The band-edge excitons observed in few-layer NiPS$_3$

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Band-edge excitons of few-layer nickel phosphorous trisulfide (NiPS$_3$) are characterized via micro-thermal-modulated reflectance (μTR) measurements from 10 to 300 K. Prominent μTR features of the A exciton series and B are simultaneously detected near the band edge of NiPS$_3$. The A exciton series contains two sharp $A_1$ and $A_2$ levels and one threshold-energy-related transition (direct gap, $E_s$), which are simultaneously detected at the lower energy side of NiPS$_3$. In addition, one broadened B feature is present at the higher energy side of few-layer NiPS$_3$. The A series excitons may correlate with majorly $d$-to-$d$ transition in the Rydberg series with threshold energy of $E_s \cong 1.511$ eV at 10 K. The binding energy of $A_1$ is about 36 meV, and the transition energy is $A_1 \cong 1.366$ eV at 300 K. The transition energy of B measured by μTR is about 1.894 eV at 10 K. The excitonic series A may directly transit from the top of valence band to the conduction band of NiPS$_3$, while the B feature might originate from the spin-split-off valence band to the conduction band edge. The direct optical gap of NiPS$_3$ is ~1.402 eV at 300 K, which is confirmed by μTR and transmittance experiments.

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INTRODUCTION

Two-dimensional (2D) semiconductors exhibit immense functionalities and practicalities of large area, ultra-thin, smooth surface, high carrier mobility and thickness-tunable band-gap modulation that have gradually received blooming attention in semiconductor technological studies and development in the post-silicon era. Among the 2D semiconductors, transition-metal dichalcogenides (TMDCs) MX$_2$ ($M = W, Mo, Re$ and $X = S, Se, Te$) comprising a monolayer structure with $X-M-X$ and layered III–VI compounds $N$ ($N = Ga, In$ and $X = S, Se, Te$) that are composed of fundamental units of $X-N-X$ might be two of the important braches of 2D materials that require further research and development in electronics and optoelectronics devices applications. The TMDC of ReSe$_2$ has been proven to be a bipolar channel material for application in analog and digital integrated circuits. The layered TMDCs of WSe$_2$ and Cr-doped WSe$_2$ possess the flexibility on bandgap tuning and also stacking phase change from 2H to 1T with the increase of the chromium content. A plasma-treated MoS$_2$ device was proposed to be a multibits memory that applied for improving computation and artificial synapse functions in an InSe FET device. The layered III–VI GaSe$_{1-x}S_x$ ($0 \leq x \leq 1$) series compounds are optically sensitive and can be applied in photodetectors and light-emission devices in the visible-to-ultraviolet region. Recently, as an additional class of 2D layered materials with a monolayer structure between that of TMDCs and III–VI compounds, metal phosphorus trichalcogenides (also known as metal phosphotrichalcogenides) M$_2$P$_2$X$_6$ ($M = V, Mn, Fe, Co, Ni, Cd, Mg$, or $Zn; X = S$ or $Se$) have attracted considerable attentions. In the metal phosphotrichalcogenides $M_2P_2X_6$, each $P_2X_6$ unit has the valency of 4 — i.e., $[P_2X_6]^{4+}$. It is necessary to have $M_{2+}$ ions for achieving the whole $M_2P_2X_6$ structure, e.g., Mg$_2$P$_2$Se$_6$, Zn$_2$P$_2$Se$_6$, and Ni$_2$P$_2$Se$_6$, etc. However, the $M_{4+}$ ions are not usually the same metal elements, thus some of the compounds like CuInP$_2$Se$_6$, CuCrP$_2$Se$_6$, and AgInP$_2$Se$_6$ etc. also belong to the metal phosphotrichalcogenide family. According to theoretical and experimental results, the bandgap values of $M_2P_2X_6$ (as well as $MPX_3$) range from 1.2 to 3.4 eV, which may considerably enhance the absorption efficiency and wavelength absorption region compared with those of layered TMDCs having bandgap values of 1.2 to 2 eV. These materials typically own chemical bonding that is intermediate between covalent and ionic as well as exhibit unusual behavior of intercalation–substitution ions, which can render them suitable for applications in Li-ion batteries. Moreover, some of the metal elements in this family are usually magnetic (e.g., $M = Fe, Ni, Mn$ and $Co$). As these metal ions are formed in the van der Waals sheet of $M_2P_2X_6$, each metal atom would have three equal-distance $M$ neighbors and exhibit stable magnetic phases in the hexagonal lattice. Therefore, layered MPX$_3$ has been proposed to exhibit specific applications in magneto-optics, magnetic storage, and 2D magnetism. The Néel temperature ($T_N$) is an index of the magnetic transition from antiferromagnetic to paramagnetic. The values of $T_N$ are ~78 K for MnPS$_3$, ~123 K for FePS$_3$, ~155 K for layered NiPS$_3$, NiPS$_3$ exhibits the highest Néel temperature, and the magnetization axis of the ordered states lies along the van der Waals plane, which differs from those of layered MnPS$_3$ and FePS$_3$ with out-of-plane axial magnetization.

