Band Mapping and Quasiparticle Suppression in the One-Dimensional Organic Conductor TTF-TCNQ

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Dispersing 1D bands have been observed for the first time in an organic conductor by high resolution photoemission experiments on TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane). Their properties are extremely unusual: the bandwidth is much larger than traditional estimates, and the quasiparticle states are strongly renormalized, with no weight at the chemical potential. A deep pseudogap around the Fermi energy persists, and even increases, up to room temperature. We also report a direct determination of k_F in this material, and the observation of the opening of a Peierls gap in the low-temperature charge density wave phase. [S0031-9007(98)07275-5]

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Strongly correlated low-dimensional organic materials are of enduring interest for their rich phase diagram and peculiar properties. Early studies of these materials have focused on the various broken symmetry states. Recently, the metallic phase is attracting more attention, due to theoretical suggestions that the *normal* state of these systems may be unusual. Exact solutions of theoretical models show that 1D conductors are not Fermi liquids like normal metals, but Luttinger [1] or Luther-Emery liquids [2], with distinct physical properties. But is this conjecture valid for real quasi-1D or even 2D materials? Some recent results suggest that this may be the case [3,4]. However, crucial questions about the single particle excitations remain open.

Angle-resolved photoelectron spectroscopy (ARPES) can address this issue, and there is growing evidence that the spectral properties of quasi-1D materials are qualitatively different from those of 3D systems. Ever since the early work of Grobman *et al.* [5], photoemission has systematically revealed a strong suppression of quasiparticle states near the chemical potential [6–12]. High-resolution ARPES studies of the strongly correlated organic Bechgaard salts revealed no dispersion [13]. Peculiar 1D correlations, intrinsic effects of the photoemission process, disorder, and surface-related effects are possible causes of this unusual behavior. Extensions of these mechanisms have been proposed to explain similar observations in some 2D organic conductors [14].

In this Letter we present high-resolution ARPES results on a prototypical organic conductor. TTF-TCNQ was chosen for the abundance of experimental data on the normal state [15]. The choice is also justified *a posteriori* by the fact that all but one of the proposed mechanisms, among them spurious surface effects, can be ruled out in this particularly favorable case. We observe, for the first time in an organic conductor, one-dimensional bands dispersing with the periodicity of the lattice, and the opening of a Peierls gap in the low-temperature phase. Having thus established that ARPES does probe intrinsic bulk properties of this material, we proceed to discuss the unconventional spectral features of the metallic state in the framework of theoretical models of correlated fermions in low dimensions.

TTF-TCNQ contains planar TTF and TCNQ molecules, stacked to form segregated chains parallel to the crystallographic **b** direction of the monoclinic structure, with almost ideally 1D bands. Charge transfer—0.55 el/molecule from TTF to TCNQ at room temperature—leads to a large metallic conductivity along the chains, and to a large resistive anisotropy. A charge density wave (CDW) with wave vector $2k_F$ develops below $T_P = 54$ K on the TCNQ chains and eventually brings the system into an insulating ordered state below 38 K [15].

The properties of TTF-TCNQ have been thoroughly explored. Different experiments have led to different suggestions on the nature of the metallic state. dc transport data have been interpreted in terms of a simple anisotropic metal [16]. Optics indicates that 1D Peierls precursor fluctuations [17] must be important, at least near the CDW transition [18]. The enhanced magnetic susceptibility, and especially the observation of $4k_F$ fluctuations up to room temperature [19], indicates that electronic correlations must play an important role [20].

In our experiments, we mounted high quality single crystals of TTF-TCNQ, of typical dimensions $4 \times 0.8 \times 0.2$ mm^3, on a He cryostat, and cleaved them at a base pressure of 1×10^{-10} torr to expose the (001) surface. We performed ARPES measurements at the Wisconsin Synchrotron Radiation Center and, with high resolution ($\Delta E < 15$ meV), at Lausanne. In both cases the angular resolution was $\pm 1°$, and the Fermi energy was determined to 1 meV accuracy by measuring the Fermi cutoff of an evaporated, polycrystalline Ag film.

