Detecting photoelectrons from spontaneously formed excitons

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Excitons, quasiparticles of electrons and holes bound by Coulombic attraction, are created transiently by light and play an important role in optoelectronics, photovoltaics and photosynthesis. They are also predicted to form spontaneously in a small-gap semiconductor or a semimetal, leading to a Bose–Einstein condensate at low temperature, but there has not been any direct evidence of this effect so far. Here we detect the photoemission signal from spontaneously formed excitons in a debated excitonic insulator candidate, Ta2NiSe5. Our symmetry-selective angle-resolved photoemission spectroscopy reveals a characteristic excitonic feature above the transition temperature, which provides detailed properties of excitons, such as the anisotropic Bohr radius. The present result provides evidence for so-called preformed excitons and guarantees the excitonic insulator nature of Ta2NiSe5 at low temperature.

The concept of quasiparticles is an essential building block in our understanding of solids, allowing us to unravel complex many-body interactions. An exciton—a bound state of an electron and a hole—is a common quasiparticle in semiconductors that is formed transiently when excited by light within the bandgap. This quasiparticle excitation not only lets us understand the fundamental optical responses of semiconductors and photosynthesis, but also supports a range of device applications, including photodetectors, photovoltaic solar cells, light emitters and excitonic lasers. One can also make a macroscopically coherent condensate of excitons—a Bose–Einstein condensate (BEC)—using double layers of electrons and holes, respectively, in artificial structures with strong fields, such as semiconductor quantum wells, graphene and transition-metal dichalcogenides. The BEC of excitons may bring fundamental optical responses of semiconductors and photosynthesis, to form an insulating state with a finite number of steady-state excitons. Such an excitonic insulator (EI) is a fundamental many-body insulating state of solids, as theoretically proposed as early as the 1960s for a small-gap semiconductor or a semimetal. However, evidence for the predicted properties of EI—such as diverging electronic susceptibility, anomalous optical transitions, quenching of plasmonic modes and renormalized valence band dispersions—has been obscured by the coexisting structural phase transitions, and direct experimental identification of spontaneously formed excitons has been lacking.

In this Article, we utilize temperature- and polarization-dependent angle-resolved photoemission spectroscopy (ARPES) to investigate the formation and symmetry of the quasiparticles in a major EI candidate, Ta2NiSe5 (TNS), across its anomalous phase transition. Our experimental results below the transition temperature (Tc = 327 K) confirm the hybridization between the valence and conduction band orbitals near the Fermi level. This interband hybridization has been debated in terms of an excitonic or structural origin. By contrast, the band structure above Tc shows no clear sign of such band hybridization, ruling out a substantial structural effect, but the bandgap persists. Moreover, we identify the emergence of a characteristic photoelectron signal, which can only be explained by direct photoemission from excitons. This is a direct signature of spontaneously formed excitons, the so-called ‘preformed excitons, preceding the emergence of a BEC at lower temperature’. The present results therefore guarantee an excitonic insulator transition in TNS at low temperature, without any ambiguity related to the structural transition occurring at Tc (refs. 27–30). This is in line with a recent theoretical proposal of a BEC-type EI transition for a semimetallic TNS and indicates the existence of a many-body quantum state of preformed excitons at high temperature. Based on our ARPES results and recent theory, the effective radius of excitons is determined to be very small and anisotropic, ~7.5 Å and ~3.0 Å parallel and perpendicular to the Ta and Ni chains, respectively (Fig. 1a). This is attributed to the many-body interaction between excitons and phonons. The present work opens up a way to characterize spontaneously formed excitons with direct photoemission probes and to exploit coherent excitons at room temperature and preformed excitons at high temperature.

