transition observed at low temperatures is associated with a tetramerization ($2k_F$ Peierls transition) of the perylene chains, as observed in the Ni and Cu compounds by x-ray diffuse scattering.[17] In the case of $M(\mathrm{mnt})_2$ paramagnetic units, a dimerization of these units, as in a spin Peierls transition, also occurs at the same critical temperature.[14]

II. EXPERIMENTAL RESULTS AND DISCUSSION

Single crystals of (perylene)$_2$Pt(mnt)$_2$ have been obtained by electrocrystallization using standard procedures for this class of compounds.[12] Crystals appear as long needles with typical size $4\times0.05\times0.025$ mm^3, with the crystallographic b axis as the long direction. Four gold pads were evaporated around the needle, and gold wires 25 μm in diameter were attached to the evaporated areas with Pt paint. The current contacts covered the whole area of both ends of the needle. Typical contact resistance was ~30 Ω at room temperature. Nonlinear conductivity and noise measurements were performed at 4.2 K by slowly immersing the sample into liquid helium, to avoid Joule heating, using dc and pulse-current methods. For the pulse-current measurements the computer-controlled arrangement consists of a HP 214B rectangular pulse generator, Tektronix AM 502 differential amplifiers, and a Tektronix 2230 digital-storage oscilloscope. A constant current was applied to the sample using a large resistance in series with the pulse generator. The noise voltage was detected at constant current using a Rhode-Schwarz spectrum analyzer.

A typical I-V characteristics obtained by pulse-current measurements is shown in Fig. 1. Two nonlinearities are observed, a smooth one at $E_{t1}=8.9$ V cm^{-1} and a rather abrupt one at $E_{t2}\sim30$ V cm^{-1}. The broad-band noise (BBN), measured in the frequency range 100 Hz–10 kHz, with an ac voltmeter, also presents a rapid rise and decreases smoothly for larger fields, as shown in Fig. 1. Below E_{t1} the voltage response is rectangular. Above threshold, the response shows an overshoot at the leading edge [Fig. 2(a)]. For slightly larger fields, superimposed on the transient response, asymmetric voltage spikes of large amplitude appear [Figs. 2(b), 2(c), and 2(d)] for increasing current values. The onset of these quasiperiodic oscillations corresponds to that of the BBN. One should note that the onset of these voltage oscillations is delayed by a time τ_1 with respect to the leading edge of the pulse. τ_1 decreases rapidly as the current-pulse amplitude is increased, as shown in Fig. 3, and is found to depend on the width of the current pulse. While a delay of the order of 150 μs is found for a pulse width $t_w=500$ μs, no delay is observed for a pulse width $t_w=350$ μs for the same current-pulse amplitude.

The second threshold E_{t2} is marked by a sudden decrease of the voltage across the sample after a time delay τ_2 [Fig. 2(e)]. τ_2 decreases with increasing current values. The amplitude of the voltage oscillations observed above E_{t1} seems to vanish as the second threshold E_{t2} is approached, but, in some samples, these oscillations are still observed above E_{t2} and they appear superimposed on the rapid voltage drop in the transient response. I-V characteristics measurements performed on four different samples have shown similar behavior with an average value of $E_{t1}=9$ V cm^{-1} and E_{t2} in

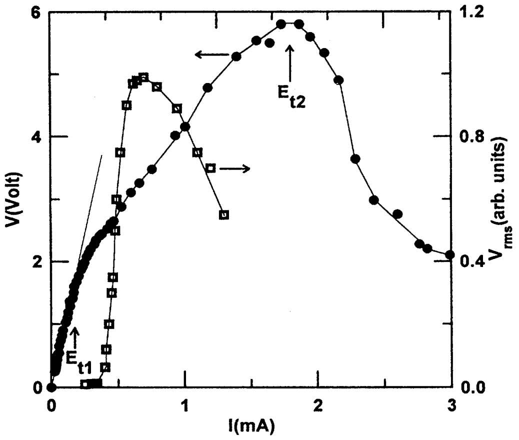

FIG. 1. Left scale: Voltage-current characteristics showing two threshold fields E_{t1} and E_{t2} obtained by pulse-current measurements in (perylene)$_2$Pt(mnt)$_2$ at $T=4.2$ K; pulse width $t_w=350$ μs. Distance between voltage contacts, 1.8 mm. Right scale: low-frequency broad-band noise as a function of dc bias current for the same sample.

