Absence of Quasiparticles in the Photoemission Spectra of Quasi-one-dimensional Bechgaard Salts

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We measured typical quasi-one-dimensional organic metals (Bechgaard salts), using high resolution angle-resolved photoemission spectroscopy. We observe neither quasiparticle features near the chemical potential nor traces of a Fermi surface. The spectra, indicating a deep pseudogap around the Fermi energy, are incompatible with a Fermi liquid picture. None of the alternative interpretations we explored can fully explain the experimental data. [S0031-9007(97)04502-X]

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The Fermi liquid (FL) theory and the underlying concept of weakly interacting quasiparticles are cornerstones of modern solid state physics. The FL theory is extremely general and robust, so any indications of its possible failure are of obvious interest. In this context, the investigation of the electronic properties of quasi-one-dimensional (1D) systems is of prime importance, since in 1D the FL does not exist and is replaced by the Luttinger liquid (LL) as a paradigm for correlated fermions [1]. Also, exact solutions are available in 1D, whereas the corresponding 2D problem is difficult to solve, and only approximate results exist.

High resolution angle-resolved photoelectron spectroscopy (ARPES), which probes the single-particle spectral function $A(k,\omega)$, provides a crucial test. The theoretical predictions have been quantitatively verified in a typical Fermi liquid system [2]. Even in the high-T_c cuprates, where the spectral line shape is not fully understood, dispersing spectral features clearly identify a Fermi surface. By contrast, photoemission studies of quasi-1D metals have yielded puzzling results. Angle integrated PES spectra reveal a strongly renormalized intensity in the vicinity of the Fermi level, and no Fermi edge, the usual fingerprint of the metallic state [3–6]. ARPES reports have confirmed that the 1D systems exhibit spectral functions qualitatively different from "normal" metals [7–11]. However, these investigations have generally been performed on inorganic charge density wave systems, which may be regarded as fluctuating Peierls insulators [12], or on Mott insulators. In this Letter, we present a high-resolution investigation of 1D organic metals, and of an organic 1D Mott insulator. Our main result is that the ARPES data are incompatible with a standard Fermi liquid picture. We also explore possible alternative scenarios.

The Bechgaard salts are strongly anisotropic organic materials. Their low-energy physics is believed to be 1D over a wide temperature range [13]. Highly unusual NMR [14], optical [15], and magnetoresistance [16] data have already prompted suggestions of non-FL behavior [17]. We investigated three members of this family: $(\mathrm{TMTSF})_2\mathrm{PF}_6$, $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ (where TMTSF is tetramethyltetraselenafulvalene), and $(\mathrm{TMTTF})_2\mathrm{PF}_6$ (where TMTTF is tetramethyltetratiafulvalene). Based on electron counting, they are metals, with a formally $3/4$ filled conduction band. The actual band filling is $1/2$ if a weak dimerization along the 1D chains is taken into account. Electronic correlations, however, modify this simple picture.

In $(\mathrm{TMTSF})_2\mathrm{PF}_6$ the electrical resistivity is metallic along the **a** (1D) and **b** axes, but not along **c**. A dimensional crossover is observed below 80 K, and a spin density wave develops at 12 K. $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ has similar properties, but a lower crossover temperature, and a superconducting ground state ($T_c = 1$ K). $(\mathrm{TMTTF})_2\mathrm{PF}_6$, by contrast, exhibits a resistivity minimum below room temperature, indicative of a charge gap, while the spins are left unaffected. The estimated value of the charge gap, $\Delta E \sim 100$ meV, is larger than the renormalized transverse hopping parameter, and $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is viewed as a 1D Mott insulator.

The synthesis of the TMTTF molecules and the growth of the single crystal samples of the charge-transfer salts were carried out at UCLA. Transport and NMR measurements were used to verify the quality of the samples. The resistivity of $(\mathrm{TMTTF})_2\mathrm{PF}_6$ was consistent with localization, with a well-defined gap. Sample size was typically 10 mm along the chain direction, and up to 2 mm in the perpendicular ($\mathbf{b}'$) direction. Typical thicknesses ranged from 0.1 to 0.2 mm, and up to 0.5 mm for $(\mathrm{TMTSF})_2\mathrm{PF}_6$. Samples were cooled to 150 K and cleaved at a base pressure $<1 \times 10^{-10}$ torr. The cleaved (001) surfaces were shiny and, except for $(\mathrm{TMTSF})_2\mathrm{PF}_6$, flat; the $(\mathrm{TMTSF})_2\mathrm{PF}_6$ surfaces exhibited steps when observed under the microscope.

We performed ARPES measurements using highly (>95%) linearly polarized uv light from the 4 m normal incidence monochromator beam line at the Wisconsin

Synchrotron Radiation Center. We used a 50 mm mean radius hemispherical analyzer, mounted on a two-axis goniometer, with a total combined (electron + photon) energy resolution better than 30 meV and an angular resolution of ±1°. The Fermi level position was determined with an accuracy of ±5 meV by measuring a gold reference film.