Beyond the study of magnetic properties, few-layer semiconductor NiPS$_3$ also has been fabricated as an ultraviolet photoconductive photodetector with a high detectivity of 1.22 × 10$^{12}$ Jones as determined via Jones testing with a 254-nm laser. The heteroatom doping of carbon on the NiPS$_3$ surface activates the photocatalytic activity of the basal plane and enhances the hydrogen evolution efficiency in the KOH solution. The catalytic behavior of NiPS$_3$ also can be exploited to perform water splitting. A resistive-type humidity sensor with a high sensing speed constructed using layered NiPS$_3$ also has been proposed, and an n-channel NiPS$_3$ FET with an on/off ratio reaching 10$^3$ to...
10^5 also has been reported. Although a few application studies of layered semiconducting NiPSe3 have been reported, the fundamental band-edge nature and optical properties of the nickel phosphotrichalcogenide are not well understood. This in turn limits the development of electronic and optoelectronic devices prepared using NiPSe3. Some studies have claimed that the bandgap of NiPSe3 is 1.6 eV; however, the experimental band-edge structure and excitonic transitions in layered NiPSe3 have not been explored in detail.

In this paper, the band-edge excitons of few-layer NiPSe3 are first observed by temperature-dependent microthermal-modulated reflectance (μTR) measurements in the temperature range between 10 and 300 K. Owing to the reduced dimensionality serving to weaken the dielectric screening effect of electron–hole pairs, 2D materials usually have strong Coulombic interactions in excitons and trions, among others, to form a many-body system, thereby achieving increased excitonic (trionic) binding energy in the layer plane. Excitonic transitions are thus frequently constructed and exist in 2D layered semiconductors. The most renowned cases of this include the A and B excitons that are present in layered MoS2, which are also clearly present in the entire series of Mo1−xX2S2 (0 < x ≤ 1) layers with an energy blue-shift behavior with the increase in the W content. Another typical case is the five dipole excitons of E1ex, E2ex, E3ex, E3*ex, and E5ex, respectively, with a mutual orthogonality of polarization in the layered 2D TMDCs of ReS2 and ReSe2. In this study, prominent and clear excitonic transitions of few-layer NiPSe3 (t = 15 ± 5 nm) are observed by μTR measurements at 10 K near the band edge. The band-edge excitons of NiPSe3 contain three excitonic features denoted as A1, A2, and E, respectively. In the A series excitons, when a broadened feature correlates with the band-to-band feature of B. The A1, A2, and E, μTR features display the Rydberg-series-like transitions with the first level at A1, the second level at A2, and the continuum band at E, respectively. The B μTR feature may originate from valence-band splitting to the direct conduction-band edge transition. The temperature dependences of the energies and broadening parameters of the A series and B obtained via μTR measurements of few-layer NiPSe3 also are analyzed. In addition, temperature-dependent transmittance (optical absorption) measurements of layered NiPSe3 are conducted to verify and identify the absorption edge and excitonic transitions of the A series from 10 to 300 K. The direct optical gap Ec of NiPSe3 is determined to be around 1.402 eV at 300 K. According to thickness-dependent microphotoluminescence (μPL) measurements, an indirect-like E3d emission peak that merged with A1 is detected at ~1.23 eV, while a direct emission of B band also appears at ~1.825 eV at 300 K (i.e., t = 10–200 nm). With changing the layer thickness of NiPSe3, the PL intensities of the E3d emission are also changed, while the intensity of the B-band emission is unchanged from t = 10–200 nm. The Ni 3d e_g* band may be located intermediate between Ec of S 3p* + P 3p* + Ni 3d* and E0 of Ni 3d + S 3p + P 3p to result in the E3d indirect-like emission in the layered NiPSe3.

RESULTS
Crystal information and structure
Layered single crystals of nickel phosphosulfide NiPSe3 were grown by the chemical vapor transport (CVT) method using l2 as the transport agent. Supplementary Fig. 1a in the supplementary information (SI) shows the crystal morphology of the as-grown NiPSe3 layered crystals for illustration. The outline of the layered NiPSe3 single crystals essentially reveals a hexagonal shape, and the powdered X-ray diffraction (XRD) pattern shown in Supplementary Fig. 1b exhibits a monoclinic structure (symmetry C2/m), with calculated lattice constants of a = 5.761, b = 10.06, c = 6.576 Å, and β = 107°. These values are in agreement with results obtained previously for NiPSe3. Supplementary Figs. 2–4 in the SI also include content analysis conducted by energy-dispersive X-ray analysis and structural characterization using Raman spectroscopy for comparison (see Supplementary Notes 1–2).

The A-series excitons and B band transition in NiPSe3 at 10 K Figure 1a shows the low-temperature μTR spectrum of a few-layer NiPSe3 sample (i.e., black solid line) measured at 10 K. The upper inset shows a microscope image of the few-layer NiPSe3 nanoflake exfoliated on a SiO2/Si substrate for the μTR experiment, while the lower inset shows the thickness information determined by atomic force microscopy (AFM). The thickness is about 23 monolayers (t = 15 ± 5 nm) of the layered NiPSe3 crystal. As shown in Fig. 1a, the black solid line is the experimental spectrum, and the green-dashed curve is the least-square fit to a first-derivative Lorentzian line-shape function appropriate for the excitonic transitions expressed as follows:

$$\frac{ΔR}{R} = \Re\left[\sum_{i=1}^{n} A_{ex,i} e^{iΔϕ_{ex,i}} (E - E_{ex,i} + iΔϕ_{ex,i})^{-2}\right].$$

