

Observation of Charge Density Wave Solitons in Overlapping Tunnel Junctions

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We report on direct observation of microscopic solitons in single electronic processes of the coherent interlayer tunneling in charge density waves. Special nanoscale devices were fabricated from the chain compound NbSe₃ using focused ion beams. The spectra were drastically refined by working at high (up to 27 T) magnetic fields. Internal quantum tunneling of electrons can go through solitons that are energetically more favorable quantum particles than electrons. In addition to the interband tunneling across the gap 2Δ , we observe a clear peak at the intermediate voltage $\approx 2\Delta/3$, which we associate with the creation of microscopic solitons, the energy of which must be $2\Delta/\pi$. These solitons might correspond to the long sought special quasiparticle—the spinon.

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The possibility of constructing elementary particles from continuous matter fields is one of the paradigms in physics. Such hypothetical objects, known as solitons (or instantons for related transient processes), have been discussed in field theory, high energy physics, cosmology, synthetic conductors, and for biological macromolecules. In solid state physics, the solitons might be some nonlinear, topologically nontrivial, stable local configurations of the multielectronic system. Their natural background is a degenerate ground state (GS) due to a spontaneous symmetry breaking that is typical for many strongly correlated electronic systems. It allows for topologically nontrivial solitons exploring the possibility of traveling among different equivalent GSs. Their most known forms are plain domain walls, lines of vortices, or dislocations, which are still macroscopic objects extending in two or one dimensions. Of great interest, however, are totally localized and truly microscopic objects, topological solitons, which can carry single electronic quantum numbers: either spin or charge or both.

The solitons would determine electronic properties if they are energetically favorable with respect to electrons, which is expected theoretically in one-dimensional (1D) electronic systems [1,2]. Experimentally, solitons were first identified in conducting polymers, where spin- or charge-carrying solitons in polyacetylene appear under doping, optical pumping, and charge injection [3]. Domain walls of spin solitons appeared in experiments under high magnetic fields on spin-Peierls systems [4]. A new impact [5] came from organic metals showing a ferroelectric transition with charge ordering where diverse solitons are observed as spinless charge carriers in conductivity and presumably in optical excitations.

All those were systems with a discrete GS degeneracy where solitons are the kinks between opposite signs of the order parameter, and they can be created only in pairs. Of

particular interest are systems with a continuous degeneracy like incommensurate charge density waves (ICDW) [6], where single solitons can be created via one-electron processes. Until now, there was no experimental proof for solitons in systems with a continuous degeneracy (although the search by optical techniques [7] looks promising). Moreover, in neither case were there indications for solitons in dynamics. Here we report their first direct observation from tunneling experiments performed on quasi-1D materials with ICDW, namely NbSe₃ and TaS₃. In the more general context of strongly correlated electronic systems, this kind of soliton corresponds to the expected, but never clearly observed, special quasiparticle—the spinon [8].

A CDW is an electronic crystal formed by singlet pairs of electrons. The crystalline order amplitude A is weak, so the oscillating electronic density and the associated lattice deformation are nearly sinusoidal $\sim A \cos(Qx + \phi)$. The optimal CDW wave number Q corresponds to two electrons per period $2\pi/Q$, hence $Q = 2P_F$ is the Fermi surface diameter of the parent metal. The GS energy is gained by the CDW formation because the gap $2\Delta_0 \sim |A|$ is opened at the Fermi level, decreasing the energy of occupied electronic states with $E < 0$. For a ICDW the phase is arbitrary, which characterizes the freedom of translation $\delta x = -\delta\varphi/Q$ of the ICDW as a whole. Phase distortions $\delta\varphi$ form the collective gapless mode, which is responsible for such effects as the gigantic electric response and the collective Fröhlich conductivity.

