

Optical signatures of magnetic phase transitions in transition metal phosphorus sulfides

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Summary

Two-dimensional materials are of great interest due to their unique properties and potential applications in various fields, including nanocatalysis, optoelectronics, and spintronics [1]. The selected van der Waals antiferromagnets NiPS₃, CrPS₄, MnPS₃ and FePS₃ are ideal candidates for the study of magnetic phase transitions with varying inter-layer coupling and exotic magnetic orders. The materials can be easily exfoliated down to two-dimensional monolayers.

With bandgaps in the optical and near-infrared regions optical measurement techniques offer promising opportunities for fast in situ measurements of the magnetic structure on a limited probe volume. Polarized photoluminescence has been identified as the most promising optical measurement technique for studying the magnetic phase transition in the selected materials. The magnetic splitting of the photoluminescence line of NiPS₃ has been demonstrated to be more interesting than previously thought, with different splitting observed for different linear polarization directions.

In CrPS₄ the circular dichroism of the photoluminescence line is shown to be proportional to the magnetization, which allows the entire magnetic phase diagram to be studied with optical methods.

Zusammenfassung

Zweidimensionale Materialien erwecken aufgrund ihrer einzigartigen Eigenschaften und potentiellen Anwendungen in verschiedenen Bereichen wie der Nanokatalyse, der Optoelektronik und der Spintronik großes Interesse [1]. Die ausgewählten van-der-Waals Antiferromagnete NiPS₃, CrPS₄, MnPS₃ und FePS₃ sind ideale Kandidaten für die Untersuchung magnetischer Phasenübergänge mit unterschiedlicher interlayer-Kopplung und exotischen magnetischen Ordnungen. Die Materialien lassen sich leicht auf zweidimensionale Monoschichten exfolieren. Mit Bandlücken im optischen und nahinfraroten Bereich bieten optische Messmethoden vielversprechende Möglichkeiten für schnelle in-situ-Messungen der magnetischen Struktur in einem begrenzten Probenvolumen. Polariserte Photolumineszenz wurde als vielversprechendste optische Messmethode zur Untersuchung des magnetischen Phasenübergangs in den ausgewählten Materialien identifiziert.

Die magnetische Aufspaltung der Photolumineszenzlinie von NiPS₃ hat sich als interessanter herausgestellt als bisher angenommen wurde, da für verschiedene lineare Polarisationen unterschiedliche Aufspaltungen beobachtet wurden.

In CrPS₄ wird gezeigt, dass der zirkuläre Dichroismus von der Photolumineszenzline proportional zur Magnetisierung ist, was es ermöglicht, das gesamte magnetische Phasendiagramm mit optischen Methoden zu untersuchen.

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Especially I appreciate Dr. Mateusz Goryca for always quickly helping me with advice and assistance despite his busy schedule. His mentorship and encouragement, along with the freedom to explore independently, have been invaluable.

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1 Introduction

Antiferromagnetic van der Waals materials such as transition metal phosphorus sulfides are of great interest due to their unique combination of magnetic, optical, and structural properties [1, 3]. The structure of a specific material, NiPS₃, is illustrated in Figure 1.1 [2], demonstrating strong layers in the *a*-*b* plane, bonded by weak van der Waals interactions along the *c* axis. This allows for easy exfoliation of the flakes and enables the investigation of property changes resulting from the transition from three-dimensional to two-dimensional structures [1]. The magnetic properties of these materials are dominated by the spins of the transition metal ions in the lattice [3]. They exhibit a wide range of thickness-dependent exotic magnetic orders [4], influenced by the varying anisotropy for different materials [3, 5].

However, determining these orders is challenging due to the antiferromagnetic structure, which results in a net magnetization of zero [3]. Especially fast measurements in the monolayer limit without disturbing the sample is challenging [4, 5], but is important for studying phase changes and exploring applications in spintronics [4]. Optical measurements emerge as the most promising methods, as they can be used for in situ measurements on a small sample volume and even offer spatial resolution. However, the commonly used Kerr effect faces limitations, as detecting small polarization rotations in thin layers, in the order of 5 μ rad, is challenging [4].

The goal of this project is to identify optical signatures of magnetic order or magnetic phase transitions in the selected transition metal phosphorus sulfides, with the aim of developing a method suitable for fast in situ measurements and potentially extending to monolayers in the future. This project focuses on identifying and demonstrating a suitable measurement technique, rather than on studying the magneto-dependent light-matter interaction process. Various optical measurement techniques were evaluated in the methodology section, with polarized photoluminescence spectroscopy identified as the most promising method. Subsequently, this method was applied to NiPS₃ and CrPS₄ in the results section. While the phase transition in NiPS₃ was out of the experimental capabilities, the circular dichroism of the photoluminescence of CrPS₄ was successfully used to observe phase transitions.

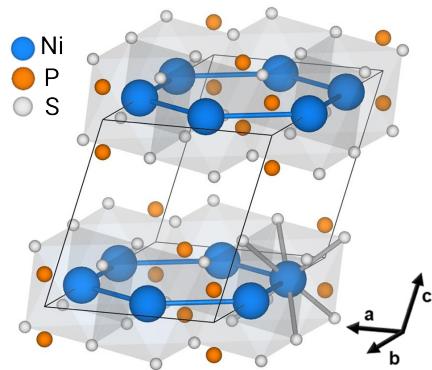


Figure 1.1

Crystal structure of NiPS₃ as an example for the studied materials. The image is adapted from [2].

Magnetic Properties

Optic Properties

2 Methodology

2.1 Sample Preparation

Prior to measurements, the samples have to be prepared. The initial measurements were done on bulk crystals. Subsequently, the samples were exfoliated, to expose a clean surface. The bulk crystals were provided as shown in [Figure 2.1a](#). They were grown using the vapor transport method which is a conventional method for the manufacture of these materials [1, 4].

The bulk crystals have dimensions of approximately $4 \times 2 \times 0.5$ mm. The thickness was quantified using thin-film interference, as detailed in [Section 2.2.2](#).

For the initial measurements, the crystals were mounted to minimize strain below a piece of black paper with a hole that was glued to a holder on the corners as depicted in [Figure 2.1b](#).

Examined under a microscope the surface of NiPS₃, CrPS₄ and MnPS₃ samples was smooth like [Figure 2.2a](#) and the FePS₃ appeared rough like [Figure 2.2b](#).

The surface appeared to be contaminated by a rough, oxidized layer. To remove this, mechanical exfoliation was used.

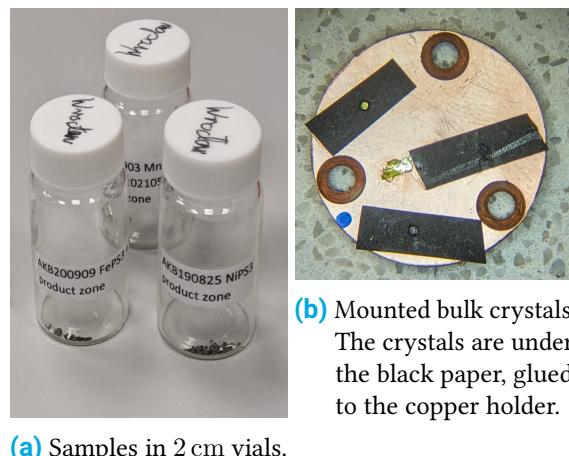
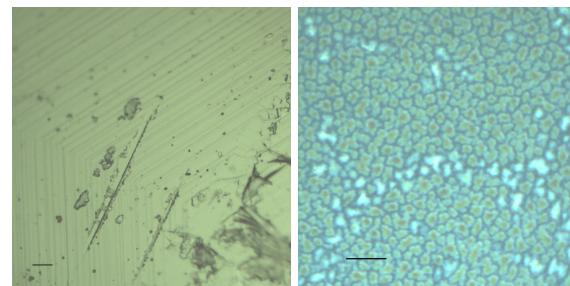
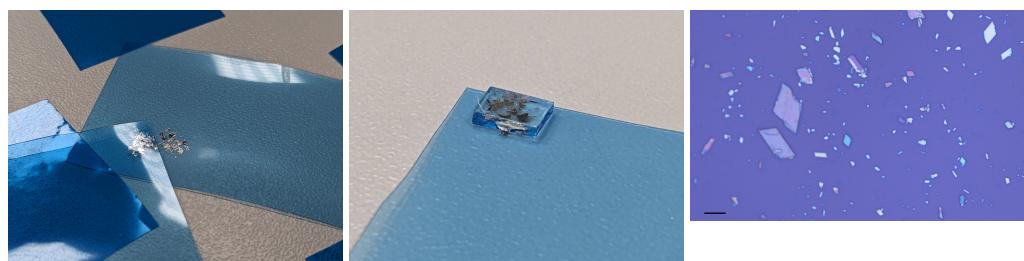


Figure 2.1 Bulk Samples, as received and mounted for first measurements.



(a) NiPS₃: Smooth surface with characteristic features from the hexagonal crystal lattice.
(b) FePS₃: Rough surface, probably due to contamination.

Figure 2.2 Optical images of the bulk sample surface. Scalebar 10 μm.



