ZnPSe$_3$ was identified as a two-dimensional material wherein valley and spin can be optically controlled in technologically relevant timescales. We report an optical characterization of ZnPSe$_3$ crystals that show indirect band-gap characteristics in combination with unusually strong photoluminescence. We found evidence of interband recombination from photoexcited electron–hole states with lifetimes in a microsecond timescale. Through a comparative analysis of photoluminescence and photoluminescence excitation spectra, we reconstructed the electronic band scheme relevant to fundamental processes of light absorption, carrier relaxation, and radiative recombination through interband pathways and annihilation of defect-bound excitons. The investigation of the radiative processes in the presence of a magnetic field revealed spin splitting of electronic states contributing to the ground excitonic states. Consequently, the magnetic field induces an imbalance in the number of excitons with the opposite angular momentum according to the thermal equilibrium as seen in the photoluminescence decay profiles resolved by circular polarization.

ZnPSe$_3$ | 2D materials | photoluminescence

The band structure theory of semiconductors introduces the concept of a valley, which exists as an extremum in the valence or conduction band. Most commonly, multiple valleys are found in the band structure of semiconductors and insulators and they can host electrons and holes partaking in processes that define the structural, optical, electrical, or magnetic properties of crystals. Charge carriers residing at various valleys can hold very different properties, as they are characterized by their specific effective mass and orbital/spin composition of wave functions (1). Moreover, multivalley effects, such as the modification of the excitonic states via band nesting (2), contribute to the variety of plausible excitations. Creating, detecting, and manipulating excitations within particular valleys are desirable for gaining a fundamental understanding of the unique characteristics of charge carriers in various types of materials as well as enabling their novel functionalities. For that reason, a discipline of valleytronics (3) was established, treating the valley degree of freedom as a quantum number that determines the behavior of charge carriers.

Early exploration of valleytronics was conducted for silicon and germanium (4), where the accessibility of valleys is limited by their weak optical response. Recently, a nontrivial valley structure was uncovered in representatives of two-dimensional materials (5, 6). Particularly interesting for optoelectronic applications (7, 8) are monolayer transition metal dichalcogenides (TMDCs) (9–11), which were found to display robust luminescence as direct band-gap systems in monolayer limit and significantly suppressed luminescence as indirect band-gap systems in multilayer limit (12–17). It is a common finding that indirect electron–hole recombination is often quenched by nonradiative processes. The long lifetime of indirect states puts the radiative recombination in competition with nonradiative processes, which usually occur within shorter timescales. Importantly, from a practical perspective, longer lifetimes are needed for creating optoelectronic devices where the operation time is defined by the response time of electronic components. These typically do not exceed gigahertz regimes; hence, optical control of charge carriers in the timescales of nanoseconds and beyond is crucial.

Here, we demonstrate that ZnPSe$_3$ acts as a two-dimensional indirect band-gap semiconductor while displaying robust yellow photoluminescence (PL), observable with the naked eye in ambient conditions under weak laser excitation. A comparative study of PL and quasi-absorption characteristics unveils optical resonances due to selective excitations at Γ and K points of the Brillouin zone and radiative recombination from indirect Γ–K transition. The lifetime of the fundamental electron–hole state is found to be in the microsecond range, about six orders of magnitude longer than in monolayer TMDC (18, 19). In the presence of an external magnetic field, a polarized emission is observed for the radiative transition indicative of a spin splitting that is preserved throughout the lifetime of the electron–hole pair. Importantly for photovoltaic functionalities,
the absorption spectrum of ZnSe correlates well with the solar emission spectrum (18, 19). Generally, through an in-depth optical study we found that ZnSe is a uniquely bright two-dimensional (2D) indirect system ideal to be employed as a platform for inspection of fundamental excitations in solids combined with potential applications within domains of photonics, optoelectronics, or photovoltaics.

Identification of Optical Resonances

In this study, we inspect bulk crystals of ZnSe grown via a chemical vapor transport technique. We cleave the crystals along the plane perpendicular to the 0001 direction of the crystal lattice and remove the top layers via mechanical exfoliation to obtain a clean crystal surface. Samples prepared via such a method displayed stable and homogenous optical response in cryogenic and ambient conditions. No discernable degradation was observed within 1 mo from the first experiments on cleaved crystals.