Figure 1b presents an overview of the band structure of TNS, revealed by our ARPES measurements along the Γ–X and Γ–Y directions (x and y directions in Fig. 1a, respectively) over multiple Brillouin zones. The valence band near the Fermi level is characterized by a hole-like band centred at Γ with strongly anisotropic dispersions along the Γ–X and Γ–Y directions—a much stronger dispersion along the Ta/Ni atomic chains. As is well known, the band structure below Tc is insulating, with the valence band top located at ~0.16 eV (Fig. 1b). A distinct flattening of this valence band top, deviating substantially from a normal parabolic dispersion, is observed, as shown in Fig. 2 in more detail. Together with
the existence of the bandgap, the band renormalization indicates a hybridization of the conduction and valence bands. The interband hybridization itself can be more directly evidenced by revealing the orbital characteristic of the valence and conduction band edges, which are dominated by Ni 3d and Ta 5d orbitals, respectively, if there is no excitonic interaction. This corresponds to the high-temperature orthorhombic crystal structure well above $T_c$, where the hybridization between these two bands is forbidden by the crystal symmetry. On the other hand, below $T_c$, the crystal structure changes to a monoclinic symmetry, allowing the hybridization of Ni 3d and Ta 5d bands. A previous scanning tunnelling spectroscopy study showed that the orbital (more accurately atomic) contributions of the valence (Ni 3d) and conduction band (Ta 5d) edges are inverted below $T_c$. This verifies the interband hybridization, which was interpreted as indirect but important evidence of the EI state. However, the recent works pointed out that this hybridization itself can be explained largely by the orthorhombic–monoclinic structural transition.

ARPES with linearly polarized light can be utilized to determine the mirror symmetry of wavefunctions for occupied bands through...
the dipole selection rule in photoemission. We performed ARPES measurements along the \( \Gamma-X \) direction for the low-temperature phase, with four different linear polarization geometries (shown schematically in Fig. 1a). The data in Fig. 2a–d show that the photoelectron intensity of the valence bands exhibits a huge difference between the ‘flat-top’ part centred at the \( \Gamma \) point and the ‘dispersive’ parts away from \( \Gamma \). These apparent cross-sectional contrasts are independent of the photon energy (50–90 eV, Supplementary Section 1) and so are attributed to the symmetry selection rules between the light polarizations and orbital symmetries\(^{56,57}\). Based on the selection rules, the mirror parities of the valence and conduction bands, respectively, are determined to be even (odd) about the \( y-z \) plane and even (odd) about the \( x-z \) plane (Supplementary Sections 2.1 and 3). These observations are fully consistent with the hybridization of the valence and conduction bands below \( T_c \).

We then track the temperature dependence of the hybridization crossing the phase transition (Supplementary Section 4.1). Figure 3 shows the results of the polarization-dependent ARPES data above \( T_c \) at 380 K. The flattening of the valence band top and the bandgap persist well above \( T_c \) (Supplementary Section 4.2 provides a comparison between the non-interacting phase (that is, metallic\(^{27} \)) and the valence band renormalization (the flat-top dispersion itself) persisting above \( T_c \).

In the following, we provide direct evidence of excitons formed spontaneously above \( T_c \), which explains this extra interaction and most of the other anomalous behaviours of this material. We particularly focus on the extremely broad spectral feature at \( \Gamma \) on the flat-top part of the valence band (appearing clearly only above \( T_c \) in the \( xz \) polarization; dashed box in Fig. 3a). This feature is clearly distinguished from the dispersive parts away from \( \Gamma \), which is a usual spectroscopic feature for an electron band in ARPES (Supplementary Section 4.2 provides a comparison between the flat-top and dispersive features). The broad feature shows only marginal dispersion and does not cross the Fermi level (Fig. 4c,e), resulting in an unusual and characteristic shape in energy–momentum space. Moreover, as discussed above, this part does not have the symmetry of a Ta 5d orbital (as is clearly visible with \( xz \) polarization). Thus, the conduction band origin can be clearly ruled out, in contrast to a previous work where only part of the symmetry was probed\(^{38}\) (Supplementary Section 2.2). Furthermore, we can retaining the Ni 3d orbital character. This observation tells us that the spontaneous orbital hybridization occurs only below \( T_c \). Because \( T_c \) was determined by the orthorhombic–monoclinic structural transition, the present result is consistent with the picture that the interband hybridization has a structural origin—the hybridization is indeed symmetrically forbidden in the orthorhombic structure\(^{11}\). On the other hand, because the non-interacting phase (that is, assuming the absence of electron–hole interactions) of TNS is semimetallic\(^{27}\), there must be another interaction to explain the bandgap and the valence band renormalization (the flat-top dispersion itself) persisting above \( T_c \).

