Multiple mobile excitons manifested as sidebands in quasi-one-dimensional metallic TaSe$_3$

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Charge neutrality and their expected itinerant nature makes excitons potential transmitters of information. However, exciton mobility remains inaccessible to traditional optical experiments that only create and detect excitons with negligible momentum. Here, using angle-resolved photoemission spectroscopy, we detect dispersing excitons in the quasi-one-dimensional metallic trichalcogenide, TaSe$_3$. The low density of conduction electrons and the low dimensionality in TaSe$_3$, combined with a polaronic renormalization of the conduction band and the poorly screened interaction between these polarons and photo-induced valence holes leads to various excitonic bound states that we interpret as intrachain and interchain excitons, and possibly trions. The thresholds for the formation of a photo-hole together with an exciton appear as side valence bands with dispersions nearly parallel to the main valence band, but shifted to lower excitation energies. The energy separation between side and main valence bands can be controlled by surface doping, enabling the tuning of certain exciton properties.

Low-dimensional electronic systems with a low density of charge carriers $n$ exhibit interesting many-body effects. Indeed, their Fermi energy is low compared to the strength of the Coulomb interaction, which is poorly screened. Moreover, the low dimensionality enhances interaction effects. They manifest themselves in non-Fermi liquid gapless ground states such as metallic Luttinger liquids, or gapped ground states such as insulating Wigner crystals and other kinds of charge density wave$^{1,2}$. Not only do the ground state of such strongly interacting systems exhibit interesting strong coupling phenomena, but also their excitations do. In particular, the attraction between negatively charged electrons and positively charged holes can lead to bound states in the excitation spectrum, usually referred to as excitons$^{3-8}$, and this tendency is enhanced in low dimensions.

The creation in insulators of non-moving excitons (that is, bound states from electrons and holes located at the minimum and maximum of the conduction band (CB) and valence band (VB), respectively) by optical excitation is fairly standard$^{6,8}$. Very recently, distinct branches of dispersing excitons have been observed in free-standing monolayer WSe$_2$, a two-dimensional Dirac band insulator, by momentum-resolved electron energy-loss spectroscopy$^7$. However, the observation of mobile bound states with sharp dispersions in metals has remained elusive for various reasons. Higher-dimensional metals are unlikely to host excitons. First, their creation requires an exceedingly strong (despite screening) Coulomb interaction that is not pre-empted by an interaction-driven instability to an insulator. Second, the excitation of moving excitons with light involves higher-order processes, whose cross-sections are very weak, unless low dimensionality and low carrier density (as present in TaSe$_3$) allow for strong Coulomb interactions with small momentum transfer. The heavy quasiparticles (QPs) (polarons) constitute a third favourable attribute of TaSe$_3$, as their mass increases the binding energy of the resulting excitons (see Supplementary Information for a more detailed discussion).

The interplay of dilute conduction electrons, low effective dimensionality and heavy QPs in TaSe$_3$ makes this quasi-one-dimensional (Q1D) material a prime candidate for probes of excitonic effects by angle-resolved photoemission spectroscopy (ARPES).

We have systematically studied the metallic phase of TaSe$_3$ using ARPES and observed the following features at low temperature. (1) Several side VBs (SVBs) appear exclusively above a pronounced VB, in contrast to most ARPES spectra that report sidebands (Supplementary Information). (2) Their dispersions are roughly parallel to the VB. (3) When the surface carrier density is increased by doping, the energy separations between the SVBs increase. (4) Close to the Fermi level, the CB is heavily renormalized and the coherent QP peak follows a W-shaped dispersion. As we will argue,

