

Neutron instrumentation and study on perovskite systems

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Abbreviations

The abbreviations used in this thesis are listed as follows in the alphabetic sequence:

AFM	antiferromagnetic, antiferromagnet
AP	ambient pressure
bcc	body-centred cubic
CAF	columnar antiferromagnetic, columnar antiferromagnet, often also called collinear antiferromagnet
CryoPAD	cryogenic polarisation analysis device
CW	Curie-Weiss
DGS	direct-geometry spectrometer
DMI	Dzyaloshinskii-Moriya interaction
ESS	European Spallation Source
FC	field-cooled
FCC	field-cooled cooling
FCH	field-cooled heating
FCW	field-cooled warming
FSL	frustrated square lattice
FM	ferromagnetic
FWHM	full width at half maximum
GKT	Gaussian Kubo-Toyabe
HP	high pressure
HP-HT	high-pressure-high-temperature
HTE	high-temperature series expansion
HWHM	half width at half maximum
ILL	Institut Laue-Langevin
ISIS	ISIS Neutron and Muon Source
LF	longitudinal-field, longitudinal field
IGS	indirect-geometry spectrometer
LP	low pressure
LKT	Lorentzian Kubo-Toyabe
INS	inelastic neutron scattering

LRMO long-range magnetic order
MiniMuPAD rectangular miniaturised mu-metal polarisation analysis device
MiniPAD cylindrical miniaturised polarisation analysis device
MLZ Heinz Maier-Leibnitz Zentrum
MuPAD mu-metal polarisation analysis device
MVF magnetic volume fraction
 μ SR muon spin spectroscopy
NAF Néel antiferromagnet, Néel-antiferromagnetic
NMO nested-mirror optics
NN nearest neighbour
NNN next-nearest neighbour
NPD neutron powder diffraction
NSE neutron spin echo
NSF non-spin-flip, non spin slip
PG pyrolytic graphite
PSD position-sensitive detector
PSI Paul Scherrer Institute
QSL quantum spin liquid
r.l.u reciprocal lattice units
RT room temperature
SANS small-angle neutron scattering
SF spin-flip, spin slip
SG space group
SNP spherical neutron polarimetry
SD standard deviation
SQL square lattice model
TAS triple-axis spectrometer, three-axis spectrometer/spectroscopy
TF transverse-field, transverse field
TLAF triangular-lattice antiferromagnet
ToF time-of-flight, time of flight
ToF-DGS time-of-flight direct-geometry spectrometer
ToF-IGS time-of-flight indirect-geometry spectrometer
uud up-up-down
VSM vibrating sample magnetometer
wTF weak-transverse-field, weak transverse field
XRD X-ray diffraction
ZF zero-field, zero field
ZFC zero-field cooled

Abstract

This thesis presents novel concepts in neutron scattering instrumentation and investigations into frustrated antiferromagnets using techniques including neutron scattering.

The study investigates the Mushroom concept, an indirect-geometry spectrometer designed for the reactor-type neutron source, FRM II. This concept aims to enhance the efficiency and flexibility of inelastic neutron scattering measurements by leveraging its unique super flat-cone analyser. Furthermore, the latest development of the MiniPAD are discussed. This compact device for spherical neutron polarimetry can be seamlessly integrated into a standard cryostat, thereby expanding the capabilities of instruments equipped for neutron polarimetry.

In addition, the thesis presents the investigations conducted on the layered perovskite related antiferromagnets $\text{Ca}_3\text{NiNb}_2\text{O}_9$ and PbVO_3 , employing various probing techniques, including neutron scattering. On the one hand, the triangular-lattice system of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ exhibits distinct ground states dependent on the conditions of crystal growth. The ordered specimen has been studied using neutron single-crystal diffraction techniques. On the other hand, the square-lattice compound PbVO_3 underwent analysis using techniques such as neutron powder diffraction and muon spin relaxation in order to study its ground state and the potential spin-liquid scenario.

Zusammenfassung

Diese Dissertation präsentiert neuartige Konzepte in der Instrumentierung für Neutronenstreuung und Untersuchungen an frustrierten Antiferromagneten unter Verwendung von Methoden einschließlich Neutronenstreuung.

Die Studie betrachtet das Mushroom-Konzept, ein Spektrometer mit indirekter Geometrie, welches für den Forschungsreaktor FRM II entwickelt wurde. Dieses Konzept zielt darauf ab, die Effizienz und Flexibilität von Messungen der inelastischen Neutronenstreuung durch Nutzung seines einzigartigen Analysators in Form von einem Super-Flachkegel zu verbessern. Darüber hinaus werden die neuesten Entwicklungen des MiniPAD diskutiert. Dieses kompakte Gerät für sphärische Neutronenpolarimetrie kann nahtlos in einen Standard-Kryostaten integriert werden und erweitert damit die Fähigkeiten von Instrumenten, die für die Neutronenpolarimetrie ausgestattet sind.

Zudem präsentiert die Dissertation die Untersuchungen an den geschichteten Perowskit-verwandte Antiferromagneten $\text{Ca}_3\text{NiNb}_2\text{O}_9$ und PbVO_3 unter Verwendung verschiedener Methoden einschließlich Neutronenstreuung. Einerseits besitzt das dreiecksgitterige System von $\text{Ca}_3\text{NiNb}_2\text{O}_9$ unterschiedliche Grundzustände, die von den Wachstumsbedingungen der Kristalle abhängen. Zur Untersuchung der geordneten Probe wurde Einkristalldiffraktion mit Neutronen verwendet. Andererseits wurde das quadratisch-gitterige System PbVO_3 unter Anwendung von verschiedenen Methoden, unter anderem Pulverdiffraktion mit Neutronen und der auf Muon-Spin-Relaxation basierenden Technik, analysiert, um ihren Grundzustand und das mögliche Szenario eines Zustands der Spinflüssigkeit zu untersuchen.

Introduction

Neutron scattering, dating back to the early twentieth century, remains a powerful technique across various fields, notably in material science and condensed matter physics. This method probes matter at atomic and molecular scales by harnessing the interactions between neutrons and atomic nuclei. Its sensitivity to magnetic properties amplifies its investigative capabilities. Over time, various neutron instruments have emerged, each tailored to address the intricate demands of studying material properties. This thesis introduces advancements geared towards enhancing the efficiency and adaptability of neutron scattering techniques. Additionally, it reports investigations into frustrated antiferromagnetic materials using neutron scattering methods.

The thesis investigates the Mushroom concept, a pioneering approach in inelastic neutron scattering to unveil dynamic material properties. Established instruments like triple-axis spectrometer (TAS) and time-of-flight direct-geometry spectrometer (ToF-DGS) have traditionally dominated momentum and energy space measurements. The Mushroom concept explores a uniquely designed secondary spectrometer employing a super flat-cone analyser with pyrolytic graphite crystal segments. This design boosts count rates and facilitates measuring the out-of-plane component of the scattered wavevector ($\mathbf{k}_f$). It assesses primary spectrometer options - crystal monochromators and time-of-flight choppers - with the former offering location flexibility and the latter enabling a broader range of incoming wavelength coverage. The resolution, crucial in neutron scattering, undergoes meticulous analysis considering wavevectors ($\mathbf{k}_i$ and $\mathbf{k}_f$), momentum transfer ($\mathbf{Q}$), and energy transfer ($\hbar\omega$). The performance of the concept is evaluated through Monte-Carlo simulations using the McStas software.

Furthermore, this work introduces the cylindrical miniaturised polarisation analysis device (MiniPAD), a novel approach to spherical neutron polarimetry (SNP). Neutron polarimetry is critical in studying complex magnetic systems featuring nuclear-magnetic interference and chiral terms. This thesis develops a compact MiniPAD that can seamlessly integrate into standard cryostats, enhancing instrument flexibility for SNP implementation. The design, operational principles and performance of MiniPAD, demonstrated by measuring nuclear and magnetic

reflections of a single-crystal MnSi sample, showcase its potential in advancing neutron polarimetry.

Moreover, this thesis investigates layered perovskite antiferromagnets, particularly focusing on $\text{Ca}_3\text{NiNb}_2\text{O}_9$ and PbVO_3 . The spin-1 triangular-lattice system $\text{Ca}_3\text{NiNb}_2\text{O}_9$, a derivative of the perovskite structure ABO_3 , offers diverse ground states based on crystal growth conditions. This investigation utilises neutron single-crystal diffraction to unravel the ordered state of $\text{Ca}_3\text{NiNb}_2\text{O}_9$, paving the way for comprehensive studies across various ground state scenarios. In contrast, the frustrated spin- $\frac{1}{2}$ square-lattice system PbVO_3 , with competing antiferromagnetic exchange energies (J_1 and J_2), displays promising spin-liquid characteristics due to the ratio $\alpha = \frac{J_2}{J_1}$ being close to 0.5. The thesis provides extensive overviews of previous studies, followed by crystal property investigations using neutron powder diffraction, supplemented by physical property and muon spin relaxation measurements.

In conclusion, this thesis strives to advance neutron scattering techniques through innovative instrumentation concepts and novel findings in material investigations.

Chapter 1

Mushroom spectrometer

1.1 Motivation

There are two types of interactions between a neutron and matter. Firstly, as a nucleon, a neutron directly interacts with atomic nuclei via the nuclear force. The length scale associated with the interactions, in the order of 10^{-15} m (fm), is notably smaller than the wavelength of a thermal or cold neutron, which is typically within the interatomic range at 10^{-10} m (Å) [1]. Within this region, only the s-wave components contribute to scattering, enabling the description of isotropic scattering using a single parameter, the scattering length b [1, 2]. Thus, the differential cross-section of nuclear scattering between a neutron and an atom can be expressed as [3]:

$$\frac{d\sigma}{d\Omega} = b^2. \quad (1.1)$$

Here, the scattering length b relies on the scattering atom with its atomic number Z and weight A . The influence of nuclear spins, though existent, can be usually neglected due to their random ordering. The value of b lies typically in the order of [3] at almost all atomic numbers (Fig. 1.1) 10^{-14} m. This characteristic makes neutron scattering particularly effective for studying light atoms and isotopes such as ^1H and ^2D compared to alternative probing techniques like X-rays, where b rises monotonically with Z [1]. Moreover, the electric neutrality of the neutron grants it a penetration depth of a few centimetres [1], facilitating the examination of bulk materials inaccessible to charged particles, which are predominantly sensitive only to surface characteristics.

Secondly, a neutron possesses a magnetic dipole moment that interacts with magnetic fields originating from unpaired electrons within a sample. This property endows neutron scattering with the capability to analyse nuclear and magnetic properties, with more details of the theory discussed in the next chapter.

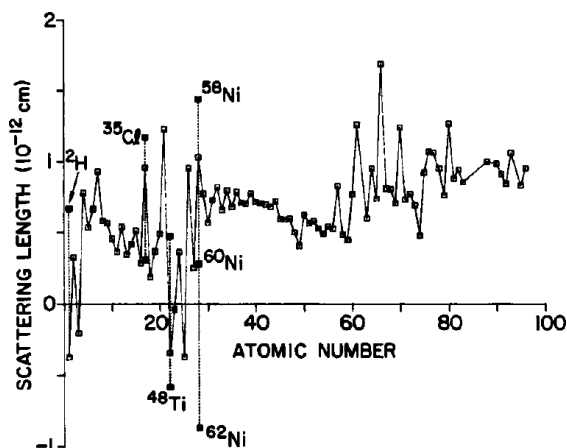


Figure 1.1: Scattering lengths for different elements with naturally abundant isotopes in the neutron nuclear scattering. Figure taken from [3].

The fundamental principle behind neutron scattering techniques involves measuring the incident $\mathbf{k}_i$ and final $\mathbf{k}_f$ wavevectors of a neutron beam with respect to its scattering by a sample. These wavevectors provide information about the wavevector transfer

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f \quad (1.2)$$

and the energy transfer

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m_n} (k_i^2 - k_f^2), \quad (1.3)$$

where $\hbar$ represents the reduced Planck constant and m_n denotes the mass of the neutron. The value of $\hbar\omega$ distinguishes between elastic scattering processes with no energy transfer ($\hbar\omega = 0$) and inelastic scattering processes with non-zero $\hbar\omega$. Neutron diffraction, where elastic neutron scattering dominates, facilitates the study of structural features of the sample, while the techniques involving inelastic scattering offer insight into dynamical properties.

Neutron diffraction can be performed on a single-crystalline or powder sample, providing insights into its nuclear and/or magnetic structure. The relation among the scattering angle, neutron wavelength and lattice spacing is described by Bragg's law [4]:

$$\begin{aligned} n\lambda &= 2d \sin \theta \\ Q &= \frac{2n\pi}{d}, \end{aligned} \quad (1.4)$$

where n denotes the diffraction order, λ stands for the neutron wavelength, d rep-

resents the lattice spacing, and θ refers to the scattering angle^{1 2}. A diffractometer is typically not equipped with components to analyse the energy transfer during scattering. Instead, the neutrons are recorded by a neutron detector, providing the intensity in dependency of θ , providing the structural information.

Since a diffractometer cannot analyse neutron energy, it cannot provide the dynamical information about the sample. Hence, to explore such information, spectrometers are equipped with components determining the energy transfer, giving access to the $(\mathbf{Q}, \omega)$ -spectra through inelastic neutron scattering (INS). In this chapter, we focus on INS.

1.2 Instruments for inelastic neutron scattering

Throughout the decades, various spectrometer designs have been tailored for INS, harnessing different aspects of neutron properties and leveraging the unique characteristics of neutron sources. These instruments grant access to diverse regions within the $(\mathbf{Q}, \omega)$ -space, as summarised in Fig. 1.2. The smallest accessible scales in Q and ω are contingent on the resolutions of individual instruments. In the subsequent discussion, we first review the working principles of triple-axis spectrometers (TASs) and time-of-flight direct-geometry spectrometers (ToF-DGSs), which have been pivotal designs among spectrometers. Following this, we explore alternative spectrometer approaches, including our Mushroom concept.

1.2.1 Triple-axis spectrometers

As its name suggests, a TAS operates on three rotational axes positioned at the monochromator, sample, and analyser. The monochromator and analyser consist of crystals operating according to Bragg’s law (Eq. 1.4). Goniometers control the orientation of each component at these rotational axes, allowing movement of the parts after this component around the respective axis. This control facilitates the manipulation of scattering angles at the monochromator, sample, and analyser, enabling access to various $(\mathbf{k}_i, \mathbf{k}_f)$ -combinations. This characteristic offers a TAS significant flexibility in measuring the sample within the $(\mathbf{Q}, \omega)$ -space using INS. Some commonly used notations of the angles employed for neutron scattering measurements³ are illustrated in Tab. 1.1. A photo in Fig. 1.3 showcases the

¹In the context of inelastic scattering, it is essential to specify whether θ or 2θ is discussed, especially considering the differing incident and outgoing angles.