where i is the respective transition; A_{ex,i} and Δϕ_{ex,i} are the amplitude and phase of the line shape; and E_{ex,i} and Γ_{ex,i} are the energy and broadening parameter of the i-th exciton transitions, respectively. As analyzed by the Lorentzian line-shape fitting using Eq. (1), the energy values of two prominent excitonic features (i.e., A1 = 1.475 eV and A2 = 1.495 eV) together with one higher-energy transition (i.e., E, at 1.511 eV) are clearly detected in the A series of few-layer NiPSe3 by μTR. One broadened μTR feature (denoted as B at ~1.894 eV) is also found at the higher-energy side of NiPSe3 at 10 K. The transition amplitudes A_{ex,i} of the A series excitons gradually decrease from the maximum n = 1 level, progressing to the subsequent n = 2 transition, and finally the E feature follows the general transition probability of the exciton sequence in semiconductors. Modulated TR measurements of semiconductors have been proven to be effective for the characterization of excitons, direct band edge, and interband transitions in the semiconductor’s band structure. The derivative spectral line features suppress the unintentional spectral background and emphasize the direct critical-point transitions in the band structure. The TR modulation spectroscopy can be regarded as a physical derivative approach to the reflectance spectrum of semiconductor dielectric function by directly applying thermal perturbation to the crystal lattice periodically (i.e., ΔR). The well-derivative ΔR signal (AC) of sample is thus measured and normalized to the sample reflectance R (DC) for obtaining ΔR/R at each wavelength using lock-in amplifier. The TR modulation spectroscopy is different from that of reflectance contrast method with firstly measuring ΔR/R = (R_{sample} − R_{substrate})/R_{substrate} and then implementing mathematical derivative to the line shape using d/dE (ΔR/R)^2. The μTR technique is directly responsive to the physical derivative nature of direct transitions in the band structure of the few-layer sample, and thus possesses less substrate effect coming from the SiO2/Si substrate. Supplementary Fig. 5 shows the bulk TR results of NiPSe3 without any substrate. Essentially the results measured by μTR (with substrate) and measured by conventional TR (without substrate) are similar (Supplementary Note 3). As shown in Fig. 1a, the sharp features of the A series excitons and the extremely broadened B transition reveal that the A and B excitons exhibit different origins in NiPSe3. The crystal structure of NiPSe3 can be realized as a stacking structure of one-layer trigonal (1 T) phase TMDCs such as TiS2. Figure 1b shows the atomic arrangements of the side (upper parts) and top (lower part) views of the layered NiPSe3 structure. As the 1T–TiS2 stacking formula, the NiPSe3 phase is taken as the layered MS2 (as TMDCs) with the Ti atom replaced by Ni, while 1/3 of the Ni atoms are substituted by the P–P pairs (P2 dimers) to form P2S2 + NiS2 + NiS2 = Ni2P2S6 structures that connect and

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extend to the entire lamella sheet (monolayer). This situation is clearly demonstrated in the side view of the monolayer NiPS$_3$ that is displayed in the upper parts of Fig. 1b. Considering the bonding structure of NiPS$_3$, the P–P pairs are covalently bonded to six sulfur atoms, and each P atom is tetrahedrally coordinated with three S atoms to form opposite triangles, as shown by the 1T phase shown in the top view of Fig. 1b. Therefore, a $(\text{P}_2 \text{S}_2)^{\text{+}}$ fundamental unit exists, and it requires two Ni$^2+$ to construct the complete Ni$_2$P$_2$S$_6$ layer compound. Because the P$_2$S$_2$ is occupied in the 1/3 lattice of layered Ni$_2$P$_2$S$_6$, the perfect hexagonal 1T phase is thereby transformed into a monoclinic layered structure of C2/m symmetry. The P$_2$ dimers also may contribute to the band-edge electronic states of layered NiPS$_3$. Therefore, the antibonding states of S 3p$^\pi + P$ 3p$^\pi + \text{Ni}$ 3d$^\pi$ may consist in conduction band while the valence band is composed by hybridization of Ni 3d + S 3p + P 3p bonding states. Excepting the incorporation of the P–P pairs, the band-edge contributions of electronic states in $E_C$ and $E_V$ of NiPS$_3$ can also refer to the TMDCs as MoS$_2$,$^{55}$ where the largely Mo 4d$^\pi$ and minor S 3p$^\pi$ are simultaneously consisted in $E_C$ bottom while major Mo 4d and S 3p are positioned at the top of $E_V$. For the spin–orbit splitting band ΔSOV the band contributions may consisted of 60% Mo 4d$_{3z^2}$ and 40% S 3p$_x$. The main difference between the band-edge structures of MoS$_2$ and NiPS$_3$ is maybe the magnetic structure of Ni 3d states that contributed to the antiferromagnet layered NiPS$_3$.

According to the analysis of exciton series A observed in Fig. 1a, a modified hydrogen Rydberg model of 2D$^{55}$ derived from 3D case$^{56}$ may be used to analyze optical transitions and to evaluate binding energy of the observed excitons. In the 2D case, the model employs an effective Hamitonian $H = -\hbar^2 \nabla^2 / \mu + V_e(r)$, where $\mu^{-1} = m_e^{-1} + m_h^{-1}$ ($\mu$ reduced mass) and $V_e(r) = -e^2 / (\epsilon_{\text{eff}} \cdot r)$ is the locally attractive Columbic interaction between electron and hole. The term $\epsilon_{\text{eff}}$ is the effective permittivity of the material available for excitons. The 2D model of exciton predicts an excitonic binding energy expressed as follows:

$$E_b^n = \mu \cdot e^2 / \left[ 2 \hbar^2 \cdot \epsilon_{\text{eff}}^{-2} \cdot (n - 1/2)^2 \right] = E_{\infty} - E_{\text{ho}}.$$  