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Fig. 1 | The crystalline and electronic structures of TaSe$_3$ at 15 K. **a**, Crystal structure projected onto the ac plane. The crystallographic axes are a, b and c. **b**, Crystal structure with its 1D chains oriented along the b axis. **c**, The BBZ and the 2D SBZ of the cleavage surface (normal to (101)). **d**, ARPES intensity at the Fermi energy $E_F$ as a function of the momentum $k_e$ in SBZ for incoming photon energy $h\nu = 40$ eV. The momenta $k_x$ and $k_y$ are conjugate to the (101) and the (010) direction, respectively. **e,f**, ARPES intensities at $h\nu = 40$ eV as a function of the energy $E - E_F$ and the momentum component $k_y$ in the SBZ, along the cut $\Gamma Y$ ($k_y = 0$) (e), and along the cut XS (f). **g**, ARPES intensity as a function of the momentum $k_y$ and of the incoming photon energy $h\nu$, which tunes the momentum $k_y$ perpendicular to the planes. The intensity contour is seen to be very elongated along $k_y$, suggesting that the equal energy contour near the Fermi level is essentially an elliptical cylinder with axis parallel to $k_y$. **h–j**, ARPES intensities as a function of the energy $E - E_F$ and the momentum $k_y$ along the cut XS in the SBZ for photon energies $h\nu = 40$ eV (h), $h\nu = 37$ eV (i) and $h\nu = 34$ eV (j). **k** Superimposed band dispersions from h–j (shown as coloured continuous lines as guide to the eye). The variation with $h\nu$ implies a finite dispersion along $k_y$.

**Results**

**Material characterization.** The trichalcogenide TaSe$_3$ consists of covalently bonded layers, stacked and held together by weaker van der Waals forces along the direction (101) (refs. 12,13). Each layer consists of chains oriented along the b axis (Fig. 1a,b), with strongly anisotropic electric and optical responses. The natural cleavage plane is the (101) surface. The corresponding bulk Brillouin zone (BBZ) and the (101) surface Brillouin zone (SBZ) are shown in Fig. 1c. In the SBZ, $(k_x, k_y)$ denote the components of momentum along (101) and (010), respectively.

TaSe$_3$ is so far the only known trichalcogenide that is a metal at high temperature and becomes superconducting below 2 K without forming a charge density wave (CDW)\textsuperscript{14–20}. However, it is close to such a transition, as suggested by CDW-like signatures observed on doping with Cu (refs. 21,22), application of strain\textsuperscript{14}, and our own surface doping results reported below. We note that topological surface states\textsuperscript{14} have been observed in refs. 25,26 in the gap between the top of the VB and the bottom of the CB of TaSe$_3$, where band inversion occurs. However, as we will argue, they are clearly distinct from the excitonic features we focus on here.

**Overall band structure from ARPES.** We have studied the electronic structure of TaSe$_3$ with ARPES on the in situ cleaved surface (101). The intersection of the small three-dimensional (3D) Fermi surface with a plane spanned by momenta conjugate to the crystal-line directions b and $a + c$ is seen as the region of highest intensity in Fig. 1d. Figure 1e ($\Gamma Y$ cut) shows hole-like VBs with maxima at the zone centre $\Gamma$, dispersing from 0.1 to 2 eV. Figure 1f (XS cut) shows an electron-like CB with minimum at the mid-point X on one zone edge of the BBZ. The strong anisotropy in the ac plane results in a Fermi surface in the form of an elongated elliptical electron pocket centred at X (Fig. 1d), see the minor axis along the XS direction reflecting the strong dispersion along the b axis. There is no good nesting wave vector for the Fermi surface of TaSe$_3$ shown in Fig. 1d. This might rationalize the absence of a CDW phase in pristine TaSe$_3$. The coupling between stacked layers is weak. This is seen both by the elongated Fermi surface in a cut with the plane $k_z = 0$ (Fig. 1g) (the photon energy $h\nu$ being used to explore momenta normal to the cleavage plane), as well as in the similarity of the spectra in Fig. 1h–j, corresponding to different normal momenta. Nevertheless, Fig. 1k shows a definite, if small, dependence on the...
incoming photon energy, which we take as evidence for these bands being bulk as opposed to surface bands.