We have studied quasi-1D materials of MX_3 -type, NbSe₃ and TaS₃, which are formed by conducting chains of MX_3 prisms with weak interchain interaction at both structural and electronic levels. NbSe₃ is a layered compound with a stronger intraplane coupling of chains and a weaker interplane coupling. The conductivity anisotropy in the interlayer (a^*) direction reaches $r \sim 10^4$ at low T [9]. NbSe₃ has two incommensurate CDWs that develop below

$T_1 \approx 145$ K and $T_2 \approx 59$ K, opening the gaps Δ_1 and Δ_2 correspondingly. The CDWs' wave numbers Q_1 and Q_2 are not locked at any T : they are located nearly symmetrically with respect to $1/4$. A very specific feature of NbSe_3 is the remnant metallic conductivity at low T . It is associated with small (relative concentration of ungapped electron $\sim 10^{-3}$) pockets of nonequal numbers of electrons and holes, which are highly coherent and mobile even in the interplane direction. The perfect crystalline structure of NbSe_3 allows for a remarkably precise identification of the observed features upon which we concentrate below.

Tunneling experiments give access to properties of electrons in solids by measuring their transition rates [the current $I(V)$] between weakly coupled parts of a sample under an applied voltage V . Usually the tunneling is external: it occurs between two different conductors across their heterojunction. The recent method [10] applied here is the *internal tunneling* within the same material and even the same single crystal. It is particularly effective in studies of strongly anisotropic (quasi-2D or quasi-1D) materials where the neighbor elementary conducting layers are well separated with only a weak hybridization of electronic wave functions. Experimentally, the transport across such a layer is studied with *mesa* structures, which are also often referred to as *overlap junctions*, with micron scale lateral sizes [11]. The new method of *interlayer tunneling* provides the possibility of accessing electronic condensed states formed at elementary conducting layers. This technique has been extended to studies of CDW states in NbSe_3 [12]. At low temperatures a zero-bias conductance peak (ZBCP) was found at low voltage V . The structures at higher V have been identified as the upper ($2\Delta_1$) and the lower ($2\Delta_2$) CDW gaps. The ZBCP was attributed to the coherent tunneling of remnant pocket carriers uncondensed into CDWs.

In the present work the stacked structures have been fabricated using the focused ion beam technique developed previously [11] for fabrication of mesa structures from thin single crystals of high- T_c superconductors. The main elements are the stacked junction with two thicker leads connecting it to current terminals; *all of them are pieces of the same single crystal whisker*, which is the essence of the method. The typical sizes of our stacked junctions were $L_{a^*}, L_b, L_c = 0.05\text{--}0.2, 1, 1 \mu\text{m}$ (Fig. 1). For the thinnest stacks, that includes a few tens of elementary tunneling junctions (20–30 interlayer atomic spaces). Figure 1 shows the device picture obtained by scanning electron microscopy. Two types of devices were fabricated: (1) a simpler longitudinal geometry where the currents enter the junction via the in-plane direction b along the chain axis; (2) a sophisticated transverse geometry where the current, before entering the junction, changes the in-plane direction to the c axis transverse to b , Fig. 1. The results are basically similar, which proves the intrinsic nature of tunneling processes within the junction. Another tool that contrasts

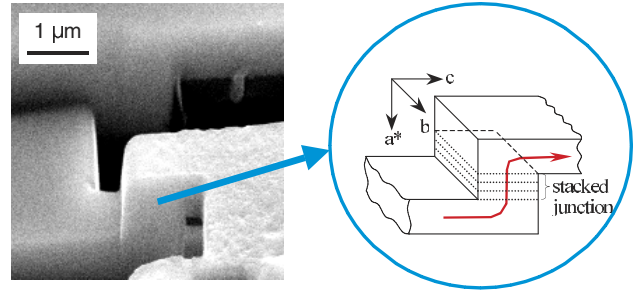


FIG. 1 (color online). Scanning electron microscopy picture of the transverse device (left) and its scheme (right). The stepwise arrowed line shows the currents in the junction area. a^* , b , c are crystallographic axes of NbSe_3 ; (b , c) is the conducting plane, b is the chain direction.

the presented studies from conventional tunneling experiments is the use of high magnetic fields (HMF), up to 27 T with different orientations. We found that the c - or a^* -directed HMFs drastically narrow or suppress the ZBCP, recovering and sharpening the structures at higher V [Fig. 2(a)]. The ZBCP can also be suppressed by elevating the temperature, which also recovers similar structures [Fig. 2(b)].

