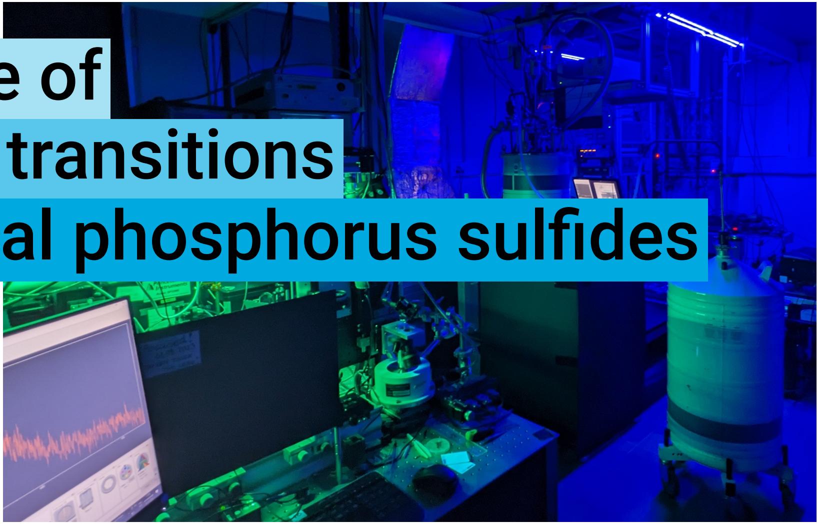
UNIVERSITY OF WARSAW

Universität Konstanz

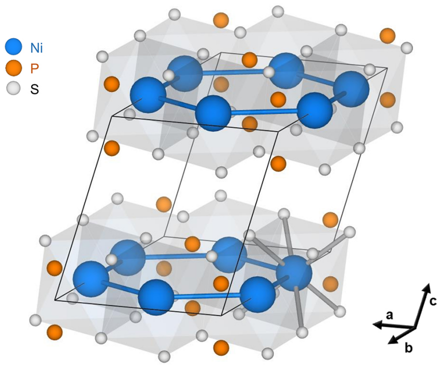
Optical signature of magnetic phase transitions in transition metal phosphorus sulfides



Bachelor Project of Leon Oleschko
11.04.2024

Supervised by Dr. Mateusz Goryca
to be reviewed by Prof. Dr. Sebastian Gönnenwein

Transition Metal Phosphorus Sulfides

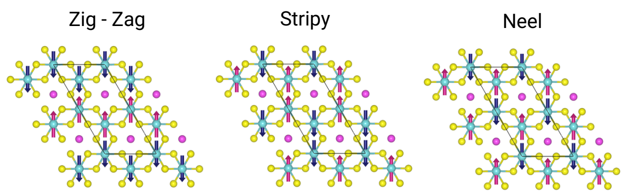


Soonmin Kang et al. “Coherent many-body exciton in van der waals antiferromagnet NIPS3”. In: **Nature** 583.7818 (July 2020), pp. 785–789. DOI: 10.1038/s41586-020-2520-5

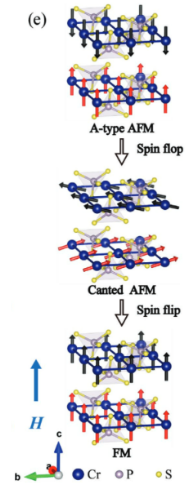
$MPS_{3/4}$ with M = Ni, Cr, Mn, Fe

- Van-der-Waals layered materials
  $\Rightarrow$ easy exfoliation
- Bandgaps in the visible range to near infrared
  $\Rightarrow$ Easy to optically study
- Anti-ferromagnetic order with different anisotropic coupling
  $\Rightarrow$ Complex magnetic structures, especially around single layers

$\Rightarrow$ Higher Probability of Excitons due to constrain in layers



Christopher Lane and Jian-Xin Zhu. “Thickness dependence of electronic structure and optical properties of a correlated van der waals antiferromagnetic NiPS3 thin film”. In: **Physical Review B** 102.7 (Aug. 2020). DOI: 10.1103/physrevb.102.075124

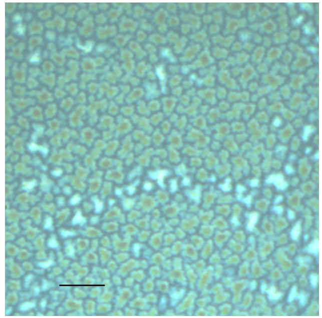


Yuxuan Peng et al. “Magnetic structure and metamagnetic transitions in the van der waals antiferromagnet CrPS4”. In: **Advanced Materials** 32.28 (June 2020). DOI: 10.1002/adma.202001200

Sample preparation

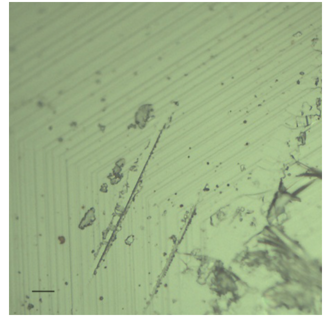
Bulk samples in 20mm vials

Not prepared by me using vapour transport method



$FePS_3$, Scalebar 10μm

Dirty Surface of bulk sample

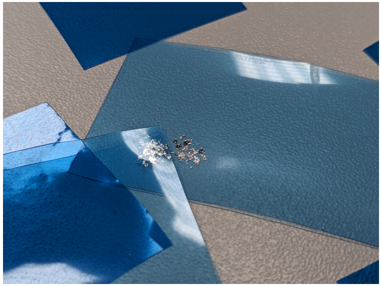


$NiPS_3$, Scalebar 10μm

Clean surface of a different sample for comparison

Exfoliation

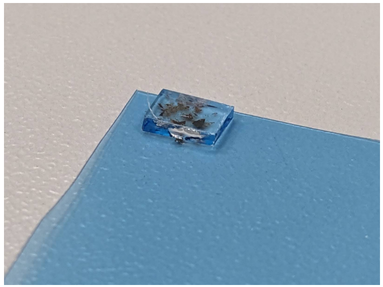
Subdividing the bulk crystal into thin flakes



Every subdivision reduces the mean thickness by a factor of 2
$N \sim 6$

$$d \approx 400 \text{ um} \mapsto \langle d \rangle = d \cdot 2^{-N} \approx 6 \text{ um}$$

Transferring the flakes onto a substrate

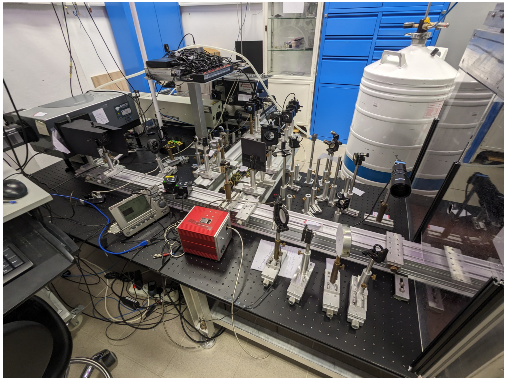


Transferring filters the flakes roughly by thickness:

$$6 \text{ um} \mapsto 400 \text{ nm}$$

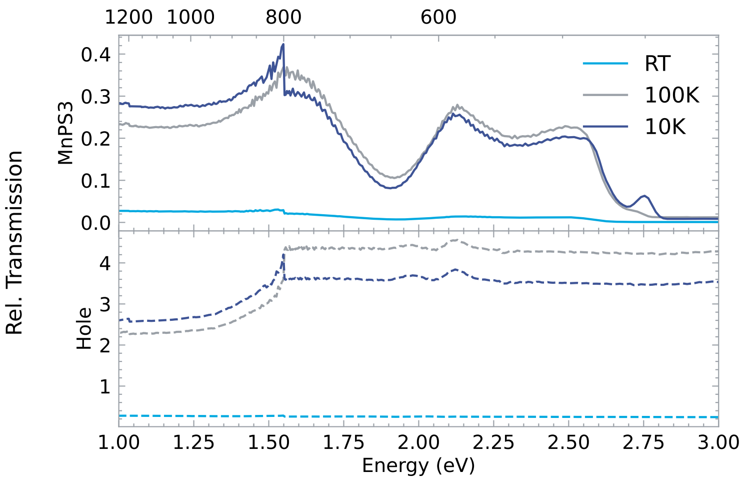
$CrPS_4$ flakes on Si/SiO_2 substrate, Scalebar 10μm