where $n$ is the principal quantum number, $E_{\infty}$ is the threshold energy of the excitonic sequence, and $E_{\text{ho}}$ is the transition energy of the exciton level detected by the layered sample. According this 2D model, a typical case for estimating A series excitons in monolayer (1 L) WS$_2$ is $E_{\text{ho}} = 2.41 \pm 0.04$ eV and binding energy $E_b^n = 0.32 \pm 0.04$ eV. However, for the thick-layer bulk case ($>10$ L), because the effects caused by 3D hydrogenic Hamitonian and excitonic Bohr radius, etc. the direct gap reduces to $E_{\infty} = 2.10$ eV and $E_b^n$ decreases to 0.05 eV$^{53}$. For the $n = 2$ level, the energy separation between $n = 1$ and $n = 2$ is increased with the layer thickness decreases when $t \leq 4$ L. The energy splitting of $n = 1$ and $n = 2$ will remain the same in bulk case in layered WS$_2$ ($t > 10$ L)$^{57}$. For NiPS$_3$, the A series and B transitions are correlated with majorly Ni 3d states constructed in $E_C$ and $E_V$. The A series originates from largely d-to-d transitions correlated with the spin orientation in the antiferromagnetic NiPS$_3$. As shown in Fig. 1a, the $A_1$ level is tentatively assigned to be the $n = 1$ level, the $A_2$ exciton is inferred to be the $n = 2$ level, and $E_{\text{ho}}$ feature is correlated with the direct band gap of NiPS$_3$. The lower inset below Fig. 1a depicts the representative scheme of the $A_1$, $A_2$, and continuum band of bulk NiPS$_3$. 

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**Fig. 1 Low-temperature excitonic series observed in NiPS$_3$.** a Band-edge excitons of the A series and B transition in few-layer NiPS$_3$ observed via μTR measurements at 10 K. Insets show the microscopic image and AFM results of the few-layer sample on a SiO$_2$/Si substrate. b Atomic arrangements of the side and top views for the layered Ni$_2$P$_2$S$_6$ structure. c Representative band-edge scheme for the A series exciton and B transition in NiPS$_3$. Published in partnership with FCT NOVA with the support of E-MRS

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NiPS₃ for analog to the detected A series excitons at 10 K. The A₁ exciton of NiPS₃ has also recently been detected by PL measurement to locate between 1.475 and 1.478 eV with the thickness changing from 3 L to 8 L at 10 K. For the bilayer and monolayer NiPS₃, the PL emission of the A₁ exciton is missing to lend evidence that monolayer NiPS₃ is maybe an indirect-like 2D material. The excitonic PL emission of A₁ also showed linearly-polarized light along the crystal’s a axis. The polarized behavior of the A₁ exciton is different from the A series exciton in the layered MoS₂. The A₁ exciton had been assigned as a Zhang-Rice triplet to a Zhang-Rice singlet transition that correlated with the spin directions in the Ni 3d states of NiPS₃. The excitonic PL emission of A₁ also showed linearly-polarized light along the crystal’s a axis. The polarized behavior of the A₁ exciton is different from the A series exciton in the layered MoS₂. The A₁ exciton had been assigned as a Zhang-Rice triplet to a Zhang-Rice singlet transition that correlated with the spin directions in the Ni 3d states of NiPS₃. Figure 1c shows the representative band scheme of NiPS₃ appropriate for the transitions of the A series and B observed in Fig. 1a by μTR. The band block array of NiPS₃ is proposed to be the S 3p⁺ + P 3p⁺ antibonding states combined with the lower Ni 3d* band that is positioned at the bottom of EC, whereas the fully occupied Ni 3d (t₂g + e_g) followed by the S 3p + P 3p bonding state comprises the main EV. The Ni 3d electron state is d⁸, which separates into the lower fully-occupied t₂g in EV (i.e., EV is mainly Ni 3d t₂g + P 3p + S 3p) and the higher half-filled e_g band hybridization with EC (i.e., EC is major in Ni 3d* e_g + P 3p* + S 3p*), where P 3p₂⁺ antibonding state contributes to the EC of NiPS₃. Not only the Ni 3d state but also the P 3p state hybridizes with the S 3p orbital still contributing to the band edge of layered NiPS₃. As shown in Fig. 1c, the A series excitons of the A₁, A₂, and E∞ transitions may originate from the top of EV by Ni 3d to the EC bottom of NiPS₃, while the B feature is inferred to originate from the spin–orbital splitting of EV to the EC bottom. The transition of spin–orbital splitting band to EC is rather flat to obtain a more broadened B feature as compared to the sharp features of the A series excitons in Fig. 1a.