Figure 2(a) shows the tunneling spectra of NbSe_3 at 4.2 K at several magnetic fields B up to 27 T applied in the junction plane. Figure 2(b) shows the temperature dependence of tunneling spectra at $B = 0$. We see sharp peaks at 50–60 mV and at 120–150 mV [12], which are readily identified with the intergap tunneling at $V_2 = 2\Delta_2$ and $V_1 = 2\Delta_1$ for the two CDWs. The singularities become more pronounced at lower T and/or higher B . At low T , the peak value is well consistent with the double CDW gap $2\Delta_2$ which is vaguely known from optical and STM measurements, and from the point contact spectroscopy [12,13]. Moreover, the temperature dependence of the peak position for each CDW in NbSe_3 is well fitted to the BCS formula [12]. This peak, therefore, can be attributed to the double CDW gap $2\Delta(T)$ at any T . Behavior of this type is expected for a conventional macroscopic CDW/Insulator/CDW junction [14].

Besides these generally expected, while surprisingly sharp, features, there is an additional singularity at $V = V_{AS} \approx 2\Delta/3$ that appears on both CDWs when ZBCP is suppressed by high magnetic field parallel to the layers [Fig. 2(a)], or by temperature [Fig. 2(b)]. This unexpected peak finds a natural interpretation in the picture of solitons as special elementary excitations of the CDW state [1], as we discuss below.

The scheme for the intergap coherent tunneling is shown in Fig. 3. The regular momentum conserving absorption (the vertical arrow) takes place between spectral branches modified by the CDW formation and the shadow (reflected with respect to P_F) branches that are peculiar to the CDW presence. The remnant pocket of ungapped electrons, specific to NbSe_3 , is shown near the zone center, $P = 0$

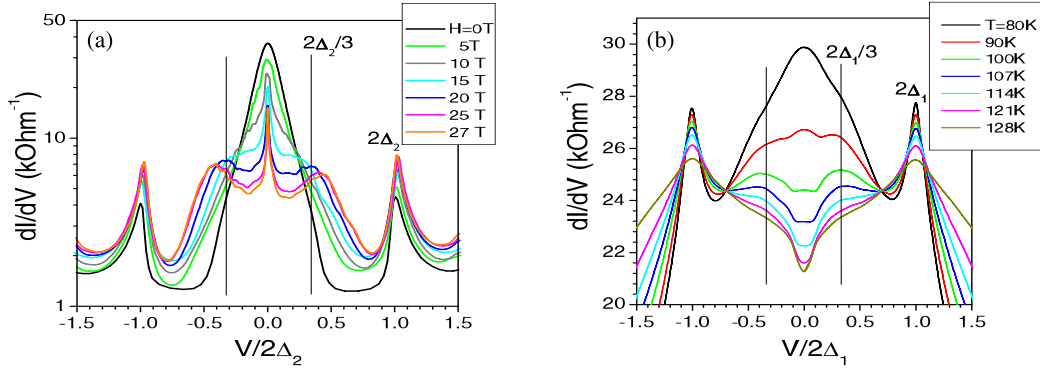


FIG. 2 (color online). Spectra of the tunneling conductivity dI/dV of NbSe_3 stacks; the voltage V is normalized to the corresponding CDW gap: $2\Delta_2$ or $2\Delta_1$. (a) Transverse geometry, at various magnetic fields $H \parallel c$, at $T = 4.2$ K, in the V range of the CDW2. The ZBCP around $V = 0$ narrows strongly with the HMF application, revealing the intergap peak at $V_{AS} = (2/3)\Delta_2$ ascribed to solitons. (b) Longitudinal geometry, at various temperatures, in the V range of the CDW1. At $120 > T > 90$ K the spectra exhibit the intragap peak at $V_{AS}(T) = (2/3)\Delta_1(T)$.