**Side VBs (SVBs).** Here, we focus our attention on SVBs, which are remarkable spectral features visible in the energy distribution curves (EDC) of the ARPES spectra. In Fig. 2a we show the band structure of TaSe₃ along the XS direction in the BBZ predicted by density functional theory (DFT), as explained in the Methods section. There is one CB (green), lying above five VBs. The VB closest to the CB (purple) is referred to as the main VB (MVB). The lower lying VBs are coloured in blue. These DFT bands match the five bands measured in Fig. 2b. The EDC along the vertical green line with fixed \( k_y \approx -0.2\ \text{Å}^{-1} \) in Fig. 2b is shown in the boxed inset. The arrows indicate local maxima of this EDC. They move as \( k_y \) varies, defining SVB dispersions. The SVBs are bounded from below by the MVB, which is stronger in intensity. The MVB and the SVBs become better visible in the curvature intensity plot of Fig. 2c associated with the data of Fig. 2b, (the colour scale being related to the curvature of the ARPES intensity). For reference, Fig. 2d shows a schematic of the band dispersion of the MVB (purple arrow) and three SVBs (tilted red arrows) are approximately symmetric about X. The Supplementary Information shows more EDCs illustrating how the SVBs are identified and evolve with doping. We only observe sidebands of the MVB, but none associated with the CB, or the deeper VBs. Close to the X point, there is no observable intensity that could be clearly assigned to either SVBs or to the MVB. In Fig. 2d, the evolution of the MVB away from large momenta (where its peak is well resolved) is indicated by a dashed segment, delineating the ‘nose’ predicted by DFT. We also indicate the possible continuation of SVBs as they approach the spectral features associated to the CB, both coloured in green in Fig. 2c,d. The latter are of a polaronic origin and play an important role for the excitonic features seen in ARPES.

**Polaron band.** In typical members of the family XT₃, such as NbSe₃ (ref. 19), Fermi surface nesting induces a CDW instability at fairly high temperatures, pointing toward a substantial electron–phonon coupling in these materials.
In pristine TaSe₃, the conduction electrons give rise to two branches of excitations, as traced by the maxima of the EDCs in Fig. 2e,f. The branch of ‘bare’ electron excitations yields a parabolic CB with a fairly short life time, showing up as a broad hump as a function of energy. Much sharper, phonon-dressed QP excitations form a strongly renormalized, weakly dispersive polaron branch close to the Fermi energy, separated by a dip from the hump of bare electron excitations. The spectral weight of the heavy polaron band is strongly peaked close to the Fermi energy, separated by a dip from the hump of bare electron excitations. 

Effects of surface doping. Crucial insight into the nature of the SVBs is gained by increasing the density of surface electrons. This is achieved by evaporating potassium (K) in situ on the cleaved surface of TaSe₃. Here we focus on moderate doping (evaporation times of 1 min or less), while stronger doping data (up to 5 min of evaporation) are reported in the Supplementary Information.

Figure 3a,b shows the ARPES intensity after evaporation for $t_1 = 1$ min, for the same range of momenta and energies as in Fig. 2b. The evaporated atoms chemically dope electrons onto the surface, which increases the filling of the CB. The incoming photons in Fig. 3a are
Schematic of how mobile excitons show up in the form of SVBs in photoemission. 

Fig. 4 | Schematic of how mobile excitons show up in the form of SVBs in photoemission. a, Toy model with parabolic VB and CB. The drawing shows excitonic excitations for total momenta $K > K'$ where a VB hole with velocity $v_h > v_F$ binds to a CB electron above the Fermi level. The SVB is constructed graphically. Starting from a VB state, the partner state with equal group velocity (slope of the dispersion) in the CB is determined. The energy-momentum transfer from the left Fermi point to that state is combined with a vertical shift by the (momentum independent) binding energy to obtain a point on the excitonic side branch. b, The same procedure applied to a more realistic model of TaSe$_3$. The simple parabolic Fermi sea is replaced by high intensity islands in the polaronic band, its diameter $\Delta k$ playing the role of $2k_F$ in a. The binding energy now depends on the curvature of the VB and the CB at the momenta involved in the exciton pair. The SVB construction results in an excitonic branch that is an almost parallel translation of the simple hole dispersion, the MVB. c, Proposed origin of the MVB and the various SVBs. The MVB (i) results from a single VB hole excitation. It costs less energy (at given momentum $K$) if it is accompanied by particle-hole excitations in the CB of the same or neighbouring chains. The binding of the CB particle(s) with the VB hole results in various types of excitonic mode, namely intrachain exciton (ii), interchain exciton (iii) and possibly interchain trion (iv).