(a) First Step: subdividing the crystal multiple times.
(b) Second Step: transferring the flakes to a substrate.
(c) Result: CrPS₄ flakes on Si/SiO₂ substrate, Scalebar 10 μm

Figure 2.3 Photos at different stages in the exfoliation process.

2.1.1 Exfoliation

In order to prepare a surface that was free of contamination, particularly necessary on the FePS₃ crystals, mechanical exfoliation was used. The stages of this process are photographed in [Figure 2.3](#).

Initially, a crystal with thickness d_0 is placed on an adhesive tape.

Subsequently, a second piece of tape is placed on top of the crystal and removed n times. This process is depicted in [Figure 2.3a](#). The flakes are divided each time into thinner flakes with the average thickness $\langle d_n \rangle = 1/2 \langle d_{n-1} \rangle$.

For most samples n was approximately 8. This technique allows to produce monolayers with $\langle d_n \rangle = 0.8 \text{ nm}$ [6] from a $d_0 = 400 \text{ nm}$ thick crystals, requiring just $n = \log_2 d_0 / \langle d_n \rangle \approx 19$ steps.

The utilized adhesive tape is specially designed for exfoliation, although the use of a special adhesive tape is not necessary. The main difference to normal *commercial grade* adhesive tape is the availability of variants with different adhesive strengths and the tape material is flexible to

prevent excessive pressure from being applied to the flake edges, thereby reducing the likelihood of breaking them.

Finally, the flakes are transferred to a substrate. In [Figure 2.3b](#) the flakes are transferred to a glass substrate. In this step, only the thinner flakes adhere to the substrate when the tape is removed, as they are more flexible and can better deform to the substrate.

The ratio of adhesion between the flakes and the substrate and the flakes and the tape determines the yield of flakes that remain on the substrate.

The adhesion between the flake and the substrate can be tuned by selecting different substrates. For instance, the yield on glass was 10 – 100 lower than on a Si/Si₂ substrate. To alter the adhesion between the flakes and the tape, a different adhesive can be used. To get even more granularity the transfer was tried at elevated temperatures to reduce the adhesion.

To increase the yield even more this transfer step was repeated multiple times for the glass substrate.

The results are flakes on a substrate, as seen under a microscope in [Figure 2.3c](#). The resulting flakes have a thickness of approximately 500 nm and can be considered bulk material when compared to the thickness of monolayers.

2.2 Measurement Techniques

In order to identify the optical signatures of phase transitions, an optical measurement technique is used. A few different methods were tried.

2.2.1 Transmission

To measure a signal independently of the surface quality transmission spectroscopy can be used. Specifically a commercial transmission spectrometer, the *Cary 5000*, was utilized. *Jan Sufczynski* was a great help in getting me up to speed with the machine and the cooling loop of the closed-cycle cryostat. The spectrometer has two user-accessible beam paths, one is the reference and one the sample. A relative transmissivity is reported from the instrument, defined as $T = T_{\text{Sample}}/T_{\text{Reference}}$. For the initial measurements, MnPS₃ was selected because the 0.5 mm bulk crystals are already visually transparent.

The data is shown in Figure 2.4 for a MnPS₃ crystal in the sample path and for a hole in the sample path.

Surprisingly the relative transmission of the hole is not constant.

The only difference between the paths are the Quartz windows of the cryostat in which the sample was mounted and the aperture of the sample holder. This does not explain the nonuniform transmission spectrum.

The machine changes from infrared to visible mode at 800 nm, and there have been rumors that a technician from the company had serviced the machine and mixed up some filters.

Irrespective of the underlying cause, the measurement was reproducible and the signal can be corrected by dividing it with a calibration spectrum of the hole and aligning the visible and infrared spectra in software.

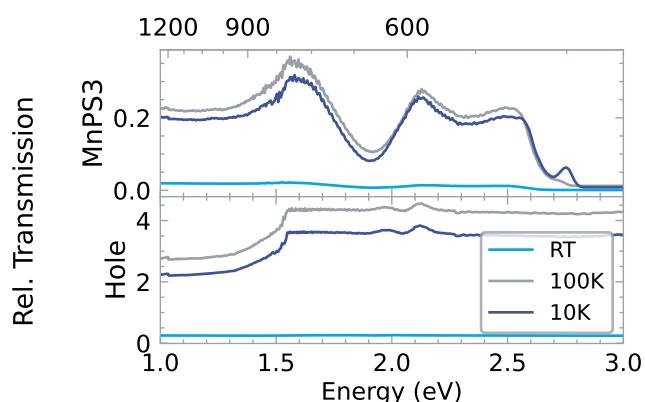


Figure 2.4 Unprocessed relative transmission spectra directly from the spectrometer. Note the non-constant relative transmission of the hole.

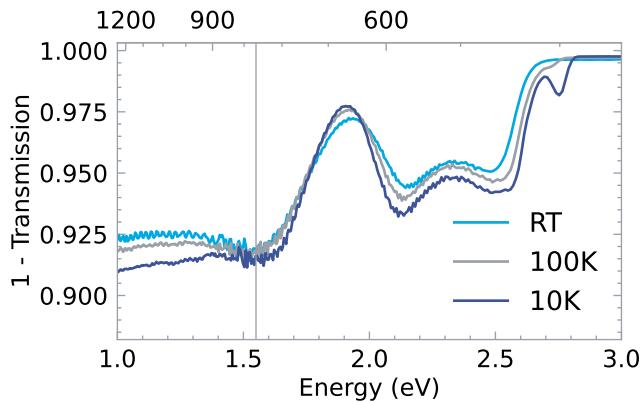


Figure 2.5 Corrected absorption spectrum ($\approx 1 - T$) of MnPS₃. The bandgap is at 2.6 eV.

The corrected absorption spectrum ($\approx 1 - T$) is depicted in [Figure 2.5](#) and reproduces the shape of the absorption spectrum in [7]. The bandgap is at 2.6 eV above which the spectrometer saturates due to insufficient signal through the sample.

For the other samples the features measured in [Figure 2.7](#) correspond with those recorded in the literature [8–10].

The main problem with this setup is that the spectrometer saturates quickly in the sample or the reference path when the sample is too thin or too thick.

It also has no way to individually display the intensity for the sample or reference path which

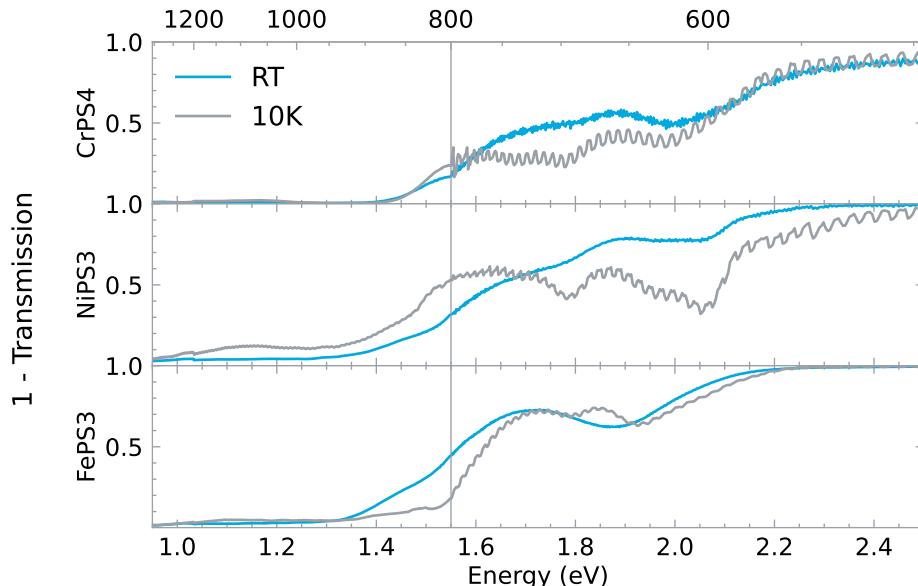


Figure 2.7 Processed absorption spectra of different materials.

makes adjustments difficult.



Figure 2.6

Mounted samples for transmission measurements.

From left to right: FePS₃, NiPS₃ and CrPS₄ exfoliated to the same transparency.

In order to obtain any usable measurements, the samples were exfoliated to a specific optical transparency, as shown in [Figure 2.6](#). Additionally, a compensating aperture was placed in the reference beam.

To hold the thick exfoliated flakes they were not transferred to a substrate but mounted with the adhesive tape used for exfoliation. This method was successfully used down to 10 K without any issues.

However, this workflow is rather tedious and there is no way to use a magnet with the spectrometer away.

It was planned to rebuild the transmission setup on the magnet, but this was not completed due to the time required for the unexpected measurements for [Section 3.2.1](#).

Nevertheless, this technique remains promising as it allows for the independent measurement of the bandgap, circumventing

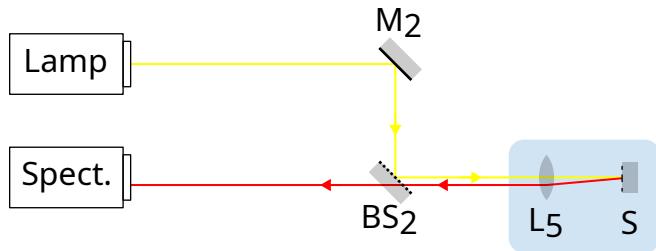


Figure 2.8 Setup used for reflection measurements.