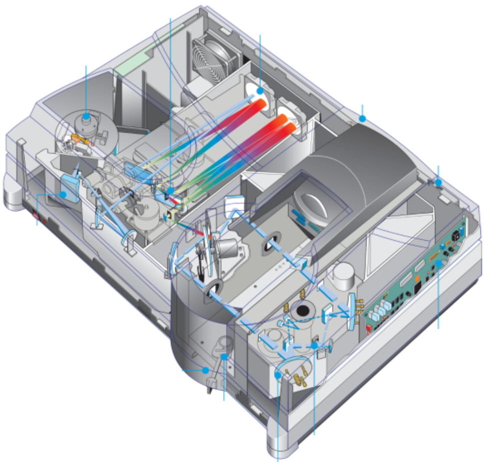
- Easy to exfoliate on Si/SiO_2 substrate at room temperature
- Glass substrates has lower yield
- Samples degraded after a couple days at room conditions



Raw measured relative Transmission

$$T_{Relative} = \frac{T_{\text{Sample}}}{T_{\text{Reference}}}$$

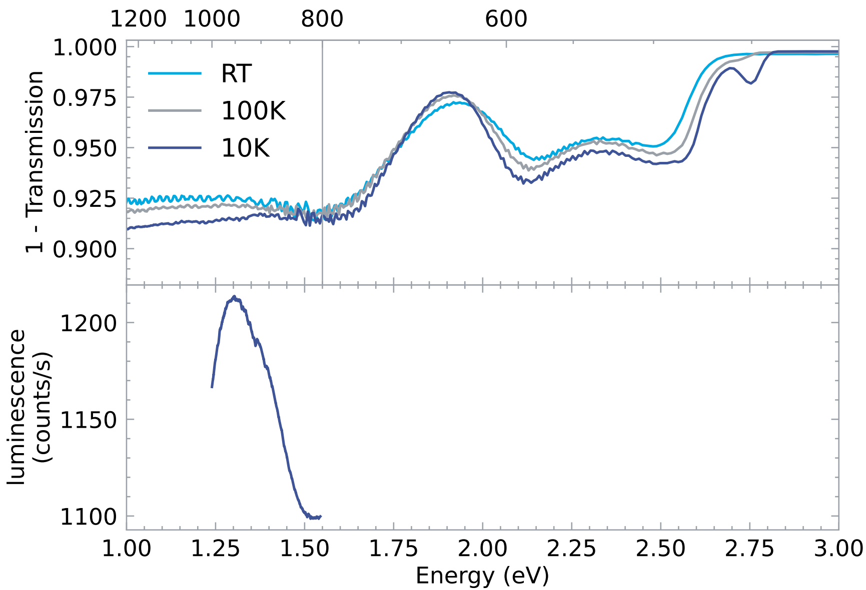




Inc. Agilent Technologies. **Agilent Cary 4000/5000/6000i Series UV-VIS-NIR Spectrophotometers**. 2020. URL: https://www.agilent.com/cs/library/brochures/5990-7786EN_Cary-4000-5000-6000i-UV-Vis-NIR_Brochure.pdf

Corrected Absorbance

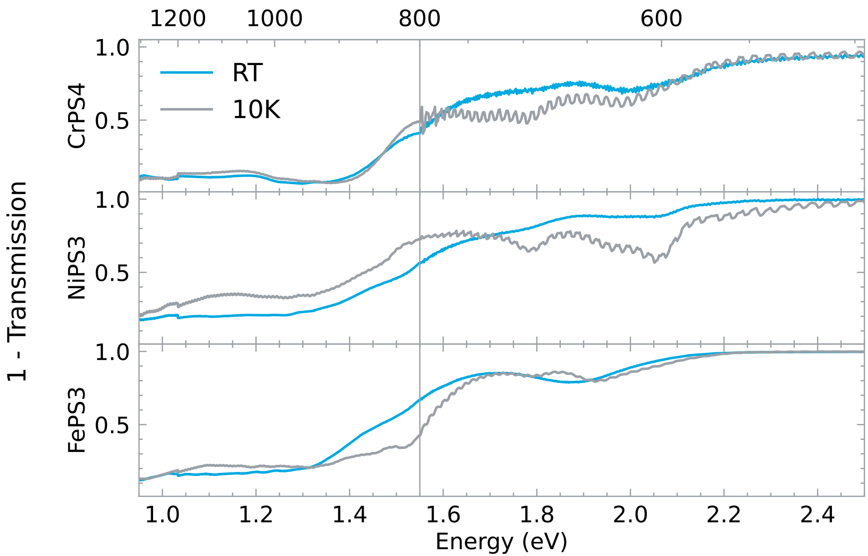
$MnPS_3$ Absorbance with Photoluminescence:

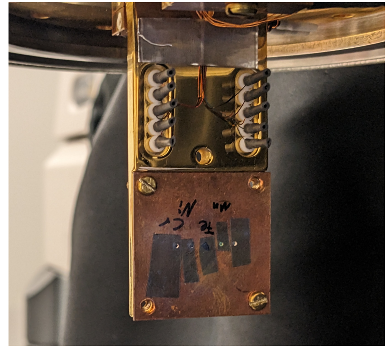


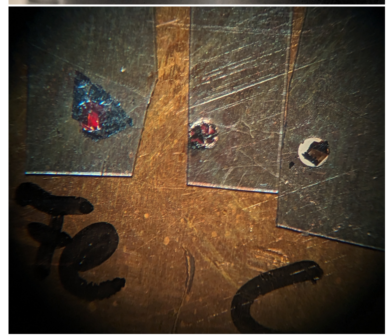
$$T_{Relative} = \frac{T_{\text{Sample}}}{T_{\text{Reference}}}$$

$$T_{Measured} = T_{\text{R, Sample}} \div T_{\text{R, Hole}}$$

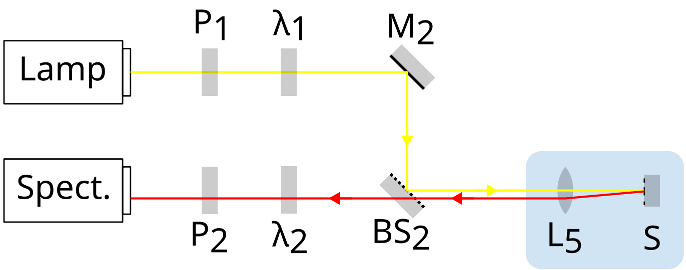
Different Samples





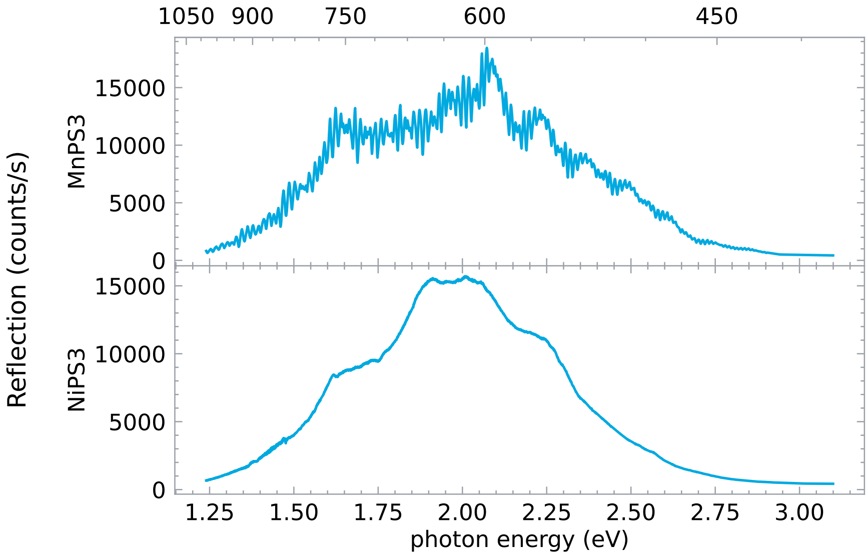


Setup for Reflection



- Polarizer P_1 and Retarder λ_1 remove excitation polarisation dependence
- Polarizer P_2 and Retarder λ_2 allow to detect different polarisations
- Beamsplitter BS_2 is a Polka-dot mirror to minimize the influence on polarisation
- Lens L_5 has strong Chromatic Aberration