We first inspect the optical response of the ZnSe crystal in a backscattering microscopic configuration at a temperature of 1.6 K, where an apochromatic cryogenic objective with a high numerical aperture is used for the PL excitation and detection. While exciting the system with a 3.06-eV laser, we found that the photoluminescence spectrum is composed of two distinct emission bands at 2.00 and 2.36 eV as presented in Fig. 1 A and B. Further investigation by photoluminescence excitation (PLE) revealed multiple contributions to the processes of light absorption within the ZnSe crystal. We performed a deconvolution of the excitation spectrum measured for the higher energy emission band of about 0.4 eV. Such resonance is typically located at higher energy than the single-particle band gap and the exciton binding energy. Such resonance is typically located at higher energy than transitions arising due to any midgap states. For those reasons, we tentatively attribute the PL band at 2.36 eV to the indirect exciton recombination. We further corroborate this attribution by investigating the impact of laser power and temperature on the PL spectra together with the measurements of the PL decay time, discussed later in the text.

Based on the DFT calculations there are two direct gaps at the Γ and K points that give rise to absorption processes occurring very close in energy (within 40 meV) (21). Indeed, we observe two excitonic-like resonances, X_Γ and X_K, in the PLE spectra at 2.71 and 2.80 eV, respectively. Notably, the resonances differ significantly by their line widths of 91 ± 8 meV (X_Γ) and

![Diagram of light absorption, carrier relaxation, and radiative recombination processes occurring in ZnSe](image)

Fig. 1. PL and PLE (quasi-absorption) characterization of ZnSe crystals. The low-temperature spectra were measured in backscattering geometry with a 3.06-eV energy laser focused to a spot of 1-μm diameter. (A and B) They are correlated with PLE spectra for (A) higher-energy and (B) lower-energy PL bands. For the PLE spectra, the intensity of the PL is integrated at the lower-energy tail for both bands, as highlighted with orange and red strips A and B, respectively. The light blue, dark blue, and yellow shaded areas represent Lorentzian functions fitted to the PLE curves as described in SI Appendix. (C and D) The PL is observable with the naked eye in ambient conditions as illustrated by photographs of the crystal under white light illumination (C) and under 3.06-eV macroscopic laser excitation in darkness with a long-pass filter placed in front of the camera to reduce reflected and scattered laser light (D). (E) A comparative analysis of PL and PLE data, together with DFT calculations found in the literature, allows us to construct a minimal diagram of light absorption, carrier relaxation, and radiative recombination processes occurring in the ZnSe.
64 ± 6 meV (X_{\Gamma}). The linewidth of the absorption resonance is directly linked with the lifetime of the electron–hole pair by the Heisenberg uncertainty principle. Typically, spatially localized electronic states exhibit longer lifetimes leading to the broadening of absorption and/or emission resonances. In this view, the K-valley charge carriers, which are built predominantly from the d-orbitals of the Zn atom, are localized in real space and the corresponding interband optical transition is characterized by a broad linewidth. Similarly, \( \Gamma \)-valley charge carriers are composed of s- and p-type wave functions of P and Se atoms, which are delocalized in real space, hence presenting narrow absorption resonances. Therefore, we identify the two absorption resonances as X_{\Gamma} and X_{K}, which correspond to direct interband absorption excitonic resonances at \( \Gamma \) and K points, respectively.

From the analysis of the optical resonances in emission and quasi-absorption spectra, we established a diagram of absorption, carrier relaxation, and radiative recombination processes that determine the optical response of ZnPSe_{3} crystals as presented in the schematic in Fig. 1E. The absorption processes create electron–hole pairs at the \( \Gamma \) and K points of the Brillouin zone followed by a relaxation of the electron for the K excitation or the hole for \( \Gamma \) excitation onto the fundamental states in the conduction and valence bands, respectively. The relaxation time of the electron and the hole constitutes a contributing factor to the lifetime of direct K and \( \Gamma \) excitons, respectively. Based on Heisenberg uncertainty principle \( \tau \geq \frac{\hbar}{2\pi\Delta E} \), the lower bound for the characteristic time of this process can be estimated from the linewidth to be \( \tau_{\text{relax}} \geq 3.6 \text{ fs} \) and \( \tau_{\text{relax}} \geq 5.1 \text{ fs} \).