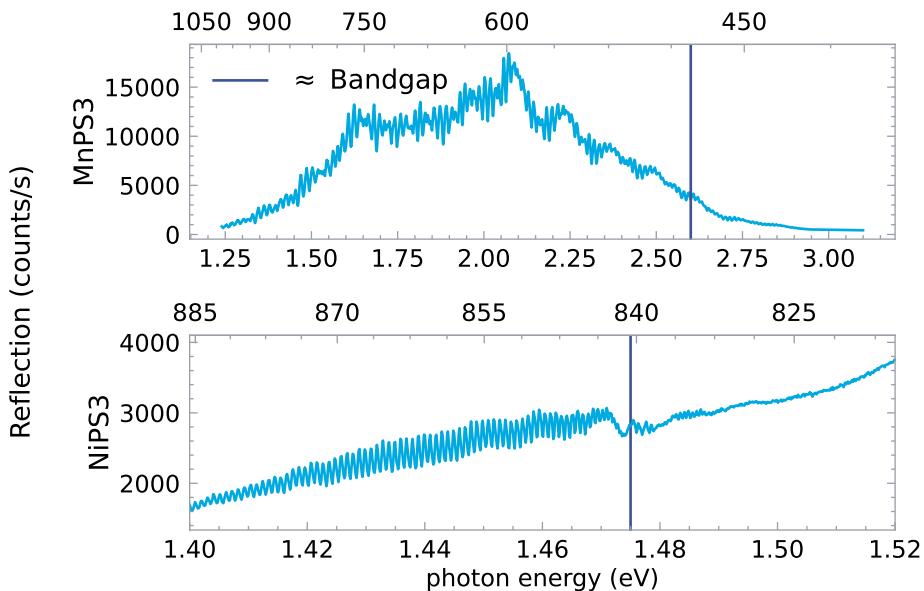


Figure 2.9 Unprocessed reflection spectra from bulk crystals. With bandgap from transmission measurements.

2.2.2 Reflection

Subsequently, reflection spectroscopy using the setup shown in Figure 2.8 was evaluated. In this instance, a halogen lamp was utilized to illuminate the sample. The light was focused by a lens (L_5) with a high numeric aperture on a small (in the order of $10\text{ }\mu\text{m}$) spot. The reflected beam passed through a beam-splitter (BS_2) into a spectrometer. This technique only needs access to the sample from a single side, which simplifies the setup.

The unprocessed recorded spectra for bulk crystals of highly transparent $MnPS_3$ and the material with the strongest bandgap edge $NiPS_3$, are represented in Figure 2.9. Below the bandgap, the crystals are transparent, and a thin-film interference pattern is visible.

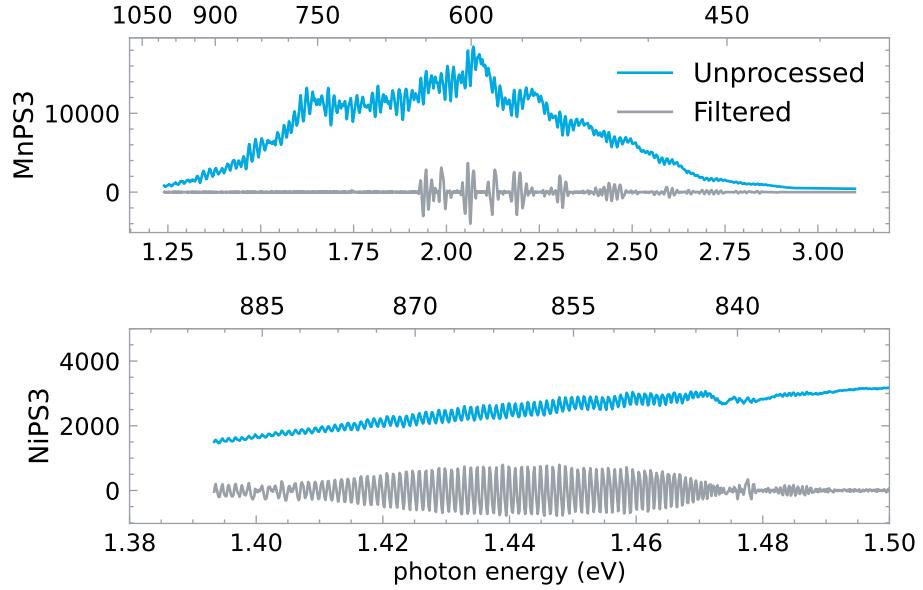


Figure 2.10 Reflection spectra filtered with empirical mode decomposition.

Deconvolving the spectral shape of the lamp by dividing the signal from the sample with the spectrum of a mirror was attempted, but the objective lens L_5 in Figure 2.8 has a strong chromatic aberration, which alters the spectrum too much.

In order to remove the lamp spectrum, a filter function, for example, the *Empirical Mode Decomposition*, can be employed [11]. The result of the filtered signal is presented in Figure 2.10.

However, even with the filtering, the bandgap edge remains difficult to detect precisely, which makes the technique unsuitable for the detection of the expected small shifts in the bandgap.

Thickness Estimation

The thin film interference pattern can be utilized to estimate the thickness of the sample. In order for the total reflection to be strong, the top reflection and the bottom reflection have to be in phase. Specifically $2nd/\lambda \in \mathbb{N}$ with the refractive index n and 2 times the thickness d . Therefore the filtered reflected signal should be something like this:

$$R(\lambda > \lambda_{\text{Bandgap}}) \approx \cos\left(2\pi \cdot \frac{2nd}{\lambda}\right) \quad (2.1)$$

which can be decomposed into the components for different thicknesses:

$$S(nd) = \mathcal{F} \left[R \left(\frac{1}{\lambda} \right) \right] (2nd) \quad (2.2)$$

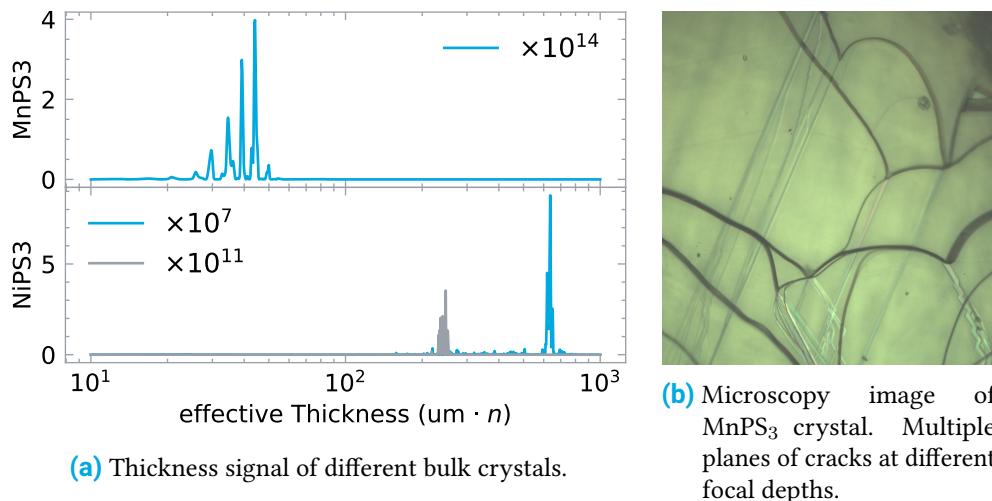


Figure 2.11 Thickness Estimation on thick crystal samples, where multiple breaks are visible in the MnPS₃ crystal.

Where the Fourier Transform \mathcal{F} is evaluated using the Lomb-Scargle method [12] because the data is not evenly spaced.

Even for evenly spaced data this method is useful as it is less sensitive to intensity noise than the discrete Fourier transform [12].

The thickness signal for different samples is depicted in Figure 2.11a. The NiPS₃ samples each have one effective thickness in the range of ~ 400 um.

In contrast, the MnPS₃ sample displays multiple peaks in the range of 40 um. When observed with an optical microscope in Figure 2.11b, the MnPS₃ sample has multiple layers of cracks at different depths, indicated by the varying focus. This matches with the recorded thickness signal.