²In some literature, the signs of the initial and final terms in Eq. 1.2 and 1.3 are reversed. This thesis adopts the notation outlined in Eq. 1.2 and 1.3.

³They are utilised at neutron sources such as Heinz Maier-Leibnitz Zentrum (MLZ), Institut Laue-Langevin (ILL), Paul Scherrer Institute (PSI).

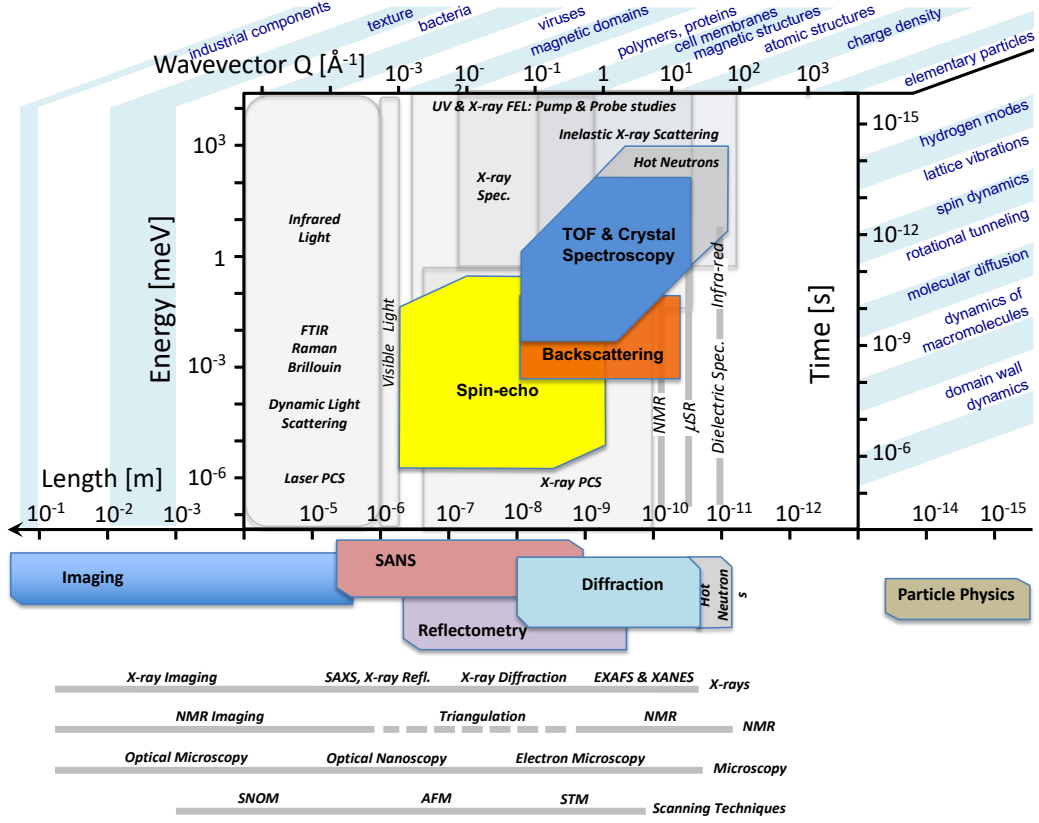


Figure 1.2: Dynamic range accessible using various microscopic probes in studies of condensed matter systems, where the techniques using neutrons, e.g. neutron spin echo (NSE) and small-angle neutron scattering (SANS), are highlighted with colours. The horizontal axes at the top and bottom correspond to the norm of the wavevector transfer Q and the length scale l , respectively, with the relation $l = \frac{2\pi}{Q}$. The vertical axes on the left- and right-hand sides show the energy $\hbar\omega$ and time t scales, respectively, with the relation $\hbar\omega = \frac{2\pi\hbar}{t}$. Figure taken from [5].

MIRA beamline at FRM II, MLZ, Garching, Germany [6, 7], providing a visual representation of TAS geometry.

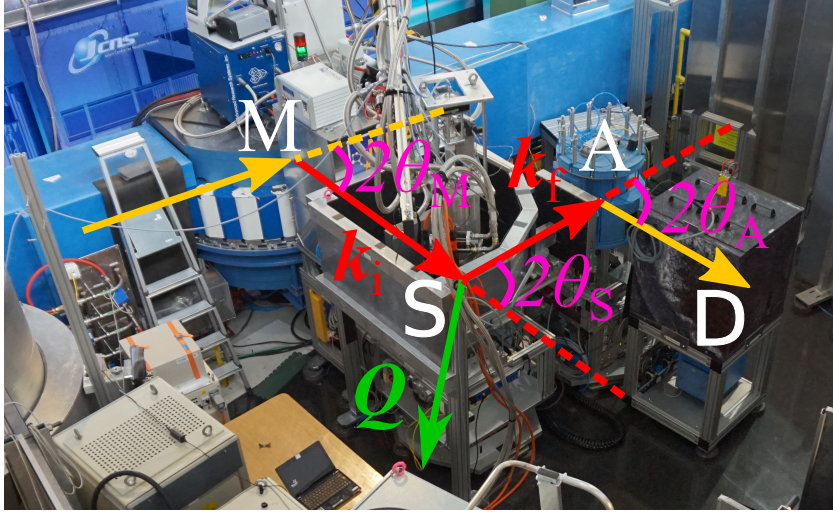


Figure 1.3: Photo of the MIRA beamline at FRM II, MLZ, Germany [6, 7]. The yellow arrows denote the neutron beam coming from the neutron guide NL6 and eventually detected by the detector (“D”), respectively. The red arrows denote the flight paths relevant to the scattering process at the sample, with $\mathbf{k}_i$ and $\mathbf{k}_f$ the incident and outgoing wavevectors, respectively, and $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ (green) the wavevector transfer. The angles 2θ (pink) label the scattering angles at the monochromator (“M”), sample (“S”) and analyser (“A”). Figure edited based on [7].

Component	Monochromator		Sample		Analyser	
Definition	Orientation	$2\theta_M$	Orientation	$2\theta_S$	Orientation	$2\theta_A$
MLZ	meth	mtt	sth	stt	ath	att
ILL and PSI	A_1	A_2	A_3	A_4	A_5	A_6

Table 1.1: Definition and notation of angles at components of a TAS. Other instruments (e.g. ToF-DGS) often use the same notations. The notations at MLZ, ILL and PSI are listed. The angle at one component denotes either the orientation of the stage, where the component is placed, or the scattering angle 2θ (often called the take-off angle).

A collimator, often a Soller collimator [8] featuring parallel absorbing plates, is typically positioned along an arm connecting adjacent components within a TAS. This collimation strengthens the inherent restriction during Bragg scattering at the

crystal monochromator and analyser [1]. Consequently, a TAS is able to achieve a high resolution of approximately $\Delta\lambda/\lambda \approx 1\%$ [6, 7], complementing its substantial flexibility in exploring different positions within the $(\mathbf{Q}, \omega)$ -space. During TAS measurements, it is critical to evaluate the attainability of the desired $(\mathbf{Q}, \omega)$ -point that is directly affected by the resolution of the instrument. The Takin software is commonly utilised for this assessment [9–14].

One limitation of a TAS is its sequential approach to measurements, recording one $(\mathbf{Q}, \omega)$ -point at a time, which can become time-intensive when aiming to encompass a large $(\mathbf{Q}, \omega)$ -area in a measurement. For example, in the study of the magnon and spinon dispersion relations in SeCuO_3 (Fig. 1.4) conducted by M. Boehm *et al.* at ThALES, ILL [15], each black point in the 2D spectrum in Fig. 1.4b corresponds a data point in an energy scan (Fig. 1.4a) at a constant Q . This instance highlights the necessity of instruments capable of capturing more significant spectral regions with high resolution.

1.2.2 Time-of-flight direct-geometry spectrometers

The time-of-flight (ToF) spectrometers possess the capability to simultaneously scan a vast area in the $(\mathbf{Q}, \omega)$ -space. There are two types of ToF spectrometers: direct-geometry spectrometers (DGSs) and indirect-geometry spectrometers (IGSs), with their operational principles illustrated through a distance-time diagram in Fig. 1.5. The DGSs are one of the most frequently implemented instrument types due to their straightforward working principle, which will be discussed in this section, whilst IGSs will be introduced in the next section among other alternative approaches.

The primary spectrometer of a DGS comprises choppers that create an incident beam with a desired wavelength, as showcased in Fig. 1.5a. Its secondary spectrometer features a cylindrical ^3He detector bank encircling the sample. This detector bank, capable of discerning the time of neutron detection triggered by the chopper, provides information on both the wavelength λ_f and direction $\hat{\mathbf{k}}_f$ of the outgoing beam. Many modern setups utilise position-sensitive detectors (PSDs), further improving the resolution by distinguishing the vertical positions where neutrons arrive at the detector, so that the ToF due to different travel lengths can also be considered.

The configuration of the IN5 instrument at ILL, Grenoble, France [18], serves as an example of DGSs (Fig. 1.6). The instrument employs a chopper arrangement to generate a monochromatic incoming beam. While the direct comparison of count rates between a DGS and a TAS varies based on instruments and their sources and guides, a DGS records a (Q, ω) -area generally faster than a TAS due to its capacity to cover an extensive range of scattering angles $2\theta_s$ and final wavelengths λ_f .

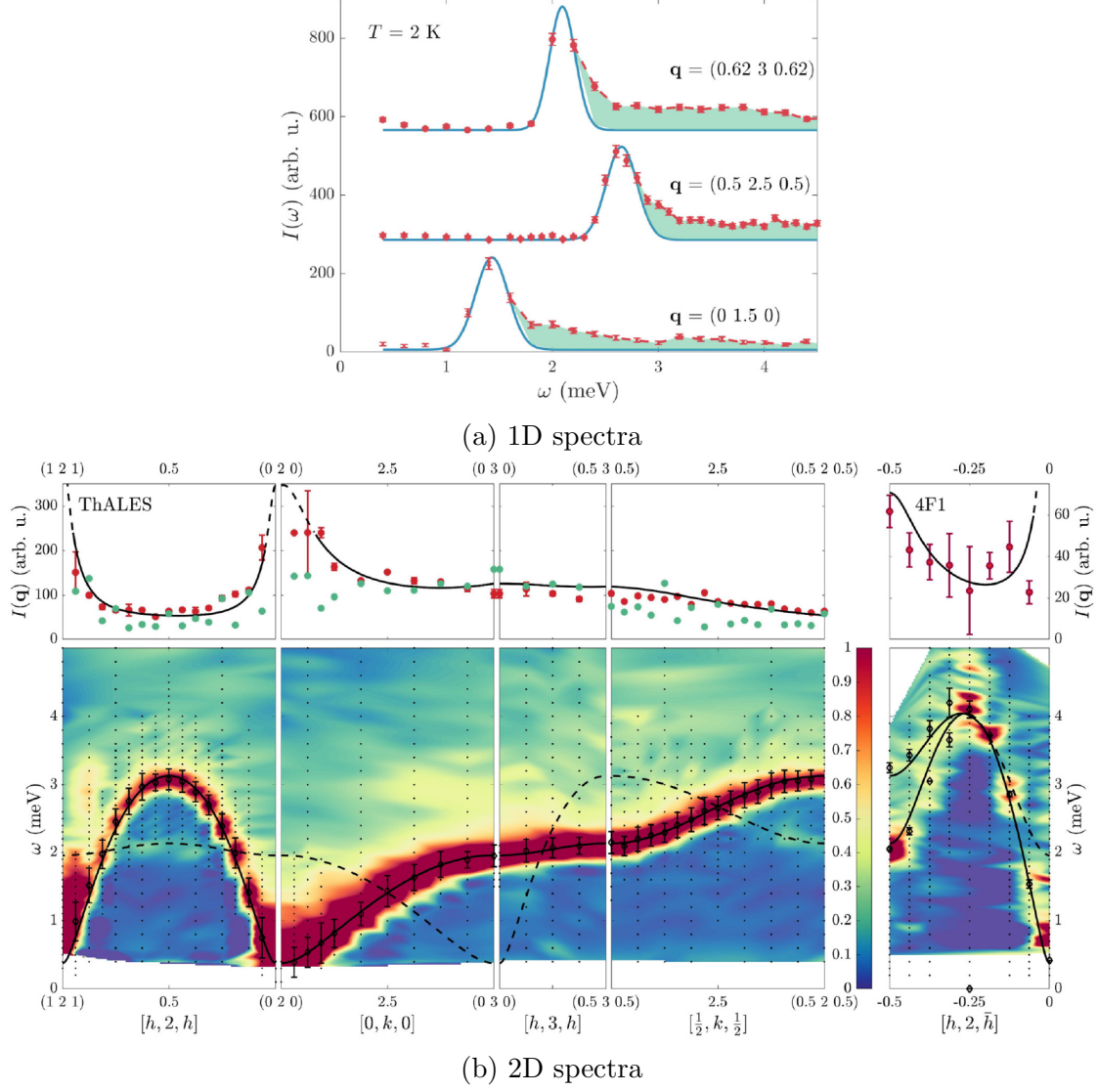


Figure 1.4: Magnon and spinon spectra, taken from [16]. Panel a: Energy scans at three different $\mathbf{Q}$ positions for magnons. Panel b: Contour maps of magnon and spinon measurements, with each black point corresponding to a data point in measurements like in Fig. 1.4b. The colour bars in the 2D spectra indicate the scattering intensity $I(\mathbf{Q}, \omega)$.