ARPES spectra, measured along the **b** axis at 150 K, in the metallic phase [Fig. 1(a)] show a prominent feature which disperses symmetrically about Γ, the center of the Brillouin zone. This feature approaches, but never reaches, the chemical potential, E_F. At larger wave vectors, it disperses away from E_F, to a maximum binding energy of 0.75 eV at the zone boundary (Y). Spectra measured perpendicular to the chains [Fig. 1(b)] do not exhibit any dispersion, indicating that these states have a strong 1D character. Figure 1(c) reproduces spectra from Fig. 1(a), at the high symmetry points Γ and Y. To enhance the dispersing feature an identical parabolic inelastic background was subtracted from the raw spectra; the exact background subtraction used did not affect any of our conclusions. Both at Γ and at Y the spectral line shapes are anomalous, with additional emission (marked by arrows) between the main peak and the chemical potential. A careful inspection of the spectra of Fig. 1(a) reveals a weak, shallow component at all angles. The spectrum at Y exhibits a linear tail extending to E_F, similar to that of the Bechgaard salt $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ [13].

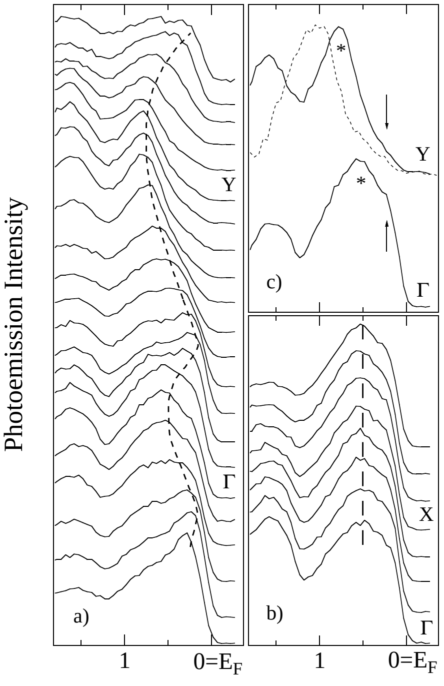

FIG. 1. (a) ARPES spectra ($T = 150$ K, $h\nu = 20$ eV) of TTF-TCNQ along the chain direction. Γ and Y are the center and boundary of the Brillouin zone, respectively. The dashed line outlines the dispersion of the main spectral feature. (b) ARPES spectra along the perpendicular **a** direction. (c) Selected spectra from (a), after background subtraction. The asterisks mark the main dispersive peak, and the arrows mark emission not accounted for by band theory. The dashed line is a spectrum of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ from Ref. [13].

Figure 2 shows an intensity plot of the data of Fig. 1(a). We observe two bands, which form electron pockets around both Γ and Y, in agreement with the schematic band structure shown in the inset [15]. Overall charge neutrality requires that the acceptor (TCNQ) and donor (TTF) bands cross exactly at the Fermi surface, thus defining the Fermi wave vector k_F. The band crossing and the minimum binding energy occur at $k = \pm(0.25 \pm 0.02)$ Å^{-1}, in agreement with previous indirect determinations of k_F from x-ray diffraction studies of the CDW superstructure [19].

Surface effects are a common concern with photoemission. Scanning tunneling microscopy of TTF-TCNQ has shown that the cleaved surfaces are highly ordered and retain the periodicity of the bulk [21]. We took special care to minimize surface exposure and found TTF-TCNQ to be less sensitive to radiation damage than other organic materials [13,14]. Aging of the cleaved surfaces was negligible on the time scale of the measurements (2–4 h). The results of Figs. 1 and 2 prove that the lattice periodicity and the charge balance between the TTF and TCNQ chains are not perturbed by the surface. Even the creation of impurities, acting as simple perturbations of the *low energy* electronic states can be dismissed: any finite quantity would strongly suppress the Peierls transition at the surface [15], an effect which we do not observe here (see below). The possibility of an insulating surface is also ruled out [14]. Therefore, concerns about possible spurious surface effects in the spectral function, which have been raised for other materials [22], can be dismissed in this particularly favorable case. We can conclude that ARPES probes intrinsic bulk properties of TTF-TCNQ.

