Spectroscopic Indications of Polaronic Carriers in the Quasi-One-Dimensional Conductor $(TaSe_4)_2I$

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Angle-resolved photoemission (ARPES) on the quasi-one-dimensional conductor $(TaSe_4)_2I$ shows a hidden Fermi-surface crossing in its metallic state and the opening of a Peierls gap at low temperatures. The underlying quasiparticles have vanishing spectral weight and extremely short coherence lengths. They are interpreted as polarons in the strong-coupling adiabatic limit, and almost all their ARPES weight is incoherent. These observations suggest a scenario where the long-standing contradictions between ARPES and other experiments on Peierls materials could be resolved.

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The low-energy properties of a solid are determined by its elementary excitations. They can broadly be classified into quasiparticles — evolving continuously out of electrons when interactions are turned on — and collective modes — with no counterparts in noninteracting electron systems. High-resolution spectroscopy is required for their accurate characterization. The spectral function $A(k, \omega)$ measured by angle-resolved photoemission (ARPES) contains unique wave-vector and energy-resolved information on the quasiparticles (QPs) and indirectly on interactions. Optics lacks the k selectivity of ARPES, but it probes both the single-particle and the collective response.

In standard metals, the dispersion and width of the lines determine the renormalized excitation energies and the lifetimes of the QPs [1]. The momentum width of the ARPES lines measures their coherence length. The spectral functions are well described by Fermi liquid (FL) theory [2]. There are, however, entire classes of materials whose ARPES properties are poorly understood. They include the cuprates, the colossal magnetoresistance manganites, and, quite generally, all quasi-one-dimensional (1D) materials. It is believed that strong electron-electron or electron-phonon interactions are responsible for these unusual line shapes.

Despite the diversity in the physical properties of 1D materials, previous ARPES work has shown common features: renormalized intensities, the absence of clear Fermi surface crossings in metals, and too large gaps in their insulating phases. The spectral line shapes are consistently different from the standard FL line shapes of 3D metals [3–11]. This applies in particular to the benchmark 1D conductor $(TaSe_4)_2I$. The ARPES features carry signatures of two incommensurate periodicities [12], but the energy distribution of the spectral weight has remained unexplained.

New data on $(TaSe_4)_2I$ indicate that electron-phonon interactions dominate the spectral properties, and suggest a possible solution to these puzzles. We do observe signatures of Fermi surface crossing, but only with exceedingly small intensity. Most of the spectral weight goes into an incoherent high-energy feature which is shifted from the band dispersion. These observations are consistent with the formation of a polaron liquid, with masses $m^* \sim 10\, m_e$ derived from optics. At low temperature, the polaronic quasiparticles undergo a transition to a charge-density-wave (CDW) state, which we observe by temperature-dependent high resolution spectra, and momentum distribution curves (MDCs).

$(TaSe_4)_2I$ has a chainlike structure and exhibits at $T_P = 263$ K a metal-insulator transition to an incommensurate, nearly tetramerized, CDW state [13,14]. Single crystals prepared by the chemical transport method, were cleaved at a pressure of 10^{-10} torr, with the 1D ΓZ direction lying in the surface plane. We performed the ARPES experiment at the PGM beam line of the SRC, equipped with a Scienta SES-2002 analyzer. The overall experimental energy and momentum resolutions were $\Delta E < 10$ meV and $\Delta k \sim 0.04$ Å^{-1}. MDCs were obtained by constant-energy cuts of the $I(E, k)$ intensity maps.

The ARPES spectra show bandlike dispersion throughout the Brillouin zone (BZ) with a minimum at Γ. The intensity maps in Fig. 1 resolve this band around π/c, the BZ boundary in the ΓZ direction, at 265 and 100 K. It was identified [4,12] with the 1D Ta $5d$ conduction band predicted by band structure calculations [13], but the peak does not cross the Fermi level in the metallic phase. Its minimum binding energy (0.45 eV at Z) apparently defines an energy gap of 0.9 eV, much larger than the optical or transport gap ($2\Delta = 0.25$–0.3 eV) [14,15].