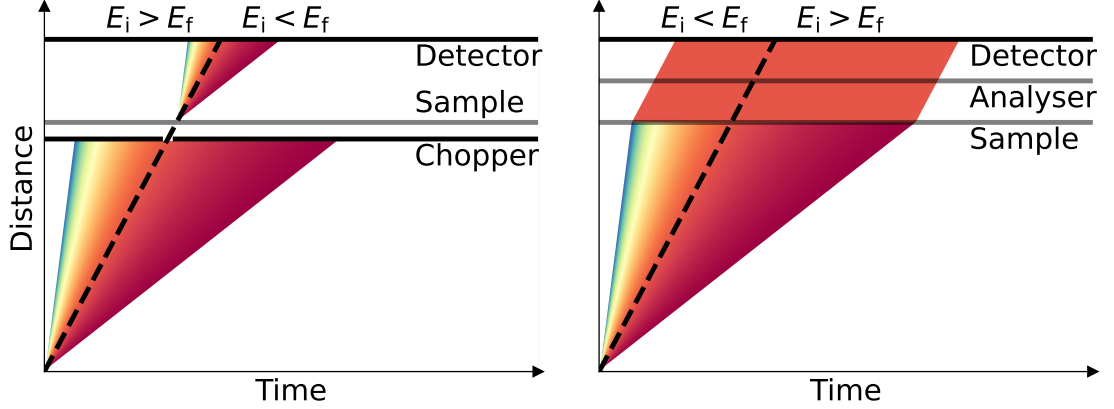


Figure 1.5: Distance-time diagram illustrating a ToF-spectrometer with direct (left) and indirect (right) geometries. The origin of each diagram signifies the beginning of time measurement, set at either the first chopper (continuous source) or the neutron source (pulsed source). The colours of the spectrum depict, in a qualitative manner, the range of neutron wavelengths, with violet indicating the fastest and red representing the slowest. The dashed line in the left panel denotes the wavelength chosen by the chopper system of a DGS, while the dashed line in the right panel signifies the wavelength selected by an analyser in an IGS. The consistent colour between the sample and detector highlights the constant wavelength. The relationships between incident (E_i) and scattered energies (E_f) of neutrons are illustrated concerning their respective arrival times at the detector. Figure reproduced from [17].

The primary limitation of a DGS lies in its resolution and physical size. The resolution of the instrument comes from two factors. Firstly, the nearly monochromatic incident beam still has a finite bandwidth in wavelength. Secondly, the ToF technique generally requires recording the time, using the same start of time-counting for neutrons within the same pulse. This mechanism makes a ToF instrument incapable of distinguishing the time difference within a pulse. With the nearly monochromatic incident beam, the ToF in the primary spectrometer is defined as $\frac{L_{1S}}{v_i}$ for all neutrons within one pulse, where L_{1S} denotes the distance between the first chopper and the sample position⁴, and v_i represents the velocity of the incident neutron beam. Hence, the time uncertainty within one pulse causes an uncertainty of ToF in the secondary spectrometer, making the time uncertainty inversely proportional to the sample-detector distance L_{SD} , which is typically smaller than L_{1S} . At the same time, attainable L_{SD} is restricted due to frame overlaps, where faster neutrons from one pulse catch up with slower ones

⁴At a pulse source, this is the distance between the source and the sample position.

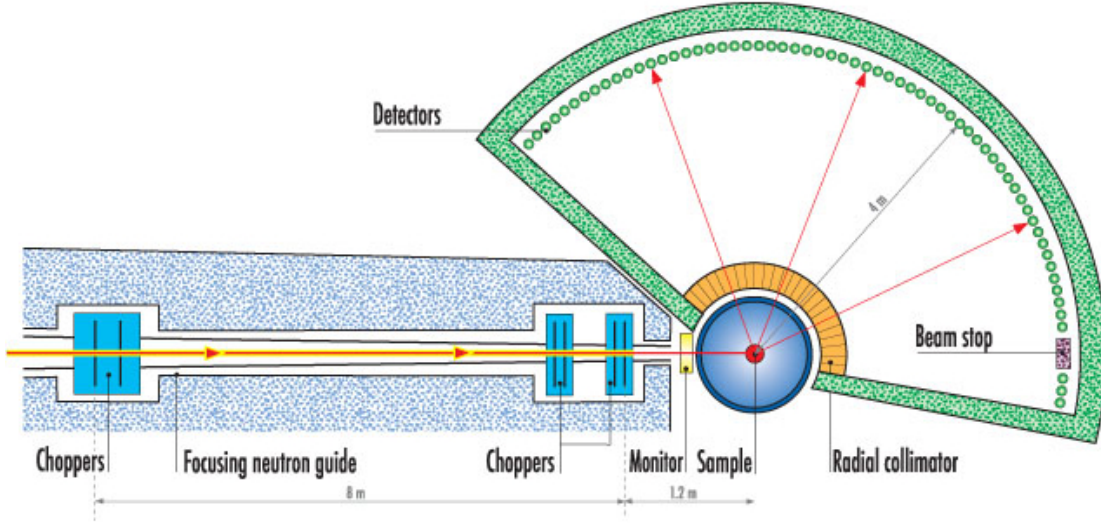


Figure 1.6: Schematic of IN5 at ILL, a ToF spectrometer with a direct geometry, where the choppers select the desired incident wavelength and the scattered wavelength is determined through the ToF channel. The red arrows denote the beam trajectory. The chopper-sample distance is 9.2 m, and the radius of the PSD tank is 4 m. Taken from [18].

from the preceding pulse. Furthermore, the rising cost of ^3He makes it more desirable to make the detector bank as compact as possible. Consequently, achieving an optimal balance between resolution, instrument size, and cost is crucial.

Typically, the DGSs offer an energy resolution ranging from 0.01 meV to a few meV [18].

1.2.3 Alternative approaches

There have been various alternative approaches to the designs of TAS and ToF-DGS, two of which will be discussed in this section. Firstly, a natural alternative is a time-of-flight indirect-geometry spectrometer (ToF-IGS). As illustrated in Fig. 1.5, this type of spectrometer utilises a polychromatic (“white”) incident beam, with its energy determined through the ToF channel. The outgoing energy is then selected by a large-area crystal analyser positioned between the sample and the detector, operating according to Bragg’s law (Eq. 1.4).

In the indirect geometry, the distance L_{1S} between the first chopper and the sample determines the relative time resolution. Integration of the first chopper into the neutron guide enables reaching distances of $L_{1S} \approx 10$ m or more. This allows for a more compact secondary spectrometer with a better resolution than a typical

DGS. Such a geometric configuration has already found successful implementation in near-backscattering instruments such as OSIRIS (Fig. 1.7) at ISIS Neutron and Muon Source (ISIS), Rutherford Appleton Laboratory, Didcot, UK [19].

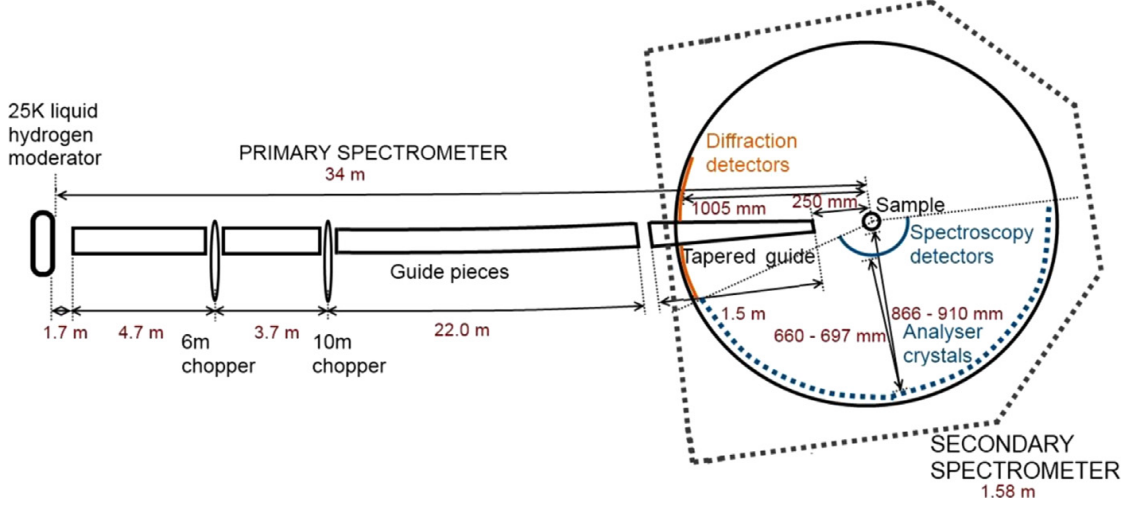


Figure 1.7: A not-to-scale schematic of OSIRIS at ISIS, a near-backscattering ToF-IGS. The incident beam is pulsed intrinsically from the neutron source, while the choppers help to eliminate frame overlaps. The instrument has two detector banks, offering diffraction or indirect-geometry spectroscopy options. Taken from [20].

Secondly, another instrument type gaining significant interest in recent years is an extended design of the TAS featuring multiplexing analysers placed sequentially along the outgoing beam, each set for different scattering angles $2\theta_A$. An analyser reflects neutrons according to Bragg’s law while allowing others to pass through, while the next analyser, set for another scattering angle, reflects neutrons with another wavelength. This design enhances the efficiency of TASs by simultaneously analysing multiple λ_f -values [21]. This design has been realised in instruments such as the multi-analyser system at PUMA, MLZ [22].

This concept has been further advanced by integrating layers of analysers, each in a cylindrical form covering an A_4 -angle of tens of degrees. This implementation enables the measurement of various directions and magnitudes of $\mathbf{k}_f$ simultaneously. Such a design has been integrated into instruments like BAMBUS at PANDA, MLZ [23], the FLATCONE add-on for several instruments at ILL (e.g. ThALES, IN8, IN14, and IN20) [24], as well as CAMEA at PSI and BIFROST European Spallation Source (ESS) [25]. The visual representation of the concept is depicted by a simplified schematic of CAMEA in Fig. 1.8.

Our approach, the Mushroom concept, seeks to enhance the utility of the neu-

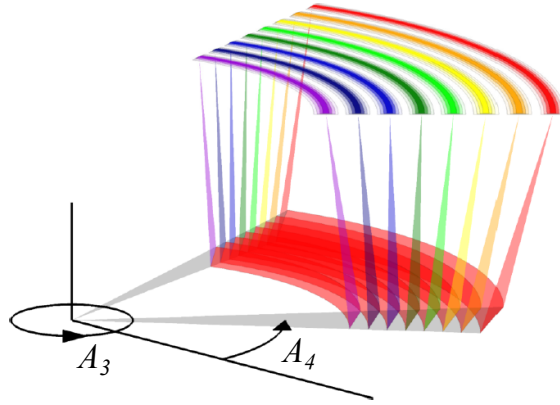


Figure 1.8: Schematic of the secondary spectrometer of CAMEA at PSI [25], where the angles A_3 and A_4 correspond to the notations listed in Tab. 1.1. The analyser arcs cover a large range of scattering angles $31^\circ < 2\theta_A < 128^\circ$ and reflect the neutrons upwards, where the neutrons with different E_f -values are detected by a detector array. The varying E_f -values reflected by the analyser arcs are visualised by the colours (from red to violet with increasing energies). Figure taken from [25].

tron beam by broadening the solid-angle coverage of the scattered beam within a spectrometer employing an indirect geometry. This design not only expands the coverage of the in-plane scattering angle but also grants access to the out-of-plane component of $\mathbf{k}_f$. Initially introduced by R. Bewley [17] in comparison to LET, a ToF-DGS at the pulsed neutron spallation source ISIS, the term “Mushroom” derives from the super flat-cone shape of the analyser in the secondary spectrometer, complemented by a PSD bank at its base (Fig. 1.9). This unique analyser system covers solid angles of the scattered beam that are approximately twice as large as those in a conventional ToF-DGS setup.

In the following discussion, we discuss the practical implementation of the Mushroom concept at FRM II, a continuous neutron source of the reactor type. The insights and methodologies discussed in this section are also relevant to similar continuous spallation sources like SINQ. Our examination begins with a detailed analysis of the secondary spectrometer, the fundamental element from which the Mushroom concept derives its name. Subsequently, we focus on the primary spectrometer, considering the options of both ToF and monochromator. Our evaluation encompasses parameters including wavevector and energy resolution, supported by analytical calculations and Monte Carlo simulations.

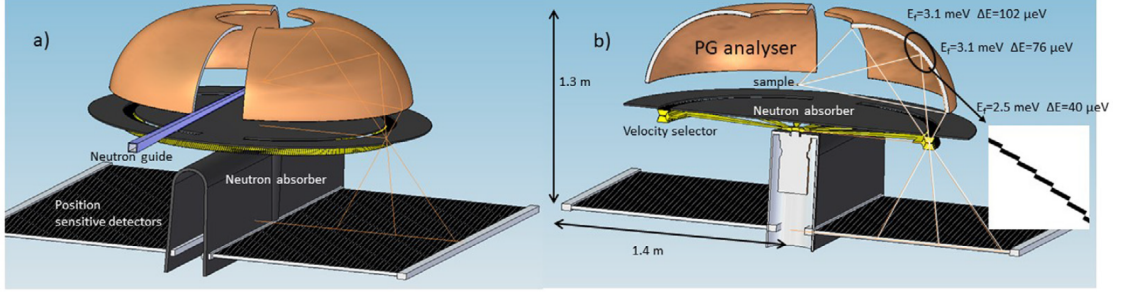


Figure 1.9: A schematic of the Mushroom concept by R. Bewley [17]. A 3D representation is shown in panel (a), while its sectional view is displayed in panel (b). The PG analyser is configured such that it reflects over a large solid angle for neutrons with energies between 2.5 meV and 3.1 meV. The diameter of the secondary spectrometer is approximately 2.8 m and the total height is approximately 1.3 m.

1.3 Mushroom - secondary spectrometer

The secondary spectrometer of the Mushroom concept consists of a super flat-cone analyser, an order selector, PSD banks, and shielding. In the following, the working principle of the secondary spectrometer will be illustrated, followed by details of the components.

1.3.1 Working principle

The secondary spectrometer, with its schematic illustrated in Fig. 1.10a, plays a crucial role in determining the wavevector $\mathbf{k}_f$ of the scattered neutrons. For the wavenumber k_f , a super flat-cone analyser is employed, reflecting neutrons following Bragg's law (Eq. 1.4). In order to distinguish k_f unambiguously, it is essential to ascertain the diffraction order n_A , as the parameter n described in Eq. 1.4, during neutron reflection by the analyser. This is achieved through an elliptic design of the analyser in the vertical sectional view, where one of its two focal points aligns with the sample position. After the analyser reflects the neutrons, they pass through the other focal point of the ellipse, where an order selector is installed to select the order n_A . The neutrons reflected by the analyser and accepted by the velocity selector finally reach the PSD banks. The positions on the detector pinpoint the positions of the analyser segments, effectively discerning the direction of the scattered neutrons, denoted as $\hat{\mathbf{k}}_f$. In this manner, the secondary spectrometer can provide the complete information of the final wavevector $\mathbf{k}_f$.