We now turn to the interpretation of the lower-energy band at 2.00 eV, which exists beyond the insofar described processes. We note first that the PLE spectrum for the lower-energy band is qualitatively similar to the recombination of the indirect interband states, which indicates that the excitation path also originates from photocation of X_{\Gamma} and X_{K} states. However, a closer look at the X_{\Gamma} resonance reveals that it is shifted toward lower energy by 25 meV and broadened by 36% compared to the X_{\Gamma} resonance observed for the interband free exciton state. Based on these observations we speculate that the lower-energy band corresponds to the radiative recombination of donor bound excitons (22). The introduction of the lattice defect can locally reduce the band gap through the increase of the interatomic distance and, consequently, the reduction in the overlaps of the valence orbital wave functions, leading to the redshift of absorption resonances. Also, an inhomogeneous broadening is expected to occur as the excitons localized by the defects may initially be created at a distance away from the defect; hence the photoexcited carriers statistically probe a variation of the band gap from the minimum at the defect site to the maximum at the pristine lattice site.

We further validate this interpretation by inspecting the power dependence of the PL intensity comparatively in the resonant \( \Gamma \)-gap excitation regime and below the direct-gap excitation regime. The qualitative difference between the free interband excitons and defect-bound excitons manifests as superlinear and sublinear dependence of the emission intensity on power, respectively. Such a finding is common in semiconductors, as the midgap defect states can trap a limited number of excitons when compared to the density of states of free interband excitons. This effect is observable in Fig. 2A, where the PL spectra obtained under resonant \( \Gamma \)-gap excitation (3.03 eV excitation energy) are normalized by the excitation power. In the low-power regime, both bands of defect-bound excitons and free excitons are comparable in intensity. With the increase of power, the population of the defect-bound states increases sublinearly (with the power coefficient close to 1), while the intensity of the free exciton transitions grows superlinearly (the trends can be followed in Fig. 2C; the extracted power factor equals 1.25). In the regime of excitation below direct gaps (2.58 eV excitation energy), the free excitons band becomes significantly quenched, while the defect-bound states remain

Fig. 2. Laser excitation power and temperature dependence of the ZnPSe_{3} PL spectra. (A and B) The PL data are normalized by the excitation power and inspected in two excitation regimes, in resonance with the direct \( \Gamma \) transition (A) as seen in the PLE spectrum and in nonresonance, with subdirect-gap excitation (B). (C and D) The detailed dependence of the PL intensity determined as the area under the PL curve across four orders of magnitude of excitation power is presented for resonant (C) and nonresonant (D) excitations. The experimental data are fitted with the function \( I(P) = I_0 + P^n \) represented by the red lines. (E) A false-color map of the PL response of ZnPSe_{3}, together with a few selected characteristic spectra, measured as a function of temperature in the range from 1.6 K up to 300 K, is presented for resonant \( \Gamma \) excitation. (F) The redshift of the emission energy of the higher-energy band is depicted with the result of Gaussian fitting of the emission peak in the temperature range where it can be clearly distinguished in the PL spectrum.
weakened excited through an alternative excitation process that is discernible in PLE spectra for the defect band as a broader resonance at 2.49 eV as illustrated by the yellow Lorentzian resonance in Fig. 1B. This weaker excitation channel may be related to the transition from the defect states into the higher-energy conduction subbands. The detailed evolution of the PL intensity with the excitation power, highlighting the qualitative energy conduction subbands. The detailed evolution of the PL intensity with the excitation power, highlighting the qualitative differences between resonant and under-gap excitation regimes, is presented in Fig. 2 C and D.