(according to [15]). The peak at V_{AS} appears from the tunneling between the Fermi level (middle of the gap) state of the electronic pocket and the nonlinear multi-electronic complex called the amplitude soliton (AS) (the inclined arrow at Fig. 3). The AS is a topologically non-trivial configuration of the order parameter $\sim A(x) \times \cos[Qx + \varphi(x)]$ with $A = \tanh(x/\xi_0)$ (see Fig. 4); it is allowed in 1D because of the ICDW GS degeneracy with respect to the phase φ . By definition, the soliton is a self-localized object, here at the scale of the microscopic coherence length $\xi = \hbar v_F/\Delta_0$ of the CDW. The wave function $\psi_0(x)$ of the associated trapped electronic state is localized over the same scale. Its form factor, the mo-

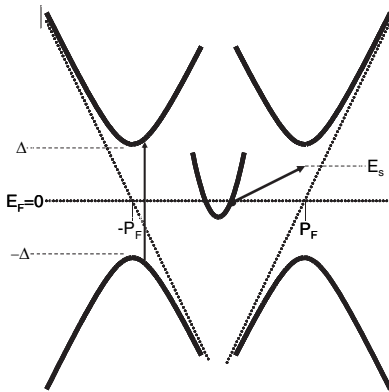


FIG. 3. Electronic spectrum of a rigid CDW. Inclined dotted straight lines are the branches for the bare metal; they cross the Fermi level $E_F = 0$ (the horizontal line) at points $\pm P_F$. Thick lines with extrema of $\pm\Delta$ on the verticals of $\pm P_F$ are the modified spectrum $E(P)$ in the CDW state. The band penetrating below E_F near the zone center $P = 0$ is the electron pocket specific to NbSe_3 . The vertical arrow shows an intergap tunneling or optical transition of free electrons. The inclined arrow shows the transition from the electron pocket at $E \approx 0$ to the soliton energy E_s ; the momentum increment is compensated by the width of the electronic midgap state within the soliton.

mentum k distribution $|\psi_k|^2 \sim \exp(-k\xi_0)$, has a tail long enough at $k = P_F$ to compensate the momentum deficit. This is the reason why, in the coherent tunneling of this device, we see the transition pocket \rightarrow soliton and do not see the transition pocket \rightarrow single electron expected at a higher $V = \Delta_0$. The last process is prohibited by momentum conservation.

The origin of solitons is partly due to anomalously strong interactions between electronic and collective (amplitude A and phase φ) degrees of freedom, which is set up if all of them are modified or formed by spontaneous formation of a new GS [1]. The resulting self-trapping of electrons explains the occurrence of two basic energies. A high one can be observed, as $2\Delta_0$ or Δ_0 , only for instantaneous processes like optics, tunneling (external and internal) or photoemission when the ground state has no time to adapt itself to injected free particles. The lower energy of fully dressed particles will show up only in thermodynamic and kinetic effects. The relaxed excitation will be observed by instantaneous probes as well, while with a reduced intensity and a broader peak—both due to the necessity to excite multiple collective modes. In our case this is the AS which energy is expected to be $\Delta_{AS} = (2/\pi)\Delta_0 \approx 0.65\Delta_0$; thus, the energy $\approx 0.35\Delta_0$ is gained

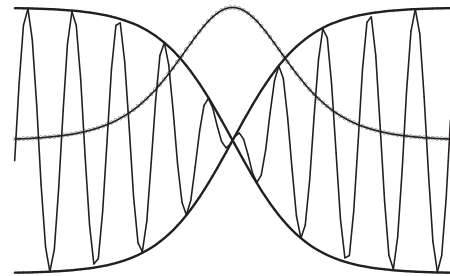


FIG. 4. Profiles of the AS: oscillating electronic density (thin line); its envelope (thick line) and the spin density distribution of the unpaired electron at the midgap state (dotted line).

by converting the electron into the soliton. All this is adequate to explain the present experiments as well as the other information available in CDWs.