Figure 2 shows the spectrum measured at k_F and 100 K in the CDW phase, where the features are sharper. The line shape is almost independent of wave vector. It exhibits a main peak (A), which corresponds to the dispersing feature of Fig. 1, and a distinct shoulder (B) at 0.3 eV, consistent

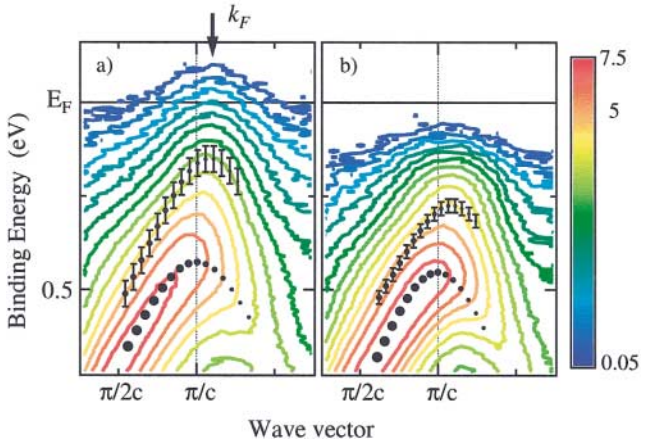

FIG. 1 (color). ARPES intensity maps of $(TaSe_4)_2I$ at 265 K (a) and 100 K (b), around $Z = (\pi/c)$, normalized to beam current and acquisition time. The lines measure constant ARPES intensity, in a logarithmic scale. The dispersions of features "*A*" and "*B*" are estimated from Gaussian fits as in Fig. 2, and their intensities are indicated by the size of the symbols.

with previous data [4,16]. An excellent fit of the spectrum is achieved with two Gaussian lines with identical width FWHM = 0.17 eV. The weaker feature *B* has a maximum at $k = k_F = 1.085\ \pi/c$. They represent the parallel bands formed by bonding and antibonding combinations of 1D states on adjacent chains [13]. Their estimated dispersions are indicated by dots in Fig. 1 [12].

The high-energy end of the spectrum exhibits nontrivial temperature-dependent changes below T_P (Fig. 1). To analyze them quantitatively we measured ARPES intensity maps between 265 and 100 K. By constant energy cuts, integrating within a narrow 20 meV energy window, we extracted MDCs as in Fig. 3a. The $T = 265$ K MDC is obtained for $E = 0$, on the extreme tail of the spectrum. Even if the intensity is quite small and the spectrum is featureless around this energy, the MDC exhibits a Lorentzian line shape centered at $k = k_F$. This is the expected fingerprint of a quasiparticle on the Fermi surface, and indeed intensity spilling across the Fermi level is evident in Fig. 1a. The properties of such a QP, however, are quite unusual. Besides its extremely small intensity, the broad linewidth $\Delta k = 0.1$ Å^{-1} indicates a very short coherence length $\lambda = 1/\Delta k = 10$ Å, close to just 3 times the Ta-Ta distance ($3\ d_{\text{Ta-Ta}} = 9.6$ Å). This value is much shorter than for a clean metal (10^2–10^3Å). At 100 K there is no ARPES signal at $E = 0$, due to the shift of the leading edge of the spectrum (Fig. 1b). The intensity *and line shape* of the MDC can be recovered by a cut at finite binding energy. Repeating this procedure at intermediate temperatures yields $\Delta E(T)$ (Fig. 3b), a phenomenological, but objective indicator of the spectral shift. Its temperature dependence and the saturation value $\Delta_0 = 0.12$ eV are consistent with the optical and transport gaps. This conclusion is not affected by the uncertainties of the procedure.