Exfoliated Flakes

The reflection spectra of exfoliated flakes were also measured. It is possible to normalize the spectrum from the flake to the reflection of the bare substrate next to the flake:

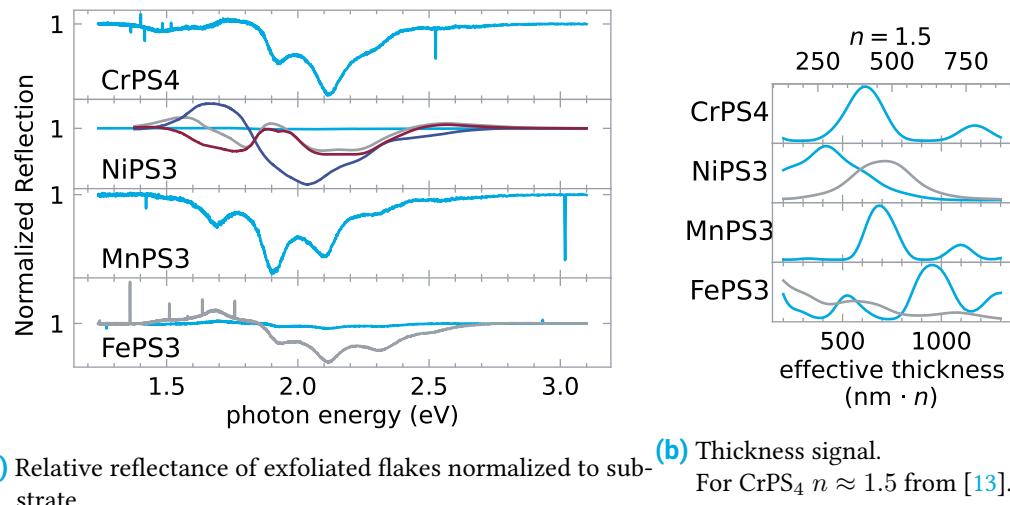
$$R_{\text{Normalized}} = \frac{R_{\text{Flake}} - Bkg}{R_{\text{Substrate}} - Bkg} \quad (2.3)$$

Where Bkg is a signal measured without illumination. The Bkg signal consists of an electronic dark noise from the spectrometer and stray light present in the room.

The results are displayed in Figure 2.12a. It is not possible to measure the bandgap edge in the signal.

The hard to interpret shape is due to the thin film interference pattern of three interfaces. The

not clear



(a) Relative reflectance of exfoliated flakes normalized to substrate.
(b) Thickness signal.
For CrPS₄ $n \approx 1.5$ from [13].

Figure 2.12 Reflectance spectra from exfoliated flakes on Si/SiO₂ substrate with calculated thickness signal.
The thickness of the CrPS₄ flake is between 200 nm to 700 nm.

first interface is the vacuum-flake, the next is the flake-SiO₂ of the substrate, and the last is the SiO₂-Si interface.

This is also visible in the thickness signal in Figure 2.12b. For CrPS₄ the thickness of the flake is found to be between 200 nm to 700 nm, as confirmed by subsequent measurements with atomic force microscopy Figure 3.10b.

Additionally, a second peak at 1180 nm · n is observed, which may be attributed to the SiO₂ layer of the substrate. However, the substrate was derived from the same wafer for all samples, and there is no reason for the thickness of the SiO₂ layer to vary between the different samples.

Reflection spectroscopy is not a suitable method for measuring the bandgap edge, even for the thick flakes used here and even less so for monolayers. Therefore, an alternative approach is required.

2.2.3 Photoluminescence

The photoluminescence process is more complex than the absorption process and is therefore more susceptible to the influence of a magnetic field. Combined with the ease of identifying changes in an isolated peak, this makes photoluminescence a promising technique for probing the magnetic field.

A setup to measure polarization-sensitive photoluminescence is illustrated in Figure 2.13.

The excitation laser at 532 nm or 647 nm is polarization-controlled using the polarizer P₁ and the retarder λ_1 .

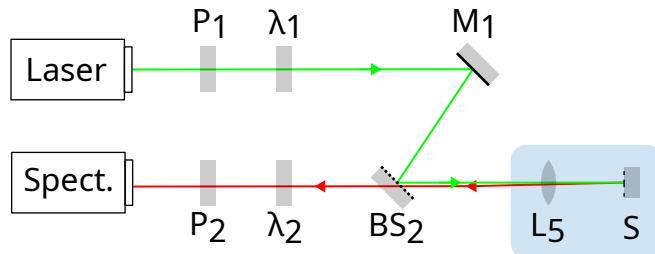


Figure 2.13 Used setup for photoluminescence measurements.

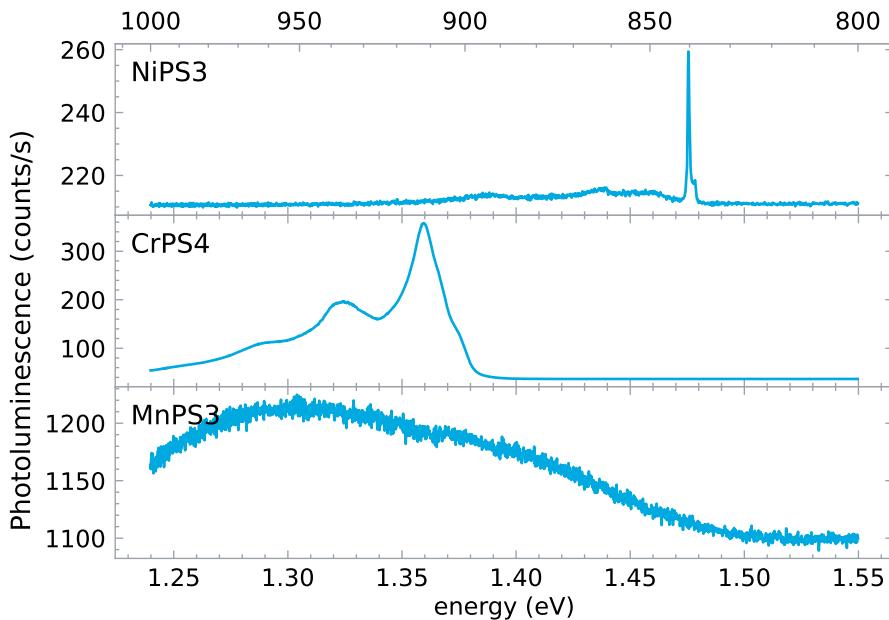


Figure 2.14 Measured Photoluminescence spectra at 10 K.

The mirror M_1 with the beam splitter BS_2 is located at a small angle to preserve the polarization as much as possible. The beam splitter BS_2 is a polka dot mirror because it minimizes the changes in polarization compared to a glass wedge.

The analysis path to the spectrometer is also polarization controlled with the retarder λ_2 and the polarizer P_2 .

The retarders were configured to excite with circular polarization and detect with linear polarization or vice versa to prevent any bias in the excitation.

While this may not be necessary given that the excitation polarization is lost in the complex luminescence process [14], it is a good practice to ensure that the measurements are not biased.

Figure 2.14 depicts the photoluminescence spectra of various samples at 10 K. This is selected as the peaks get sharper with decreasing temperature.

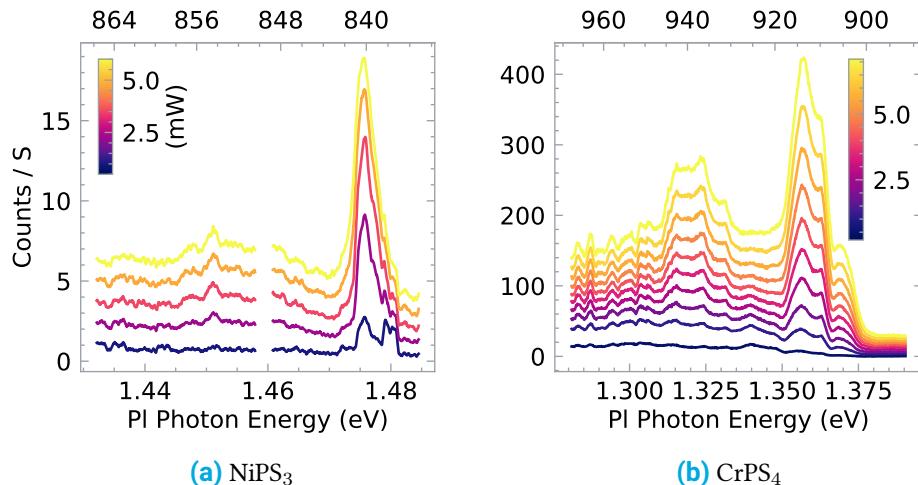


Figure 2.15 Excitation power dependence of the photoluminescence signal at 10 K.

A main peak is observed, with different widths for the different materials. This Peak is caused by the exciton photoluminescence process [15, 16].

Next to the main peak, multiple smaller peaks are visible. These are more complex structures such as excitons in higher energy levels, charged excitons, or biexcitons [2, 15–17].

For this project, only the respective main peak is considered.

Despite exfoliation to remove the rough surface, no pH which is consistent with the findings reported in [18].

It is standard practice to use an excitation power in the range of 5 uW to 5 mW to prevent damage to the sample [15, 17].

However, the damage threshold is dependent on the power density, and neither the beam size nor the damage threshold is known. In order to get an understanding of the saturation of the sample the power scaling was measured.

The resulting spectra for different excitation powers are shown in Figure 2.15. No unexpected drastic changes that would indicate damage to the sample are visible.

To gain a more comprehensive understanding, the main peak can be integrated. This is shown relative to the excitation power in Figure 2.16.

For NiPS₃, a quadratic function fitting indicates a linear scaling that begins to saturate at higher excitation powers.

For CrPS₄, the scaling is faster than linear, which can be explained by a scaling probability of creating biexcitons additionally to the exciton photoluminescence process [19].

Since a power law fit is commonly used to describe the scaling the fit is also shown.

In order to achieve a good signal-to-noise ratio while avoiding saturating the sample, the excitation power was selected to be in the range of 1 mW to 4 mW.