The identification of the free exciton band and defect-bound exciton band is further supported by the inspection of the temperature dependence of the PL spectra. As typically observed for semiconductors with a radiative ground state, the PL intensity decreases with temperature. From the fitting of this temperature dependence of the PL spectra, we performed an analysis of the spin properties of the charge carriers partaking in the optical processes by inspecting the magneto-optical effects in ZnPSe3. Using excitation resonant with \( \Gamma \) transition (excitation energy 3.03 eV) with circularly polarized light we observe the magnetic-field evolution of the PL spectra resolved by circular polarization. The obtained results showcase that the emitted light becomes circularly polarized under the influence of the magnetic field regardless of the polarization state of excitation photons. We can interpret this finding in a simple picture of magnetic-field–induced splitting of individual valence and conduction bands that we describe with a splitting \( g \) for the electron (e) or hole (h) in the \( \Gamma \) or the K valley, respectively; \( \mu_B \) is the Bohr magneton, and \( B \) is the value of the magnetic field. The relevant states in the presence of a magnetic field, together with the associated optical transitions are illustrated in Fig. 4C. The values of the \( g \) for individual bands are determined by the spin, orbital, and/or valley effects (27, 28). As seen in Fig. 4 A and B, the absorption strength is equal for \( \sigma^+ + \sigma^- \) excitation at 1.9 eV, which indicates that the oscillator strength for both \( \sigma^+ \) and \( \sigma^- \) transition is independent of the magnetic field and the split valence states remain equally populated. The emergent circularly polarized emission from the interband \( \Gamma-K \) recombination can be understood in a simple single-particle picture. The initial state of the recombination process splits into \( \sigma^+ + \sigma^- \) active components with a differential exciton g factor \( g_X^{\Gamma,K} = g_\Gamma + g_K \). The final state of the recombination process is given by a magnetic-field–independent vacuum level if we assume a neutral exciton state. In such a case, the emergent circular polarization degree of the emitted light is indicative of the thermal distribution of excitons on the levels split by the magnetic field. As previously noted, no significant effects of excitation polarization can be observed in both emission and absorption-type spectra. Hence we describe the relative population of \( \sigma^+ + \sigma^- \) active

**Magneto-Optical Effects in ZnPSe3**

Having established the origin of the optical resonances seen in PL and PLE spectra, we performed an analysis of the spin properties of the charge carriers partaking in the optical processes by inspecting the magneto-optical effects in ZnPSe3. Using excitation resonant with \( \Gamma \) transition (excitation energy 3.03 eV) with circularly polarized light we observe the magnetic-field evolution of the PL spectra resolved by circular polarization. The obtained results showcase that the emitted light becomes circularly polarized under the influence of the magnetic field regardless of the polarization state of excitation photons. We can interpret this finding in a simple picture of magnetic-field–induced splitting of individual valence and conduction bands that we describe with a splitting \( g \) for the electron (e) or hole (h) in the \( \Gamma \) or the K valley, respectively; \( \mu_B \) is the Bohr magneton, and \( B \) is the value of the magnetic field. The relevant states in the presence of a magnetic field, together with the associated optical transitions are illustrated in Fig. 4C. The values of the \( g \) for individual bands are determined by the spin, orbital, and/or valley effects (27, 28). As seen in Fig. 4 A and B, the absorption strength is equal for \( \sigma^+ + \sigma^- \) excitation at 1.9 eV, which indicates that the oscillator strength for both \( \sigma^+ \) and \( \sigma^- \) transition is independent of the magnetic field and the split valence states remain equally populated. The emergent circularly polarized emission from the interband \( \Gamma-K \) recombination can be understood in a simple single-particle picture. The initial state of the recombination process splits into \( \sigma^+ + \sigma^- \) active components with a differential exciton g factor \( g_X^{\Gamma,K} = g_\Gamma + g_K \). The final state of the recombination process is given by a magnetic-field–independent vacuum level if we assume a neutral exciton state. In such a case, the emergent circular polarization degree of the emitted light is indicative of the thermal distribution of excitons on the levels split by the magnetic field. As previously noted, no significant effects of excitation polarization can be observed in both emission and absorption-type spectra. Hence we describe the relative population of \( \sigma^+ + \sigma^- \) active

**Fig. 3.** PL decay transients in ZnPSe3 crystals. (A and B) The PL decays have been inspected for the higher-energy (2.36 eV) (A) and lower-energy (2.0 eV) (B) PL bands under 2.33-eV excitation with a picosecond pulsed laser (pulse width of 570 ps). Both PL transients were fitted with a biexponential decay function:

\[
i(t) = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right)
\]

with characteristic decay times \( \tau_1 \) and \( \tau_2 \).