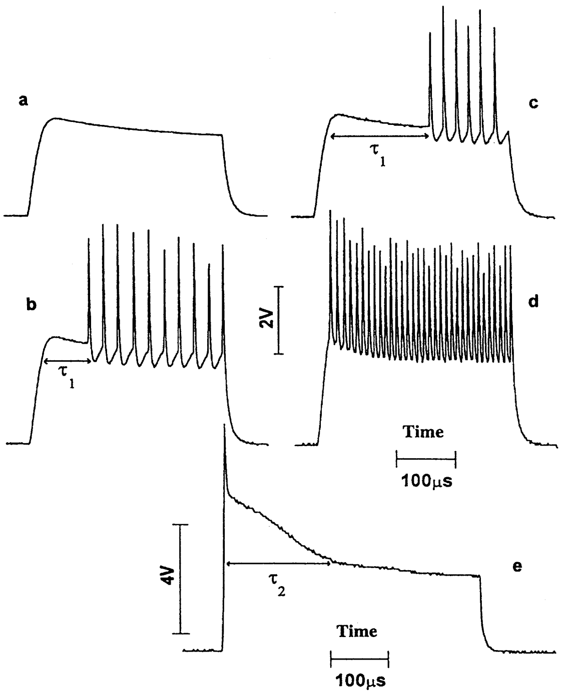

FIG. 2. Voltage wave-form response in (perylene)$_2$Pt(mnt)$_2$ at 4.2 K for different values of the current-pulse amplitude i; pulse width $t_w=350$ μs (a)–(d); and 500 μs (e). (a) $i=0.428$ mA; (b) $i=0.464$ mA; (c) $i=0.496$ mA; (d) $i=0.672$ mA. (e) $i=2.24$ mA.

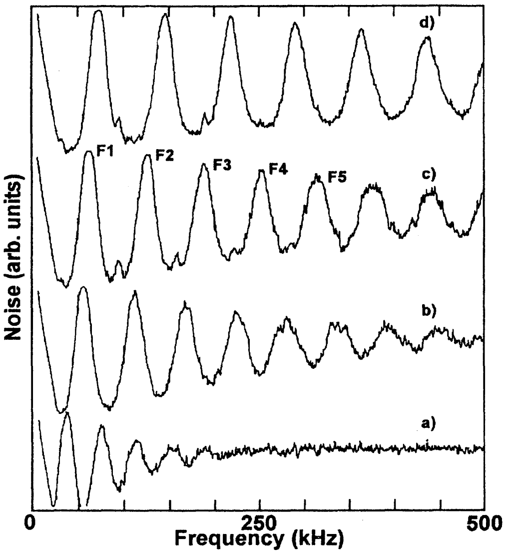

FIG. 3. Voltage-noise amplitude (arbitrary units) as a function of frequency for different values of the applied dc bias current at 4.2 K. (a) $i=0.52$ mA; (b) $i=0.59$ mA; (c) $i=0.627$ mA; (d) $i=0.685$ mA.

the range of 2–3.5 E_{t1}. The current injection homogeneity varies from sample to sample, and, as a consequence, in some cases the voltage spikes appear more irregularly. For some samples, upon an increase of the current-pulse amplitude, additional quasiperiodic spikes appear. They correspond to additional frequencies which increase with the current. For a given current, the onset of the additional spikes also shows a time delay that increases with their frequency. In all cases, the frequency of the oscillations increases with the current and at larger current these oscillations vanish gradually. The results reported here were obtained on a high-quality sample with highly homogeneous current injection.

Typical Fourier spectra of the voltage noise when the same sample is driven by a dc current provided by batteries with large series resistance are shown in Fig. 3 for various dc bias currents. Slightly above E_{t1}, for the same current where the BBN shows a rapid rise together with the onset of the voltage oscillations, the Fourier spectra show clearly one fundamental frequency and several harmonics. This type of narrow-band noise is clearly observed up to ~ 1.2 mA. Above this value, the peaks in the Fourier spectrum broaden noticeably. Figure 4 shows that these frequencies increase linearly with the excess CDW current density with a slope $F_1 J_{\mathrm{CDW}} = 18$ kHz $\mathrm{A}^{-1}\,\mathrm{cm}^2$ for the fundamental frequency F_1. The frequency of the quasiperiodic voltage oscillations obtained directly from the pulse response increases at a similar rate with the current-pulse amplitude.

The nonlinear conductivity above a threshold field E_{t1} accompanied by an overshoot in the transient voltage response, as well as the broad-band and narrow-band noise, are very similar to those already observed in CDW conductors such as $\mathrm{NbSe_3}$, $\mathrm{TaS_3}$,[1] or the blue bronze $\mathrm{K_{0.30}MoO_3}$.[7] We therefore ascribe the results described above to the depinning of the CDW above E_{t1}. In the isostructural compound with $M=\mathrm{Au}$, similar phenomena were also observed.[12] However, the real-time voltage oscillations were not detected, and the amplitude of the narrow-band noise was very weak with frequencies not harmonically related, denoting a poor sample current homogeneity. The observation of large voltage spikes is the most striking feature of the nonlinear transport in this system. Among the various CDW systems studied during the past decade, the direct observation of voltage oscillations has been scarce and the amplitude of the oscillations was smaller.[1] Although the CDW in $M=\mathrm{Au}$ and Pt compounds is commensurate,[12–16] we believe that the dominant pinning mechanism is by impurities or lattice defects, since these samples may contain more impurities or defects than in inorganic CDW conductors.