1.3.2 Analyser

The analyser stands out due to its distinctive mushroom-like shape that covers a large solid angle of the scattered neutron beam. The analyser segments are crafted from pyrolytic graphite (PG), a widely used material for neutron crystal monochromators and analysers. In order to maintain a high resolution, the segments have a small size in the range of a few centimetres, ensuring a reasonable divergence. Given the overall size of the analyser array spanning a few metres in diameter, a considerable amount of crystals is essential, thus favouring the use of flat PG crystals to simplify procedures like alignment.

As depicted in Fig. 1.10b, the analyser has a rotational symmetry around the vertical axis going through the sample position, except for the openings at the neutron guide for an incoming beam and the beam stop shielding against the direct beam after sample. Benefiting from the symmetric design, a spherical coordinate system (Fig. 1.10b) is introduced for discussing the secondary spectrometer, where the sample is at the origin of this coordinate system, the z -axis points upwards, the x -axis is parallel to the wavevector $\mathbf{k}_i$ of the incident beam, and the y -axis completes a right-hand system. With this configuration, the coordinate system can be used not only to define the positions of the analyser segments by their azimuthal (horizontal, ψ) and polar (vertical, φ) angles, but also to describe the direction of $\mathbf{k}_f$ of a beam using the same angles as of the segment reflecting this beam, yielding:

$$\mathbf{k}_f = \begin{pmatrix} k_{f,x} \\ k_{f,y} \\ k_{f,z} \end{pmatrix} = \begin{pmatrix} k_f \cos \varphi \cos \psi \\ k_f \cos \varphi \sin \psi \\ k_f \sin \varphi \end{pmatrix}. \quad (1.5)$$

Considering the fact that $\mathbf{x} \parallel \mathbf{k}_i$, we have:

$$\mathbf{k}_i = \begin{pmatrix} k_i \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{Q} = \begin{pmatrix} k_i - k_f \cos \varphi \cos \psi \\ -k_f \cos \varphi \sin \psi \\ -k_f \sin \varphi \end{pmatrix}. \quad (1.6)$$

In order to separate the wavenumber k_f from the vertical angle φ , thereby decoupling the out-of-plane component Q_z from the energy transfer $\hbar\omega$, the analyser operates with a constant wavenumber k_f across all φ -values. This is accomplished by arranging the analyser segments on distinct ellipses that share identical foci. This contrasts with the polygonal design, where the ends of neighbouring analyser segments share the position, forming approximately one elliptical arc in the vertical view. The two designs are compared in Fig. 1.11. The geometries of these two designs are depicted in Fig. 1.11a, while the panels b and c of Fig. 1.11 illustrate k_f and $k_{f,z}$, respectively, as functions of φ . Fig. 1.11 demonstrates that a constant- k_f design successfully decouples the terms $k_{f,z}$ and k_f (Eq. 1.5 and 1.6), whilst these two terms in a polygonal design are entangled. As a result, a constant- k_f design

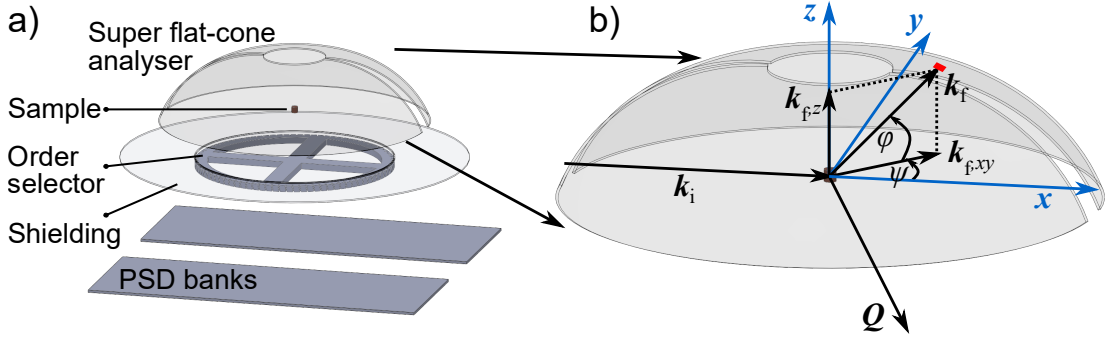


Figure 1.10: Panel a: a schematic of the secondary spectrometer of the Mushroom. Panel b: An enlarged picture of the analyser illustrating the coordinate systems. The Cartesian system is defined with its origin at the sample position, the z -axis pointing upwards, the x -axis being collinear to the wavevector $\mathbf{k}_i$ of incoming beam, and the y -axis completing the right-hand rule. The analyser has a mirror symmetry with regard to the xz - and yz -planes, with the angular position (ψ, φ) -of one of its segments highlighted in red. For simplicity, the analyser is depicted as a single entity on either side of the direct beam, adopting an elliptical form in a vertical sectional view. Consequently, the azimuthal angle ψ signifies the angle between the wavevector $\mathbf{k}_f$ of scattered beam and the xz -plane, while the polar angle φ denotes the angle between $\mathbf{k}_f$ and the xy -plane.

offers access to various Q_z values at the same $\hbar\omega$ -value, significantly simplifying experiment planning compared to using a polygonal design.

When calculating the analyser segments, there can be only one point in each segment that can ideally match the scattering angle for the target value of k_f , for which its position and orientation can be calculated in dependency on the vertical angle φ . The centre of each segment is set to fulfil the Bragg condition, so that the deviations on other positions of the same segment are minimised in total.

It is crucial to examine the effect due to an interplay between neighbouring analyser segments, especially if a segment is placed in the way of the neutron reflected by its neighbour with a higher φ . With the indexing starting from the highest φ to the lowest φ , an arbitrary segment and its neighbour can be denoted by indices i and $(i + 1)$, respectively. These two segments are not parallel due to their distinct orientations, but their differences are minor. Hence, the neutrons reflected by the i -th segment may be scattered by the $(i + 1)$ -th segment, depending on the mosaicity of analyser crystals. This effect is showcased in Fig. 1.12a, where the third segment (“Seg 3”) does not reflect the neutrons coming from the second segment (“Seg 2”), with the neutron trajectory denoted in blue. In contrast, some of the neutrons reflected by the 16th segment (“Seg 16”) can be reflected on the back side of the 17th segment (“Seg 17”), with the beam with and without double

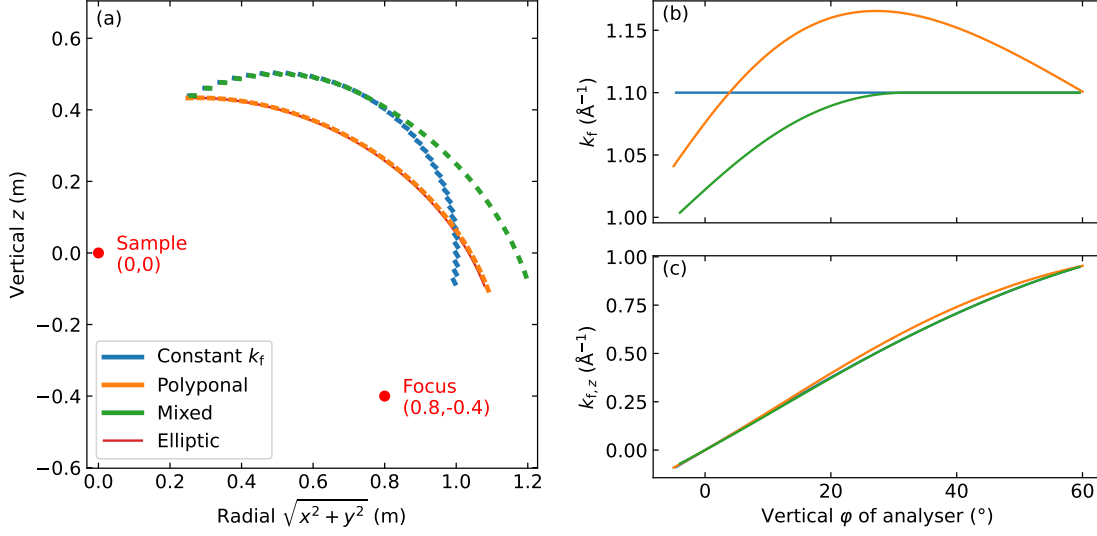


Figure 1.11: Comparison between “Constant k_f ”, where analyser segments are designed for a constant $k_f = 1.1 \text{ \AA}^{-1}$ when using PG 002, “Polygonal”, where the end of an analyser segment is at the same position as the start of its neighbour, and “Mixed”, where the segments are arranged for a constant k_f only if interferences between neighbouring segments are absent, and the segments have a polygonal design to avoid such interference. Panel a: The geometries of these three designs, with every third segment plotted, each segment having a size of 1 cm. The sample position at (0,0) and the other focal point at (0.8 m, -0.4 m) are the two foci of respective ellipses. Panel b: The k_f -values as a function of the vertical angle ϕ of the analyser segments reflecting scattered neutrons. Panel c: The out-of-plane component of $\mathbf{k}_f$, denoted by $k_{f,z}$, as a function of the vertical angle ϕ of analyser segments.

reflections denoted in orange and green, respectively.

To examine the effect on the intensity of the neutron beam, the configuration with $l_S = l_A = l_F = 1 \text{ cm}$ and a mosaicity $\eta_A = 60'$ of analyser crystals (with a reflectivity of 70 % for $k_f = 1.1 \text{ \AA}^{-1}$) has been simulated using McStas, depicted in Fig. 1.12b. The simulation considers each segment (i) and the next one ($i + 1$), where the neutron beam scattered by a vanadium sample is focused onto the i -th segment only, abandoning other neutrons in the simulation. The two segments are implemented either as a component group in McStas, where only the first segment that a neutron encounters reflects the neutron ⁵, or as two individual components,

⁵The i -th segment is considered first, while the $(i + 1)$ -th segment is considered only if the i -th segment does not scatter the neutron beam. However, since the scattered beam is focused onto the i -th segment, it does not hit the $(i + 1)$ segment.

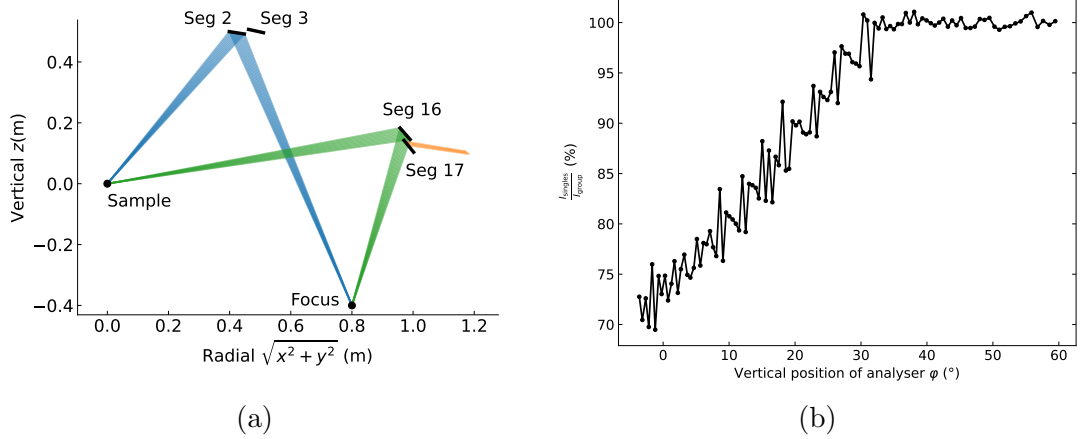


Figure 1.12: Panel a: Examples visualising possible multi-reflections due to neighbouring analyser segments. Neutrons reflected by the second segment (“Seg 2”, indexed from high φ to low φ) are not reflected by the third segment (“Seg 3”), as shown by the blue trajectory. Some neutrons reflected by the 16th segment (“Seg 16”) may be reflected by the 17th segment (“Seg 17”), depicted by orange and green for beams with and without double reflections, respectively. Panel b: Simulations comparing the intensity of neutrons reflected by a single analyser segment (I_{single}) with the intensity where the neutron beam reflected by this segment may also be reflected by the next one (I_{double}). Further details on the simulations are provided in the text.

where double reflections are possible ⁶. In this manner, the first situation provides the intensity due to the i -th segment only, while the second situation considers a reduction of intensity due to double reflections.

The results illustrated in Fig. 1.12b indicate no reduction of intensity at high φ -values, which can be understood by the fact that the $(i + 1)$ -th segment at a high φ is not between the i -th segment and the focal point. At low φ -values, the intensity decreases down to 70 %, which can be explained by the overlap between the i -th and $(i + 1)$ -th segments at low φ . A reduction of intensities by 30 % can be accepted but has to be corrected for data analysis. Besides, it is necessary to install radiation shielding, e.g. made of boron (B), around the analyser. A compromise is to keep a constant k_f only as long as this interference between neighbouring segments is absent and to employ a polygonal design for the rest of the segments. This design is depicted in Fig. 1.11, where approximately half of the segments are associated with a constant k_f .

⁶Since the scattered beam is focused onto the i -th segment, it can hit the $(i + 1)$ segment only if it is reflected by the i -th one.

1.3.3 Order selector

The order selector operates based on the principle of a mechanical velocity selector. Its traditional design involves multiple blades arranged to permit the passage of neutrons travelling at a specific velocity v_0 [26]. In order to prevent higher-order contaminations where neutrons with velocities nv_0 ($n \in \mathbb{N}$) also pass the final plate, the design necessitates more than two plates with their openings phased only for the target v_0 .

Modern designs of mechanical velocity selectors feature a spiral formation of blades crafted from neutron-absorbing materials, such as gadolinium (Gd), as depicted in Fig. 1.13. This design features an opening angle α , a spiral phase angle γ and an angular velocity ω (Fig. 1.13). The selector is calibrated to allow the transmission of neutrons satisfying the condition:

$$\frac{D}{v_0} = \frac{\gamma}{\omega} = t_0, \quad (1.7)$$

where D represents the length of the selector, v_0 denotes neutron velocity, and t_0 signifies the time taken to pass through. The fastest and slowest neutrons capable of passage have travel times given by:

$$t_{\min} = \frac{\gamma - \alpha}{\omega}, \quad t_{\max} = \frac{\gamma + \alpha}{\omega}. \quad (1.8)$$

As a result, the time resolution, measured by relative uncertainty, is determined by:

$$u_r = \frac{\Delta t}{t} = \frac{(t_{\max} - t_{\min})/2}{t_0} = \frac{\alpha}{\gamma}. \quad (1.9)$$

The resolution of a velocity selector is commonly around 10 % [27, 28], yet employing highly collimated slits allows achieving a higher resolution of approximately 2.5 %, which is particularly beneficial for SANS instruments [28].

