Scanning-Tunneling Microscope Imaging of Single-Electron Solitons in a Material with Incommensurate Charge-Density Waves

Serguei Brazovskii,[1] Christophe Brun,[2,3,*] Zhao-Zhong Wang,[2] and Pierre Monceau[4]

[1]*Laboratoire de Physique Théorique et Modèles Statistiques, CNRS and University Paris-Sud, bat. 100, 91405 Orsay, France*
[2]*Laboratoire de Photonique et de Nanostructures, CNRS, route de Nozay, 91460 Marcoussis, France*
[3]*Institut des Nanosciences de Paris, CNRS-UMR 7588, Université Pierre et Marie Curie-Paris 6 UPMC, 4 place Jussieu, 75252, Paris, France*
[4]*Institut Néel, CNRS and University Joseph Fourier, 25 Avenue des Martyrs, B.P. 166, 38042 Grenoble cedex 9, France*
(Received 19 October 2011; published 27 February 2012)

We report on scanning-tunneling microscopy experiments in a charge-density wave (CDW) system allowing visually capturing and studying in detail the individual solitons corresponding to the self-trapping of just one electron. This "Amplitude Soliton" is marked by vanishing of the CDW amplitude and by the π shift of its phase. It might be the realization of the spinon—the long-sought particle (along with the holon) in the study of science of strongly correlated electronic systems. As a distinct feature we also observe one-dimensional Friedel oscillations superimposed on the CDW which develop independently of solitons.

DOI: 10.1103/PhysRevLett.108.096801 PACS numbers: 73.20.−r, 71.45.Lr, 07.79.Cz, 73.22.Gk

Most of strongly correlated electronic systems show various types of symmetry breaking giving rise to degenerate ground states: superconductors, electronic crystals [1]—charge- and spin-density waves (CDW, SDW), Wigner crystals, Mott antiferromagnets, or crystals hosting charge ordering with ferroelectricity. Flexibility of these states allow their local modification when electrons or holes are added to the system via doping, optical pumping, or injection. The degeneracy leads to topologically nontrivial perturbations induced by the possibility of swapping between different allowed ground states. These perturbations take the form of plane domain walls, vortex lines or dislocations; the latter are still macroscopic objects extended in one or two dimensions. Of special interest, however, are totally confined and truly microscopic objects, which energies and quantum numbers (charge, spin) are on the one-electron scale. In theory of one-dimensional (1D) models and in physics of quasi-1D systems these microscopic objects are known under the name of "solitons." Having energies below the bare electronic gap Δ, solitons should determine the observable properties, which are usually ascribed to conventional electrons. In $D = 1$, the solitons would carry either a spinless charge e or a neutral spin $1/2$, thus realizing the long-sought particles—holons and spinons—hypothesized for strongly correlated electronic systems [2,3]. Bringing these concepts beyond quasi-1D systems to general dimensions will require understanding the effects of the topological coupling between various degrees of freedom and the related effects of spin-charge reconfinement.

Solitons in electronic systems [4,5] were first found in experiments on conducting polymers. New motivations came from discoveries of the ferroelectric charge ordering [6,7] in organic conductors, from nanoscale tunneling experiments in CDWs [8], from optical [9] and high-field [10] studies of new conducting polymers. Former experiments were performed upon dimerized systems having the simplest two-value $\pm A_0$ symmetry breaking characterized by a real order parameter A. In this case the observation of solitons was facilitated by their underlying topological stability [11], but this latter property also put forward a limitation: solitons can be created and exist only in pairs. Superconductors and incommensurate CDWs (ICDW, that is a CDW with an arbitrary CDW wave number Q corresponding to a fractional band filling) are more complicated systems with a continuous degeneracy of the order parameter—a complex field $\Psi = A\exp(i\varphi)$. Now the possibility to "wind" or "unwind" the phase erases the topological stability [11] of kinks of the amplitude A, see below; this reason could explain what prevented the observation of solitons in such systems till now. Nevertheless, the same absence of topological constraints enables the direct transformation of single electrons into solitons, which dynamics was discovered in experiments on internal tunneling [8].