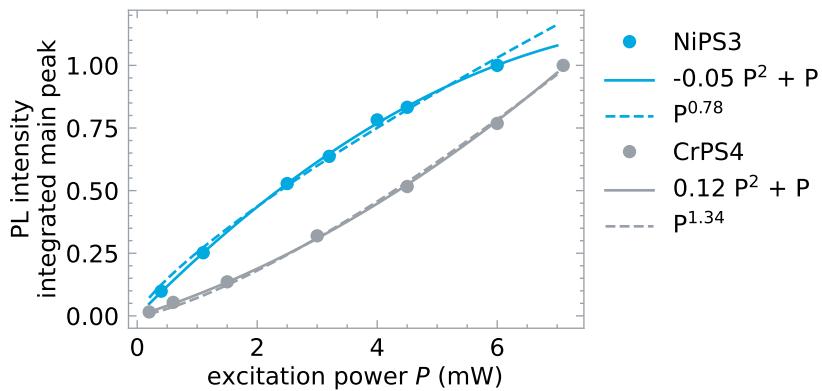


Figure 2.16 Excitation power dependence of the main photoluminescence line at 10 K with a quadratic and power law fit.

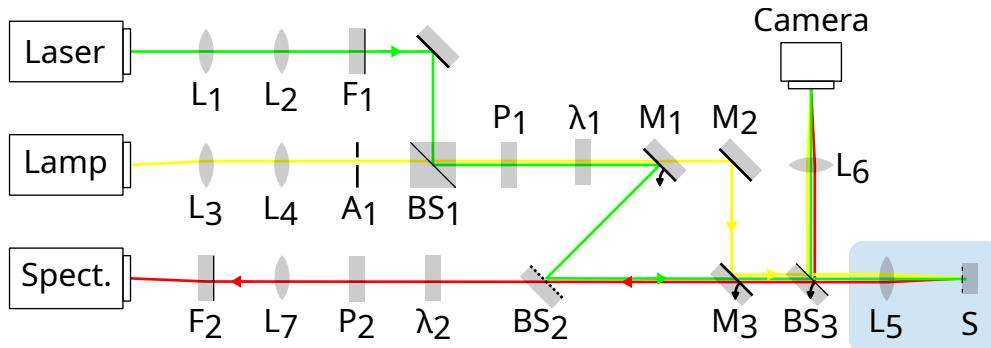


Figure 2.17 Full schematic at the end of the measurements.

Even when illuminated with 20 mW, the sample did not exhibit any signs of damage.

However, following multiple measurements, the photoluminescence ceased in some NiPS₃ flakes.

This is not due to the excitation, as this also occurred in flakes that were not excited. It is caused by oxidation during storage and manipulation of the samples.

There were no visible changes to those samples on optical microscope images.

2.3 Measurement Setup

Upon completion of the measurements, the optical table had a few additional components not depicted on the simplified schematic Figure 2.13. The full schematic is presented in Figure 2.17.

make left on page

The sample S could be illuminated with a fiber-coupled array of diode lasers, a fiber-coupled halogen lamp, and subsequently a white LED. The lenses L_{1-4} were used to expand the cross-section in order to utilize the entire size of L_5 .

F_1 was a film filter used to block out the detection wavelengths from the excitation light. Additionally, it creates a sharper spectral edge on the laser line for Raman spectroscopy.

The aperture A_1 was mounted off-center to illuminate the sample in a dark-field configuration, thereby increasing the contrast in the camera image. Thanks to *Mateusz Raczyński* for showing me this trick.

These two illumination paths were combined with cube beam splitters BS_1 . The polarizer P_1 and the retarder λ_1 were used to control the polarization of the light.

Then the mirror M_1 and the beam splitter BS_2 were used to introduce the light into the detection path without changing the polarization too much.

To get more light for the camera M_1 could be flipped out and M_3 could be flipped in. This obstructs the spectrometer and compromises the polarization of the light, but increases the intensity by a factor of two.

BS_3 was just used to image the sample with the camera. It was a film beam splitter with a large aperture that has to be removed for polarization-sensitive measurements, as it is strongly polarizing.

The objective lens L_5 was on an x-y-z piezo stage in the cryostat to move and focus on different flakes of the sample.

The cryostat and the magnet are combined in a single unit since the 10 T superconducting magnet needs a helium reservoir. The sample was in a variable temperature insert (VTI) with a controllable helium cooling flow and an electric heater. The magnet has metal heat shields in the vacuum isolation layer and a nitrogen jacket to isolate it even more. Both isolation methods had problems:

The metal heat shield was bent on the magnet that was supposed to be used for the measurements. This bridged the nitrogen and helium reservoir, which caused the helium to boil off pretty quickly. But only when the VTI was cooled down, due to thermal contraction.

At the end of the measurements, somebody forgot to renew the contract with the company delivering the nitrogen, but they still delivered to the end of my measurements.

The light from the sample then goes through the retarder λ_2 and the polarizer P_2 to control the analyzed polarization.

The retarder λ_2 was mounted on a computer-controlled rotation stage and connected to the PyLUMS software stack originally developed by *Tomasz Kazimierczuk*, who was also of great help in solving numerous technical problems.

The light then was focused by the lens L_7 into the spectrometer. L_7 had a focal length of 20 cm arbitrarily chosen by the previous user.

The interference filter F_2 was used to block out the excitation light from the spectrometer and is placed as close to the spectrometer as possible to block out all the stray excitation light.

For Raman measurements, the filter was tuned by rotating it to change the effective thickness of the interference film. *Jan Suffczyński* helped to set up the Raman measurements, as he has measured it on NiPS₃ before.

The used spectrometer was a *ANDOR SR-500i* with a piezo-cooled CCD sensor and a 1200 lines/mm grating.

3 Results

3.1 NiPS₃: Splitting and Rotation

First NiPS₃ was investigated due to the sharp photoluminescence (PL) line. This was done with exfoliated flakes on a Si/SiO₂ substrate for easier handling.

When an external magnetic field H is applied to the sample in the natural a - b plane of the crystal, the photoluminescence line observed from the plane normal splits into two lines. This is shown in [Figure 3.1](#) for different detection polarizations P .

The amount of splitting ΔE is different for different polarization directions. In the polarization direction where the external magnetic field H is aligned with the electric field of the photoluminescence signal $P \parallel H$, the splitting ΔE is larger than in the perpendicular direction $P \perp H$.

To directly determine ΔE the sum of two Gaussian peaks was fitted, with the peaks centered at $E \pm \Delta E/2$ with the same amplitudes I and widths σ . As the recorded line was much narrower

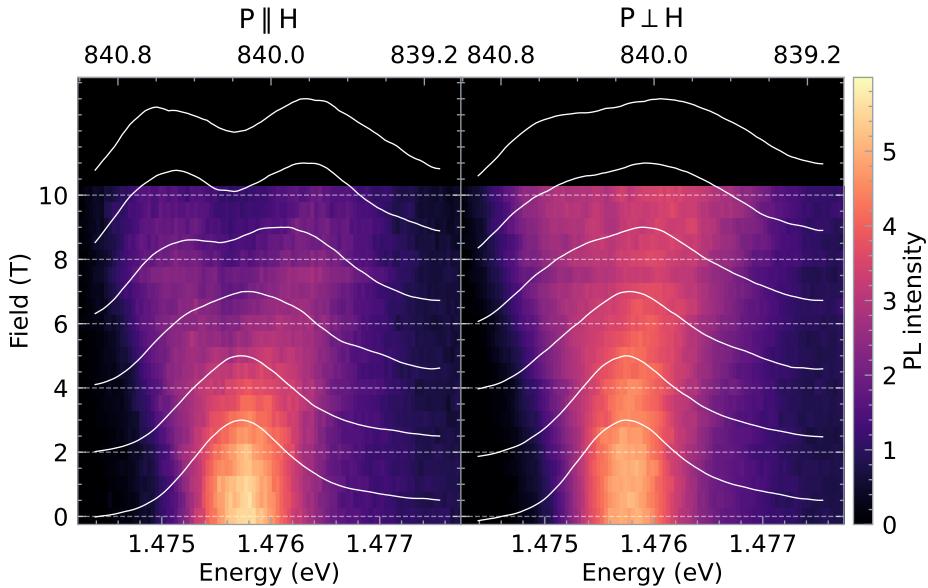


Figure 3.1 Photoluminescence intensity in NiPS₃ for different polarization directions P to applied external magnetic field H at 5 K.

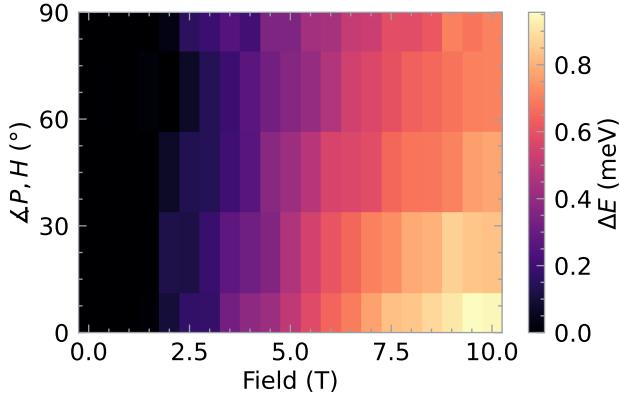


Figure 3.2 ΔE measured with bi-gaussian fit.

than the focus of the spectrometer, σ was fixed at a constant value [20]. E and I were fitted independently for each measurement over field and polarization angle, as the turning retarder and the field-dependent moving sample holder altered the position of the focus on the spectrometer and the focus on the sample, thereby changing E and I respectively. The resulting splitting ΔE is shown over the field and polarisation angle in Figure 3.2.