A standard mean-field scenario of the Peierls transition would require a sharp QP peak at $k = k_F$ and $E = 0$ in the metallic phase above T_{MF}, the mean-field transition temperature, and at $\Delta(T)$ below T_{MF}. The picture which emerges from ARPES is quite different, whether we refer to the peak of the ARPES line (signal *A*) or—more correctly—to the position of signal (*B*). The leading edge defines the temperature evolution of the gap. We now discuss the possible origins of these inconsistencies, namely: (i) extrinsic effects; (ii) fluctuations of the order parameter;

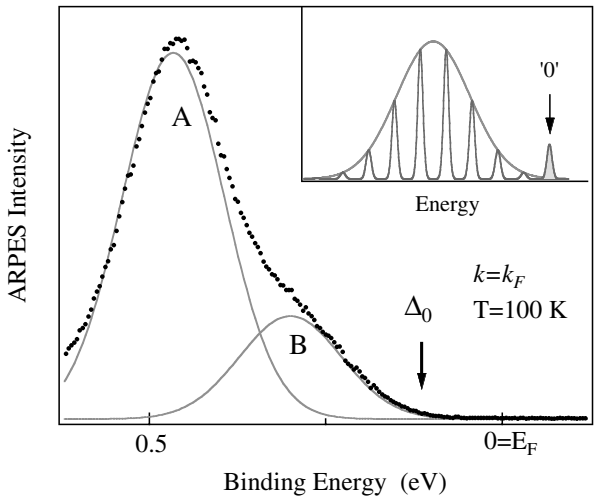

FIG. 2. High-resolution ARPES spectrum of $(TaSe_4)_2I$ at 100 K and $k = k_F$. The line shape can be fit by two Gaussian lines. The extrapolation of the leading edge defines an energy gap $\Delta_0 = 0.12$ eV. Inset: Schematic spectral function of an electron coupled to a harmonic oscillator in the strong-coupling limit. The "zero-phonon" line ("0") should also lie under the general Gaussian envelope, and it was arbitrarily rescaled to enhance its visibility. Its weight is exponentially reduced with the coupling strength.

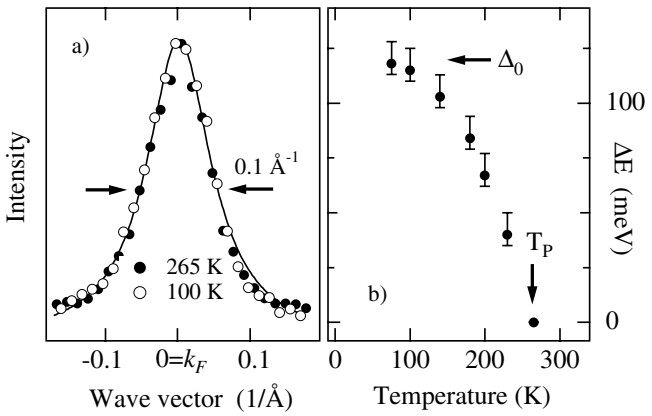

FIG. 3. (a) Momentum distribution curves measured at $E = 0$ (265 K) and $E = 0.12$ eV (100 K); the solid curve is a Lorentzian with FWHM = 0.1 Å^{-1}. (b) Temperature-dependent position of the energy window producing identical MDCs as in (a). The error bars reflect the uncertainties associated with different normalization procedures.

(iii) a strong renormalization of the QP line shape from interactions.

It was recently suggested by Joynt [17] that dissipation by screening currents induced by the photoelectron may distort the spectrum of poorly conducting materials and suppress the spectral weight at E_F. This classical effect depends on the photon energy, but we found no changes in the line shape when the energy was changed by a factor 4 (not shown). This also excludes possible final-state effects. Spurious surface effects are ruled out by the observation of the bulk periodicity and of clear signatures of the transition.