A related aspect is the difference existing between states containing even and odd numbers of particles, which is a common issue for correlated electrons particularly at the nanoscale. Because of solitons, this issue is spectacularly manifested in CDWs. Two types of solitons resulting from the self-trapping of either one or two electrons are expected. (i) An additional pair of electrons or holes can be accommodated to the extended ground state for which the overall phase difference becomes $\pm 2\pi$. Phase increments of 2π are produced by dynamic phase slips which require the CDW amplitude $A(x, t)$ to pass through zero, at which instance the complex order parameter has the shape of the amplitude soliton (AS)—the kink $A(x = -\infty) \Rightarrow -A(x = +\infty)$. (ii) The instantaneous configuration of the AS can become a stationary state when an unpaired spin is added to the system. Its ''raison d'être'' is that, instead of keeping the unpaired electron at the minimal energy $E = \Delta$ allowed by the rigid CDW, it is preferable to make a node in $A(x)$ and to place the excess electron at the resulting midgap state $E = 0$. The gained electron energy Δ surpasses the energy lost to create the AS, the net energy being $E_{AS} \approx 2/3\Delta < \Delta$. The AS extension is the microscopic coherence length $\xi \sim \hbar v_F/\Delta$ (v_F is the Fermi velocity of the parent metal). Here the collective charge is entirely concentrated which compensates exactly the charge of the bound electron, thus producing a neutral particle carrying a spin 1/2. Then, this new electronic state is the realization of the spinon.

Up to now, the solitons—either spinons or holons—were never directly observed neither in continuously degenerate systems nor in simple cases of dimerization; their existence was guessed by indirect evidences. In the present work we demonstrate the existence of microscopic amplitude solitons, imaged locally in real space by scanning-tunneling microscopy (STM), in the ICDW material $NbSe_3$. We also observed strong 1D Friedel oscillations, allowing us to discriminate unambiguously generic solitons from impurities-induced CDW defects.

$NbSe_3$ undergoes the two independent CDW transitions at $T_1 = 144$ K and at $T_2 = 59$ K. By STM we could previously identify the three types of chains lying in the ($\boldsymbol{b}$, $\boldsymbol{c}$) surface plane [12]. The surface CDW wave vectors are $\boldsymbol{q}_1 = 0.24\ \boldsymbol{b}^*$ and $\boldsymbol{q}_2 = 0.26\ \boldsymbol{b}^* + 0.5\ \boldsymbol{c}^*$, in excellent agreement with the bulk x-ray diffraction results [13]. A new interference modulation defined by the wave vector $\boldsymbol{u} \simeq 2 \times (0.26 - 0.24)\ \boldsymbol{b}^*$ was observed [12] and a split-off surface CDW transition was evidenced for the $\boldsymbol{q}_2$ CDW [14].

The present work was performed with an Omicron low-temperature ultrahigh vacuum (UHV) STM system equipped with two UHV separated chambers. $NbSe_3$ single crystals with typical dimensions of $0.01 \times 10 \times 0.05\ mm^3$ were selected, cleaved *in situ* at room temperature along the ($\boldsymbol{b}$, $\boldsymbol{c}$) planes and cooled down to 5, 63, or 78 K. Samples were further thermalized at temperatures between 5 and 140 K. Electrochemically etched W tips were used for this study. All the STM images shown in the following are measured with constant current and with a negative bias voltage applied to the sample, $V_{bias} = -0.3$ V, enabling to probe the occupied states of the sample in the energy range of 0.3 eV below the Fermi level. As the CDW energy gap of the high-temperature CDW is $\Delta_1 =$ 100–120 meV [15–17], it is seen that our chosen bias voltage allows us to measure by STM the integrated local density of states (LDOS) over an energy interval $2.5\Delta_1 - 3\Delta_1 = 0.3$ eV, the latter range accounting well for the bandwidth of the electron bands leading to the $\boldsymbol{q}_1$ nesting measured by ARPES (see bands 2 and 3 in Fig. 4 of [18]). Hence in all our data we probe the occupied electronic states contributing to the whole bands responsible for the $\boldsymbol{q}_1$ CDW. In addition we have shown that in the ($\boldsymbol{b}$, $\boldsymbol{c}$) plane of a single $NbSe_3$ layer, the surface Se atoms (because they are located by 2 Å closer to the STM tip than the closest Nb atoms) are expected to contribute the largest to the tunneling current and hence to determine the contrast of the STM images [12].

Figure 1(a) shows an STM image measured at 83 K. The $\boldsymbol{q}_1$ CDW superlattice, which period is about 4 times the lattice constant, is clearly observed along the 1D chains ($\boldsymbol{b}$ direction) as bright regular protrusions [12]. Whereas all over this area the CDW maxima form a regular lattice, an extra CDW period is observed (see inside the ellipse). To analyze in details the CDW deformation occurring at this location, we have plotted in Fig. 1(b) the STM profiles extracted along the defected chain and its next-neighbor chains. It is seen that the CDW amplitude is strongly reduced at the location of the defect. On going away from this extra CDW periodicity, the distorted amplitude and phase are progressively restored on a length of a few CDW periods, recovering values similar to those observed on the first-neighbor chains, the latter appearing to be not affected by the defect. We interpret this CDW deformation as a trapped amplitude soliton.