circularly polarized with positive helicity, while they are linearly polarized in the incident plane in Fig. 3b (the scattering geometry is reported in the Supplementary Information). EDCs, such as those shown in Fig. 3c, allow location of the MVB and the SVBs. More EDCs for the same evaporation time $t_1$ can be found in the Supplementary Information. The curvature intensity plot in Fig. 3d shows that the two SVBs (indicated by the red arrows) are more pronounced than in the undoped case of Fig. 2c. A heavy, but non-monotonically dispersing polaron band close to the Fermi energy is still present, but the size of the high intensity islands of diameter $\Delta k$ within the polaron band increases together with $k_F$, as is apparent in Fig. 3d. The measured dispersions are traced in Fig. 3e. Note that the non-renormalized CB branch is essentially parabolic, apart from the polaronic effects close to the Fermi energy and the avoided level crossings with some SVBs, where the ARPES intensity is suppressed. For large enough momenta, one identifies two SVBs roughly parallel to the MVB. At small momenta close to $X$, there are two nose-like dispersing pieces of an excitation branch. They might be continuations of the SVBs seen at larger momenta, as hinted at in Fig. 3f.

Figure 3g shows the ARPES intensity at $hv = 37$ eV after doping. Here, the first SVB is clearly visible.

The doping strongly affects the average energy separations $\Delta_1$ and $\Delta_2$ between the MVB and the first SVB, and the first and second SVBs (if detectable), respectively. We measure these spacings in the regime of large momenta relative to $X$. In Fig. 3h, $\Delta_1$ and $\Delta_2$ are seen to substantially increase with doping or, equivalently, with the Fermi wave vector $k_F$. In particular, $\Delta_1 \approx 180$ meV and $\Delta_2 \approx 70$ meV, in the presence of potassium doping ($t_2$) are much larger than the spacings $\Delta_1 \approx 70$ meV and $\Delta_2 \approx 37$ meV in undoped TaSe$_3$.

Effects of stronger doping are presented in the Supplementary Information. The QP-dip-hump features at the Fermi energy described above evolve into a CDW at $t_3 = 2$ min. This observation supports the interpretation of these polarons as originating from an electron–phonon coupling in TaSe$_3$. More empirical evidence for electron–phonon coupling in TaSe$_3$ is provided by the evolution of Raman intensities in the Supplementary Information. Doping increasingly separates the QP-dip-hump features at the Fermi energy from the region of band inversion between the bottom of the CB and the top of the MVB, confirming that they are distinct, mutually independent characteristics. In particular, SVBs are clearly distinct from topological surface states. The doping dependence of the ARPES spectra also rules out an interpretation of the SVBs in terms of states bound to a surface layer detached from the bulk (see Supplementary Information for further discussion). Finally, doping reveals that, while CB and MVB are shifted by roughly the same energy at $t_1 = 1$ min, their shift differs from the
nearly rigid energy shift of the lower VBs. This suggests that the lower VBs are nearly uncorrelated with the carriers at the Fermi level, while MVB and CB are more strongly correlated with new doped carriers. This may be the reason why we observe excitons only associated with the MVB, but not with the other VBs (Supplementary Information).