This measurement was repeated for different samples and at different temperatures. Representative results are shown in Figure 3.3. In most flakes, the splitting was not as clear as in Figure 3.1. It was either a broadening of the line as shown in Figure 3.3a or multiple overlapping splitting curves as shown in Figure 3.3b for 50 K.

At higher temperatures, the photoluminescence peak was broader and the splitting was not visible, as shown in Figure 3.3c. Above 50 K the photoluminescence could not be measured over the field, and thus the phase transition to paramagnetic at the Néel temperature of 155 K [3] can not be observed with this method.

No hysteresis was observed over the magnetic field in any of the measurements.

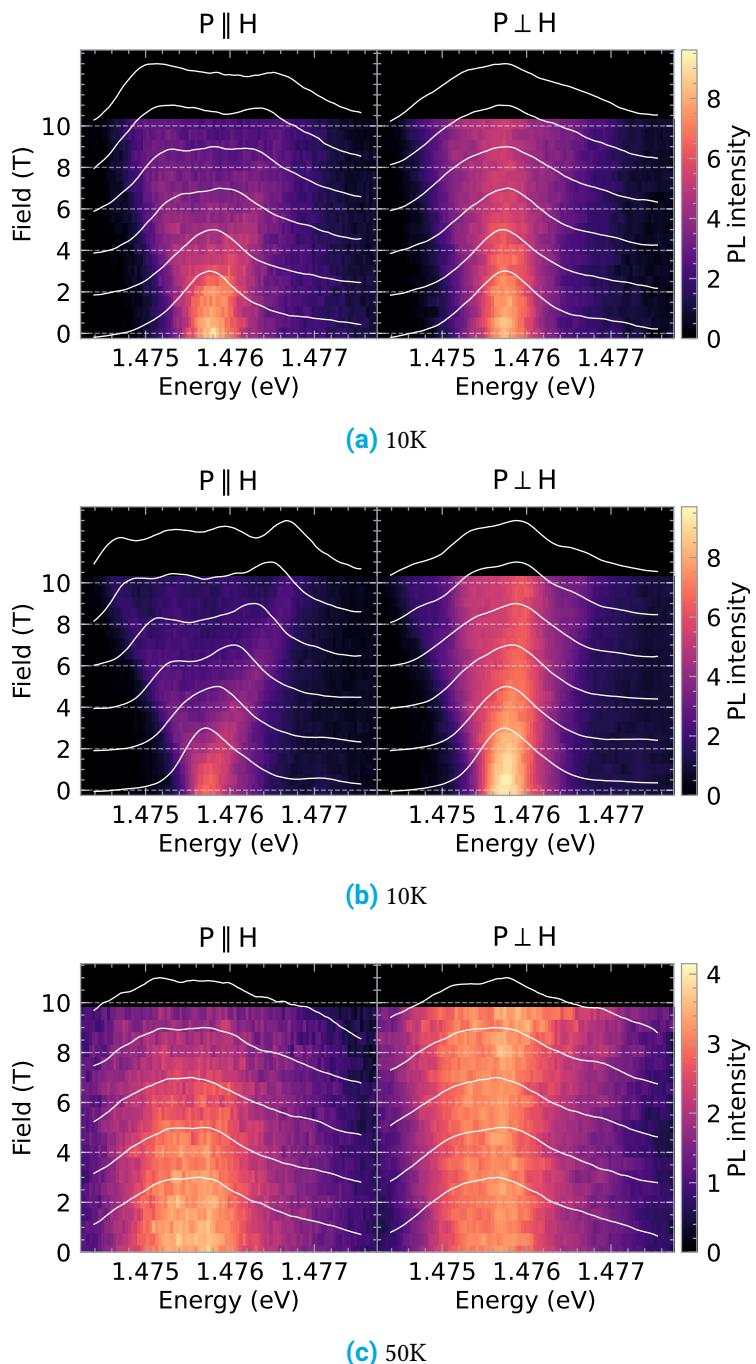
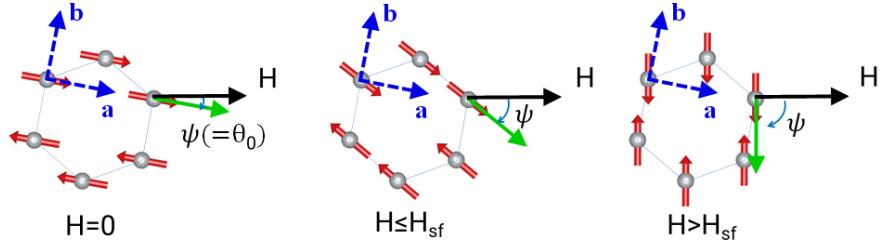
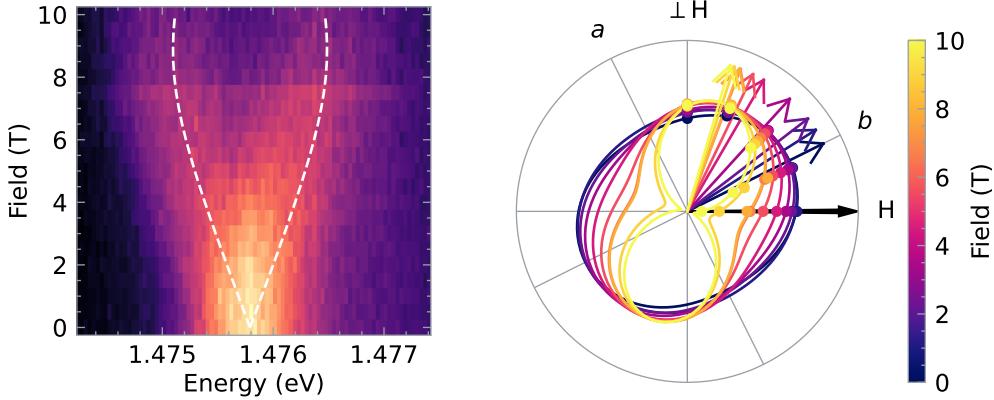


Figure 3.3 Splitting of the NiPS₃ photoluminescence line at different temperatures on different flakes.



(a) Model for the photoluminescence signal in NiPS₃, with the spins of the Ni²⁺-ions in the *a*-*b* crystal plane. Adapted from [20, Figure S2].



(b) Recorded data for $P \parallel H$ at 5 K, with (c) fit for ΔE with $\theta_0 = 27^\circ$ according to model Equation 3.2 from [20].

(c) Integrated photoluminescence signal of the main peak for different polarizations. With a \cos^2 fit, to show the polarization axis. The *a* and *b* crystal axis are inferred from the polarisation at $H = 0$ [14].

Figure 3.4 Different models for the photoluminescence signal in NiPS₃.

To understand the observed splitting of the photoluminescence line, a model from [20] can be used, as the splitting was already observed there. A mean-field biaxial antiferromagnet model was proposed, that defines the angle ψ shown in Figure 3.4a between the spin of the Ni²⁺-ions and the external magnetic field \vec{H} . For $H = 0$ the spin aligns with the *a*-crystal axis, and thus, the initial angle $\theta_0 = \psi(H = 0) = \angle(a, H)$ can be defined. The coupling constants along the axis of the model reduce to an effective g factor and a spin-flop field H_{sf} . Consequently, the proposed model [20] yields the following results:

$$\tan 2\psi = \frac{\sin 2\theta_0}{\cos 2\theta_0 - \frac{H}{H_{sf}}^2} \quad (3.1)$$

$$\Delta E = \mu_B g H \cos \psi \quad (3.2)$$

This model does not include polarization-resolved differences as ΔE is independent of the polarization angle. This is not observed in Figure 3.2. Nevertheless, by selecting a single polarization the model fits the data, as shown in Figure 3.4b. Even the same $H_{sf} = 10.55$ T and $g = 2.0$ from [20] fit the data.

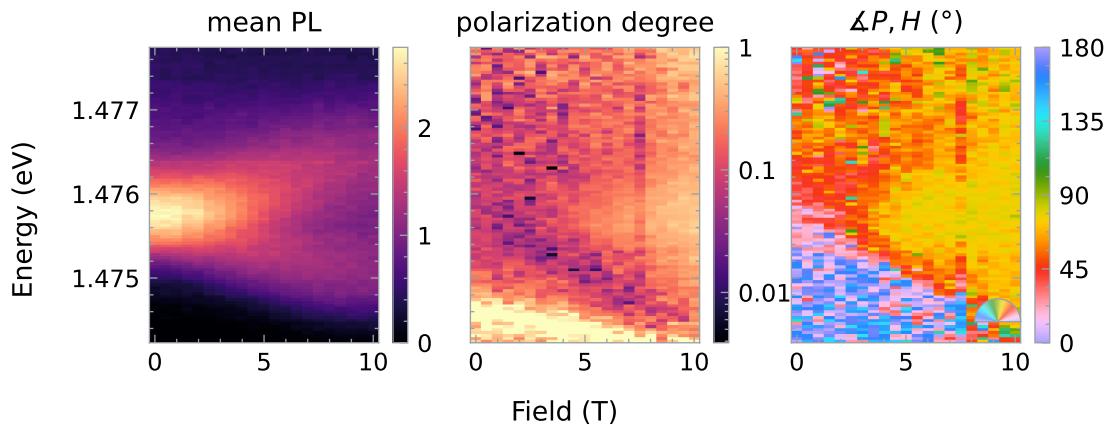


Figure 3.5 Results from the \cos^2 fit spectral resolved at 5 K.