The AS profile can be simulated [see Fig. 1(c)] according to the formula

$$- \tanh(x/\xi) \sin[2\pi x/\lambda + \arctan(x/l)], \qquad (1)$$

where x is the running coordinate along the chain, λ is the CDW period and l is the length over which the CDW phase adjusts to its equilibrium value. At large $\|x\| \gg l$, the nonperturbed CDW taken as $\cos 2\pi x/\lambda$ is recovered: the π shifts from both the amplitude and the phase compensate each other. It is seen that the simulation reproduces well the qualitative features of the observed CDW defect; the parameters used in the simulation are $\xi = 3\lambda$ and $l = 5\lambda$. Our extracted value of $\xi \approx 4$ nm is in good agreement with the one deduced from the CDW gap Δ_1 [8]. The larger phase-recovery distance $l \sim \hbar v_F/T_c$ is consistent with the fact that the observed T_c is lower than the expected mean-field value corresponding to Δ_1.

Within 1D models [4] the AS is a neutral spin-carrying particle—the spinon; it is a topologically nontrivial configuration creating locally a π phase shift seen in our images as a displacement by half a CDW period near the AS center. However, in the long-range 2D and/or 3D environment surrounding the AS chain, ordering interactions with the neighboring chains require the AS to be dressed with two compensating $\pi/2$ phase tails, hence concentrating the total charge e. Therefore, the AS in the ICDW with the 2D-3D long-range order is a composed particle: (i) an amplitude node surrounded by a zone ξ of π-phase increment, corresponding to the amplitude