Temperature-dependent microthermal-modulated reflectance spectroscopy of few-layer NiPS₃

Figure 2a, b shows the temperature-dependent μTR spectra of the few-layer NiPS₃ sample in the temperature range between 10 and 300 K near the band edge. The dashed lines are the experimental spectra, and the solid curves are the least-square fits using Eq. (1). The obtained transition energies Eᵢ of A₁, A₂, E∞, and B transitions from 10 to 300 K are depicted in Fig. 3a and temperature-dependent broadening parameters Γᵢ of the A₁ and B μTR features are shown in Fig. 3b, respectively. The obtained transition energies of A₁, A₂, E∞, and B at 10 K are indicated by arrows in

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**Fig. 2  Temperature-dependent μTR spectra of NiPS₃ near band edge.** a Temperature dependence of the band-edge excitonic transitions of the A series and B observed in few-layer NiPS₃ via μTR measurements. The solid lines are the least-square fits of the experimental data to a derivative of the Lorentzian line-shape function in Eq. (1). b Magnification of the B transition feature in a. c 2D contour plot of the μTR spectra of the A series excitons from 10 to 300 K to illustrate the temperature-energy shift and intensity change. d Representative scheme of the experimental setup for the temperature-dependent μTR measurements.
Fig. 3 Temperature dependence energies and broadening parameters of the A series and B features obtained by μTR. a Temperature-dependent transition energies of the A series and B features obtained by μTR measurements. The symbols are the data points, solid lines are the least-square fits of the Varshni type, and dashed lines are those of the Bose–Einstein fitting. b Temperature dependence of the line-width broadening parameter of the A, B features obtained by μTR experimentation.

Fig. 2a, b. The energy values are $A_1 = 1.475$ eV, $A_2 = 1.495$ eV, $E_{\infty} = 1.511$ eV, and $B = 1.894$ eV, respectively. As shown in Fig. 2a, with the increase in the temperature from 10 to 300 K in the few-layer NiPS$_3$, band-edge excitons of the A series reveal energy reduction and line-shape broadened characteristics. Figure 2b shows the magnification of the μTR features of the B exciton from 1.6 to 2 eV (blue box in Fig. 2a): Energy reduction and line-shape broadened characteristics are clearly observed from 10 to 300 K. The transition amplitudes $A_{i}^{\text{ex}}$ of the A series and B features in Fig. 2a, b also demonstrate degradation with the increase in the temperature. Figure 2c shows the 2D contour plot of the μTR spectra of the A series excitons, $A_1$, $A_2$, and $E_{\infty}$ from 10 to 300 K. The energy separation of the $n = 1$ and $n = 2$ levels of NiPS$_3$ is about 20 meV (Fig. 2a(a)). The $n = 2$ exciton level is ionized at $T > 175$ K (Fig. 2a, c). The value of the thermal energy $kT$ (where $k$ is the Boltzmann constant) is in agreement with the energy separation of the $n = 2$ level and $E_{\infty}$ ($\sim$16 meV) to facilitate the thermal ionization of the $A_2$ exciton level. The binding energy of the $A_1$ level obtained from the Rydberg-series analysis of NiPS$_3$ in Eq. (1) is about 36 meV. Therefore, the $A_1$ exciton (i.e., $A_1 \approx 1.366$ eV) can be detected in Fig. 2a for the layered NiPS$_3$ at 300 K. Figure 2d shows the representative scheme for the experimental setup of the μTR measurement for the few-layer NiPS$_3$. A tungsten halogen lamp dispersed by a monochromator provided the monochromatic light, and which was then guided to a CCD-equipped microscope using optical fiber. The detailed descriptions of the experimental setup are stated in “Methods” section.

Temperature-dependent analysis of A series and B in NiPS$_3$

Fig. 3a shows the experimental data points of the transition energies of the temperature-dependent A series ($n = 1, 2$) and $E_{\infty}$ and B features in the few-layer NiPS$_3$ obtained by the analysis of the derivative Lorentzian line-shape fitting using Eq. (1) that was derived from Fig. 2a, b. The solid lines correspond to the least-square fits to the Varshni empirical relationship:

$$E_i(T) = E_i(0) - a_i \cdot T \cdot \left(1 - \frac{T}{T_m}\right),$$

where $E_i(0)$ is the energy at 0 K, $a_i$ is related to the strength of the electron (exciton)–phonon interaction, and $T_m$ is closely related to the Debye temperature. Table 1 lists the obtained fitting parameters for comparison. More rapid temperature-energy shift of the $E_i$ top than that of the spin–orbit splitting in the NiPS$_3$ band indicates that the exciton–phonon interaction strength of the A-series are slightly larger than that of the B band transition. According to the energy difference between B and $E_{\infty}$ in Fig. 3a, the spin–orbit splitting ($\Delta_{\text{SO}}$) of the few-layer NiPS$_3$ is about 0.383 eV. This value is greater than that of about 0.19 eV in the energy separation of the A and B excitons in MoS$_2$. The temperature dependence of the band-edge transition energies of few-layer NiPS$_3$ also can be analyzed using another expression containing the Bose–Einstein occupation factor for phonons:

$$E_i(T) = E_i(0) - a_i \cdot \left[1 + \frac{1}{\exp(\theta_i/T) - 1}\right],$$

where $\theta_i$ represents the strength of the electron (exciton)–phonon interaction, and $\theta_i$ corresponds to the averaged phonon temperature. Figure 3a shows the fitted results represented by the red dashed-dotted curves. The obtained values of $E_i(0)$, $a_i$, and $\theta_i$ also are listed in Table 1 together with the layered compounds MoS$_2$, WS$_2$, and Mo$_{1-x}$W$_{x}$S$_2$, while GaAs$_6$ and ZnSe$_6$ are included for comparison. The values of the Varshni parameter $a_i$ and Bose–Einstein type constant $a_i$ of the A series excitons ($A_1$, $A_2$, and $E_{\infty}$) in NiPS$_3$ are greater than those of the layered TMDCs MoS$_2$, Mo$_{0.5}$W$_{0.5}$S$_2$, and WS$_2$. The energy difference of the A exciton between 10 and 300 K is about 110 meV in NiPS$_3$, which is greater than those of 70–80 meV for MoS$_2$, Mo$_{0.5}$W$_{0.5}$S$_2$, and WS$_2$. The incorporation of the additional P$_2$ pairs in layered Ni$_{1-x}$P$_x$S$_6$ is potentially the main reason for causing a more rapid temperature–energy gap shift compared to the other layered TMDCs in the environment of a crystal lattice-constant change.
**Table 1.** Values of the Varshni and Bose–Einstein type fitting parameters that describe the temperature dependences of the excitonic transition energies of the $A_1$, $A_2$, $E_\infty$, and $B$ in the few-layer NiPS₃ together with those previously obtained for MoS₂, WS₂, Mo₀.₃W₀.₇S₃, GaAs, and ZnSe.