Fig. 1.14 illustrates the design modified for the order selector of Mushroom, featuring a radius R and a thickness D . Each slit has a width s , a tilting angle β , and a phase difference $d = D \tan \beta$ between its two ends. The order selector requires the same time for the plate to rotate across distance d as the time for the neutron beam to travel across the distance D . Denoting the rotation frequency as f , these parameters yield:

$$\frac{D}{v_0} = \frac{d}{2\pi R f}. \quad (1.10)$$

The resolution, measured as the relative uncertainty, yields:

$$u_r = \frac{s}{d}. \quad (1.11)$$

For our purpose of selecting the diffraction order n_A of PG 002 and PG 004, a moderate resolution of about 25 % is already sufficient.

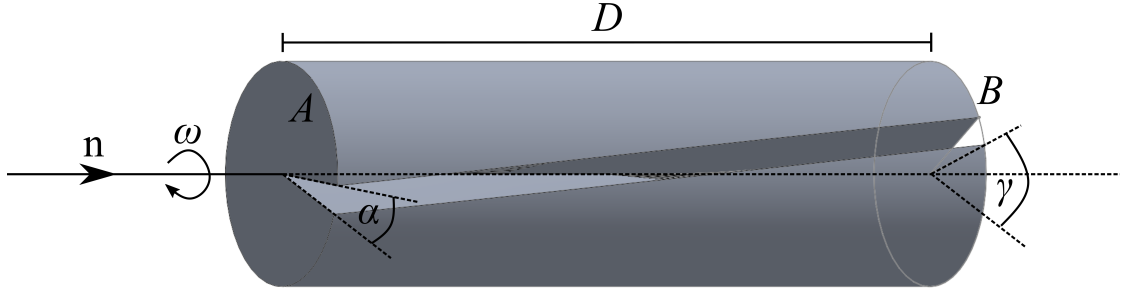


Figure 1.13: Schematic of a spiral velocity selector with the thickness D and rotational frequency ω . The neutron (“n”) travels from left to right. The opening angle is α , and the phase shift between the two surfaces, A and B , is γ . Figure reproduced from [26].

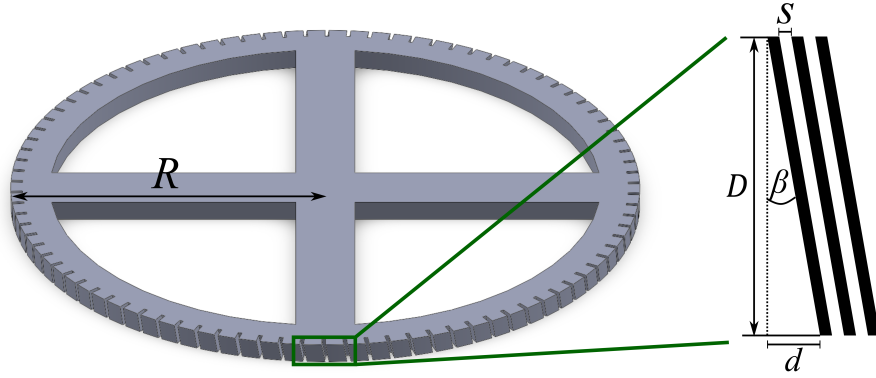


Figure 1.14: A simplified schematic of the order selector, featuring a radius R and thickness D , for the secondary spectrometer of Mushroom. The size and number of slits are adjusted for the schematic to improve visibility, with the enlarged version illustrated on the right-hand side. The geometry of a slit is defined by its width s , tilting angle β , and phase difference $d = D \tan \beta$ between its two ends.

1.3.4 Detector and shielding

In addition to the analyser and order selector, the detector and shielding play essential roles. The bank of PSDs has a size of several metres in both xy dimensions. Commercially available PSDs can fulfil this requirement and offer a sufficient spatial resolution in the millimetre to centimetre range [29]. If a resolution finer than the analyser segments is used, a plasma design can be possible, further improving the resolution of the secondary spectrometer.

Alongside the order selector positioned at the common focal point of the ellipses, shielding becomes imperative to remove undesired neutrons – for instance, the neutrons coming from the sample without being reflected by the analyser –

from reaching the detectors. The shielding, exhibiting a round shape, incorporates a radially symmetrical slit around the focal point to accomplish this task.

1.3.5 Geometrical parameters

The geometrical parameters are carefully selected to match the components mentioned above with the working principle of Mushroom. According to Bragg's law (Eq. 1.4), a larger k_f (or a smaller λ_f) implies a reduced θ_A , leading to a larger L_{SD} . This expansion demands more space around the sample position for a cryostat, thereby increasing the size of the secondary spectrometer for the same diffraction order n_A . Therefore, meticulous consideration of geometrical parameters is essential to fulfil multiple requirements:

- The analyser should cover a vertical angle as large as possible.
- The coverage of the azimuthal angle ψ should be as close to 360° as feasible, except around positions for the neutron guide (incident beam) and beam stop.
- The installation of a cryostat for the sample with a diameter of approximately 0.5 m should be ensured.
- The outer diameter of the secondary spectrometer should not exceed 3 m;
- The total height should not exceed 2 m;
- The PG analyser (PG 002) should select $1.0 \text{ \AA}^{-1} < k_{f,002} < 1.5 \text{ \AA}^{-1}$, and $2.0 \text{ \AA}^{-1} < k_{f,004} < 3.0 \text{ \AA}^{-1}$ using PG 004, operating for the range of cold neutrons;
- The size of an analyser segment and the aperture of an order selector should be comparable to provide a suitable resolution;
- The incident angle of neutrons at PSD should be as close to $\frac{\pi}{2}$ as possible to minimise the spreads on PSDs, which helps to reduce the overlap among neutrons arriving from distinct analyser segments at PSDs.

The setup shown in Fig. 1.15 fulfils the requirements, offering $k_{f,002} = 1.1 \text{ \AA}^{-1}$. In this configuration, the sample position is labelled as the origin (0, 0), and the other focal point is positioned at (0.8 m, -0.4 m). The analyser segment sizes and the opening at the other focal point measure 1 cm. Below the sample position, the PSD bank extends to 1.24 m and has an outer radius of 1.35 m. The analyser provides coverage of vertical scattering angles spanning from -5° to 60° . If needed,

geometrical parameters can be adjusted to achieve a different desired k_f -value, depending on the available instrument space and other factors when realising the instrument.

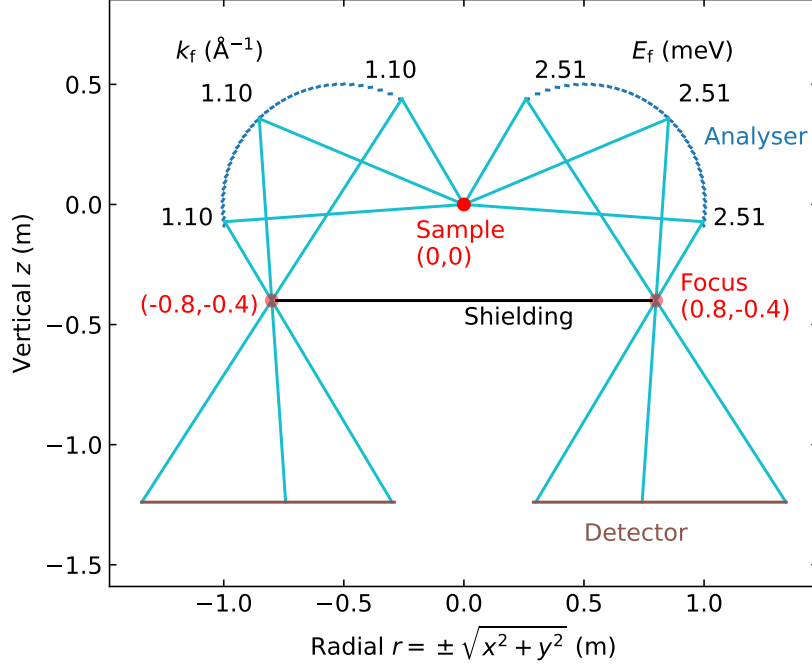


Figure 1.15: Schematic of the Mushroom secondary spectrometer in a sectional view. The dark blue dashed lines denote the analyser segments (every third segment is plotted for a better visual clarity), the light blue lines showcase some representative trajectories of the neutron beam, the brown lines illustrate the PSD banks, the black line indicates the shielding, and the red points depict the sample position at $(0, 0)$ as well as the other focal points at $(\pm 0.8 \text{ m}, -0.4 \text{ m})$. The geometrical parameters correspond to a configuration for $k_f = 1.1 \text{ \AA}^{-1}$ and $E_f = 2.51 \text{ meV}$.

Considering a resolution of the order selector of $u_r \approx 25\%$, the frequency for PG 002 is approximately $f_{002} \approx 29.3 \text{ Hz}$, hence $f_{004} \approx 58.6 \text{ Hz}$. With $s = 3 \text{ mm}$, this results in $d = 12 \text{ mm}$ and $D \approx 56 \text{ mm}$.

1.4 Mushroom - primary spectrometer

As shown in Fig. 1.10, the wavevector $\mathbf{k}_i$ of the incident beam maintains a fixed direction. The determination of the wavenumber k_i can be achieved through multiple methods.

Firstly, the wave nature of neutrons allows a crystal monochromator to establish wavelength, similar to a conventional TAS. Secondly, the particle nature of neutrons permits the determination of incoming velocity by a mechanical velocity selector or the ToF chopper system, providing the wavenumber as:

$$k_i = \frac{mv_i}{\hbar}. \quad (1.12)$$

A mechanical velocity selector can be employed as explained in Sec. 1.3 for a nearly monochromatic beam. The configuration of the ToF chopper system determines whether it delivers a nearly monochromatic beam as in a ToF-DGS or a polychromatic beam. This section will explore the options using either a crystal monochromator or a polychromatic ToF chopper system.

1.4.1 Option 1: Crystal monochromator

Working principle and design

A crystal monochromator reflects neutrons that satisfy Bragg's law (Eq. 1.4) and transmits the others. This feature enables positioning the Mushroom spectrometer along a neutron guide before its end, provided there is no conflict in wavelengths with other instruments along the same guide. For covering elastic scattering with $k_i = k_f$, it is beneficial that the monochromator be crafted from the same material, i.e. PG, as in the analyser.

The Mushroom primary spectrometer can utilise a single or double monochromator system (Fig. 1.16). In the single-monochromator setup, components rotate around the monochromator to alter the scattering angle $2\theta_M$, enabling measurements at different k_i -values. For instance, considering a maximum spectrometer radius of $r = 1.5$ m and a monochromator-sample distance of $d = 2$ m, the scattering angle coverage becomes $2\theta_M \in (\tan \frac{r}{d}, \pi - \tan \frac{r}{d})$, corresponding to $k_i \in (1.03 \text{ \AA}^{-1}, 2.28 \text{ \AA}^{-1})$. This configuration occupies an area of approximately $5.7 \text{ m} \times 3.5 \text{ m}$, including space needed for the secondary spectrometer rotation.

Due to the complexity and time needed to move the large secondary spectrometer around the monochromator whenever k_i has to be changed, a double-monochromator system is a viable alternative. Both monochromators rotate around their vertical axes for the desired θ_M . The second monochromator adjusts to maintain the neutron beam trajectory after the first monochromator, ensuring the secondary spectrometer remains stationary regardless of k_i . This design occupies an area of $2(d \cos \theta_M + r) \cdot 2r$, corresponding to approximately $5.7 \text{ m} \times 3.0 \text{ m}$, which is smaller than the single-monochromator setup.

In the wavenumber range $(1.03 \text{ \AA}^{-1}, 2.28 \text{ \AA}^{-1})$ or wavelength range $(2.76 \text{ \AA}, 6.10 \text{ \AA})$ in the primary spectrometer, the reflectivity of PG 002 is $\gtrsim 0.75$, as shown in Fig.

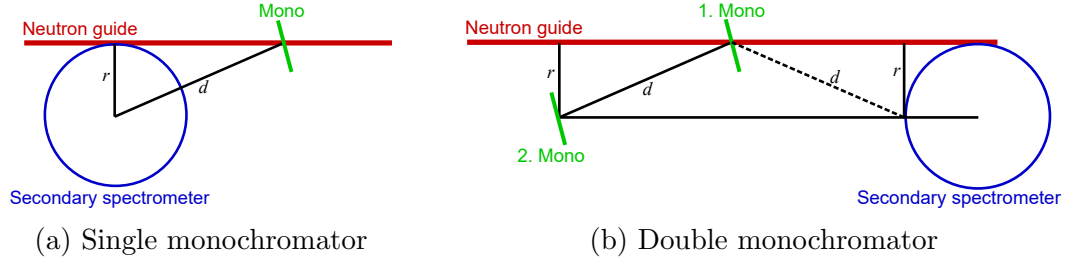


Figure 1.16: Mushroom primary spectrometer with a single- (Fig. 1.16a) or double-monochromator system (Fig. 1.16b). Fig. 1.16a: the secondary spectrometer rotates as a whole around the monochromator for changing the scattering angle $2\theta_M$ (A_4), while the monochromator rotates around its vertical axis for the respective θ_M (A_3). Fig. 1.16b: The first monochromator rotates around its vertical axis, whilst the second one not only rotates around its axis but also moves accordingly to keep the same trajectory of the neutron beam after it, so that the secondary spectrometer stays at the same position.

1.17 [30, 31]. Consequently, the double-monochromator system is able to offer a comparable neutron flux to the single-monochromator setup.

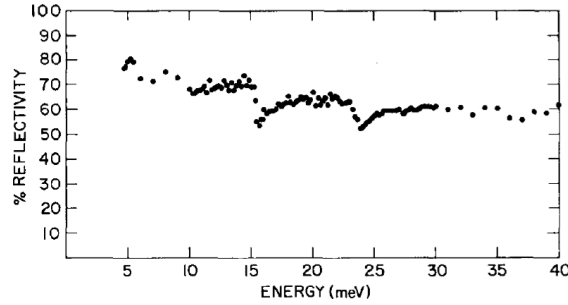


Figure 1.17: Reflectivity of pyrolytic graphite (PG 002) as a function of the neutron energy. Figure taken from [31].