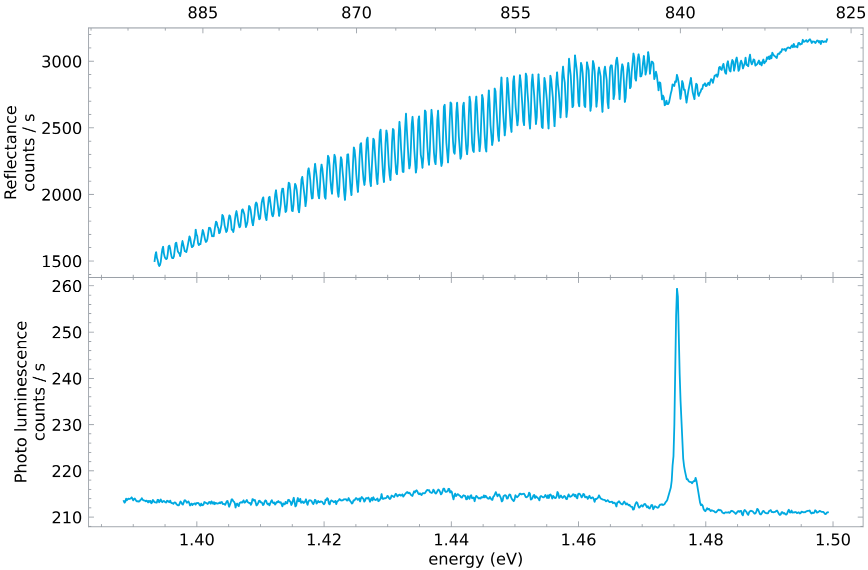
Reflection Spectra



Measured Spectra with broad shape from Halogen Lamp

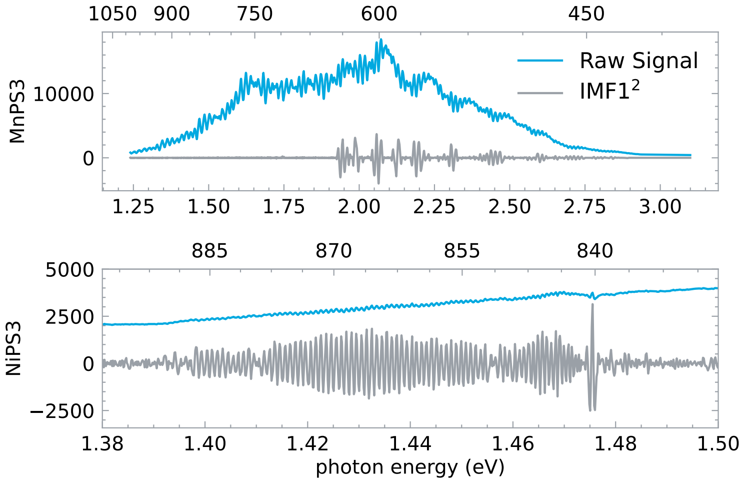
Reference using Mirror was difficult due to Chromatic Aberration of the last lens

NiPS3: Reflection of bulk sample



Thin film Interference below Bandgap, where the material is transparent

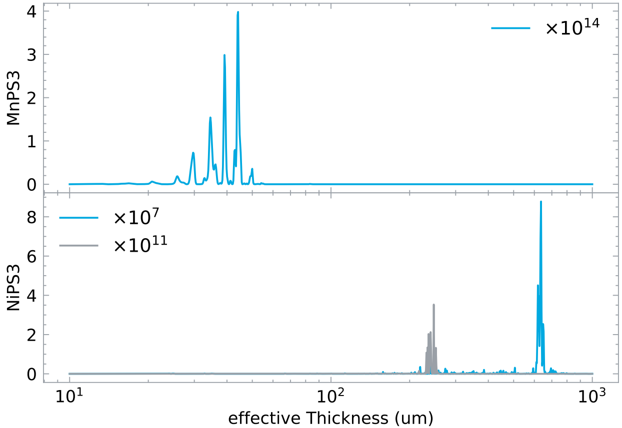
Empirical Mode Decomposition

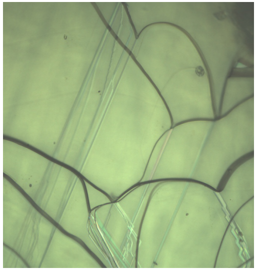


Idea for EMD: Jiaxing Sun et al. “A method for measuring and calibrating the thickness of thin films based on infrared interference technology”. In: **Results in Physics** 51 (Aug. 2023), p. 106727. DOI: 10.1016/j.rinp.2023.106727

EMD $\sim$ Low Pass filter to Filter out Spectrum of Halogen Lamp

Thickness Estimation of Bulk Crystals





MnPS$_3$

Different layers of cracks visible in a microscopy image

$$R(\lambda) = \cos 2\pi \cdot 2nd \cdot \frac{1}{\lambda}$$

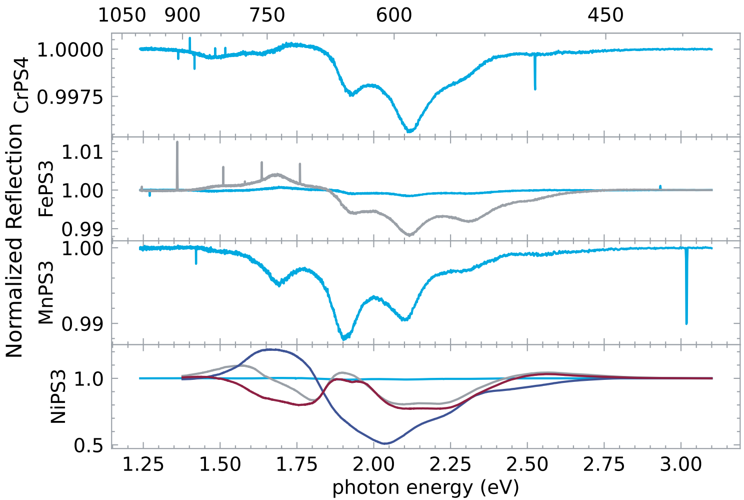
$$\Rightarrow P_\nu(nd) = \mathcal{F}\left[R\left(\frac{1}{\lambda}\right)\right](2nd)$$

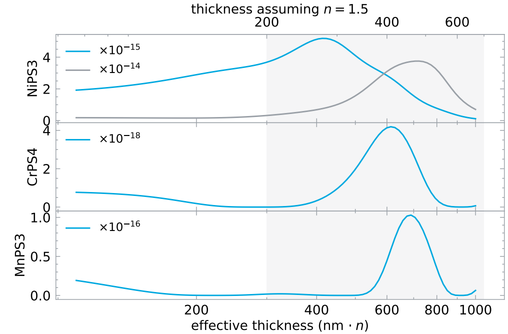
$$\approx \mathcal{F}\left[\mathrm{IMF}_1\, R\left(\frac{1}{\lambda}\right)\right](2nd)$$

$\mathcal{F}$: Lomb-Scargle method due to unevenly sampled data

Reflection on exfoliated samples

$$R = \frac{R_{\text{flake}}}{R_{\text{substrate}}}$$





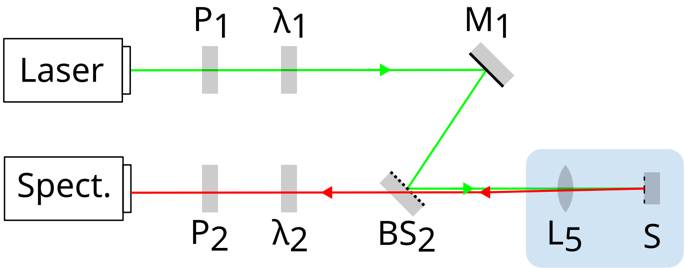
Extracted thickness matches with AFM measurements

Source for $n \sim 1.5$: A. R. Alcantara et al. "Parameter-free treatment of a layered correlated van der waals magnet: CrPS4". In: **Physical Review B** 108.15 (Oct. 2023). DOI: 10.1103/physrevb.108.155133