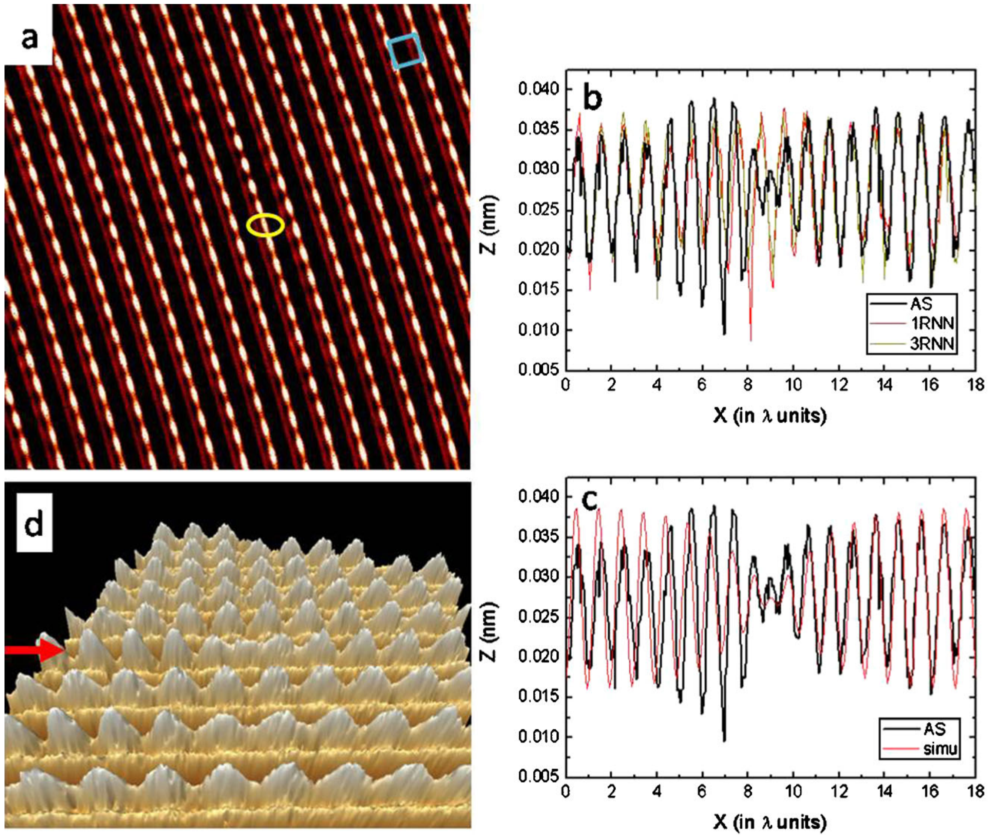

FIG. 1 (color online). Microscopic amplitude soliton in a quasi-1D CDW system. 9a) STM image of the (***b***, ***c***) plane of $NbSe_3$ measured at 83 K showing the $\boldsymbol{q}_1$ CDW superlattice (22×22 nm^2, $V = -0.3$ V, $I = 0.1$ nA) The bright regular protrusions represent the $\boldsymbol{q}_1$ CDW maxima. The blue rectangle indicates the CDW superlattice unit cell. In the center of the image an extra CDW period is observed (inside the ellipse) at the location of which an amplitude soliton (AS) is trapped. (b) Profiles extracted along the chain carrying the AS (in black) and along its neighboring chains (1RNN: 1st right nearest-neighbor (NN), 3RNN: 3rd right nearest-neighbor). At the AS center, the CDW amplitude is strongly reduced and dephased by 1/2 of the period with respect to the unperturbed profile on the neighboring chains. (c) Modeling with the Eq. (1) of the AS (simu), centered at the position of the minimum amplitude of the CDW and compared to the experimental AS profile. (d) Enlargement around the AS viewed in three dimensions with perspective, rotated by 90 degrees with respect to Fig. 1(a). The chain carrying the AS is along the arrow.

kink, and ii) wings of a longer length l with $\pi/2$ phase increments over each side. These charged wings might play a determinant role in the possibility of observing ASs by STM. Solitons are light particles with expected effective masses of the order of the band mass. To be visualized they should be immobilized by some host defects. Charged defects (e.g. isolated Se vacancies in the triangular Se prism of one of the $NbSe_3$ chains [19] or substitutional atoms replacing Nb ones) will be able to trap the amplitude soliton thanks to its charged phase tails.

A related question can be raised immediately: are we observing a generic AS or an effect produced by a hidden impurity, the latter being expected to give rise to Friedel oscillations (FO)? Fortunately, we can demonstrate that these two effects give rise to drastically different features. Recall that the FO manifests itself in a metal around an impurity as charge oscillations with a wave number equal to the Fermi diameter $2k_F$ (the same as the one of the CDW distortion). FO decay as $1/\|x\|$ for $D = 1$ at $T = 0$. In the CDW state the FO decay faster as $\exp(-\|x\|/\xi)$ while keeping the singularity $\sim 1/\|x\|$ at small $\|x\| < \xi$ [20]. Figure 2(a) shows an STM image measured at $T =$ 110 K which evidences a clear FO, centered in the circle; a strong increase of the local DOS in the immediate vicinity of the defect is seen. Profiles measured along the chain hosting the defect (in black) and along the next-neighbor chains (in lighter colors) are given in the panel 2(b). The inset shows the theoretical plot of a pure FO, which was obtained by numerical integration of the equations derived in [20]. Clearly, the maximum of the charge oscillation occurs at the defect position and is enhanced above the CDW amplitude over several periods. This feature renders the FO profile totally different from the AS one, leading their respective authentication in the STM images straightforward. From Fig. 2(b) it is seen that a 2π phase shift occurs along the chain carrying the FO; the defected chain acquires one more period, indicating an extra two-electron charge $2e$ accumulated over the two