Diffraction order

Similar to the analyser (Sec. 1.3), a monochromator also reflects neutrons with a higher diffraction order n_M (Eq. 1.4). This produces neutrons with wavelengths $\lambda_i = \frac{\lambda_0}{n_M}$ in addition to the intended λ_0 , potentially affecting intensities assigned to a wrong $(\mathbf{Q}, \omega)$ -position. Hence, choosing the diffraction order n_M becomes crucial.

Apart from employing a mechanical velocity selector (Sec. 1.3), a neutron crystalline filter [1] can be inserted as an alternative due to the fixed trajectory

of the incident beam. This filter utilises the total cross-section, describing the probability of neutron interaction with matter [1]:

$$\sigma_{\text{tot}} = \sigma_{\text{abs}} + \sigma_{\text{inel}} + \sigma_{\text{el}}. \quad (1.13)$$

Different filter types exploit distinct portions of this cross-section. Filters using the absorption and inelastic terms are effectual for fast neutrons with energies typically above $E > 50 \text{ meV}$ [1]. Conversely, filters centred on the elastic term σ_{el} become promising candidates for our purpose of using cold to thermal neutrons.

The elastic term, σ_{el} , corresponds to Bragg scattering (Eq. 1.4), enabling two filter types. The first utilises polycrystalline materials, scattering neutrons with various wavelengths out of the beam trajectory. Its upper wavelength limit, λ_{cutoff} , is determined by the largest d-spacing (d_{max}) related to the smallest Miller index of crystal planes. Above $\lambda_{\text{cutoff}} = 2d_{\text{max}}$, the cross-section σ_{el} decreases sharply. Hence, this filter scatters neutrons with $\lambda < \lambda_{\text{cutoff}}$ and allows slower neutrons to pass through [1, 32]. Typical λ_{cutoff} values for commonly used materials like beryllium (Be) range between approximately $4 \text{ \AA}$ and $8 \text{ \AA}$, as measured by A. Freund *et al.* [33] (Fig. 1.18).

The second type involves PG single crystals, orienting their c -axis parallel to the beam. This filter scatters neutrons meeting the condition:

$$2k \sin\left(\frac{\pi}{2} - \varphi_{hkl}\right) = G_{hkl}, \quad (1.14)$$

where φ_{hkl} is the angle between the reciprocal-lattice vector $\mathbf{G}_{hkl}$ and the c -axis, transmitting the remaining neutrons [1]. Consequently, lower-energy first-order neutrons pass through, while higher-order neutrons with greater energies are significantly attenuated due to scattering from other crystal planes.

Loopstra *et al.* [34] observed high efficiency of PG crystals for first-order neutrons with energies from 10 meV to 15 meV (wavelengths between $2.34 \text{ \AA}$ and $2.86 \text{ \AA}$). The efficiency begins from 4.5 meV (wavelength $4.26 \text{ \AA}$), as documented by Loopstra *et al.* [34] and Bergsma *et al.* [35].

A neutron filter working on Bragg scattering could be advantageous for the Mushroom spectrometer using cold neutrons. However, this filter is not viable for the entire range of $2.76 \text{ \AA} < \lambda_i < 6.10 \text{ \AA}$ ($2.20 \text{ meV} < E_i < 10.74 \text{ meV}$) without switching between two filters for different wavelength ranges. An alternative is a spiral velocity selector (Fig. 1.13). Its adaptability across various wavelengths, controlled by frequency tuning following Eq. 1.7, makes it a flexible choice.

A monochromator-type primary spectrometer offers flexibility in its positioning along a neutron guide. However, like a TAS, this design suffers from the limitation of measuring a single k_i at a time.

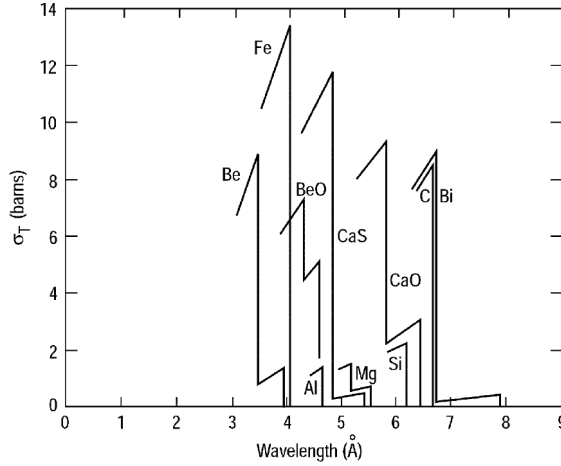


Figure 1.18: Scattering cross-section as a function of neutron wavelength of varying polycrystalline materials [33] showing the cutoff wavelengths, above which the neutrons are not scattered but transmitted.

1.4.2 Option 2: Time-of-flight system with choppers

A primary spectrometer with a chopper system for Mushroom operates like other ToF-IGSs, as mentioned in Sec. 1.2.3. At FRM II, being a continuous source, the first chopper C_1 serves to start time-counting and cut the initial beam into pulses, hence often called a pulse-cutting chopper. This contrasts with pulsed spallation sources like ISIS, where the beam arrives in pulses from the source. As a neutron beam has a finite size, it becomes necessary to incorporate either a slit or a counter chopper with an identical opening rotating in the opposite direction. Due to the minor role of the counter chopper in shaping the wavelength spectrum, the system with C_1 and its counter chopper will be referred to in this thesis as a single-chopper system.

Measuring the ToF t_{tot} between C_1 and detector yields the ToF of neutrons between C_1 and the sample:

$$t_i = t_{\text{tot}} - t_f = t_{\text{tot}} - \frac{L_{\text{SD}}}{v_f}. \quad (1.15)$$

Here, L_{SD} denotes the sample-detector distance, t_f represents the ToF in the secondary spectrometer, and v_f signifies the velocity of scattered neutrons determined by the analyser following Bragg's law (Eq. 1.4). With the distance L_{1S} between the chopper C_1 and the sample position, the velocity v_i and energy E_i of the incident beam can be determined.

The travel lengths and times concerning the instrument components are illustrated in Fig. 1.19. Since the secondary spectrometer can utilise only one k_f -value

at a time, the incident beam following the chopper system should be polychromatic to provide higher count rates. Configuring such a chopper system involves three main factors: eliminating frame overlaps, achieving good time resolution, and ensuring high transmission rates.

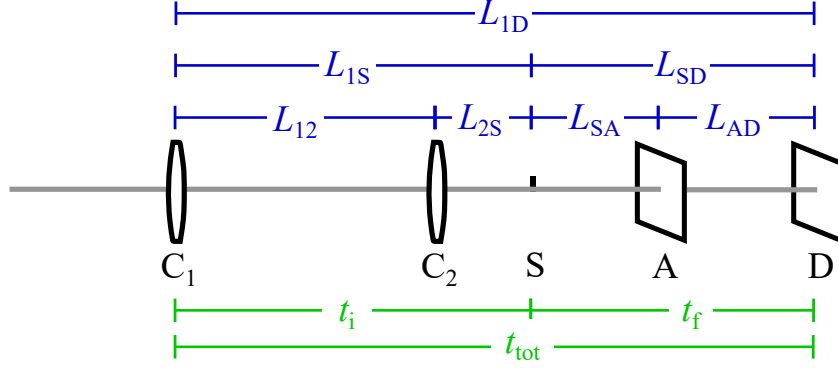


Figure 1.19: Schematic of the Mushroom spectrometer with two choppers showing the definitions of travel lengths and times of the neutron beam. For simplicity, all distances have the same order of magnitude, and all components are along the same line, with the 3D geometry depicted in Fig. 1.10. The components and abbreviations are chopper 1 (C₁), chopper 2 (C₂), sample (S), analyser (A) and detector (D). The distances between components are in blue. The travel times are in green.

Frame overlaps

Eliminating frame overlaps, where slower neutrons from a prior pulse intersect with faster ones from a subsequent pulse, is vital to differentiate between distinct pulses. Since the analyser selects a v_f -value from the scattered beam, frame overlaps have to be eliminated between chopper C₁ and the sample position in a single-chopper system, requiring:

$$\frac{L_{1S}}{v_{\max}} + T_1 - 2w_1 > \frac{L_{1S}}{v_{\min}}. \quad (1.16)$$

Here, $v_{\max}$ and $v_{\min}$ denote the maximum and minimum velocities of the incoming neutron beam, respectively, T_1 represents the repetition time of C₁, and $2w_1$ represents its opening time (Fig. 1.20). The time parameters are determined by:

$$T = \frac{1}{Nf}, \quad 2w = \frac{\varphi}{2\pi f}, \quad (1.17)$$

where f denotes the rotation frequency of the chopper, N signifies the number of openings, and φ represents the opening angle. The time uncertainty is governed

by the opening time of the pulse-cutting chopper C_1 , where the time of neutrons passing the same pulse cannot be distinguished, leading to ⁷:

$$\Delta t = w_1. \quad (1.18)$$

This time uncertainty spans the entire ToF (t_{tot}) within L_{1D} . However, owing to the minor uncertainty in the secondary spectrometer across all directions of the scattered beam, for simplicity, an approximation $\Delta t_i \approx w_1$ is adopted for discussions in this section concerning chopper parameters. A more precise expression $\Delta t_{\text{tot}} = w_1$ is reserved for the detailed discussion on resolution in Sec. 1.5.2. Employing this approximation, the relative time uncertainty in the primary spectrometer is determined as:

$$u_{r,t_i} = \frac{\Delta t_i}{t_i} \approx \frac{w_1}{L_{1S}/v_i} = \frac{w_1 v_i}{L_{1S}}. \quad (1.19)$$

When the chopper parameters φ_1 and f_1 are set, the time resolution $\Delta t_1 = w_1$ remains constant. Consequently, the relative resolution u_{r,t_i} is directly proportional to the velocity v_i in a measurement. Thus, the lowest resolution (i.e., the largest uncertainty) on the time t_i is expressed as:

$$u_{r,\text{max}} = \frac{w_1 v_{\text{max}}}{L_{1S}} = \frac{\varphi_1 v_{\text{max}}}{4\pi f_1 L_{1S}}. \quad (1.20)$$

The necessity to remove frame overlaps (Eq. 1.16) imposes restrictions on the parameters of chopper C_1 , indicated by:

$$\frac{2\pi}{N_1 \varphi_1} > \left(1 + \frac{1}{u_r} \left(\frac{v_{\text{max}}}{v_{\text{min}}} - 1 \right) \right). \quad (1.21)$$

Considering a polychromatic initial beam with $\lambda_{\text{min}} = 1 \text{ \AA}$ and $\lambda_{\text{max}} = 10 \text{ \AA}$, achieving a resolution $u_{r,\text{max}} = 5 \%$ requires:

$$N_1 \varphi_1 < 0.035 \text{ rad} \approx 2^\circ. \quad (1.22)$$

The maximum achievable transmission rate of the chopper system is determined by the total opening angle(s) divided by 2π , leading to:

$$R_t = \frac{N_1 \varphi_1}{2\pi} \approx 0.56 \%. \quad (1.23)$$

This equation indicates the drawback of the single-chopper system in flexibility, since once the parameters N_1 and φ_1 are set, the value of R_t becomes fixed, even though the resolution can be changed through the frequency f_1 .

⁷The standard deviation (SD) is actually $\sigma_t = \frac{w_1}{\sqrt{3}}$, as will be discussed in the section about the resolution. An approximated value is used to simplify the calculations.

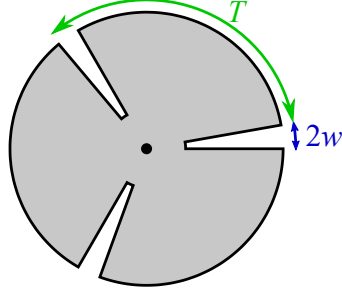


Figure 1.20: Schematic of a disk chopper with the number of openings $N = 3$, the opening time $2w$ and repetition time T .

Double-chopper system

To solve the issue of the single chopper, a second chopper C_2 rotating alongside C_1 can further divide each pulse from C_1 into sub-pulses. Each sub-pulse covers a narrower wavelength range, easing the restriction outlined in Eq. 1.16.

The design of such a system can refer to the concept by J. Copley [36], utilising a t - τ diagram. In this diagram, where t represents the time a neutron passes a reference component and $\tau = \frac{1}{v}$ is the inverse neutron velocity (Fig. 1.21), the time when a neutron passes C_1 at t_1 with the cycle index $n_1 = 1$ is between:

$$n_1 T_1 - w_1 \leq t_1 \leq n_1 T_1 + w_1, \quad n_1 \in \mathbb{Z}. \quad (1.24)$$

Similarly, the time passing C_2 at t_2 with cycle index n_2 is given by:

$$\tau_0 L_{12} + n_2 T_2 - w_2 \leq t_2 \leq \tau_0 L_{12} + n_2 T_2 + w_2, \quad n_2 \in \mathbb{Z}, \quad (1.25)$$

where τ_0 represents the nominal inverse velocity the choppers are configured to transmit, and L_{12} is the distance between them. A neutron passing C_1 at t_1 with an inverse velocity τ reaches C_2 at $t_2 = t_1 + \tau L_{12}$. This means:

$$t_2 = t_1 + \tau L_{12}. \quad (1.26)$$

Hence, the time at C_1 can also be expressed as:

$$(\tau_0 - \tau) L_{12} + n_2 T_2 - w_2 \leq t_1 \leq (\tau_0 - \tau) L_{12} + n_2 T_2 + w_2. \quad (1.27)$$

These equations are illustrated for $n_1, n_2 = 1, 2, \dots$ in Fig. 1.21. The overlaps in the diagram represent neutrons passing both choppers. In the geometry of Mushroom, this effect assists in generating a polychromatic initial beam using two adjustable-resolution choppers.