We also collected high-resolution spectra at $k = k_F$, above (70 K) and below (30 K) the CDW transition (Fig. 3). At 70 K the peak's binding energy is 0.18 eV,

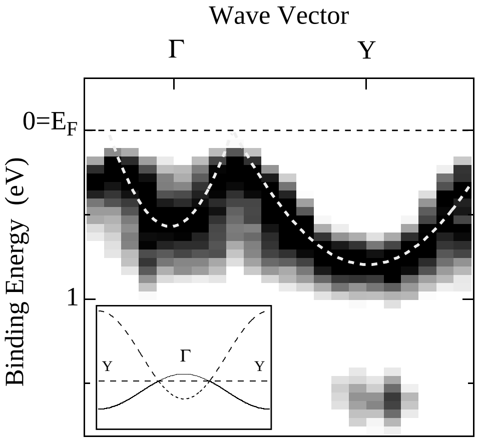

FIG. 2. Intensity plot of the spectra of Fig. 1. The dashed lines represent tight-binding cosine bands. Inset: schematic band structure of TTF-TCNQ. The donor (TTF, solid line) and acceptor (TCNQ, dashed line) bands cross at the Fermi level, thus defining the Fermi wave vector k_F.

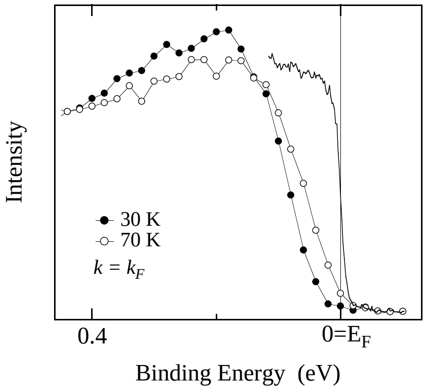

FIG. 3. High-resolution ARPES spectra measured at $k = k_F$ ($h\nu = 21.2$ eV) above (70 K) and below (30 K) the Peierls transition. The solid line spectrum is the Fermi-Dirac cutoff of an Ag film, determining the Fermi level position.

rather than zero as in a normal metal, and the intensity at the chemical potential is vanishingly small. Similar ARPES line shapes, characteristic of a pseudogap, have been observed in inorganic 1D systems [11,12], and in the normal state of underdoped cuprate samples [23]. Taking the midpoint of the leading edge as an indicator [23], we derive a pseudogap energy of ~120 meV. Between 70 and 30 K the leading edge of the spectrum shifts by 20 meV, indicating the opening of a Peierls gap of $2\Delta \sim 40$ meV, in agreement with other techniques [15].

Figure 4 illustrates the temperature dependence of the spectra at k_F in the normal state from 70 K to room temperature (RT). The quasiparticle peak progressively loses intensity, and the pseudogap effectively increases with temperature. The original spectrum is recovered upon cooling back to 70 K. These data indicate that a coherent excitation grows at low temperature inside the high-temperature pseudogap.

The periodicity of valence band states, the k_F value determined from Fig. 2, and the observation of a low-temperature gap of the right magnitude are all consistent with the known properties of TTF-TCNQ. However, other aspects of the spectral properties of the normal state are unexpected. First, a fit with tight-binding (cosine) bands, yields total widths of 2.5 eV for the TCNQ band, and 0.95 eV for the TTF band—2–4 times larger than theoretical or experimental estimates [15]. Second, the pseudogap width is at least 1 order of magnitude wider than the covalency gap expected from the coupling of the TTF and TCNQ bands [24], and this rules out any single-particle origin of the pseudogap. Third, the temperature dependence of the spectra is peculiar (see below).

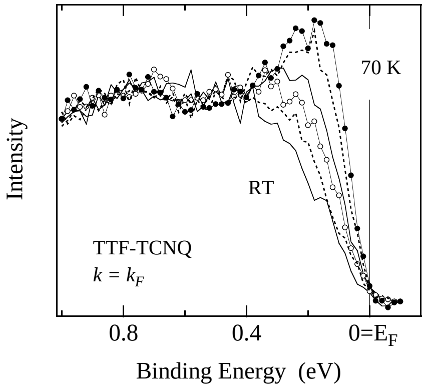

FIG. 4. ARPES spectra of TTF-TCNQ measured at $k = k_F$ between 70 K and RT.