Interpretation of SVBs. As is explained in the Supplementary Information and summarized in Fig. 4, the position, shape and doping dependence of the SVBs can best be explained in terms of a moving bound state between the photo-hole with non-zero group velocity and large momentum in the VB of a given chain, and one (or possibly several) QP/QPs in the CB on the same or neighbouring chains (Fig. 4a,b). In particular, for sufficiently large total momentum ΔK along the chain (compared to Δk, the diameter of the polaronic islands), we propose the following interpretation. The MVB arises from the excitation of a single photo-hole in the VB (Fig. 4c(i)). The topmost SVB above the MVB is the K-dependent threshold to a continuum consisting of an exciton and a free quasi-hole in the CB, the exciton being a moving bound state between a QP in the CB and a valence hole on the same chain, sharing the same group velocity Fig. 4c(ii). The SVBs closer to the MVB can be of two distinct origins. One possibility is that the particle-hole excitation in the CB is created on a chain neighbouring the one hosting the valence hole, leading to an interchain exciton Fig. 4c(iii), with lower binding energy than intrachain excitons. Alternatively, one can have thresholds to more complex continua, the simplest one consisting of a photo-hole accompanied by two particle-hole excitations on neighbouring chains Fig. 4c(iv), whereby both QPs bind to the valence hole to form a mobile trion27–29. These trions are distinct from two particle bound states (excitons) that are dressed with particle-hole excitations of the Fermi sea, occurring in optical low-momentum excitations of monolayer transition metal dichalcogenides at finite carrier densities in ref. 30. A trion threshold is expected to have a lower energy-integrated intensity, as it scales with a higher power of the density of conduction electrons (since it involves two-particle-hole excitations), an aspect that might rationalize the low intensity of the second SVB in Fig. 3c,d.

The separation of the SVBs from the MVB results from two sources, the binding energy and the kinetic energy gain from distributing the momentum between the VB and the CB. We show in Fig. 4b how these two effects combine to produce SVBs above the MVB. The binding energy is relatively strong due to the heavy mass of the polaronic QPs and the effective one-dimensionality (which entails an increase of binding energy with doping), as we discuss in the Supplementary Information. In a pristine sample, we estimate it to be of the order of 150 meV for the most strongly bound exciton.

While the polaronic reconstruction of QPs makes the formation of excitons more robust, excitonic excitations can also occur without polaronic reconstruction, provided the Fermi surface is sufficiently small.

Discussion

The material TaSe3 is a Q1D metal that combines a low density of conduction electrons with a polaronic renormalization of the low-energy QPs. All these ingredients enhance the spectral weight in photoemission for composite excitations involving an exciton and a hole from the CB. Our experiments show that the excitons come with different internal structures, presumably depending on whether the involved holes and electrons belong to the same chain or neighbouring ones, or whether the hole binds one or two conduction electrons (resulting in an exciton or a trion, respectively).

Interchain excitons are Q1D cousins of bilayer excitons in layered 2D materials, such as transition metal dichalcogenides31,32. They are of particular interest as they may have a substantially longer life time than intrachain excitons due to the spatial separation of the particle and the hole.

We have experimentally probed the evolution of these SVBs with increasing doping. This increases both the binding energy (owing to the Q1D nature of the problem) and the typical momentum transfer in the CB. Both increase the energy separation between the SVBs and the MVB. A more systematic study of the doping dependence will allow us to analyse the fate and nature of excitons as one crosses the Lifshitz transition where a second CB emerges at the Fermi level. It would also be interesting to excite the exciton bound states at low momenta by optical absorption, by using resonant inelastic X-ray scattering or exciting them by means different from light. Finally, it would be interesting to see whether dispersing excitons also exist in other trichalcogenides, at least in the regime of higher temperatures where they do not form a CDW. This will explain the extent to which the peculiar structure of the polaronic band with its strong intensity islands is crucial for the visibility of exciton branches in ARPES.