$\Rightarrow$ 3 Interface Interference: Vacuum - Flake - SiO_2 - Si

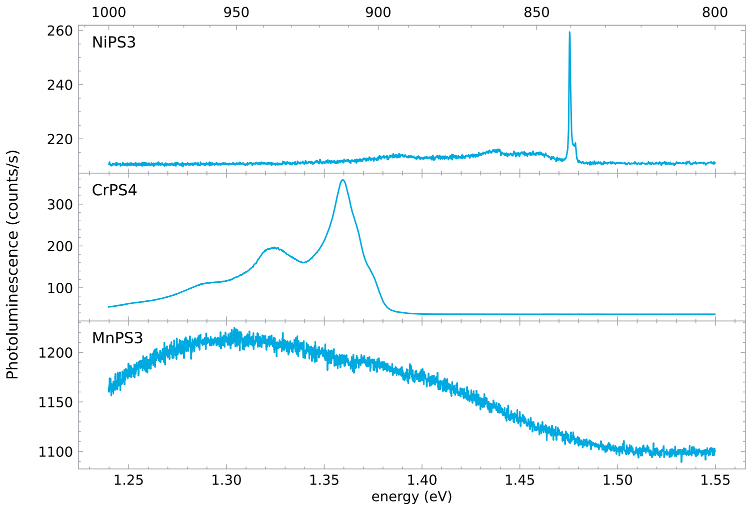
$\Rightarrow$ Bandgap not visible

Setup for Photoluminescence



- Polarizer P_1 and Retarder λ_1 remove excitation polarisation dependence
- Polarizer P_2 and Retarder λ_2 allow to detect different polarisations
- Beamsplitter BS_2 is a Polka-dot mirror to minimize the influence on polarisation
- Lens L_5 has strong Chromatic Aberration
- Laser Wavelengths: 532 nm and 647 nm with up to 10 mW before L_5

Photoluminescence at 10K



Expected splitting of the photoluminescence line
$\Rightarrow$ the $MnPS_3$ peak is too broad

Excited with 532 nm and 647 nm laser: no difference in main peak

No degradation of the sample with up to 10 mW laser power

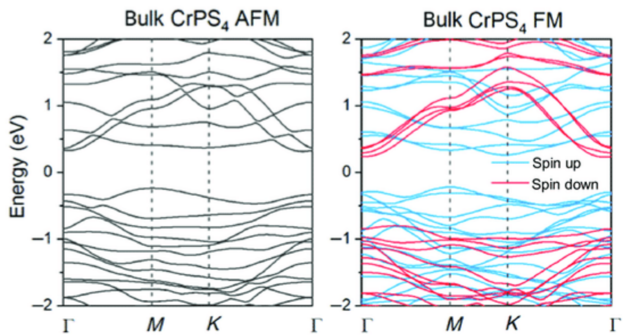
Model for Photoluminescence

Exciton Model:

- Bound electron-hole pair gets created by excitation photon $E > E_{\text{Bandgap}}$
- Exciton decays by phonon emission with $E_{\text{Bandgap}} - E_{\text{Binding}}$
- E_{Binding} split with Zeeman effect
- Exciton has a magnetic moment
  $\Rightarrow$ aligns with B field
  $\Rightarrow$ linear polarisation if M in-plane, circ. polarisation if out-of-plane

Single Particle Model:

- Field dependent (possibly complicated) band structure
  Can be calculated with DFT
- With some emitting transitions
- electron Spin dependent transitions
  $\Rightarrow$ Circular Polarisation

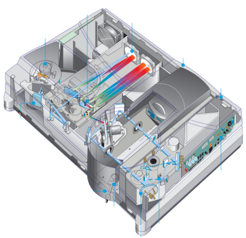


Jie Yang et al. "Layer-dependent giant magnetoresistance in two-dimensional ". In: **Physical Review Applied** 16.2 (Aug. 2021). DOI: 10.1103/physrevapplied.16.024011

Tried Techniques

Transmission

- large Sample Volume
  $\Rightarrow$ strong Signal
- Technical Problems in the setup and not enough time to build a new one



Reflection

- Multiple interferences in Flake and Si layer on Substrate
- Difficult to extract meaningful information

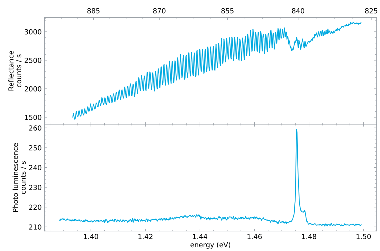
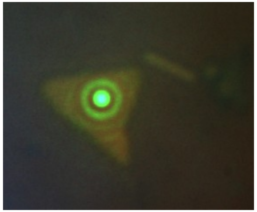
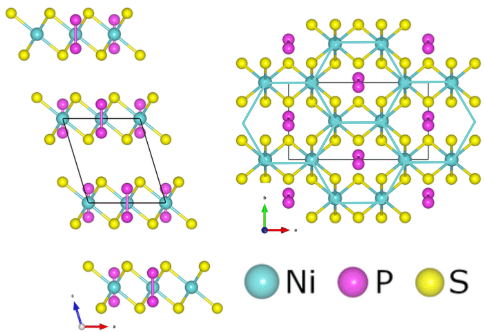


Photo-Luminescence

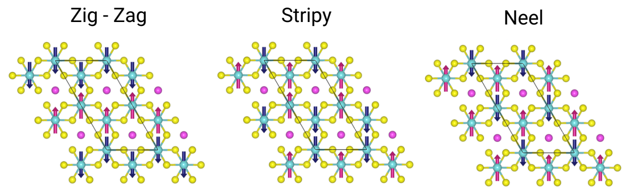
- strong enough signal
- sharp enough peak
- relatively easy to interpret



$NiPS_3$ Structure



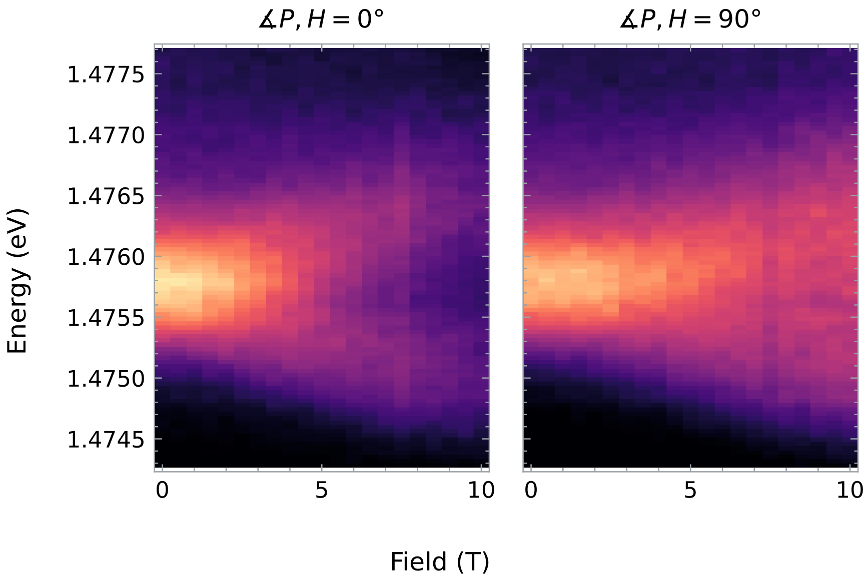
Antiferromagnetic order



Intra layer coupling $\gg$ Inter layer coupling
Anisotropic Inter layer coupling

Christopher Lane and Jian-Xin Zhu. "Thickness dependence of electronic structure and optical properties of a correlated van der waals antiferromagnetic NiPS3 thin film". In: **Physical Review B** 102.7 (Aug. 2020). DOI: 10.1103/physrevb.102.075124

Splitting of the $NiPS_3$ Photoluminescence in one polarisation Direction



The PL peak splits with magnetic Field.

But by different amounts in different polarisation directions *P* relative to the applied field *H*.

Splitting already documented

The splitting was already observed, but without the polarisation measurement:

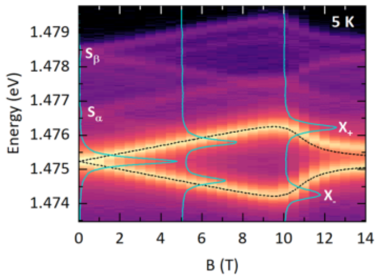
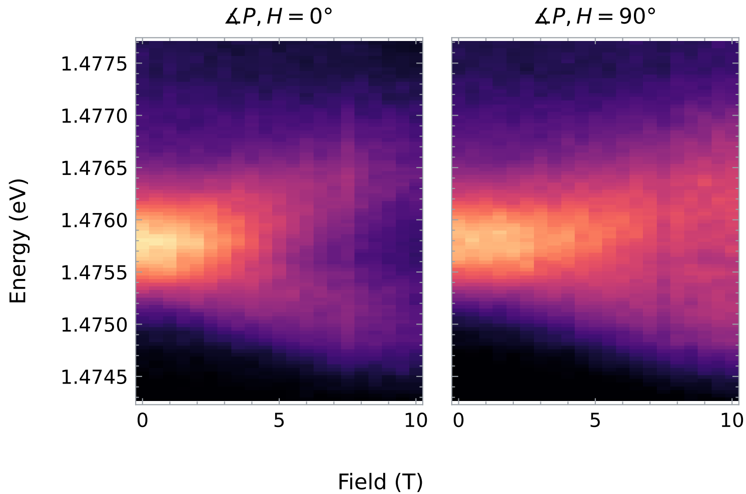


FIG. 7. False color map of low temperature (4.2 K) PL of $NiPS_3$ exfoliated flake as a function of the in-plane magnetic field. Few representative PL spectra, measured at a magnetic field strength of 0 T, 5 T, and 10 T are also plotted. Dashed lines correspond to a fit of the $E_{X_{+/-}}$ dependence according to Eq. (5) for $g = 2.0$, $B_{sf} = 10.55$ T and $\theta_B = 5°$. High energy satellite peaks are labeled as S_α and S_β.