In Fig. 3 we present evidence for strong excitonic behaviour above \( T_c \) for the measurements taken at \( \hbar \omega = 70 \) eV with \( xz \) (a) and \( y \) (b) polarizations. c, d, Corresponding second-derivative plots for \( xz \) (c) and \( y \) (d) polarizations. e, f, Stacked energy distribution curves (e) and momentum distribution curves (f) for further visualization of the intensity plot in a. The characteristic strong signal around the \( \Gamma \) point is emphasized by the blue colours in the curves in e and f, corresponding to the feature indicated by the dashed rectangle in a.
observed and characterized in detail with the pump-and-probe looks like. An excitonic feature in photoemission spectra was recently we next check what a direct photoemission feature from excitons suggests an extraordinary origin beyond an electron band and the unusual shape of this feature in both energy and momentum not induce a broad spectral feature at the edge of the gap. Thus, Excitonic photoemission simulations based on the Bohr radius of 7.5 Å along the four panels.

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Based on discussion of the excitonic interaction in this material, we next check what a direct photoemission feature from excitons looks like. An excitonic feature in photoemission spectra was recently observed and characterized in detail with the pump-and-probe photoemission method as an excited state above the Fermi level and below the bottom of the conduction band. We adopt this analysis, established for pump-excited excitons, although we are dealing with a spectroscopic feature below the Fermi level for a spontaneously formed steady-state object. We performed the peak-fitting analyses using two-dimensional (2D) excitonic wavefunctions \(|\varphi(q)|^2 \sim 1/(1 + (q a_0)^2/4)|^2 \) (where \(q\) and \(a_0\) are the momentum and excitonic Bohr radius, respectively) for momentum distribution curves at several energies across the broad feature at \(\Gamma\) dashed lines, Fig. 4a). The results in Fig. 4b show excellent fits to all the observed momentum distribution curves across the entire binding energy range of 0.13–0.34 eV with a nearly constant excitonic Bohr radius of \(a_0 = 6.5–7.5\) Å. Based on this excitonic Bohr radius, we also performed a model calculation for the ARPS spectra arising from the excitons, based on the computational method presented by Rutsagi and Kemper with only one major phenomenological parameter—a Lorentzian energy broadening of \(\sim 0.3\) eV—which will be discussed further in the following. The result is shown in Fig. 4c for the excitonic contribution alone and in Fig. 4d together with the valence band dispersion (Supplementary Section 5). The overall shape of the high-intensity region near the valence band maximum (resembling a bright up-side-down triangle) and the three-peak structure of the momentum distribution curves in the ARPS data (Fig. 4e) can be reproduced excellently (Fig. 4f). These results convincingly indicate that we are detecting the direct photoemission signal from excitons formed spontaneously below the Fermi level. This is in clear contrast to the detections of optically generated excitons in, for example, absorption spectroscopy studies.

The direct photoemission feature can enable the detailed character-
Brillouin zone centres are indicated as \( h v \) binding energy (excitons are known to be highly susceptible to self-localization in the lattice and the bands. Because the low-dimensional anisotropic chains. The anisotropy is natural given the quasi-1D structures in comparable to the distance between the Ni and Ta chains (~2.2 Å) which is about half that along the other direction (Fig. 5d). This is and (3) the finite experimental resolution. Because the experimen-
tal intensity plot along the \( \Gamma - Y \) direction (performed in a manner similar to that in the \( \Gamma - X \) direction) at a binding energy of 0.135 eV (dashed horizontal line in a). The experimental data in red dots are overlaid with the result of fit (blue line). The green peak is the best-fit excitonic wavefunction and the dashed curves are the Lorentzian fits to valence band peaks. c. The \( k_x \)–\( k_y \) map of the ARPES intensity as a function of binding energy \( (h v = 50 \text{ eV}) \). The dashed ellipse indicates the significantly anisotropic photoemission feature arising from preformed excitons. The surface Brillouin zone centres are indicated as \( \Gamma_{00} \) and \( \Gamma_0 \). d. Schematic of the spatial extent of the exciton, extracted from the ARPES momentum distribution curve analyses, scaled with respect to the underlying crystal structure.

respectively. These data reveal the giant anisotropy of the exciton photoemission feature, as characterized by its much larger extent along the \( \Gamma - Y \) direction than along \( \Gamma - \bar{X} \). Fitting analysis of the momentum distribution curve with an excitonic wavefunction, as shown in Fig. 5b, yields an excitonic Bohr radius along \( \Gamma - Y \) of ~3 Å, which is about half that along the other direction (Fig. 5d). This is comparable to the distance between the Ni and Ta chains (~2.2 Å) and signals a strong localization of excitons perpendicular to the chains. The anisotropy is natural given the quasi-1D structures in the lattice and the bands. The low-dimensional anisotropic excitons are known to be highly susceptible to self-localization in the presence of strong phonon coupling, this observation is probably associated with the self-localization of excitons due to the strong coupling of excitons to phonons, giving rise to the strong Fano resonance and broadening of the absorption peak.