Online content

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Methods

Crystal synthesis and structure. Single crystals of TaSe3 were synthesized using evenly ground stoichiometric elemental Ta (roughly 325 mesh, Beamtown Chemical, ≥99.99%) and Se (roughly 200 mesh, Beamtown Chemical, ≥99.999%) with a total mass of roughly 300 mg pressed into a pellet and placed in an evacuated quartz tube mixed with roughly 10 mg of I2 as the vapour transport medium. The tube was put into a furnace and heated up to 700°C on the sample side while the other side of the tube, in the furnace, was open to the external environment so as to generate a temperature gradient. After holding the sample at 700°C for 5 days, the furnace was shut down and cooled to room temperature. Needle-like crystals TaSe3 could be found at the cooler side of the quartz tube. The trichalcogenide TaSe3 is a representative of the family of crystals XT3, where X belongs to either the group VIA (S, Se, Te), the group IVB (Ti, Zr, Hf) or the group VB (Nb, Ta), and T is a chalcogen from the space group P2₁/m (SG11). The selenium atoms are located at the vertices of triangular prisms with three faces parallel to the b axis and a tantalum atom at their centre. These prisms are covalently stacked along the b axis and form parallel one-dimensional (1D) chains. The unit cell viewed along the b axis contains four triangular prisms, with covalent bonds along the (101) direction. Thus, the natural cleavage plane is the (101) surface.

ARPES experiments. ARPES measurements were performed at the SIS-ULTRA beamline and at the ADRESS-ARPES beamline of the Swiss Light Source, Paul Scherrer Institute, and at the beamline UE112 PGM-2b-1 at BESSY (Berlin Electron Storage Ring Society for Synchrotron Radiation) Synchrotron. The energy and angular resolutions were set to 5–30 meV and 0.1°, respectively. The samples for ARPES measurements were cleaved in situ and measured mainly in a temperature range between 15 and 25 K in a vacuum exceeding 8 × 10⁻¹¹ Torr.

First-principles calculations. The first-principles calculations were performed within the framework of the full-potential linearized augmented plane-wave method implemented in the WIEN2K simulation package. A modified Becke-Johnson exchange potential together with the local-density approximation for the correlation potential was used to obtain accurate band structures. Spin-orbit coupling was included as a second, self-consistent variational step. The radii of the muffin-tin sphere \( R_{MT} \) were 2.5 Bohr for Ta and 2.38 Bohr for Se. The \( k \)-point sampling grid of the Brillouin zone in the self-consistent process was \( 7 \times 19 \times 6 \). The truncation of the modulus of the reciprocal lattice vector \( K_{max} \), which was used for the expansion of the wave functions in the interstitial region, was set to \( R_{MT} K_{max} = 7 \). The geometry optimization including spin-orbit coupling was carried out within the framework of the projector augmented-wave pseudopotential method implemented in the Vienna Ab initio simulation package. The ionic positions were relaxed until the force on each ion was less than 0.005 eV Å⁻¹.

Data availability

The data that support the findings of this study are available in the MARVEL public repository (MARVEL Materials Cloud Archive: https://archive.materialscloud.org) with the same title as this paper.

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Author contributions

J.Z.M. performed ARPES experiments with the help of M.N., J.J., N.C.P., M.R. and W.H.F. S.M.N. and Z.W. performed first-principles calculations of the band structure. J.Z.M. plotted all the figures. X.G. and W.W.X. synthesized the single crystals. C.Y.X. performed primary high magnetic field quantum oscillation measurements with the help of J.Z.M., J.L.Z., T.S. and Y.M.X. H.H. and U.D.G. analysed the possibility of boson driven band structures with the help of D.G.-M and O.V.Y. I.K. performed Raman measurements for checking the phonon energy. N.K. and Y.S. performed primary transport measurements with PPMS. M.A.S. helped by ruling out the bosonic strong coupling scenario. C.M. and M.M. analysed different physical scenarios on the basis of bound states and worked out the theory of excitonic sidebands. All authors contributed to the discussion of this project. J.Z.M., C.M., M.M. and M.S. wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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