The rectification of frame overlaps, akin to the single-chopper scenario, involves analysing the time taken by neutrons to reach the sample ($t_s = t_1 + \tau L_{1s}$), where

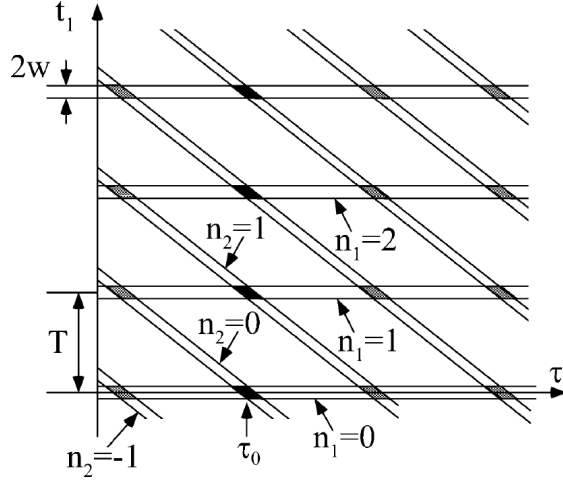


Figure 1.21: t_1 - τ diagram, where t_1 is the time of neutrons passing the first chopper and τ the inverse velocity. The indices n_1 and n_2 denote the open cycle when the neutron passes the chopper 1 and 2, respectively. Taken from [36].

L_{1S} denotes the distance between C_1 and the sample. The inequalities 1.24 and 1.27 can be reformulated concerning t_S :

$$\begin{aligned} \tau L_{1S} + n_1 T_1 - w_1 &\leq t_S \leq \tau L_{1S} + n_1 T_1 + w_1 \\ \tau_0 L_{12} + \tau L_{2S} + n_2 T_2 - w_2 &\leq t_S \leq \tau_0 L_{12} + \tau L_{2S} + n_2 T_2 + w_2, \end{aligned} \quad (1.28)$$

where $L_{2S} = L_{1S} - L_{12}$ represents the C_2 -sample distance. Post rigorous computations in Sec. 5.1, the resolution of frame overlaps elucidates two fundamental restrictions:

$$\begin{aligned} 2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) &\leq T_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) \\ 2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) &\leq T_2 - (\tau_{\max} - \tau_{\min}) (L_{1S} - L_{12}). \end{aligned} \quad (1.29)$$

This criterion aids in the optimal selection of chopper parameters for enhancing the transmission rate.

Transmission rate By utilising the t - τ diagrams, the upper limit of the transmission rate can be computed by summing the areas of the acceptance windows in the diagram and dividing this total by the entire area:

$$R_t = \frac{N_{(n_1, n_2)}}{N_{n_2}} \frac{2w_1 2w_2 / L_{12}}{(\tau_{\max} - \tau_{\min}) T_2} \approx \frac{2w_1 2w_2}{T_1 T_2}, \quad (1.30)$$

where $N_{(n_1, n_2)}$ represents the count of (n_1, n_2) -combinations accepted by the chopper system, while N_{n_2} denotes the total number of n_2 -values. The approximation holds when N_{n_2} attains a significant magnitude. With more detailed calculations available in the appendix (Sec. 5.2), the restrictions shown in Eq. 1.29 give the limit of the transmission rate as:

$$R_t \leq \frac{2w_1 L_{12}}{L_{1S} \left[2\sqrt{2w_1 (2w_1 + \Delta\tau L_{12})} + 2 \cdot 2w_1 + \Delta\tau L_{12} \right]}, \quad (1.31)$$

where the equality is achieved when:

$$\begin{aligned} 2w_2 &= \frac{L_{2S}}{L_{1S}} \sqrt{2w_1 (2w_1 + \Delta\tau L_{12})} \\ T_1 &= \frac{2w_2 L_{1S} + 2w_1 L_{2S}}{L_{2S}} \\ T_2 &= \frac{(\Delta\tau L_{12} + 2w_1) L_{2S} + 2w_2 L_{1S}}{L_{12}}. \end{aligned} \quad (1.32)$$

Here, the opening time $2w_1$ is determined by the target resolution u_r at $v_{\max}$, i.e. $\lambda_{\min}$, through Eq. 1.20:

$$2w_1 = \frac{\varphi_1}{2\pi f_1} = \frac{m_n \lambda_{\min} L_{1S} u_r}{2\pi \hbar}. \quad (1.33)$$

When the equality in Eq. 1.31 is attained, denoting the value of R_t as $R_{t, \max}$, L_{12} becomes a factor influencing $R_{t, \max}$ at a predetermined L_{1S} . This influence is depicted in Fig. 1.22 for $u_r = 5\%$ at $\lambda_{\min} = 1 \text{ \AA}$, demonstrating a marginal change of $R_{t, \max}$ when $L_{12} \gtrsim 5 \text{ m}$. Considering the dependency of other chopper system parameters on L_{12} (Fig. 1.23), $L_{12} = 10 \text{ m}$ is chosen for further deliberations.

With $u_r = 5\%$ at $\lambda_{\min} = 1 \text{ \AA}$ and $\lambda_{\max} = 10 \text{ \AA}$, alongside $N_1 = 3$ and $N_2 = 1$, the remaining parameters can be determined using Eq. 1.32. These values are summarised in Tab. 1.2. The resulting transmission rate is $R \approx 0.43\%$, with corresponding opening times of $2w_1 \approx 0.18 \text{ ms}$ and $2w_2 \approx 0.67 \text{ ms}$.

The achieved transmission rate is slightly less effective compared to a configuration that chops the entire beam once. However, it offers flexibility in adjusting the transmission rate based on the desired wavelength range and corresponding time resolution. The configuration, as described by these parameters, can be represented on a t_S - λ diagram (Fig. 1.24), illustrating the coverage of the wavelength range and allowing for an assessment of frame overlap.

Adaptive resolution

With the geometrical parameters of the choppers established for the specific configuration, namely N_i and φ_i ($i = 1, 2$), the chopper frequencies can be adjusted

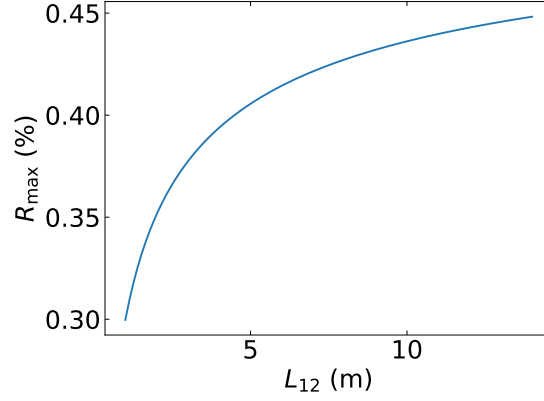


Figure 1.22: Maximum transmission rate of the chopper system $R_{\max}$ as a function of the C_1 - C_2 distance L_{12} .

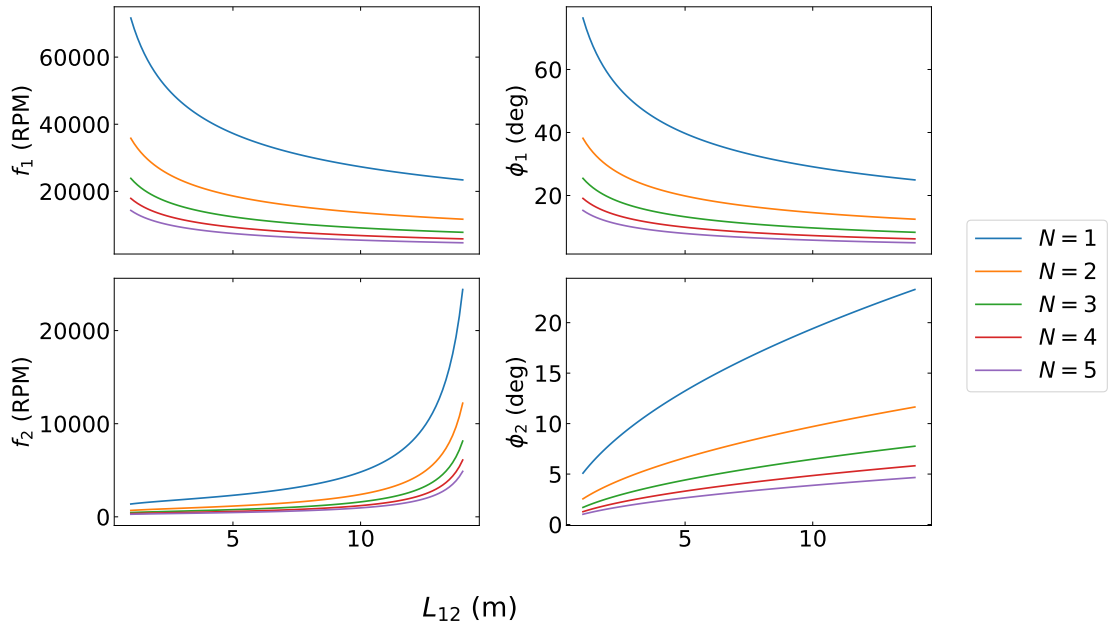


Figure 1.23: Chopper parameters as a function of the C_1 - C_2 distance L_{12} . The parameters are the chopper frequencies, f_1 and f_2 , as well as the opening angles, φ_1 and φ_2 . The situations with different numbers of openings N are treated.

to meet the target resolution at a reference wavelength. The two restrictions de-

f_1	f_2	φ_1	φ_2
219 Hz (8760 RPM)	79 Hz (4740 RPM)	9°	19°

Table 1.2: Parameters of the choppers with the given parameters in the text.

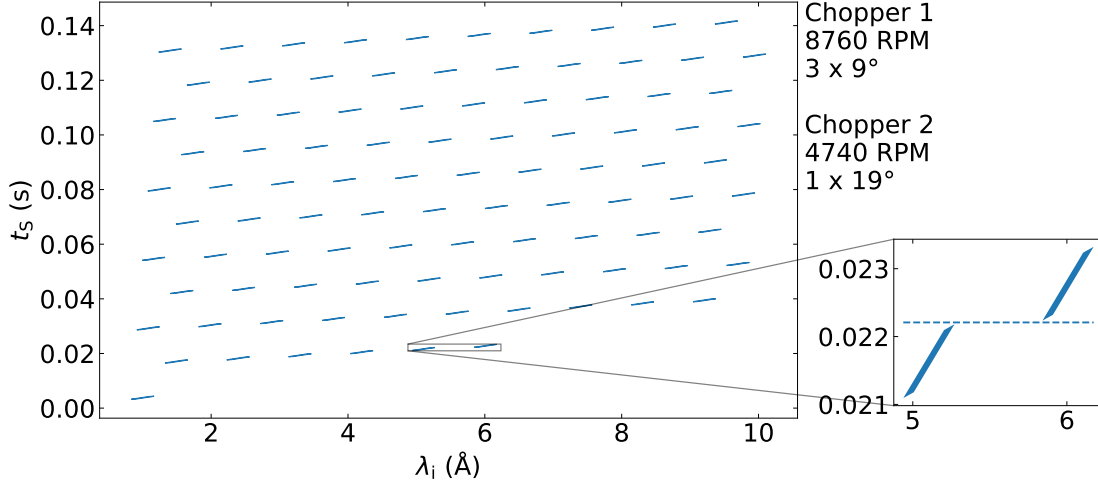


Figure 1.24: t_s - λ_i diagram at (n_1, n_2) -combinations, where t_s is the time for neutrons arriving at the sample position, λ_i the wavelengths of the incoming neutrons, and $n_1, n_2 = 1, 2, \dots, 1000$ the opening windows of the choppers C_1 and C_2 . The seeming stripes are parallelograms depicting the neutrons accepted at respective (n_1, n_2) -sets, with the zoom-in figure showing two representative pulses. The chopper C_1 with three 9°-openings each rotates with 8760 RPM, while C_2 with one 19°-opening rotates with 4740 RPM.

lineated in Eq. 1.29 are expressed as:

$$\begin{aligned}
 N_1 &\leq \frac{L_{2S}}{f_1 (2w_2 L_{1S} + 2w_1 L_{2S})} \\
 N_2 &\leq \frac{L_{12}}{f_2 [(\Delta\tau L_{12} + 2w_1) L_{2S} + 2w_2 L_{1S}]},
 \end{aligned} \tag{1.34}$$

where the C_2 -sample distance is denoted as $L_{2S} = L_{1S} - L_{12}$, and $\Delta\tau = \tau_{\max} - \tau_{\min}$. The transmission rate outlined in Eq. 1.30 is calculated as:

$$R \approx \frac{N_1 N_2 \varphi_1 \varphi_2}{(2\pi)^2}. \tag{1.35}$$

The resolution capability of the Mushroom instrument aims for adaptability within specific wavelength ranges to achieve desired resolutions by tuning the fre-

quency f_1 as per Eq. 1.33:

$$f_1 = \frac{\varphi_1 \hbar}{m \lambda L_{1S} u_r}. \quad (1.36)$$

The adaptive resolution is restricted by two main factors: the mechanical stability of the choppers and the elimination of frame overlaps. The maximum attainable $f_{1,\max}$ for a stable chopper C_1 determines the achievable time resolution:

$$u_r = \frac{\varphi_1 \hbar}{m \lambda L_{1S} f_{1,\max}}. \quad (1.37)$$

The constraint imposed by eliminating frame overlaps described in Eq. 1.29 leads to:

$$\begin{aligned} u_r &= \frac{\varphi_1 \hbar}{m \lambda L_{1S}} / f_1 \\ &= \frac{\varphi_1 \hbar (\tau_{\max} - \tau_{\min})}{m \lambda L_{1S}} / \left(\frac{2\pi}{\varphi_2 N_1 N_2 L_{1S}} - \frac{1}{N_1 L_{12}} - \frac{\varphi_1}{\varphi_2 N_2 L_{1S}} \right). \end{aligned} \quad (1.38)$$

Comparing these two limitations on resolution (Eq. 1.37 and 1.38) using the same parameters φ_1 , φ_2 , N_1 , and N_2 as shown in Fig. 1.25, illustrates that the effect resulting from eliminating frame overlaps dominates within the 1 Å to 10 Å wavelength range. Consequently, within the limitations outlined in Eq. 1.38, frequencies f_1 and f_2 can be computed based on the desired resolution at a specific wavelength. Predicting the transmission rate becomes feasible using Eq. 1.30.