With this model the overlaid splitting curves in Figure 3.3b can be understood as poly-crystalline or cracked flakes with rotated orientations of the *a* and *b* crystal axis and therefore different splitting curves. This was confirmed by manufacturing a sample with more exfoliation steps to get thinner flakes, which yielded clearer splitting curves.

The linear polarization can be explained by the origin of the photoluminescence. The main peak is caused by the transition from the Zhang-Rice triplet to the Zhang-Rice singlet state [2]. The spins of the free electrons in the Ni *d* orbital and the S *p* orbital are the same for the triplet state and the opposite for the singlet state [2], which results in a change in angular momentum during the transition. The difference in angular momentum ΔS is parallel to the spin alignment axis in the *a-b* plane. ΔS is carried away by a circularly polarized photon in the *a-b* plane and is not detected [14]. Viewed from the plane normal, this is a changing dipole that emits a linearly polarized photon with a polarization perpendicular to the spin alignment [14].

This was used to observe a magnetic field dependent rotation of the polarization from perpendicular to the *a* crystal axis to perpendicular to the magnetic field in [14]. This is reproduced in Figure 3.4c, which depicts the main peak of the photoluminescence signal measured with different polarisation angles and a \cos^2 fit. The peak was integrated from 839 nm to 841 nm.

However, the peak does not behave uniformly. To examine the polarization direction, the data can be displayed by fitting the \cos^2 function for every wavelength and field individually. The average intensity, polarization angle, and degree can be extracted. This is shown in Figure 3.5. As previously stated the photoluminescence line splits less when $P \perp H$ than when $P \parallel H$. In the $\angle P, H$ -panel this is evident as a rotation of the polarization in the center of the line from 30 to 90°. The photoluminescence background below the main peak is polarized parallel to the magnetic field, resulting in an angle of 0 or 180°. In between there is a visible line where the angle is 45 degree. This can simplify the presentation of the data, as two images in Figure 3.1 are combined into one.

In order to quantify the degree of polarization, it is necessary to define a reference level. The background level was selected as the photoluminescence signal next to the peak, evaluated as

the mean between 845 nm to 860 nm.

The much lower polarization degree in [Figure 3.5](#) compared to near unity in [17] can be again explained by poly-crystalline flakes with different orientations of the crystal axis and therefore different polarization directions.

The measurement of polarized photoluminescence shows that the luminescence process is more complex than previously understood and more theoretical work is needed to explain it fully.

3.2 CrPS₄ Circular Dichroism

CrPS₄ was examined next, as the photoluminescence behavior under a magnetic field was not yet documented. The photoluminescence signal in CrPS₄ exhibited a notably stronger and broader profile compared to NiPS₃. No observable splitting or displacement of the peak in the photoluminescence signal was detected in response to changes in the magnetic field. Additionally, even though the photoluminescence signal in CrPS₄ was strongly linear polarization (see [Figure 3.6](#)), no rotation over the external magnetic field was observed.

The circular dichroism of the photoluminescence in CrPS₄ in [Figure 3.7a](#), had a clear non-hysterical change over the magnetic field.

It is evaluated by integrating over the main photoluminescence peaks from 890 nm to 970 nm. This reduces noise and is necessary to measure such small differences with the spectrometer. However, there is no significant difference in the circular dichroism over the wavelength, so the spectrometer is not necessary. The selection of the zero level for calculating the dichroism is obvious, as there is no significant difference if it is taken sufficiently far away from the photoluminescence peak or without the excitation.

The measured circular dichroism signal correlates perfectly with magneto torque measurements of the magnetization (see [Figure 3.7b](#) from [5]) in all measured magnetic field configurations and temperatures. However, the corresponding authors have thus far not provided their data for quantitative comparison. But at least from qualitative comparison, the circular dichroism of the photoluminescence line is proportional to the magnetization in CrPS₄.

Additional theoretical work is necessary to explain this effect. The main photoluminescence peak is attributed to a simple transition between doublet states in the Cr³⁺-ions in [16]. Nevertheless, this phenomenon can already be used to measure the magnetization. The phase transitions are visible as distinct changes in the magnetization curve in [Figure 3.7a](#). The spin-flop transition at 0.8 T and the spin-flip phase transition at 7.5 T can be observed, matching the magneto torque measurements [5].

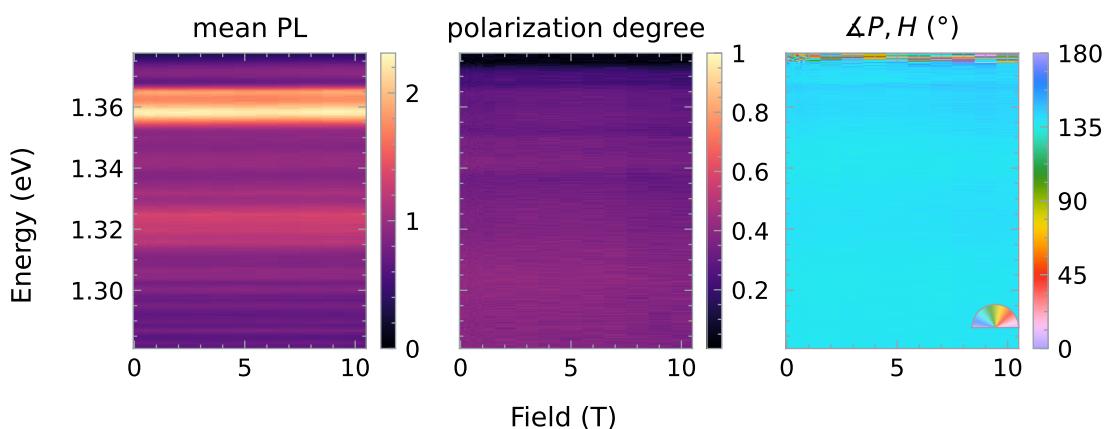
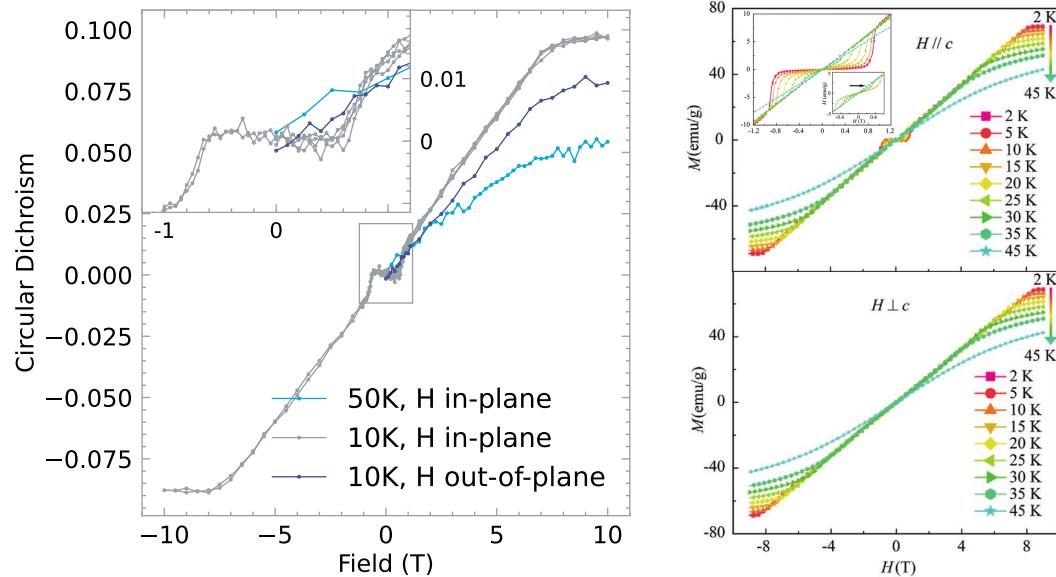


Figure 3.6 Linear polarization of CrPS₄ at 10 K.



(a) Circular dichroism of the photoluminescence in CrPS₄. (b) Magnetisation measured using magneto torque. Adapted from [5, Figure 2].

Figure 3.7 Comparison of circular dichroism of the photoluminescence line and the magnetization in CrPS₄.

The method is not yet suitable for absolute magnetization measurement, as the circular dichroism to magnetization ratio differs between flakes. This might depend on the thickness of the flakes.

At higher temperatures, the photoluminescence signal broadens and the intensity decreases, as shown in Figure 3.8. Differently to NiPS₃ the photoluminescence signal is visible up to room temperature. This is promising for studying the phase transitions to paramagnetic at the Néel temperature of 38 K [5], which allows for this method to be used to study the entire magnetic phase diagram of CrPS₄.