| Materials    | Feature | $E_i(0)$ (eV) | $a_i$ (meV/K) | $\beta_i$ (K) | $E_{\infty}(0)$ (eV) | $a_\infty$ (meV) | $\theta_\infty$ (K) |
|--------------|---------|---------------|---------------|---------------|----------------------|------------------|------------------|
| NiPS₃        | $A_1$   | 1.476 ± 0.002 | 0.7 ± 0.04    | 300 ± 50      | 1.542 ± 0.001        | 69 ± 11          | 250 ± 30         |
|              | $A_2$   | 1.494 ± 0.002 | 0.61 ± 0.05   | 300 ± 50      | 1.559 ± 0.006        | 63 ± 13          | 250 ± 30         |
|              | $E_\infty$ | 1.509 ± 0.002 | 0.68 ± 0.06   | 300 ± 50      | 1.575 ± 0.010        | 70 ± 22          | 250 ± 30         |
|              | $B$     | 1.896 ± 0.003 | 0.42 ± 0.05   | 300 ± 50      | 1.941 ± 0.008        | 48 ± 8           | 250 ± 30         |
| MoS₂ b       | $A$     | 1.935 ± 0.005 | 0.48 ± 0.05   | 180 ± 50      | 1.976 ± 0.02         | 46 ± 15          | 220 ± 50         |
|              | $B$     | 2.142 ± 0.005 | 0.47 ± 0.05   | 160 ± 50      | 2.179 ± 0.02         | 42 ± 8           | 200 ± 30         |
| Mo₀.₃W₀.₇S₃ | $A$     | 1.947 ± 0.005 | 0.47 ± 0.05   | 190 ± 60      | 1.986 ± 0.02         | 43 ± 12          | 214 ± 40         |
|              | $B$     | 2.257 ± 0.005 | 0.49 ± 0.05   | 75 ± 60       | 2.293 ± 0.02         | 39 ± 10          | 190 ± 33         |
| WS₂ b        | $A$     | 2.067 ± 0.005 | 0.47 ± 0.05   | 210 ± 50      | 2.102 ± 0.02         | 37 ± 10          | 200 ± 40         |
|              | $B$     | 2.493 ± 0.005 | 0.55 ± 0.06   | 200 ± 50      | 2.534 ± 0.02         | 45 ± 11          | 200 ± 35         |
| GaAs c       | $E_g$   | 1.512 ± 0.005 | 57 ± 29       |              |                      |                  |                  |
| ZnSe d       | $E_g$   | 2.800 ± 0.005 | 73 ± 4        |              |                      |                  |                  |

*Present work.

See ref. 43.

See ref. 64.

See ref. 64.

See ref. 64.

Figure 3b plots the analysis of the broadening parameter $\Gamma$ (half-width at half-maximum (HHWM)) of the representative $A_1$ and $B$ features in the μTR spectra of few-layer NiPS₃ between 10 and 300 K with representative error bars. The solid lines represent the least-square fitting to a Bose–Einstein-type formula, which is appropriate for the temperature-dependent line-width analysis as follows:54,65

$$
\Gamma_i(T) = \Gamma_i + \Gamma_{LO}/[\exp(\theta_{LO}/T) - 1],
$$

where $\Gamma_i$ represents the term of the line-shape broadening invoked from the mechanism of crystallinity from impurities, dislocations, electron interactions, and Auger processes, whereas the $\Gamma_{LO}$ term is related to the electron (exciton)–longitudinal optical (LO) phonon (Frohlich) interaction. $\theta_{LO}$ is related to the LO phonon temperature. The obtained fitting parameters for the line-shape broadening of the $A_1$ and $B$ transitions in NiPS₃ are $\Gamma_i = 7 ± 1$ and $96 ± 10$ meV; $\Gamma_{LO} = 98 ± 10$ and $1800 ± 800$ meV; and $\theta_{LO} = 280 ± 20$ and $584 ± 140$ K, respectively. The considerably lower value of $\Gamma_i$ of the $A_1$ exciton indicates that an extremely high-quality crystal is obtained for layered NiPS₃. The broadened $B$ feature implies that the spin–orbital-splitting band is rather flat compared to the $E_\infty$ top (in $k$ space) that exists in the band structure of NiPS₃. Because linewidth broadening contributes more significantly than the energy shift with the change in the temperature in the NiPS₃ lattice, the $\theta_{LO}$ value is therefore greater than that of $\theta_{\infty}$ due to the larger averaged phonon temperature.