Dipankar Jana et al. "Magnon Gap excitations and spin-entangled optical transition in the van der waals antiferromagnet NiPS3". In: **Physical Review B** 108.11 (Sept. 2023). DOI: 10.1103/physrevb.108.115149

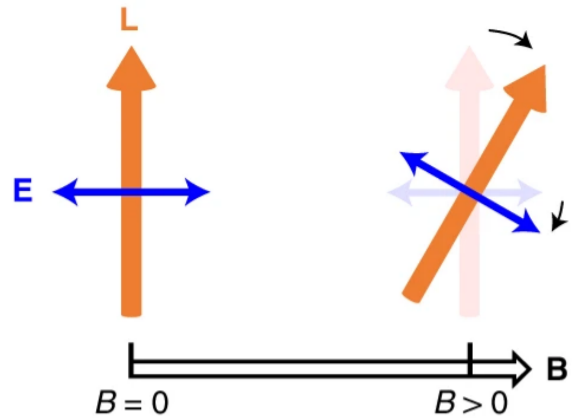


Fitting a simple model

Polarisation $\parallel$ Spin Alignment:

Neel Vector: $L = M_1 - M_2 \parallel$ Spin Alignment

$\psi = \measuredangle(L, B)$



Xingzhi Wang et al. “Spin-induced linear polarization of photoluminescence in antiferromagnetic van der waals crystals”. In: **Nature Materials** 20.7 (Apr. 2021), pp. 964–970. DOI: 10.1038/s41563-021-00968-7

Simple Biaxial Antiferromagnet Model:

$\psi = \measuredangle(N, B)$

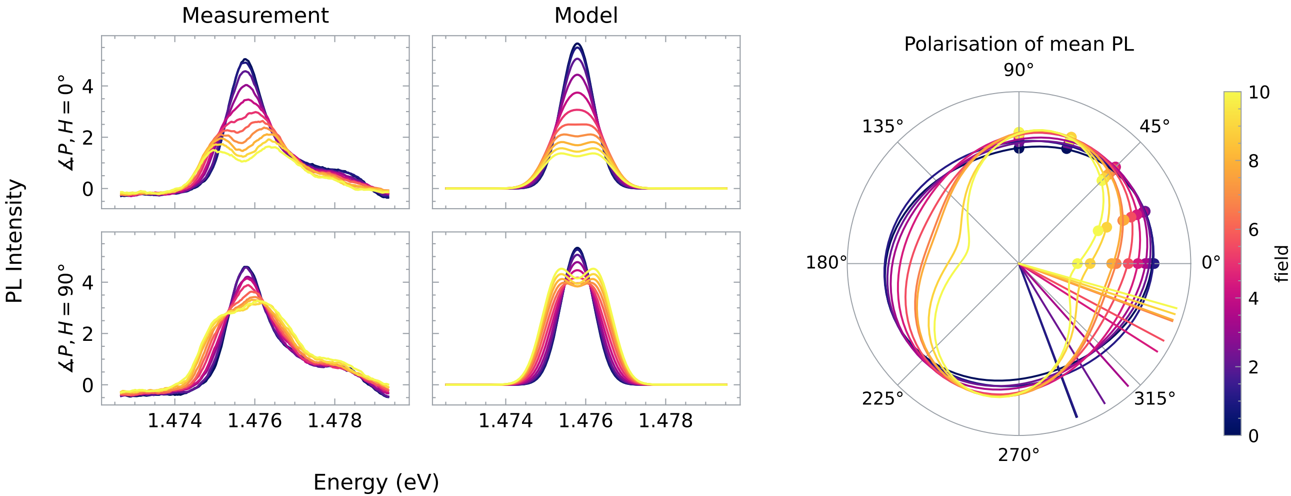
$\theta_0 = \measuredangle(a, B) = \psi(B = 0)$

$$\tan 2\psi = \frac{\sin 2\theta_0}{\cos 2\theta_0 - \frac{B}{B_{SF}}^2}$$

$$\Delta E = g\mu_B B \cos\psi$$

Dipankar Jana et al. “Magnon Gap excitations and spin-entangled optical transition in the van der waals antiferromagnet NiPS3”. In: **Physical Review B** 108.11 (Sept. 2023). DOI: 10.1103/physrevb.108.115149

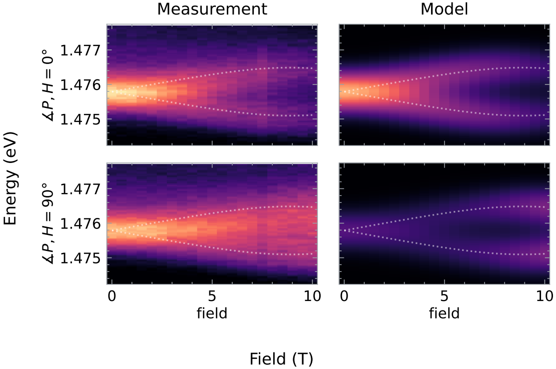
Fitting the Model



$\Rightarrow$ Model fits roughly

The Model is too simple

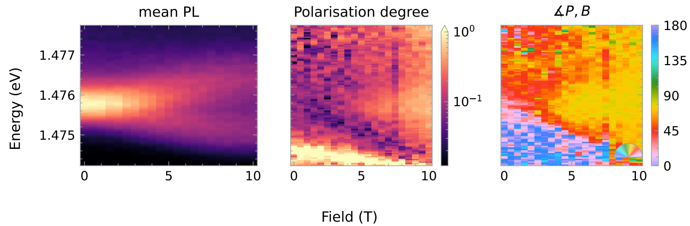
Different Splitting:



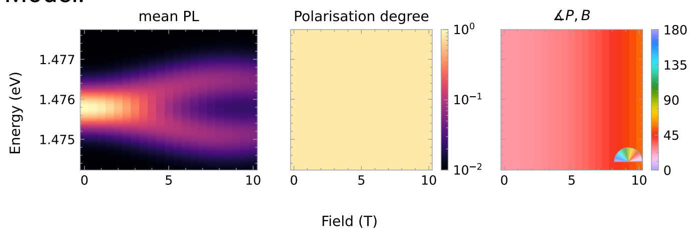
No difference in ΔE for different polarisations
$\Rightarrow$ No difference in Splitting for different polarisations

Polarisation:

Measurement:



Model:

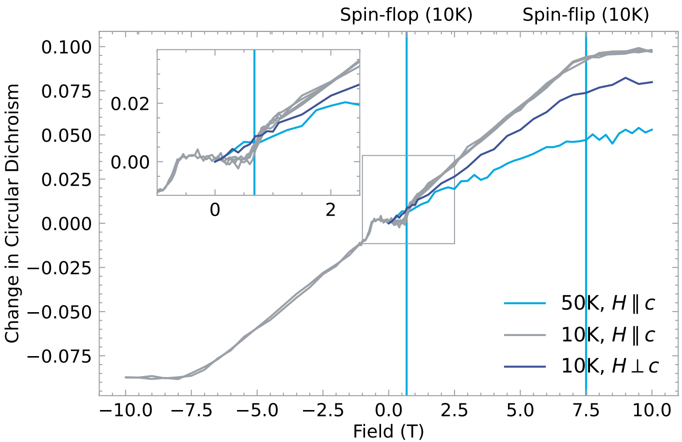


No independent Polarisation for different Wavelengths

$\Rightarrow$ Further Theorethical work is necessary

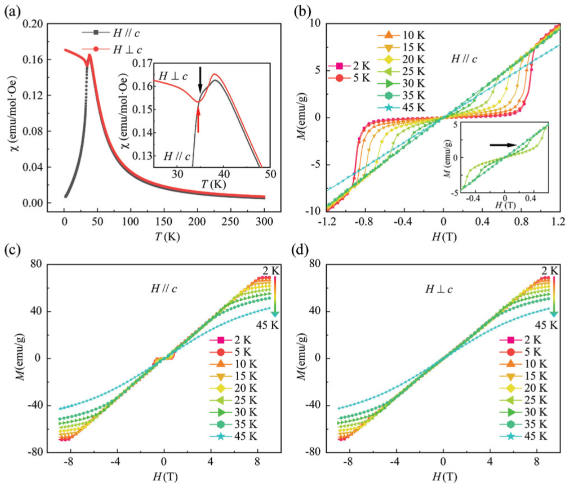
Pl Circular Polarisation in Magnetic Field