Another interesting observation is the strong broadening of the excitonic photoemission peak with an observed width of ~0.3 eV at \( \Gamma \) (extracted from the \( \Gamma \) energy distribution curve in Fig. 3c). The possible contributions to the broadening include (1) the intrinsic scattering of excitons, (2) the broadening along \( k_z \) arising from the finite extent of the excitonic wavefunction in the z direction and (3) the finite experimental resolution. Because the experimental resolution is set to ~40 meV and the \( k_z \) broadening is also a few tens of milli-electronvolts, limited by the dispersion width in the valence band in the \( \Gamma - Y \) direction (Fig. 1b, inset)~14, the sizable fraction of the 0.3 eV width should be attributed to the intrinsic exciton scattering processes. Thus, the strongly broadened excitonic photoemission feature is consistent with the presence of strong exciton–phonon coupling. The anomalous broadening of the phonon modes identified in inelastic X-ray scattering and X-ray diffraction above \( T_c \) (ref. 41) seems in line with the strong exciton–phonon coupling. The role of such a many-body interaction in the phase transition is a highly interesting topic of future research. We also note that the strong intensity of this exciton photoemission feature, comparable to that of photoelectrons from the valence band, is indicative of the substantially high exciton density necessary to guarantee exciton condensation.

The existence of high-temperature excitons above \( T_c \) is in fact embedded as an essential ingredient of a BEC-type transition of excitons, where excitons form at a much higher temperature than \( T_c \) due to the strong interactions in a material with an EI instability and condense into a macroscopic quantum state at \( T_c \). The ‘preformed’ excitons above \( T_c \) are not coherent, and the corresponding phase is a many-body quantum phase composed of spontaneously formed incoherent excitons. The present results thus provide evidence of the preformed excitons and an emerging phase composed of them in a solid. In turn, they show that the present material has a huge excitonic instability beyond the thermal and structural energy scale and unambiguously demonstrate that the TNS represents an EI state at a sufficiently low temperature. We stress that this particular support of the EI does not interfere with the structural transition occurring at 327 K, while that transition makes the ground state more complex than a pure BEC of excitons. The existence of preformed excitons is consistent with the very recent optical spectroscopy works~35 reporting the active electronic degree of freedom above \( T_c \). On the other hand, the preformed excitons can naturally explain the persisting gap at high temperature, which was suggested as evidence against the EI nature~36. A BEC-like EI is in contrast to the other EI candidate, 17-TiSe\(_2\), for which a Bardeen–Cooper–Schrieffer-type excitonic instability is suggested~46. This material
excitations is not clearly observed in the EI phase below \( T \). That is, in the low-temperature EI phase, excitons do not seem to behave as a coherent condensate and collectively behave as a single macroscopic state of matter\(^{1,2}\), as evidenced by the recent observations of coherent collective modes and their propagations\(^{51,52}\). Unfortunately, no theory is currently available for photoemission from an exciton BEC in equilibrium. On the other hand, the strong interaction with the lattice (phonons) at a lower temperature than the structural transition deviates the ground state well away from a BEC, as noted in a recent theoretical work\(^{41}\). The overall phase evolution may follow the BEC behaviour, but in a way heavily affected by the lattice degree of freedom\(^{29}\). We suggest that this may kill the direct photoemission feature from independent excitons.