Figure 1 illustrates ARPES spectra of (TMTSF)$_2$ClO$_4$, measured at 150 K along the 1D **a** direction. An identical inelastic background was subtracted from all spectra after beam current normalization. We observe nondispersive features at 4, 2.5 eV, and a prominent one at 1 eV, followed by an almost linear tail extending to the Fermi energy, E_F. Difference curves show that this tail is independent of the electron emission angle. Large, angular-dependent intensity variations, with no evidence for dispersion, occur around 1 eV. Changes at even larger energies mainly reflect the angular dependence of the background.

These results, and similar data for the perpendicular $\mathbf{b}'$ direction, are surprising in two respects: (i) the absence of any dispersing quasiparticle states near E_F, and (ii) a vanishingly small signal at E_F at all emission angles, despite the metallic nature of the sample. They are however consistent with the absence of a metallic Fermi edge in the angle-integrated spectra [4].

The data of Fig. 1 were carefully reproduced and are typical of all six TMTSF samples we studied (both ClO$_4$ and PF$_6$). We found that measuring times in excess of one hour resulted in a loss of intensity, at first within 1 eV of E_F and later of all coherent features, with an accompanying increase of background. We have therefore taken particular care to reduce sample exposure to the photon beam to a minimum. The first and last spectra (Nos. 1 and 5) of Fig. 1 were collected within 15 minutes, and are essentially identical. This indicates that there was no surface damage from irradiation over the measuring time, and that the spectra are intrinsic to the (TMTSF) surfaces.

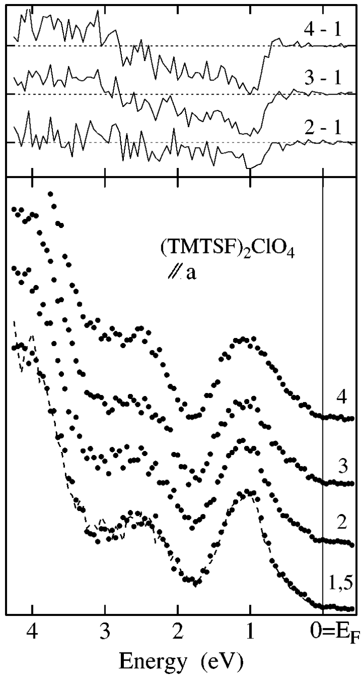

FIG. 1. Bottom: ARPES spectra of (TMTSF)$_2$ClO$_4$ along the 1D **a** direction. The spectra are labeled 1 (corresponding to the Γ point) to 4 (the zone boundary), and 5 (back to Γ, dashed line). The temperature was 150 K, and the photon energy 20 eV. Top: Difference spectra.

Our conclusion about surface quality is supported by the polarization dependence of the ARPES signal. The spectra of Fig. 2 were collected at Γ in two different geometries, with the electric field vector (**E**) of the linearly polarized light either parallel or orthogonal to the **a** axis. The strong intensity decrease of the peak at 1 eV for **E**⊥**a** is consistent with the 1D character of the conduction electrons, and with optical data [15]. The low-energy tail exhibits a less pronounced polarization dependence.

Further evidence that ARPES does probe the intrinsic properties of these materials is given by a comparison of data for (TMTSF)$_2$ClO$_4$ and (TMTTF)$_2$PF$_6$. The two compounds exhibit similar spectral line shapes, both at the Γ point (Fig. 3) and away from Γ (not shown). However, the (TMTTF)$_2$PF$_6$ spectra are almost rigidly shifted to higher binding energy, and their onset is well below E_F. A linear fit to the leading edge of the spectra (inset) indicates a difference in intersection with the baseline of 100 ± 20 meV, independent of emission angle. This value is consistent with the size of the charge gap in (TMTTF)$_2$PF$_6$. Therefore the ARPES data indicate a real energy gap in the insulating (TMTTF)$_2$PF$_6$, but only of a deep pseudogap in the metallic (TMTSF)$_2$ClO$_4$.

The absence of quasiparticle features dispersing through the Fermi level rules out any standard interpretation of the data. We now briefly discuss alternative

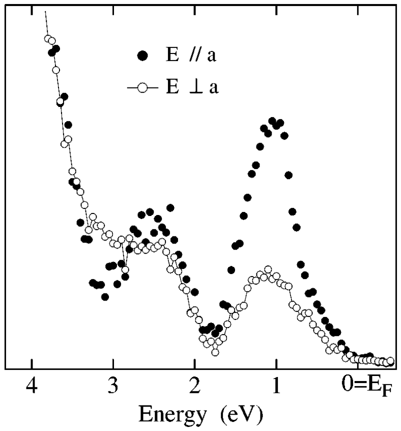

FIG. 2. ARPES spectra of (TMTSF)$_2$ClO$_4$ measured at the Γ point with the electric field of the linearly polarized radiation parallel (solid symbols) or perpendicular (open symbols) to the chain axis **a**.