Below 10%. The fitting of biexponential function yields decay times of \( \tau_1 = 0.10 \mu s \) and \( \tau_2 = 0.74 \mu s \) for the free exciton band and \( \tau_1 = 0.21 \mu s \) and \( \tau_2 = 1.36 \mu s \) for the defect-bound exciton band. Almost twice as long decay times for the lower-energy band further confirm its assignment to defect-bound transition, where the spatial localization effects of defect-bound excitons lead to an increase in the excitonic lifetimes. The high PL intensity with long carrier recombination times makes this material a promising candidate for investigating and controlling photoexcited charge carriers in timescales relevant to electronics.
excitons, which we assume to be proportional to the emission intensity, by a Boltzmann distribution function:

$$\frac{I_{\sigma-}}{I_{\sigma+}} (B, T) = A \exp \frac{-g_X^{\Gamma \rightarrow K} \mu_B B}{k_B T + T_{\text{eff}}} + (1 - A),$$

where $g_X^{\Gamma \rightarrow K}$ is the excitonic $g$ factor, $\mu_B$ is the Bohr magneton, $k_B$ is a Boltzmann constant, $T_{\text{eff}}$ acts as a measure of interexcitonic interactions, $(1 - A)$ accounts for remnant polarization degree $(\frac{I_{\sigma-}}{I_{\sigma+}} (B \rightarrow \infty, T))$ due to spin, orbital, and/or valley mixing effects, and $B$ and $T$ denote the value of magnetic field and sample temperature. Notably, we can describe the experimental data $(\frac{I_{\sigma-}}{I_{\sigma+}} (B, 1.6 \text{ K}))$ and $(\frac{I_{\sigma-}}{I_{\sigma+}} (9 \text{ T}, T))$ with the same set of parameters (Fig. 4 D and E) and we found the best fit to yield $g_X^{\Gamma \rightarrow K} = 1.1 \pm 0.2$ and $T_{\text{eff}} = 2.6 \pm 1.0 \text{ K}$. The agreement of our data with Boltzmann distribution and the small value of the effective temperature indicates that the excitons in ZnPSe$_3$ in the investigated excitation conditions behave like a weakly interacting semiclassical gas of particles (29–31). Further PL dynamics of the ZnPSe$_3$ are studied by polarization-resolved PL decay times measured in the presence of the external magnetic field. As shown in Fig. 4F at 9 T for the defect-bound excitons, the PL transients resolved in circular polarization demonstrate that the degree of polarization is conserved over long microsecond decay times in ZnPSe$_3$.

Summary

We have identified ZnPSe$_3$ as a member of the family of two-dimensional materials with unique optical properties. Most importantly, we have demonstrated that ZnPSe$_3$ is an indirect band-gap system that displays a robust PL characterized by microsecond decay times of the emitting states. Through a combination of PL and PLE spectroscopy, we could selectively create excitations within the $\Gamma$ and K valleys and probe the recombination processes of indirect interband transition and defect-bound excitons. Overall, ZnPSe$_3$ enriches the family of optically active 2D materials with the potential to study valley-selective optical processes in technologically relevant timescales or employ resonant interband light absorption residing within the solar range for photovoltaic application (SI Appendix).

Materials and Methods

The optical characterization of ZnPSe$_3$ crystals was performed in backscattering microspectroscopic geometry. The sample was cooled down by a dry cryogenic system and the temperature was controlled by heaters at the sample and variable temperature insert (VII) stages. The sample was positioned under a 50 × objective by a stack of x y z piezo positioners. The laser light was delivered into the low-temperature insert through a monomode optical fiber for photoluminescence experiments and through a multimode 50-μm fiber for PLE experiments. The sample was excited by a 514 nm (2.41 eV) single-frequency laser for monochromatic excitation and a supercontinuum source for PLE. In the latter case, the power was stabilized by a liquid crystal acting in a feedback loop with a photodiode probing the intensity of laser light after the output of the excitation fiber. The signal from the sample was collected through a multimode fiber, dispersed by a 0.75-m spectrometer with a 150-g/mm grating, and detected by a CCD camera. A set of filters, polarizers, and waveplates was used to perform polarization-resolved experiments. The magnetic field was applied to the sample in the direction perpendicular to the layers of ZnPSe$_3$ material by superconducting coils. The photoluminescence decay times were measured by an avalanche photodiode under the excitation with a picosecond 532-nm laser (2.33 eV) with kilohertz repetition rates.

Data, Materials, and Software Availability. All study data are included in the article and/or SI Appendix.

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