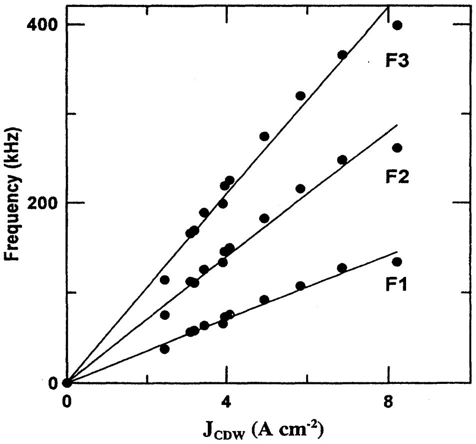

FIG. 4. Frequency of the narrow-band noise as a function of the excess CDW current density.

It is worth noting that the threshold field $E_{t1} \sim 9$ V cm^{-1} is much larger than in the Au analogue, which shows a higher transition temperature $T_p = 12$ K, and it becomes comparable to that of the organic conductor TTF-TCNQ driven through third-order commensurability under pressure: $E_t \sim 15$ V cm^{-1} at $P \sim 19$ kbar.[18] This large threshold field E_{t1} could be due to the fact that the normal carrier concentration is smaller in the platinum compound. The resistivity at $T=4.2$ K is of the order of 14 Ω cm, more than two orders of magnitude larger than in the case $M=\mathrm{Au}$. Therefore, the screening of CDW deformations may be less efficient and the CDW will be more rigid.[19] Another possible contribution to a large threshold E_{t1} in the Pt compound is the dimerization of the Pt $\mathrm{(mnt)_2}$ units below T_p (Ref. 14) not observed in the Au compound, which may contribute to an enhanced commensurability pinning in this case. A clear determination of the pinning mechanism requires additional experiments, namely, the temperature dependence of E_{t1}. The origin of the second threshold $E_{t2} > E_{t1}$ is not yet clarified. It could be due to a strongly inhomogeneous current density in the sample for large fields or to avalanche breakdown effects. From systematic studies of the possible role of pulse width and repetition rate we can exclude sample-heating effects.

Above E_{t1}, the field-dependent time delay τ_1 in the onset of the voltage oscillations is reminiscent of the delayed switching in other CDW conductors.[20] τ_1 is found to decrease with field more rapidly than the predicted power laws $\tau_1 \sim \varepsilon^{-1/2}$ for the screening or amplitude collapse models, or

$\tau_1 \sim \varepsilon^{-1}$ for the mean-field phase-slip model[20] where ε is the overdrive $\varepsilon \equiv (E - E_{t1})/E_{t1}$. The strongly asymmetric voltage spikes might result from the periodic formation of phase slips required for CDW to normal carrier conversion at contacts or near strong pinning centers. In this picture, the CDW current changes abruptly each time a phase dislocation line is created at one end or annihilated at the other end. An alternative model is that of a rigid CDW moving in a periodic pinning potential tilted by the electric field.[1] In this model, $F_1/J_{\mathrm{CDW}} = 1/ne\lambda$ where n is the concentration of carriers condensed into the CDW and λ the CDW wavelength. From the experimental value $F_1/J_{\mathrm{CDW}} = 18$ kHz A^{-1} cm^2 and from $\lambda = 4b = 16.8$ Å, corresponding to a tetramerization, we obtain $n = 2.1 \times 10^{21}$ cm^{-3}, close to the value calculated from structural data $n = 3.2 \times 10^{21}$ cm^{-3}. Taking into account the uncertainty in the sample cross-section determination, we can conclude that the CDW is depinned coherently and nearly in the entire sample. In the phase-slip process,[5] the removal of the accumulated phase difference along the sample is periodically repeated, and here also $F_1/J_{\mathrm{CDW}} = 1/ne\lambda$. The observation of a delayed onset of the voltage spikes and their strong asymmetry rather suggest that the phase-slip model is more appropriate.

In conclusion, we have presented evidence for CDW nonlinear transport in the molecular organic conductor (perylene)$_2$Pt(mnt)$_2$. Real-time voltage oscillations have been clearly observed. The Fourier analysis of these oscillations indicates that their frequencies increase linearly with the CDW current density. In high-quality samples, the CDW can be depinned coherently nearly in the entire sample. These results together with those reported previously for the isostructural M=Au compound show that the (perylene)$_2$Pt(mnt)$_2$ family of compounds provides model systems for more detailed studies of CDW transport in organic conductors.

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