Fluctuations drastically modify the mean-field scenario in the temperature range of our experiment [18,19], and there is evidence for such fluctuations from magnetic susceptibility [20] and optical conductivity [15] data. For $T_P < T < T_{\mathrm{MF}}$ the QP peak remains centered at Δ, but the fluctuations broaden it [21]. Clearly the experimental ARPES spectra do not display the predicted peak at $\Delta_0 = 0.12$ eV.

The displacement of spectral weight to much higher energies suggests the importance of interactions. Both many-body correlations and electron-phonon interactions transfer spectral weight from the coherent QP peak to incoherent structures at higher binding energies [22]. In $(TaSe_4)_2I$ there is no evidence for strong electronic correlations. On the other hand, electron-phonon interactions are obviously important in a CDW system [14].

The anomalously large width of the MDCs of Fig. 3 indicates that the photohole should be described as a wave packet with a width of only 10 Å in real space. This points to a polaron scenario, where the charge carriers move coherently with the local lattice deformation. These are the carriers which at $T < T_P$ condense into the CDW, and it is interesting that their size is comparable to the CDW period [13].

The polaron problem has a long history [23], but its spectral properties have not been systematically explored. An electron coupled to a single harmonic oscillator [1] provides qualitative insight: spectral weight is transferred from the "zero-phonon" peak to the excited states of the oscillator (Fig. 2, inset). They are equally spaced by $\hbar\Omega$, the energy of the mode, and have a Poissonian envelope. This simple picture essentially reproduces the PES spectrum of a diatomic molecule such as H_2 [22]. It also bears similarities with the spectral function of the 1D Holstein model, in the atomic limit [24,25]. In the strong coupling, adiabatic limit ($\Omega/t \ll 1$, where t is the electron hopping integral) the satellites merge into a single Gaussian peak. The separation between the peak maximum and the "zero-phonon" QP line is $\Delta\varepsilon \sim \langle n\rangle\hbar\Omega$, proportional to the average number $\langle n\rangle$ of phonons dressing the hole. The QP weight is exponentially suppressed and the spectrum is mostly incoherent. Gaussian line shapes are also expected in any realistic situation due to the overlap of several modes, and to various broadening mechanisms.

The observations of displaced Gaussian line shapes is consistent with the assumption that the charge carriers are small polarons. In this perspective almost all spectral weight in our data is in the incoherent part of the spectral function. What remains of the coherent QP is just the base of the leading edge. From the data of Figs. 1 and 3, we infer that the QP peak follows the band dispersion, while the large incoherent signals are displaced to higher binding energies by 0.18 eV. Depending on assumptions on phonon frequencies (35 meV for the highest vibration or 11 meV for the mode involved in the $2\,k_F$ instability [15]), $\langle n\rangle \sim 5{-}15$. Both numbers are compatible with the vanishing QP weight considering that, in the strong coupling regime, the reduction of the QP weight Z is much faster than the corresponding increase of the effective mass [26]. Large masses are not incompatible with a broad ARPES bandwidth, but the broad dispersion should be interpreted as the superposition of narrow polaron bands, with spectral weight distributed along the unperturbed band structure [27]. This polaronic scenario has obvious similarities with one proposed earlier by Dessau *et al.* [28] to interpret ARPES data in the manganites, but our results do not suggest the predicted narrow QP dispersion.

Optical data also support the hypothesis of heavy quasiparticles. The optical conductivity (Fig. 4) has a complex structure [15]. Besides the peaks from a quasipinned collective mode and the CDW (pseudo-)gap, one can identify two distinct zero-frequency modes. They represent the collective contribution of sliding CDW segments, and the