Transmittance and optical absorption of NiPS₃ near band edge

To further identify the band-edge nature, temperature-dependent transmittance ($T$) measurement of a bulk NiPS₃ with a thickness of about 10 μm was conducted. Figure 4a, b show the transmittance absorption edge and μTR spectra of the $A$ and $B$ excitons at 10 and 300 K, respectively, together with a mathematical-derivative transmittance ($\Delta T$) spectrum that is included for contrast. The transmittance spectrum of NiPS₃ clearly reveals the presence of the $A_1$, $A_2$, and $E_\infty$ excitonic features at the absorption edge at 10 K, similar to those detected in the μTR spectrum. In addition, the $\Delta T$ spectrum in Fig. 4a reveals the same energy position and line shape of the $A_1$, $A_2$, and $E_\infty$ features compared with those detected in the μTR measurement of NiPS₃ at 10 K. At 300 K, the $A_2$ feature is ionized, and the energy value of $A_1$ from μTR is about 1.366 eV. The transmittance edge is extremely close to the $A_1$ transition, and the $\Delta T$ spectral line shape is also similar to that of the μTR feature. These results indicate that the energies of transmittance absorption edge (measured by $T$) and direct band edge (measured by μTR) of bulk NiPS₃ are very close. This result is dissimilar to other TMDCs such as MoS₂, whose transmittance absorption edge is at 1.23–1.28 eV (i.e., optical transition assisted by emission and absorption of phonons), while the direct gap is about 1.88 eV in multilayer MoS₂. The energy difference between the indirect and direct bandgaps of MoS₂ is about 0.6 eV. The weakened layer-by-layer decoupling of layered NiPS₃ compared to MoS₂ may be the main reason for the small energy difference between the indirect and direct bandgaps of the layered compound. Figure 4c, d show the temperature-dependent transmittance and absorption spectra of the NiPS₃ sample from 10 to 300 K. The absorption spectrum of NiPS₃ at 10 K in Fig. 4d is also similar to previous absorption curve that detected by antiferromagnet NiPS₃. The absorption edge in the temperature-dependent transmittance and absorption spectra demonstrates an energy blue-shift behavior with the decrease in the temperature from 300 to 10 K, similar to the typical trend for semiconductors. The clear $A_1$, $A_2$, and $E_\infty$ transition features of the A series excitons are still observed in the low-temperature absorption spectra ($T<180$ K), verifying the μTR results of few-layer NiPS₃ in Fig. 2a. At 300 K, a shoulder peak of $E_\infty ≈ 1.402$ eV is still observed for NiPS₃ in Fig. 4d. This value is in good agreement with the direct band gap of the layered NiPS₃ obtained using the Rydberg series as $E_\infty = A_1 (1.366 eV) + E_0 \alpha \beta$ (36 meV) at room temperature.

Micro-photoluminescence result

To evaluate the origin of the band edge, thickness-dependent micro-photoluminescence (μPL) measurements of layered NiPS₃ were conducted at 300 K. Figure 5a shows the μPL spectrum of a few-layer NiPS₃ sample with a thickness of about 10 nm. Two broadened peaks at about $E_{3d} ≈ 1.23$ eV and $B ≈ 1.825$ eV are observed in the μPL spectrum of few-layer NiPS₃. The $E_{3d}$ peak is strong, but it gradually decreases with the increase of thickness in
layered NiPS₃ (Fig. 5b), whereas the B emission peak remains at a similar PL intensity with the change in the layer thickness from 10 to 200 nm. A detailed analysis of the PL line-shape fitting of the PL spectrum in Fig. 5a reveals that the A₁ peak (at 1.366 eV) is still involved in the broadened E₃d peak. The variation of PL intensity of the E₃d peak with changing the thickness of NiPS₃ implies that multilayer NiPS₃ is maybe an indirect semiconductor with an indirect-like emission of ~1.23 eV, originating from the Ni 3d₂g* band to the Eᵥ transition assisted by phonons at 300 K. The indirect-like emission of a 1.3–1.4 eV peak from indirect Eᵥ valley at Σ point was usually observed in the multilayered MoS₂ (10–200 nm) on SiO₂/Si and on Cu substrate⁶⁷. In the light-emission process, phonons are required to conserve the momentum, and photoexcited hot electrons are injection into the lower indirect valley of Eᵥ for resulting in indirect-like emission. As shown in Fig. 4b, the transmittance absorption edge of layered NiPS₃ reveals that photons almost pass through at 1.23 eV, while this value starts to decrease until the photon energy becomes 1.366 eV (A₁) at 300 K. This result implies that the Ni 3d₂g* states might form an intermediate band located between the main Eᵥ (P 3p⁸+ S 3p⁸+ Ni 3d⁴) and the top of Eᵥ. The lower indirect-like emission bands of the M d to d transitions of M₂P₂S₆ also can be observed in previous study of Cd₂P₂S₆⁶⁸. The inset of Fig. 5a shows the probable band scheme of the band edge for PL band-edge emissions. The E₃d peak is an indirect-like emission caused by the intermediate band of Ni 3d₂g* existed in NiPS₃. The A₁ and B

Fig. 4 The comparison of transmittance and μTR spectra in NiPS₃. Spectral comparison of the band-edge transitions in the transmittance (T), first-derivative transmittance (ΔT), and μTR spectra at a 10 K and b 300 K. The temperature-dependent transmittance and absorption spectra of the layered NiPS₃ sample from 10 to 300 K are shown in c and d, respectively.
and to the spin-split-off band below to-band feature of B in NiPS₃ were detected by micro-TR at 10 K. In conclusion, the band-edge excitons of A series and B transition energies of the excitons and the temperature-energy shift of the 2D layer NiPS₃ were conducted to verify the thermal ionization temperatures to sustain the detected A series excitons between 10 and 300 K. The direct optical gap of the NiPS₃ sample with a thickness of ~10 nm at 300 K. a