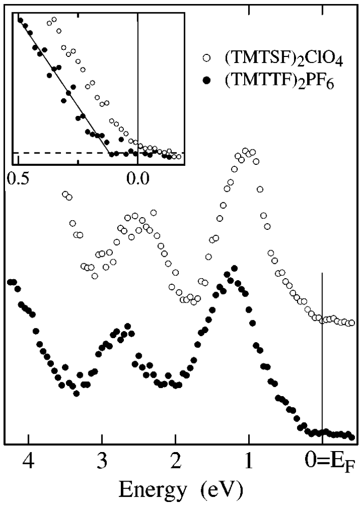

FIG. 3. Comparison of the spectra of (TMTSF)$_2$ClO$_4$ and (TMTTF)$_2$PF$_6$, at the Γ point. A linear fit to the leading edges (inset) identifies an energy shift of 100 ± 20 meV, compatible with the charge gap in (TMTTF)$_2$PF$_6$.

explanations. It was previously suggested [4] that the absence of a Fermi step in the PES spectrum could be a consequence of the peculiar electronic correlations in 1D metals. In a LL $A(k,\omega)$ reflects spin-charge separation, and depends on the renormalized coupling constant K_ρ, via the exponent $\alpha = (K_\rho + K_\rho^{-1} - 2)/4 \geq 0$. α increases from 0 to large values as the strength and the range of the electronic interactions increase [18,19]. Our data, which exhibit no quasiparticle or pronounced spinon and holon peaks, are consistent with the unusually large α values ($\alpha > 1$) suggested by PES. In this limit, the spectral function exhibits no divergencies at the spinon and holon energies, and increases roughly linearly with binding energy. However, even assuming that such large α values are realistic, this explanation is unsatisfactory in two respects: (i) calculations indicate a change of slope, which we do not observe, in this linear region as k approaches k_F; (ii) strong interactions and commensurability (with or without dimerization) will conspire to make the system insulating.

Large exponents may appear in more subtle ways. The optical conductivity of (TMTSF)$_2$PF$_6$ [15] reveals, at low temperature, a small (5–10 meV) correlation gap and a small number ($\sim$1%) of free carriers. In a slightly doped Mott-Hubbard insulator, near quarter filling, $K_\rho = 1/8$ and $\alpha = 1.53$, consistent with the photoemission spectra. But this scenario is also unsatisfactory, since we expect this exponent to be relevant only for energies less than the gap. At larger energies, both in the TMTSF and TMTTF samples, $A(k,\omega)$ should exhibit the signatures of a Mott-Hubbard insulator [11], which we do not observe. More generally, models based on a weak dimerization and moderate values of a Hubbard U consistent with the known bulk properties of the Bechgaard salts are incompatible with our data, because the spectral function of the Hubbard model exhibits divergent dispersing signals.

There remains the possibility that surface effects—intrinsic to the cleaved samples—may be relevant to our results. Scanning tunneling microscopy measurements of cleaved TMTSF samples have revealed well-ordered surfaces [20], but even a small density of defects could influence the spectrum of a 1D material in nontrivial ways. We speculate that at the surface, for structural or electronic reasons, transverse interactions may be smaller than in the bulk, thus enhancing the 1D character of the system. In this case, even weak disorder could localize electrons in finite chain segments, suppressing dispersion and leading to renormalized exponents [21,22]. A less efficient screening would also enhance the effect of the energetic intramolecular vibrations, [3,23], and lead to a transfer of spectral weight from the quasiparticle peak to the incoherent part of the spectral function. We also mention that fluctuations of the cation stoichiometry could affect band filling at the surface. One can conceive an extreme limit, where the Fermi level would be pinned outside the conduction band. This hypothesis, however, is incompatible with the absence of dispersion.

In addition to the low-energy part of the spectral function, near E_F, we considered the prominent peak at 1 eV. At such energies the lattice cannot be ignored. Band structure calculations predict a Van Hove singularity at the bottom of the conduction band [24]. A shadow band, reflecting correlations, should also be visible at about the same energy [25]. In both cases we would expect to observe dispersion, not just intensity variations. Since the binding energy of this feature is of the order of the estimated Coulomb repulsion U, it is plausible to identify it with the completely filled lower Hubbard subband of the $3/4$ filled system.

In summary, we have measured intrinsic spectral fingerprints of typical 1D organic systems. We observe a gap consistent with resistivity and optical results for the insulating (TMTTF)$_2$PF$_6$ but only a deep pseudogap in the metallic (TMTSF)$_2$ClO$_4$. The absence of any quasiparticle peak dispersing through the Fermi energy rules out a standard Fermi liquid description of our results, and no existing model seems completely consistent with our data. An interplay of surface effects and low dimensionality may be relevant, and should be explored from both the theoretical and the experimental point of view.

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