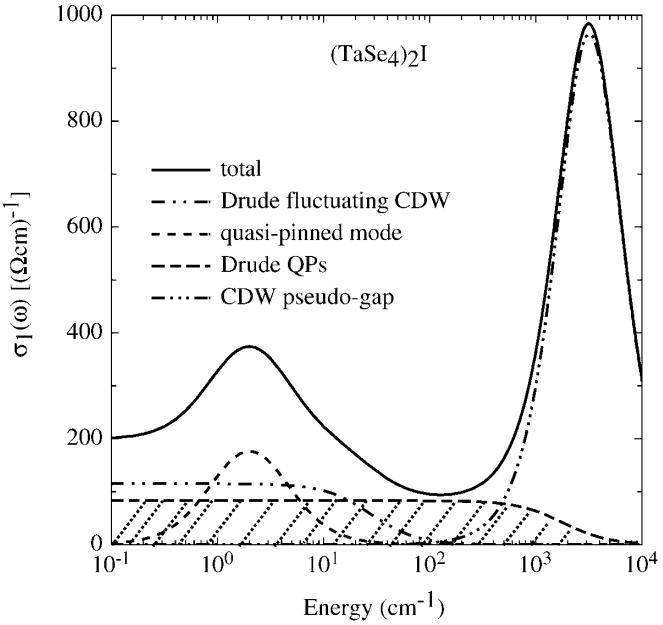

FIG. 4. Optical conductivity of $(TaSe_4)_2I$ after the Lorentz-Drude model, based on the classical dispersion theory, reproducing the experimental data at $T = 270$ K, along the chains direction (Ref. [15]). The components of the calculation are shown separately, and the quasiparticle (QPs) weight is highlighted as a dashed surface.

Drude response of uncondensed quasiparticles defining the Fermi surface, respectively. The spectral weight of the QP Drude term can be scaled with the total spectral weight up to the onset of the interband transitions. The total spectral weight corresponds to a plasma frequency $\omega_p^{\mathrm{tot}} = 2 \times 10^4$ cm^{-1} and the weight of the QP Drude term to an effective plasma frequency $\omega_p^{\mathrm{QP}} = 4200$ cm^{-1} at 300 K, so that $(\omega_p^{\mathrm{tot}}/\omega_p^{\mathrm{QP}})^2 = (n_{\mathrm{tot}}/n)\,(m^*/m_e) = 23$. Here m^* is the effective mass of the polaronic QPs, and should not be confused with the mass of the fluctuating CDW segments, discussed elsewhere [15]. Spin susceptibility [20] gives $(n/n_{\mathrm{tot}}) \sim 0.5$ at 300 K, which yields $m^* \sim 10\ m_e$, consistent with the heavy polarons deduced from ARPES. A similar analysis of the blue bronze $K_{0.3}MoO_3$, another typical CDW system, leads to a comparable mass renormalization. This, and the similarities in the ARPES line shapes, suggests that polaronic effects shape the spectral properties of 1D Peierls systems, and that the 1D signatures predicted by theory may be too weak to be observed. Clearly, these conclusions may not apply to other 1D systems dominated by electronic interactions.

In summary, we observed a Fermi surface crossing in the metallic phase of $(TaSe_4)_2I$, based on the identification of the polaronic QP dispersion with the leading edge of the spectrum. In the CDW phase we obtain a gap value which is consistent with other experiments. The peak of the ARPES spectrum is a high-energy feature related to the phonon cloud of the polaron, and not to low-energy physics. Accepting the polaron picture, we have studied its spectroscopic properties in detail: (i) despite the mass enhancement predicted by theories, the spectral features follow unrenomalized band dispersions; (ii) most of the spectral weight is in an incoherent signal which has well-defined dispersion and line shape throughout the BZ; (iii) the QP line carries vanishing spectral weight. In ARPES, one-dimensional fluctuations involve only this coherent part of the spectrum, and are therefore just a higher-order effect. Finally, numerical simulations of polaron models have produced extremely complex spectral functions. In contrast, our results indicate that polarons are surprisingly simple excitations which might be more effectively described in terms of the lowest nonvanishing moments (mean, variance, skewness, etc.) of the weighted eigenstates and their dependences on wave numbers.

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