In conclusion, the circular dichroism of the photoluminescence signal in CrPS₄ allows for fast and localized measurements of the magnetization, that were not possible with previous methods.

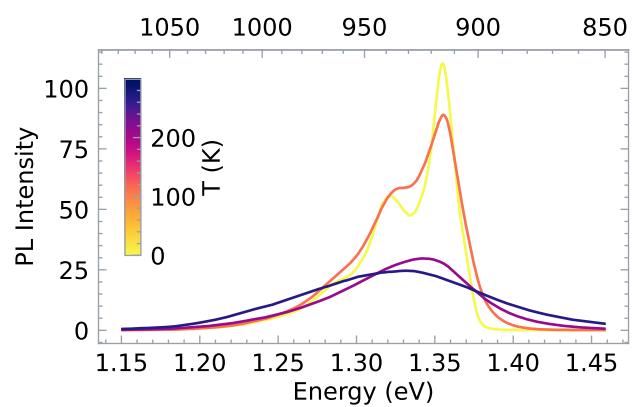


Figure 3.8 Photoluminescence for different temperatures.

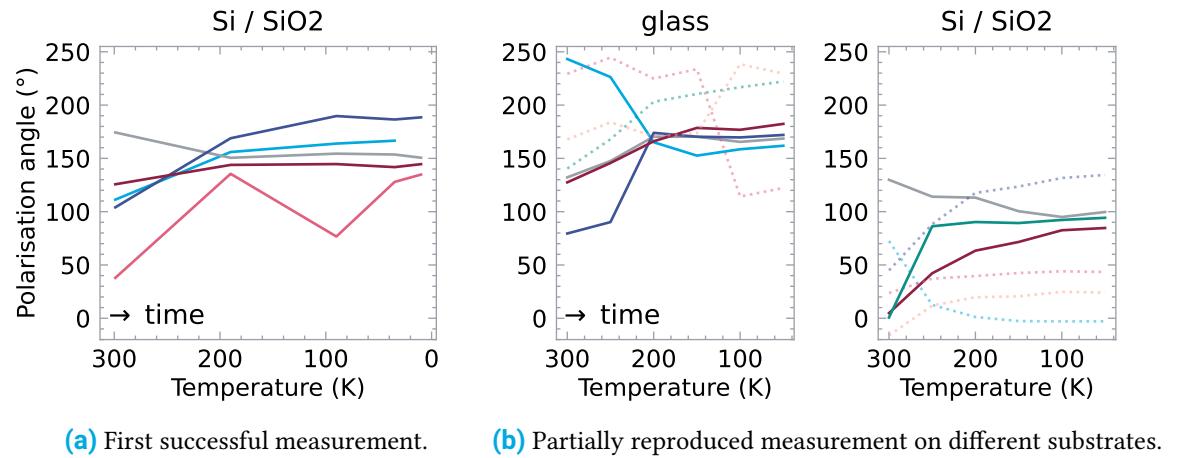


Figure 3.9 Rotation of the linear polarization of the photoluminescence signal in CrPS₄ during cooling.

3.2.1 Aligning Flakes

After a few days of measurements on CrPS₄, the linear polarization of the photoluminescence signal from all the flakes was aligned in the same direction. This is unexpected for out-of-plane magnetic field measurements, as there was assumed to be no inherent axis in the plane and therefore symmetry for the in-plane rotational degree of freedom.

This was measured more systematically by creating new samples without any alignment in the exfoliation process. For this, the adhesive tapes were rotated to arbitrary angles at each subdivision step and the transfer step was performed multiple times at different angles.

Then the linear polarization of several flakes was recorded during the cooling process, with particular care taken to ensure that no bias for one axis was introduced in the measurement. Images were taken at each temperature in order to determine if the entire flake rotated or just the photoluminescence signal.

The initial measurement [Figure 3.9a](#) confirmed that the photoluminescence of all recorded flakes, which were randomly oriented at room temperature, aligned to a single orientation at temperatures around 200 K. No rotation was observed in the images of the flakes, indicating that just the photoluminescence signal was rotating.

It was suspected that the Si lattice of the Si/SiO₂ substrate introduces an alignment direction. Therefore, a glass substrate was used, which should not have a preferred axis. The results are presented in [Figure 3.9b](#), along with a new Si/SiO₂ sample to reproduce the aforementioned result. However, in this experiment not all flakes aligned, which indicates a significant variance in the sample preparation. Nevertheless, the alignment directions are different, indicating that the directionality is not from the experimental setup. The images of the flakes show no correlation between the alignment and the shape or size of the flakes. Furthermore, the alignment does not correlate with the distance to neighboring flakes or the substrate material.

Following the measurements, *Julia Kucharek* helped me to record atomic force microscopy

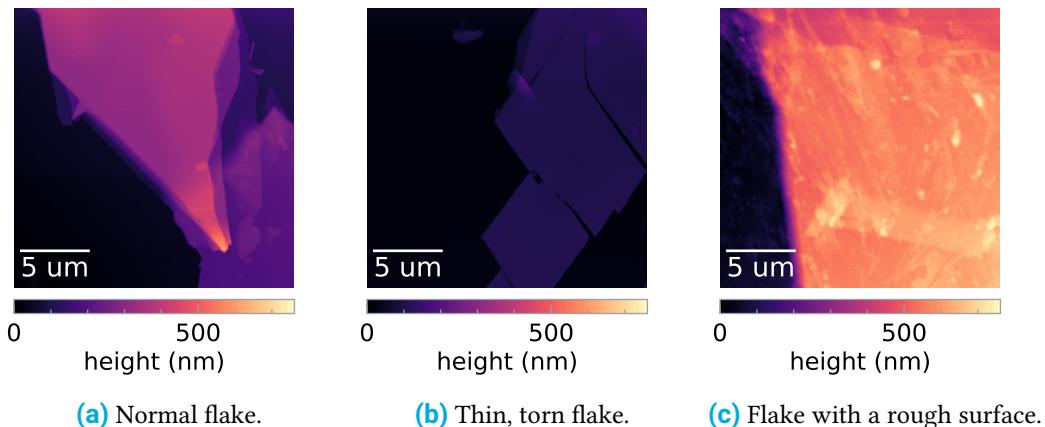


Figure 3.10 Atomic force microscopy images of CrPS₄ flakes.

images of the samples. The flakes had a thickness ranging from 200 nm to 700 nm, as shown in [Figure 3.10](#).

In the case of the sample where all flakes aligned, all flakes had a smooth surface like in [Figure 3.10a](#) and [Figure 3.10b](#).

On the samples where not all flakes aligned, some flakes had a rough surface, as shown in [Figure 3.10c](#). This rough patch extended over the flakes' boundary to the bare substrate. This is likely residue from the adhesive used in the exfoliation process.

Additionally, thinner flakes on the Si/SiO₂ substrate had cracks in the surface as shown in [Figure 3.10b](#). The observed cracks appear to be mechanical stress fractures. The origin of these cracks, whether due to unequal thermal expansion or from the mechanical exfoliation process, remains unclear.

The source of the alignment remains unknown. Further research is needed because it is an unknown influence on possibly similar measurements.

4 Conclusion and Outlook

In this work, polarized photoluminescence spectroscopy was identified as the most promising method for studying the magnetic properties of transition metal phosphorus sulfides, following an exploration of various methods. The findings reveal a higher complexity in the photoluminescence process of the studied materials than was previously understood.

Specifically, the linearly polarized photoluminescence in NiPS₃ exhibits a distinct splitting for different polarization directions, challenging current models [2, 14, 20]. Consequently, the objective now is to find a model for the photoluminescence process that can account for these measurements.

The investigation into CrPS₄ uncovered a correlation between the circular dichroism of the photoluminescence signal and the magnetization. The observed proportionality offers a novel method for measuring the magnetization that is faster and more localized than previous methods. With this method phase transitions have been observed, indicating its potential for studying the entire magnetic phase diagram of CrPS₄. However, this challenges our current understanding of the photoluminescence process in this material, necessitating further research into the underlying mechanisms. As of the time of writing, additional data is being recorded by the group in Warsaw to enhance the reliability of the results.

During these measurements, an unexpected alignment of the linear polarization of the photoluminescence signal was observed in CrPS₄ during cooling. Despite efforts, the cause of this alignment could not be identified in the scope of this work. Understanding the mechanism behind this alignment is crucial, as it may have implications for similar experiments. The next steps are obvious: Capturing atomic force microscopy images post-exfoliation to determine whether flakes are already torn. Modifying the temperature during the transfer step in exfoliation to investigate potential correlations with the rough surface, thereby confirming the presence of glue residue. Washing away the glue to confirm its stabilizing effect on the flakes. Experimenting with substrates with diverse thermal expansion coefficients to assess potential influence on the alignment. However, all these procedures necessitate a statistical argument, demanding numerous samples. Nonetheless, it presents an opportunity for a future student to continue.

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Data Availability

All the recorded data and software used for the analysis and documentation are available publicly at https://github.com/leole100/bachelorarbeit_public.

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Konstanz, den 2. Mai 2024