My measurement:



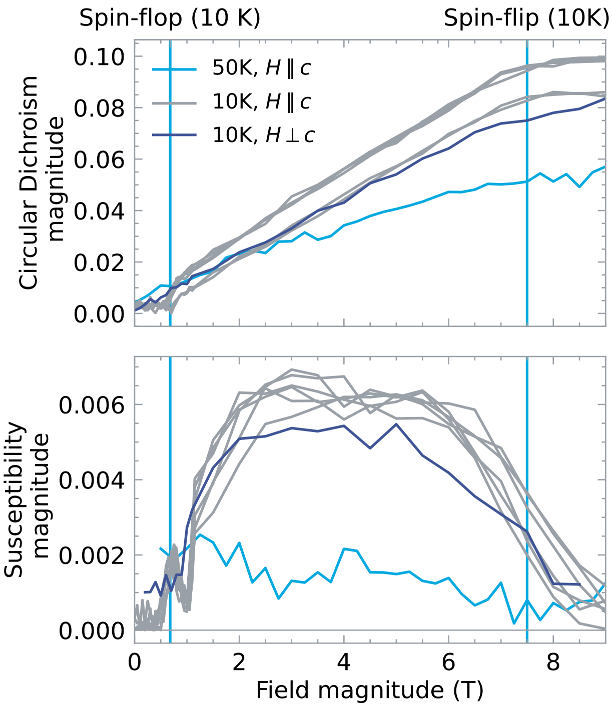
⇒ Circular Dichroism ∝ Magnetisation

⇒ Fast and Sensitive Measurement of Magnetisation in $CrPS_4$

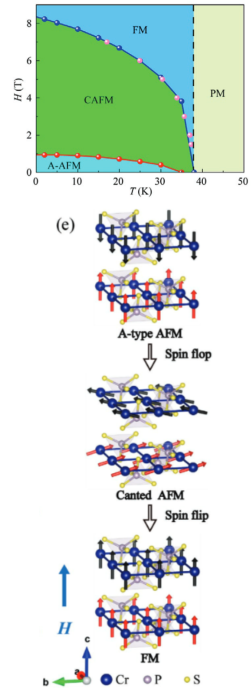


Yuxuan Peng et al. "Magnetic structure and metamagnetic transitions in the van der waals antiferromagnet CrPS4". In: **Advanced Materials** 32.28 (June 2020). DOI: 10.1002/adma.202001200

Proof of Concept: Detecting Phase Transitions



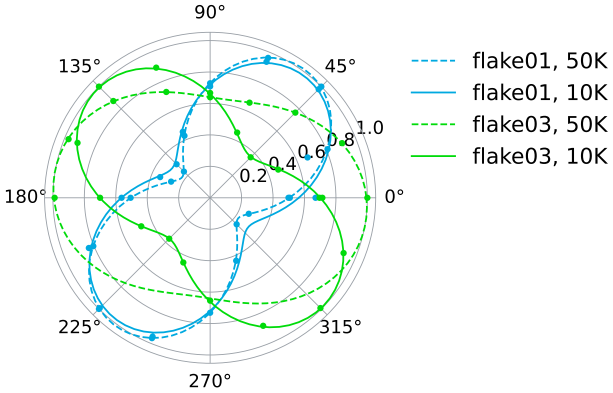
Spin-Flop at 10 K and .68 T,
Spin-Flip at 7.5 T
No Phase Transition at 50K
⇒ Demonstrates the using CD of the PL line to study Phase Transitions

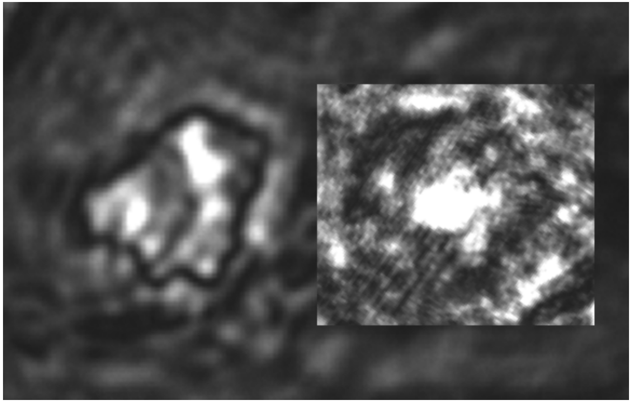


Yuxuan Peng et al. "Magnetic structure and metamagnetic transitions in the van der waals antiferromagnet CrPS4". In: **Advanced Materials** 32.28 (June 2020). DOI: 10.1002/adma.202001200

Initial Measurements: Aligning $CrPS_4$ Flakes?

Photoluminescence Signal:

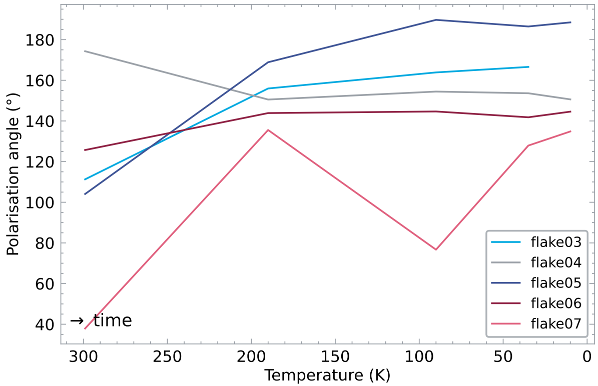


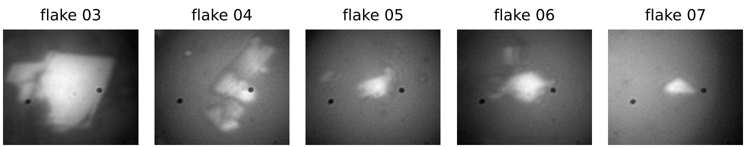


Flake 03
background: flake after cooldown
foreground: flake before cooldown

⇒ Do the entire flakes align or just their PL polarisation?

More Formal Measurement





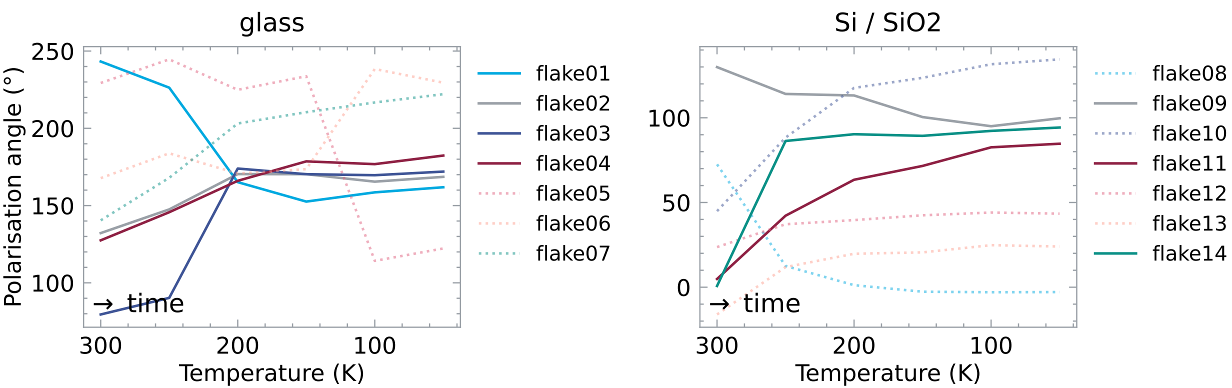
Flake 03 and Flake 04-07 were on different misaligned substrates

Setup a better imaging system using dark field illumination.

$\Rightarrow$ polarisation aligns, but flakes do not rotate in the image.

$\Rightarrow$ Maybe the Si/SiO_2 substrate has something to do with it?