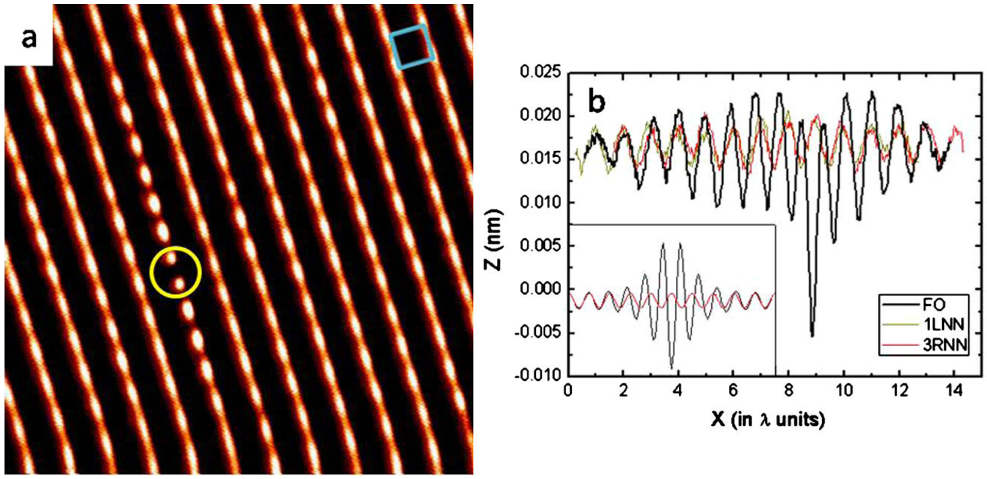

FIG. 2 (color online). 1D Friedel oscillations in a quasi-1D CDW system. (a) STM image of the (***b***, ***c***) plane of $NbSe_3$ measured at 110 K showing a defect indicated by a circle giving rise to 1D Friedel oscillations (FO) ($V = -0.3$ V, $I = 0.1$ nA). (b) Corresponding profiles along the chain hosting the defect (FO) and along the first left-nearest-neighbor (1LNN) and third right-nearest-neighbor (3RNN) of this defected chain. Inset: Theoretical profile of a pure Friedel oscillation in presence of the CDW which modulation is recovered after a few CDW periods.

wings. The underlying impurity might thus be a $+2e$ charged dopant which would correspond well to a Se vacancy expected for $NbSe_3$. At distances beyond the fourth CDW period the chains recover their transverse correlation.

We have collected numerous observations of isolated or interfering ASs and FOs. In addition to the observation that the order parameter is depressed to zero by the amplitude nodes, we have clarified the principle role of a gapless degree of freedom—here the phase—: to relax the topological perturbation induced by the amplitude soliton. These phase adaptations, induced by the long-range order, give rise to spin-charge reconfinement for the amplitude soliton and to a spinless charge in the case of Friedel oscillations.

The reported images, their analysis and comparison with existing theories demonstrate that for the CDW solitons can be the lowest energy excitations. These conclusions can be naturally generalized to the other and best-known spin-singlet ground state—the superconductor. Further extensions lead to spin-ordered states like the spin-density waves and the doped antiferromagnets; in these latter cases the soliton will be the realization of the holon [2–5] rather than the one of the spinon.

Acknowledgements. The $NbSe_3$ single crystals were synthesized by H. Berger and F. Levy (EPFL, Lausanne).

*christophe.brun@insp.upmc.fr

[1] S. Brazovskii, N. Kirova, and P. Monceau, Physica (Amsterdam) **404B**, 347 (2009).
[2] P. W. Anderson, Science **235**, 1196 (1987).
[3] K. K. Derek and P. A. Lee, J. Phys. Condens. Matter **9**, 10 421 (1997).
[4] S. Brazovskii, J. Supercond. Novel Magnetism **20**, 489 (2007).
[5] S. Brazovskii, in [1], p. 482.
[6] P. Monceau, F. Ya. Nad, and S. Brazovskii, Phys. Rev. Lett. **86**, 4080 (2001).
[7] S. Brazovskii, in *Physics of Organic Superconductors and Conductors*, edited by A. G. Lebed (Springer Series in Materials Sciences 110, New York, 2008), pp. 313–356.
[8] Yu. I. Latyshev *et al.*, Phys. Rev. Lett. **95**, 266402 (2005).
[9] O. J. Korovyanko *et al.*, Phys. Rev. B **67**, 035114 (2003).
[10] A. Choi *et al.*, Synth. Met. **160**, 1349 (2010).
[11] V. P. Mineev, *Topologically Stable Defects and Solitons in Ordered Media* (Harwood Acad. Publ., New York, 1998).
[12] C. Brun, Z.-Z. Wang, and P. Monceau, Phys. Rev. B **80**, 045423 (2009).
[13] S. van Smaalen *et al.*, Phys. Rev. B **45**, 3103 (1992).
[14] C. Brun, Z.-Z. Wang, P. Monceau, and S. Brazovskii, Phys. Rev. Lett. **104**, 256403 (2010).
[15] T. Ekino and J. Akimitsu, Jpn. J. Appl. Phys. **26**, L452 (1987).
[16] Z. Dai, C. G. Slough, and R. V. Coleman, Phys. Rev. B **45**, 9469 (1992).
[17] J. Schäffer *et al.*, Phys. Rev. Lett. **91**, 066401 (2003).
[18] J. Schäffer *et al.*, Phys. Rev. Lett. **87**, 196403 (2001).
[19] C. Brun, PhD. thesis, Université Paris Sud, http://tel.archives-ouvertes.fr/tel-00126135/fr/.
[20] I. Tütto, and A. Zawadovski, Phys. Rev. B **32**, 2449 (1985).