In summary, we have utilized symmetry-selective and temperature-dependent ARPES to identify the emergence of quasiparticles and their orbital symmetries near the Fermi level across the anomalous electronic transition in the EI candidate material, \( \text{Ta}_2\text{NiSe}_5 \). We identify unambiguously a characteristic photoemission feature coming directly from the excitons formed spontaneously above \( T \); in the absence of the structural transition and in the presence of a persisting bandgap. This clearly evidences the existence of the preformed excitons and fully validates the occurrence of an excitonic insulator phase transition in this material. Analysis of the direct excitonic photoemission feature reveals the compact and highly anisotropic size of the excitons as well as their strong scattering, indicating strong exciton–phonon coupling, even in the precursor state of the excitonic insulator and signalling the importance of a higher-order many-body interaction in this material. By demonstrating the observability of steady-state excitons in ARPES, our study presents a possibility for characterizing excitonic properties, not only in various types of excitonic insulator material, but also in future electronic and optoelectronic devices utilizing the presence of such steady-state quasiparticles.

**Online content**

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Methods

Sample growth. The single crystals of TNS were grown by a chemical vapour transport method with iodine as the transport agent. The TNS polycrystalline sample (pre-reacted at 900 °C for seven days) and an iodine chunk (∼2 mg cm⁻³) were loaded into a quartz ampoule, which was placed in a two-zone furnace with a temperature gradient of 960 to 850 °C for two weeks. The as-grown single crystals had typical dimensions of 2–3 × 0.1 × 0.01 mm³, in a long bar shape along the b axis, with crystallinity and stoichiometry confirmed by X-ray diffraction and energy-dispersive spectroscopy.

ARPES measurements. The samples were prepared by in situ cleaving to obtain a fresh surface parallel to the x–y plane, as shown in Fig. 1a. All ARPES measurements were performed at Pohang Light Source (PLS) BL-4A2. Linear horizontal, linear vertical, right circular and left circular photon polarizations were utilized. Combined with the deflector acquisition modes, the samples were investigated with six different polarization geometries as schematically illustrated in Fig. 1a for linear polarizations and in Supplementary Fig. 2 for circular polarizations. For all measurements, the incidence angles of the light were the same. Photon energies of hv = 50–90 eV were utilized and the measurement temperatures were T = 75–400 K.

Density functional theory calculations. We used the experimental crystal structure of TNS observed at room temperature and low temperature⁴⁵. The unit cell contains 8 Ta ions, 4 Ni ions and 20 Se ions. For relaxation of the initial internal coordinates, the Vienna ab initio Simulation Package (VASP), which employs the projector-augmented wave (PAW) basis set⁵³,⁵⁴, was used for density functional theory (DFT) calculations in this work. The relaxation was performed on a 14 × 3 × 4 Monkhorst–Pack k-mesh with a 400-eV energy cutoff. For the treatment of electron correlations within DFT, a revised Perdew–Burke–Ernzerhof exchange-correlation functional for crystalline solid (PBeosol) was employed⁵⁵, in addition augmented by on-site Coulomb interactions for transition-metal d orbitals within a simplified rotationally invariant form of DFT + U⁶⁶ formalism. The correlation effect of the Ta and Ni d orbitals was investigated by observing the band dispersion and density of states with various Uₜₜ values. The electronic structure of each phase (orthorhombic or monoclinic) varied widely from semimetal to semiconductor with respect to varying Uₜₜ values. Uₜₜ values of 2.25 eV for the Ta d orbitals and 4.75 eV for the Ni d orbitals were adopted, giving a 27-meV semiconducting gap in the monoclinic phase and a 72-meV semimetallic band overlap in the orthorhombic phase (consistent with the expected semimetallic non-interacting phase). Structural relaxations were performed in the presence of the DFT + Uₜₜ on-site Coulomb interaction and all atomic coordinates were relaxed until the forces exerted on all the atoms were smaller than 0.01 eV Å⁻¹. The monoclinic phase is more stable than the orthorhombic phase by 18 meV per unit cell.

Data availability

Data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request. Source data are provided with this paper.

Code availability

The numerical computation codes used to obtain the ARPES simulations in Fig. 4c,d are available from the corresponding author upon reasonable request.

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Author contributions

K.F. and R.S. measured the experimental data. K.F. analysed the data and performed the computations on ARPES spectra simulations. C.I.K. prepared the samples. K.F. and R.S. performed the electronic structure calculations. G.I.K. and J.S.K. performed the experiments. H.W.Y. and J.K. were responsible for the project planning and direction.

Competing interests

The authors declare no competing interests.

Additional information

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