DISCUSSION
In conclusion, the band-edge excitons of A series and B transition energies of the excitons and the temperature-energy shift of the 2D layer NiPS₃ were conducted to verify the thermal ionization temperatures to sustain the detected A series excitons between 10 and 300 K. The direct optical gap of 1.366 eV at 300 K. The temperature-energy shift of the A series excitons between 10 and 300 K was faster than those of MoS₂ and WS₂. From the μPL measurement of few-layer NiPS₃, the indirect-like emission was observed at 1.23 eV, while a direct B band emission was observed at 1.825 eV. The indirect-like emission possibly originates from an intermediate band of Ni 3d e₂g* to the Eᵥ top recombination. The A series excitons come from the top of Eᵥ to the Eᵥ bottom, while the B feature is originated from the spin-split-off band to the Eᵥ transition. Based on the experimental analysis, the origin of the band-edge excitons of the layered nickel phosphorus trisulfide was realized.

METHODS
Sample growth
Test samples were prepared by growing the layered single crystals of NiPS₃ via CVT with I₂ as the transport agent. First, powdered elements of Ni (99.999% purity), P (99.9999% purity), and S (99.9999% purity) were prepared. Second, the powder mixture of the starting materials and an appropriate amount of I₂ (10 mg/cm²) were cooled with liquid nitrogen and sealed in a vacuum environment at ~10⁻⁵ Torr inside a quartz ampoule. The growth temperature was set as 800 °C (heating zone) → 700 °C (growth zone) with a gradient of ~25 °C/cm for the simultaneous growth in two ampoules. The reaction occurred over 336 h to grow large single crystals. After this growth, several shiny sheet-like NiPS₃ thick crystals with areas up to a scale of square centimeters were obtained. With the weakened van der Waals bonds between the layers, different layer thicknesses of NiPS₃ can be mechanically exfoliated and transferred onto a SiO₂/Si substrate using Scotch tapes with different stickiness properties.

Microthermal-modulated reflectance
For μTR measurements, a 150-W tungsten halogen lamp served as the white light source. The white light source was dispersed by a 0.2-m Photronics International (PTI) monochromator, which was equipped with a 1200-grooves/mm grating for providing monochromatic light. The SiO₂/Si substrate decorated with few-layer NiPS₃ (size of 0.8 × 0.8 × 0.01 cm³) was closely attached onto an Au-evaporated quartz plate. The monochromatic light source was coupled onto the few-layer or multilayer sample using a silica fiber, and it passed through a light-guiding microscope (LGM) equipped with an Olympus objective lens (50x, working distance ~8 mm). It served as the interconnection coupled medium between the few-layer sample and the incident and reflected lights. The reflected light from the layered sample was collected by the LGM and then coupled to an EG&G HUV2008 Si detector using an additional silica fiber. Optical alignment was accomplished by the XYZ adjustment of the nano-flake sample using a CCD imaging camera in the LGM. A μTR measurement of ~0.5 A was periodically supplied to the Au heater for the thermal modulation of the lattice constant and band edge of the sample. Phase-sensitive detection was achieved by using an NF 5610B lock-in amplifier. A Janis open-circle liquid-helium cryostat equipped a Lakeshore 335 thermometer controller was used to facilitate temperature-dependent measurements from low temperatures to room temperature.

Optical transmission measurement
For the optical transmission measurement of bulk NiPS₃ sample, the same monochromatic light source as that employed for μTR was used. The layer sample of t ~ 10 µm was closely mounted on a copper holder with a center hole of size approximately 500 µm for light transmission. The incident light was chopped at 200 Hz with an optical chopper. The transmission light of the sample was passed to an EG&G HUV2008 Si photodetector. An NF 5610B lock-in amplifier was used to implement the phase-sensitive photodetection. An RMC 22 close-cycled He compressor system that was equipped with a Lakeshore 335 thermometer controller facilitated the low temperature and temperature-dependent measurements.

Micro-photoluminescence experiment
The μPL measurements were conducted in an integrated RAMaker microscope spectrometer with a 532-nm solid-state diode-pump laser as the excitation source. The same LGM setup as that used for μTR was utilized for the interconnection coupled medium between the few-layer NiPS₃ was determined to be Eᵥ = 1.402 eV at 300 K. The temperature-energy shift of the A series excitons between 10 and 300 K was faster than those of MoS₂ and WS₂. From the μPL measurement of few-layer NiPS₃, the indirect-like emission was observed at 1.23 eV, while a direct B band emission was observed at 1.825 eV. The indirect-like emission possibly originates from an intermediate band of Ni 3d e₂g* to the Eᵥ top recombination. The A series excitons come from the top of Eᵥ to the Eᵥ bottom, while the B feature is originated from the spin-split-off band to the Eᵥ transition. Based on the experimental analysis, the origin of the band-edge excitons of the layered nickel phosphorus trisulfide was realized.
NiPS₃ sample, the incident and reflected (scattered) lights, and the charge-coupled-device (CCD) spectrometer. The laser power was 5 mW, and the laser spot size was 3–5 μm. The measurements were obtained from 1.1 to 2.25 eV.

DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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AUTHOR CONTRIBUTIONS
C.H.H. conceived the idea and conducted the experiments. T.Y.H. grew the samples and performed the optical measurements. L.C.M. did the micro-PL experiment. C.H.H. also analyzed (calculated) the measurement data, and wrote the manuscript.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
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