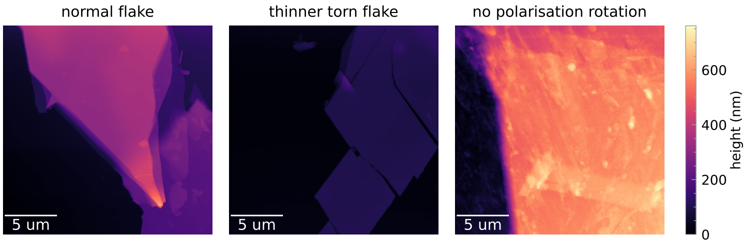
Different Substrates

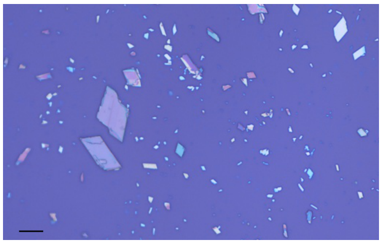


⇒ Not all flakes align, does not correlate with the size or position off the flakes
⇒ substrate independent
⇒ probably a variance in the sample preparation

AFM Results of $CrPS_4$ flakes after cooldown on Si/SiO_2 and Glass Substrates

After Cooldown:





Scalebar 10μm

On the samples where all flakes aligned:
all flakes have a smooth *"normal"* surface

On the samples where not all flakes aligned:
some flakes have a rough surface
this rough patch is larger than the flakes on the substrate

Thinner flakes appear to be torn by mechanical stress

Possible Causes of the aligning Flakes

Ruled out causes:

- Residual Magnetic Field
  The coil was turned out of plane $\Rightarrow$ no in plane torque on the flakes
- Inter flake forces
  Different densities of the flakes were used, no significant correlation
- alignment due to exfoliation
  The tape was rotated between each exfoliation step, the transfer to the substrate was done multiple, rotated times

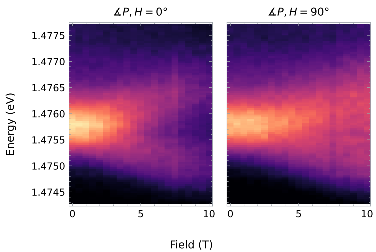
Follow up ideas:

- AFM images before cooldown: Is it already torn? Are the rough patches visible?
- Tape to Substrate transfer at a higher temperature: Are there more rough patches?
- Measure Direction using Polarized Raman, to minimize influence of strain.

Conclusion and Outlook

NiPS3

- Measured polarisation resolved splitting of the PL line
- Shown that current model does not fit the data
  ⇒ more theoretical work needed

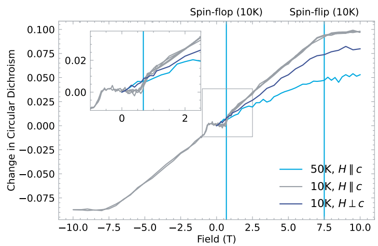


CrPS4

- Shown that CD of the PL line can be used to measure magnetisation, faster and more sensitive than previous methods

→ More measurements are being taken today

→ Noise measurements are planned



Side Projects:

- Thickness Estimation: Demonstrated a robust method for thickness estimation based on reflection spectra
- Rotating Flakes: Observed mysterious alignment force

CrPS4: magnetic order

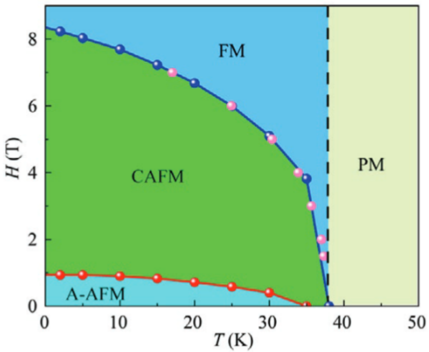
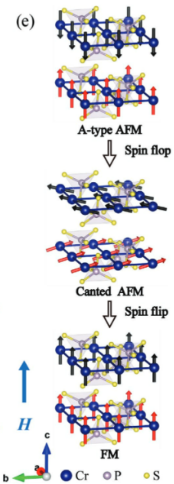
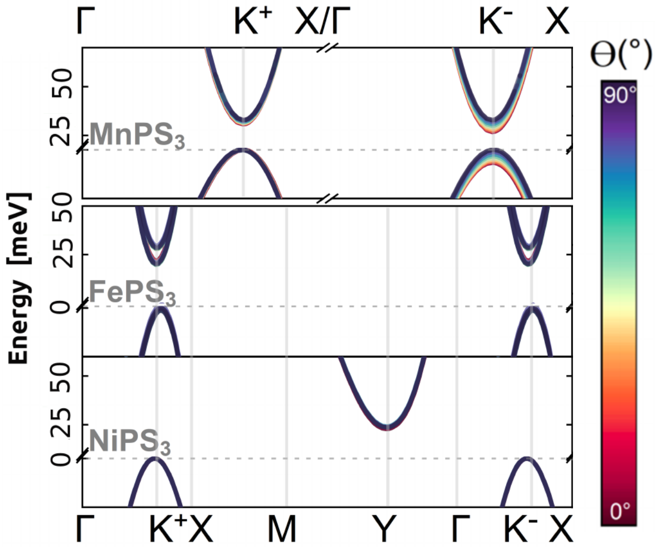


Figure 5. Magnetic phase diagram of $CrPS_4$ with applied field along the c axis. The red and blue balls are extracted from the $M(H)$ curves shown in Figure 2. Pink balls are extracted from the $M(T)$ curves. The black dashed line is for a potential boundary between the FM and PM phases at $T_N = 38$ K.



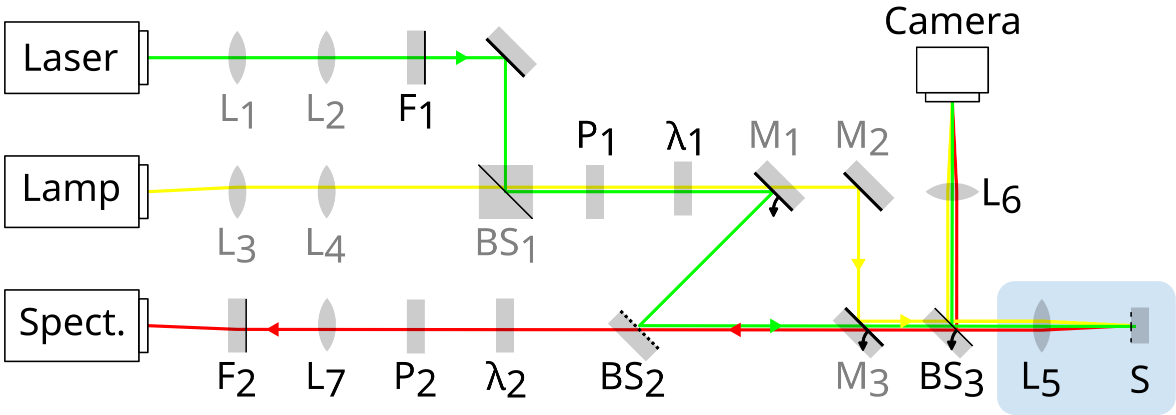
Yuxuan Peng et al. “Magnetic structure and metamagnetic transitions in the van der waals antiferromagnet CrPS4”. In: **Advanced Materials** 32.28 (June 2020). DOI: 10.1002/adma.202001200

Semiconductor Photoluminescence

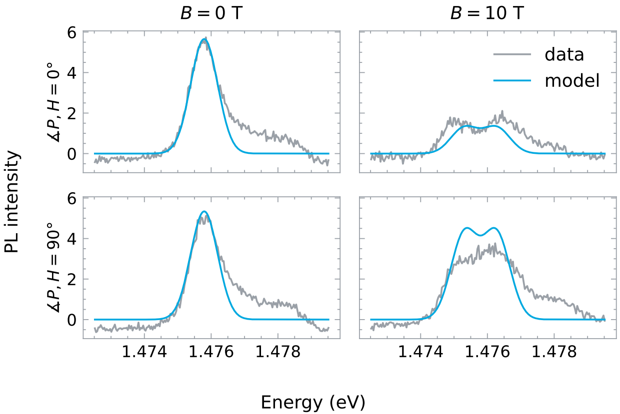


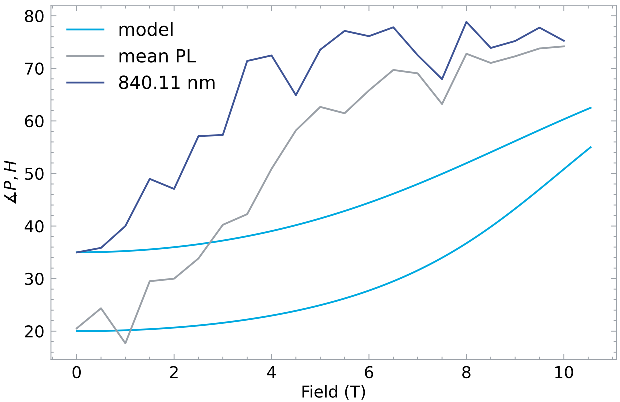
Magneto-optical anisotropies of 2D antiferromagnetic MPX3 from first principles, arXiv 2023