Our observations, namely, the suppression of spectral weight at E_F, are in clear contrast with the picture of an uncorrelated anisotropic metal. They are also not compatible with a model based on 1D fluctuations. In a 1D CDW system, phase and amplitude fluctuations of the complex order parameter below the mean field (MF) temperature T_{MF} generate the fluctuating Fröhlich conduction and a pseudogap in the density of states at the Fermi level [17]. A real gap develops from the pseudogap at the Peierls transition temperature $T_P < T_{\mathrm{MF}}$. Within the standard weak coupling BCS model, the observed gap $2\Delta \sim 40$ meV yields $T_{\mathrm{MF}} \sim 125$ K which is consistent with other estimates [15]. Therefore, the ~120 meV ARPES pseudogap—3 times the Peierls gap—must have a different origin, as also proven by the temperature dependence. In a Peierls scenario the pseudogap progressively fills in with increasing temperature and disappears above T_{MF}. The data in Fig. 4 show exactly the opposite qualitative trend. At RT, where $2k_F$ CDW fluctuations are negligible [19], the spectrum exhibits only an incoherent line shape, much broader than the temperature energy scale.

Models of (moderately strong) electron-electron or electron-phonon interactions are inconsistent with both the large increase in bandwidth and the complete suppression of spectral intensity at the chemical potential. This combination excludes a Fermi liquid scenario, where the quasiparticle weight and bandwidth are both reduced as correlations increase. The data are also qualitatively inconsistent with an interpretation based on strong electron-phonon interactions. Polaron formation, which is favored in 1D, would shift spectral weight from E_F to higher binding energies, but at the same time lead to larger effective masses and reduced dispersion. The idea of localization of the photohole by a strong intramolecular response faces an analogous difficulty [6].

An approach based on specific 1D models of correlated fermions, appears more promising. Our data do not show any transverse dispersion, and we are not aware of other evidence suggesting transverse band formation in the metallic state. NMR experiments [15] indeed suggest a very small $t_\perp \sim 5$ meV $\sim k_B T_P$, implying that a dimensional crossover is quenched by the occurrence of the Peierls transition. TTF-TCNQ therefore is ideally suited to confront 1D theory to experiment. In 1D interacting electron systems, the strong coupling to collective modes underlying the Luttinger liquid picture completely suppresses the quasiparticles. The spectral function is incoherent and exhibits interaction-dependent singularities which follow the dispersions of the collective charge (holon) and spin (spinon) excitations [25,26]. A simple 1D Hubbard model (renormalized coupling constant $K_\rho > 1/2$) would predict two peaks of roughly equal strength, dispersing with the charge and spin velocities and crossing the Fermi surface [27]. This is not observed. The Luttinger liquid picture, however, allows one to study the influence of extensions of the Hubbard model, on the low-energy physics of 1D electrons, and therefore to include the different physics of the TTF and TCNQ chains.

In this perspective, the $4k_F$ fluctuations observed up to RT on the TTF chains indicate strong, long-range interactions. Therefore, these chains may be described as a Luttinger liquid with a renormalized coupling constant $K_\rho < 1/2$ [2]. For such strong interactions, all the spectral weight is concentrated around the charge excitation energy, with a low-energy tail extending to the (lower) spin fluctuation energy (cf. Fig. 3 in Ref. [26]). The picture for the TCNQ chains is less clear. The absence of $4k_F$ CDWs indicates weaker electronic correlations, and $K_\rho > 1/2$. In a Luttinger liquid perspective, the incipient $2k_F$ CDW formation around 160 K implies that the system has opened a spin gap, and thus should be described by a Luther-Emery (LE) model. In going from a $K_\rho > 1/2$ Luttinger liquid to a LE model, the divergence at the charge excitation energy is cut off to a finite maximum, while the spin divergence remains [28]. While the ARPES line shapes are compatible with both predictions, the absence of Fermi surface crossing would favor LE. This conclusion is also supported by the analysis of NMR results [29]. As T_P is approached, one would expect a crossover to a fluctuating Peierls system due to emerging transverse two-particle coherence. It is tempting to speculate that the coherent structure forming inside the pseudogap at lower temperatures could be associated with the crossover from purely incoherent collective Luttinger (or LE) excitations to the kind of short-lived quasiparticles characteristic of a fluctuating Peierls insulator.

In summary, the data provide the first complete dispersion relation for a 1D organic conductor. They also provide direct evidence for the double chain band structure of TTF-TCNQ, and for the opening of a real gap in the CDW phase. The ARPES results draw a picture of a very unusual normal state. The different spectral line shapes of the TTF and TCNQ bands may reflect different ground states of correlated 1D systems. These results, and especially the unexpected temperature dependence of the pseudogap in the metallic phase, set a new stringent test for a future comprehensive theory of the electronic structure of 1D materials.

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