Contrary to commensurate CDWs, solitons in ICDWs are not topologically stable; they can be eliminated as well as created. *Why do they exist then?*: because their energy is smaller than the band edge Δ_0 of free electrons. A single electron or a hole with an energy near the gap edges $\pm\Delta_0$ spontaneously evolves to the AS while the original particle is trapped at a local intragap level E_0 split off from the conduction band $E > \Delta_0$. There is a continuous path in the configurational space: the instanton of the phase slip type parametrized by the chiral angle—the total phase increment θ defined as $\theta = \varphi(x = +\infty) - \varphi(x = -\infty)$, such that $E_0 = \Delta_0 \cos(\theta/2)$ [1]. The self-trapping process provides the spectral flow by transferring the split-off state between the gap edges $\Delta_0 \rightarrow -\Delta_0$ while θ evolves from 0 to 2π . Simultaneously, it provides the particle flow (conversion of normal carriers to the collective GS) between the empty and the filled bands, which crosses the gap riding upon the split-off state. Also it provides the microscopic phase slip, by adding or subtracting the 2π winding of the order parameter, i.e., one wavelength of the CDW. Since each CDW wavelength is combined with two electrons with $\uparrow\downarrow$ spins, then a pair is required to enforce the complete phase slip. In case of a single particle, an electron added at Δ_0 or a hole at $-\Delta_0$, self-trapping will still proceed but pass only halfway when the solitonic configuration takes the stable form of the amplitude soliton. The amplitude sign change $A = \Delta_0 \tanh(x/\xi_0)$ corresponds just to a phase shift of π , which is half of the CDW period. Thus the AS is an intermediate stationary step in the phase slip process, and this is what we see in the experiments. For this configuration, the local state energy resides just at the centrum $E_0 = 0$; it becomes a pure midgap state occupied by a single electron.

The AS carries the electronic spin $s = 1/2$, but the charge is zero rather than e , being compensated by the dilatation of electronic wave functions of the valence band [1]. Indeed, the AS is symmetric with respect to charge conjugation: it is the adaptation of an electron added to the GS of $2M$ particles as well as of a hole upon the GS of $2M + 2$ particles. Thus, the AS is a *realization of a spinon*, which plays a central role in phenomenological pictures of strongly interacting electronic systems [8].

In the present experiments we are working within phases with a 3D long range order that literally does not allow for topological solitons which would disrupt the interchain ordering. But, actually, the discontinuity of the amplitude $A(x)$ is compensated by gradual rotations of the phase distributed over long tails stretched in all directions. The π rotation of the phase changes the sign of the factor $\cos(Qx + \varphi)$, which exactly compensates the change of sign of A in their product; thus, the system returns to the same GS as without the soliton. This compensation adds

also the charge e distributed over the phase tails, in addition to the spin $1/2$ concentrated in the core. This is why the direct transformation of an electron to the soliton is allowed.

Still, there is the question of the creation rate, i.e., of the tunneling current magnitude [16]. The interchain tunneling to the solitonic state takes place in moments when collective quantum fluctuations create an appropriate configuration with the necessary split-off intragap state. The optimal fluctuation is more shallow than the AS full form, corresponding to the chiral angle $\theta \approx 100^\circ$ rather than 180° . Indeed, the energy conservation law requires for the voltage $V_{AS} = (2/\pi)\Delta_0 \approx 0.65\Delta_0$. But this energy is gained by the interchain transfer of a single electron; hence the split-off energy level, prepared for this electron by the optimal fluctuations, must be at $E_0 = V_{AS}$; therefore, the tunneling takes place when quantum fluctuations accumulate the chiral angle such that $\cos(\theta/2) = 2/\pi$, which gives the tunneling angle.

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