Full Setup


Camera
Laser
Lamp
Spect.
L1
L2
F1
P1
λ1
M1
M2
L6
L3
L4
BS1
F2
L7
P2
λ2
BS2
M3
BS3
L5
S

$NiPS_3$: Model Problems

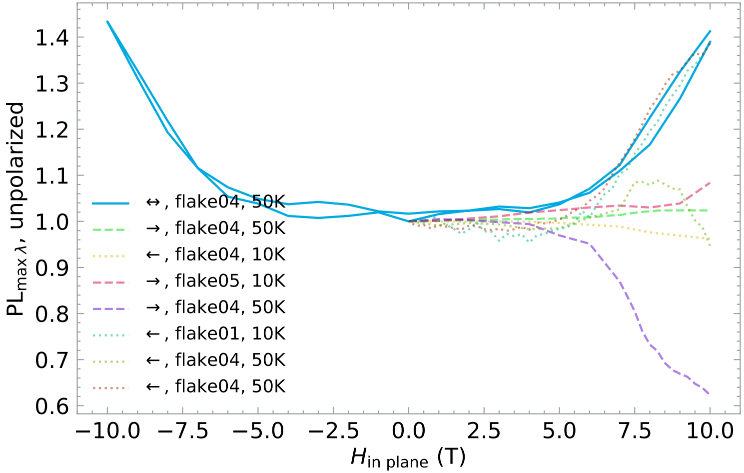




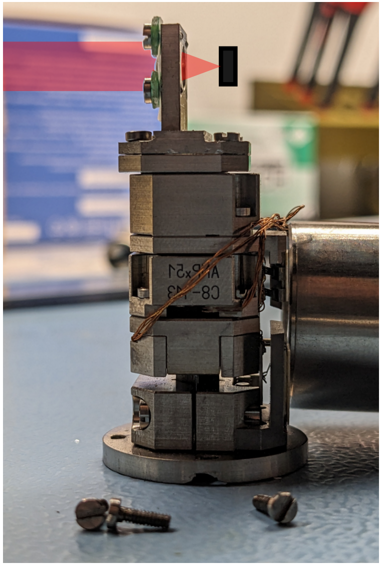
Dipankar Jana et al. "Magnon Gap excitations and spin-entangled optical transition in the van der waals antiferromagnet NiPS3". In: **Physical Review B** 108.11 (Sept. 2023). DOI: 10.1103/physrevb.108.115149

Xingzhi Wang et al. "Spin-induced linear polarization of photoluminescence in antiferromagnetic van der waals crystals". In: **Nature Materials** 20.7 (Apr. 2021), pp. 964–970. DOI: 10.1038/s41563-021-00968-7

Magnitude of Spectra is unstable

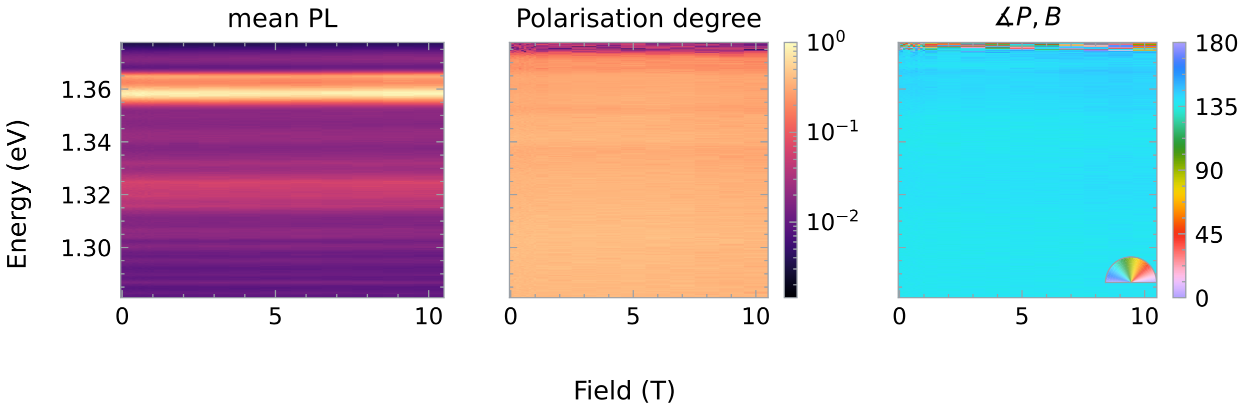


NiPS3, magnitude of photoluminescence peak

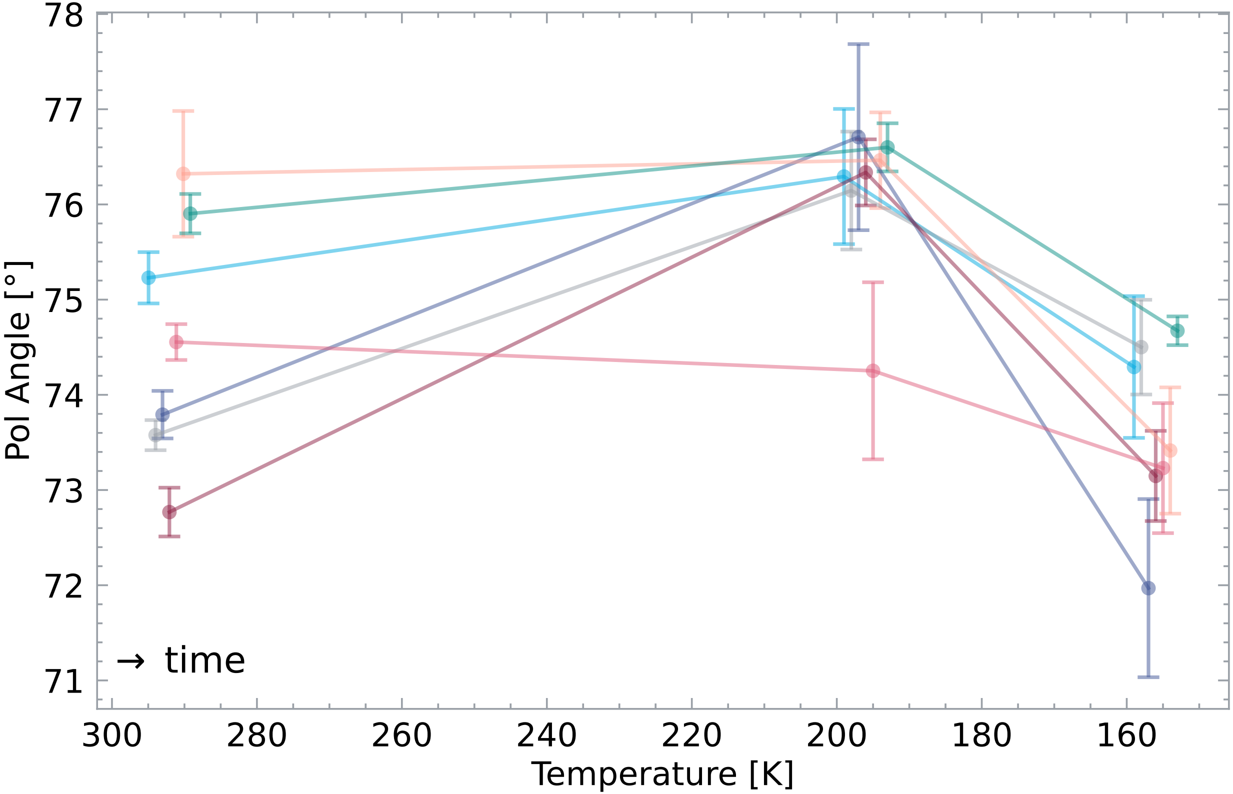


Field in plane of the image.

linear Polarisation, 10 K, in-plane field:



Flakes NiPS3, based on Raman signal



NiPS3 magneto raman