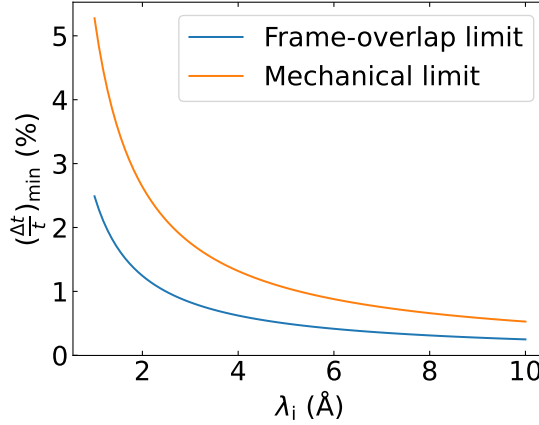
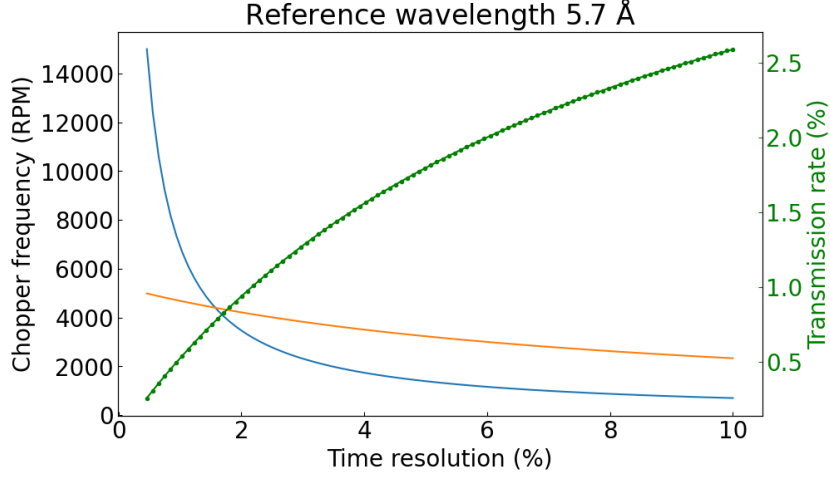
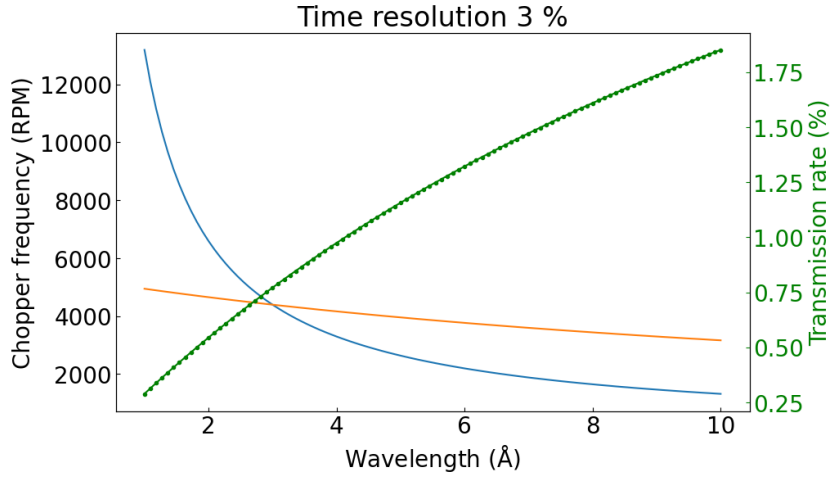


Figure 1.25: Reachable time resolution of the chopper system, which is limited by the mechanical stability and the removal of frame overlaps.

An example illustrating this process is depicted in Fig. 1.26, where chopper frequencies are calculated for varying resolution values at $\lambda_i = 5.7$ Å or for a resolution of $u_{r,t_i} = 3\%$ across different wavelengths.



(a) Chopper parameters with time resolution ranging from 1 % to 10 % at $k_i = 1.1 \text{ \AA}^{-1}$.



(b) Chopper parameters with time resolution 5 % at wavelength λ_i , which varies from 1 Å to 10 Å.

Figure 1.26: Chopper frequencies (C_1 in blue and C_2 in orange) tuning for different target resolutions at a given reference wavelength. The transmission rate in percentage is plotted in green on the right-hand side, where the lines are calculated according to Eq. 1.30 and the dots are calculated when the opening indices (n_1, n_2)-are examined up to 1000 for each configuration.

An alternative chopper system design involves incorporating more than two choppers and refining the neutron beam spectrum to allow passage of only a specific wavelength vicinity to the sample. Although the beam remains polychromatic rather than nearly monochromatic as in a DGS, this design offers adaptive resolution in a more narrow and adaptable wavelength range. This design does not conflict with the double-chopper setup, because the choppers can be installed or removed to meet varying sample feature requirements.

Optical system

In the preceding discussion, the beam size was considered infinitesimally small at the choppers. This necessitates a point-like virtual source at the position of the chopper, achievable through the utilisation of nested-mirror optics (NMO) [37]. The NMO system comprises nested supermirror segments arranged in either an elliptic or a hyperbolic shape, through which the incoming beam traverses before reaching the supermirrors. The elliptic NMO is adept at transporting the neutron beam from a point-like source to the other focal point, whereas the parabolic NMO is better suited for focusing a nearly-parallel beam onto a focal point, or vice versa [37].

Hence, presuming the incident neutron beam from the guide lacks focus, the parabolic optics can generate a virtual source at chopper C_1 . Concurrently, a double-planar (focused in both dimensions) elliptic NMO aids in transporting the beam from C_1 to the sample position. The installation of the NMO system might also be considered if the primary spectrometer is designed with additional choppers that require a focused beam at the positions of other choppers, e.g. for C_2 . However, this has to be considered together with the loss of intensity due to the optic system.

An illustrative schematic of the configuration utilising two choppers, accompanied by other significant components of the Mushroom spectrometer, is presented in Fig. 1.27.

1.5 Resolution

When estimating the resolution of an instrument for neutron scattering, the beam divergence depends on the geometry of the instrument and the sizes of the components. The contribution of a finite geometrical size (l), for example, of an opening, can be approximated by a rectangular distribution, exhibiting a variance $\sigma^2 = \frac{l^2}{12}$. The contribution is commonly approximated by a Gaussian distribution with the same SD [38], $\sigma = \frac{l}{2\sqrt{3}}$, whose full width at half maximum (FWHM) can be expressed using its SD: $\text{FWHM} = 2\sqrt{2\ln 2}\sigma$. The Gaussian approximation has the

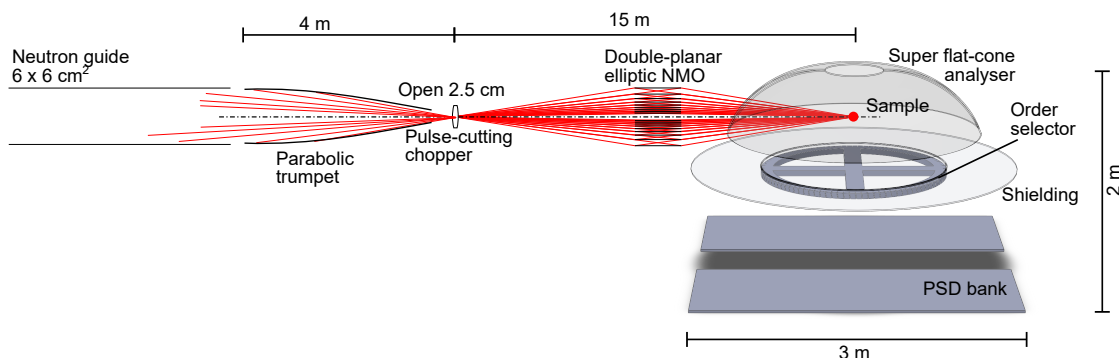


Figure 1.27: A not-to-scale schematic of the Mushroom instrument with the optics system for transporting the neutron beam. The parabolic trumpet generates a virtual source at the position of the pulse-cutting chopper (C_1). For visual clarity, only one double-planar (focused in both dimensions) elliptic NMO is shown to transport the beam from C_1 to the sample. The schematic of the secondary spectrometer corresponds to Fig. 1.10.

advantage that the resolution involving multiple contributions can be estimated using the propagation of uncertainty, where the SD of a function f with n independent variables, $x_1, x_2, \dots, x_n$, can be determined according to [39]:

$$\Delta f = \sqrt{\sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)^2 (\Delta x_i)^2}. \quad (1.39)$$

Here, $\frac{\partial f}{\partial x_i}$ represents the partial derivative of f concerning x_i ⁸. The uncertainty of x_i is denoted by its SD, Δx_i . Eq. 1.39 is valid when the SDs of all variables are small [40], which is in most cases true when discussing resolutions. In this thesis, the resolution Δx for an arbitrary variable x is represented by its SD, yielding: $\Delta x = \sigma_x$. Conversion is necessary when comparing a resolution characterised by its SD to a FWHM.

In this section, we begin by estimating the $\mathbf{k}$ -resolutions of the primary and secondary spectrometers separately, followed by discussions on resolutions related to wavevector transfer $\mathbf{Q}$ and energy transfer $\hbar\omega$. For both primary and secondary spectrometers, a $\mathbf{k}$ -resolution involves the wavenumber resolution (Δk) and its horizontal ($\Delta\psi$) and vertical ($\Delta\varphi$) angular spreads, with the angles (ψ, φ) illustrated in Fig. 1.10b. The secondary spectrometer will be discussed first.

⁸In case of $\frac{\partial f}{\partial x_i} = 0$, the next order should be used for calculating the contribution of x_i .

1.5.1 Secondary spectrometer

The resolution of the secondary spectrometer is estimated analytically and assessed using McStas, a software crafted for Monte-Carlo simulations of neutron instruments [41–45].

Wavenumber

The secondary spectrometer of Mushroom operates at a constant wavenumber k_f as long as the diffraction order n_A remains fixed. However, due to finite sizes of the sample (“S”), analyser (“A”), opening at the focal point (“F”) and the intrinsic resolution of a detector (“D”), there is some deviation in the scattering angle θ_A , resulting in a distribution of k_f -values around the target value $k_{f,002} = 1.1 \text{ \AA}^{-1}$. This deviation contributes to the k_f -resolution of the secondary spectrometer. Considering the diffraction order $n_A = 1$ in Eq. 1.4, the k_f -resolution can be derived using Eq. 1.39:

$$\frac{\Delta k_f}{k_f} = \sqrt{\left(\frac{\Delta d}{d}\right)^2 + (\cot \theta_A \Delta \theta_A)^2}. \quad (1.40)$$

The d -spacing of a PG crystal has been determined by T. Keller *et al.* to exhibit a broadening of $\frac{\Delta d}{d} \lesssim 2.5 \times 10^{-4}$ (characterised by its SD) [46]. The angular spread $\Delta \theta_A$ of scattering angles at an analyser are governed by various factors. Firstly, considering a fixed position of an analyser segment, an angular spread can be expressed as [19, 47]:

$$\Delta \theta_{A,1} = \sqrt{\frac{\alpha_{A,i}^2 \alpha_{A,f}^2 + \eta_A^2 \alpha_{A,i}^2 + \eta_A^2 \alpha_{A,f}^2}{4\eta^2 + \alpha_{A,i}^2 + \alpha_{A,f}^2}}. \quad (1.41)$$

where η_A denotes the mosaicity of the PG crystal used in the analyser and ranges typically from 0.13° to 1.3° when characterised by its SD [48]⁹. The incoming and outgoing divergences concerning the analyser are signified by $\alpha_{A,i}$ and $\alpha_{A,f}$, respectively. They can be estimated by considering the finite sizes of sample l_S and the opening of the focal point l_F . Secondly, the deviation $\Delta \theta_{A,2}$ of scattering angles at different positions of the same analyser segment can be derived by considering the finite size of an analyser segment l_A . With these two factors, the total angular spread at an analyser segment can be expressed as:

$$\Delta \theta_A = \sqrt{\Delta \theta_{A,1}^2 + \Delta \theta_{A,2}^2}. \quad (1.42)$$

⁹The mosaicity is conventionally characterised as FWHM of a Gaussian distribution. The mosaicity presented in [48] ranges from 0.3° to 3° in FWHM.

This simplified method gives a qualitative estimation of the spread of scattering angles at an analyser without accounting for the correlation between $\Delta\theta_{A,1}$ and $\Delta\theta_{A,2}$. However, since the incident and outgoing angles at different positions of a segment can be different from each other, the reflections depend on the mosaicity η_A of the crystal as well, making $\Delta\theta_{A,1}$ and $\Delta\theta_{A,2}$ correlated. Hence, this approximation is expected to be less valid at large sizes of components, i.e. l_S , l_A and l_F .

With the detailed calculations for $\alpha_{A,i}$ and $\alpha_{A,f}$ presented in the appendix (Sec. 5.3), the analytical k_f -resolution as a function of the vertical position φ of an analyser segment is depicted in Fig. 1.28. For simplicity, a spherical sample with a diameter of l_S is utilised. All analyser segments have a square shape with constant width and height, both denoted by l_A . The radial size of the opening at the focal point in a vertical sectional view is signified by l_F , while the opening is circular in the horizontal plane, with the centre being the projection of the sample position in this plane, as depicted in Fig. 1.10. Considering the small sample sizes in exotic systems, a value of $l_S = 1$ cm has been considered. Matching the sample size to optimise the resolution, the size of the analyser segment (l_A) and the aperture at the focal point (l_F) are considered as $l_F = l_A = 1$ cm for Fig. 1.28. The analytical results concerning some larger sizes l_S , l_A and l_F are summarised in the appendix (Sec. 5.4).

The diagram in Fig. 1.28 indicates an interplay between the component sizes and the mosaicity of analyser crystals. The uncertainty Δk_f exhibits a minimum when the vertical position φ of an analyser segment is close to the middle of the range between -5° and 60° , while the value increases when φ increases or decreases. This is consistent with the geometry, where the sample-analyser distance L_{SA} increases with decreasing φ , while the analyser-focus distance L_{AF} decreases. Moreover, Δk_f is almost independent of η_A , for the sizes l_S , l_A and l_F are small. The impact of η_A on Δk_f is especially small where $l_S = l_A = l_F = 1$ cm. This allows the use of analyser crystals with a relaxed mosaicity ($\eta \gtrsim 1^\circ$) without deteriorating the resolution of the secondary spectrometer, thereby reducing costs. Furthermore, more quantitatively, the SD of k_f does not exceed 0.5 % at all positions.

Angular spreads of wavevector In an ideal scenario, the direction of the wavevector $\mathbf{k}_f$ can be determined by the angles ψ and φ , which correspond to the positions of analyser segments, as illustrated in Fig. 1.10. However, discrepancies may arise between the assigned values (ψ_f, φ_f) and the values associated with the respective analyser segments. These discrepancies lead to angular spreads of $\mathbf{k}_f$, which are pivotal in defining the $\mathbf{Q}$ -resolution of an instrument. Such deviations primarily result from three factors. Firstly, the intrinsic resolution of the PSDs determines the shortest resolvable distance between the positions where neutrons

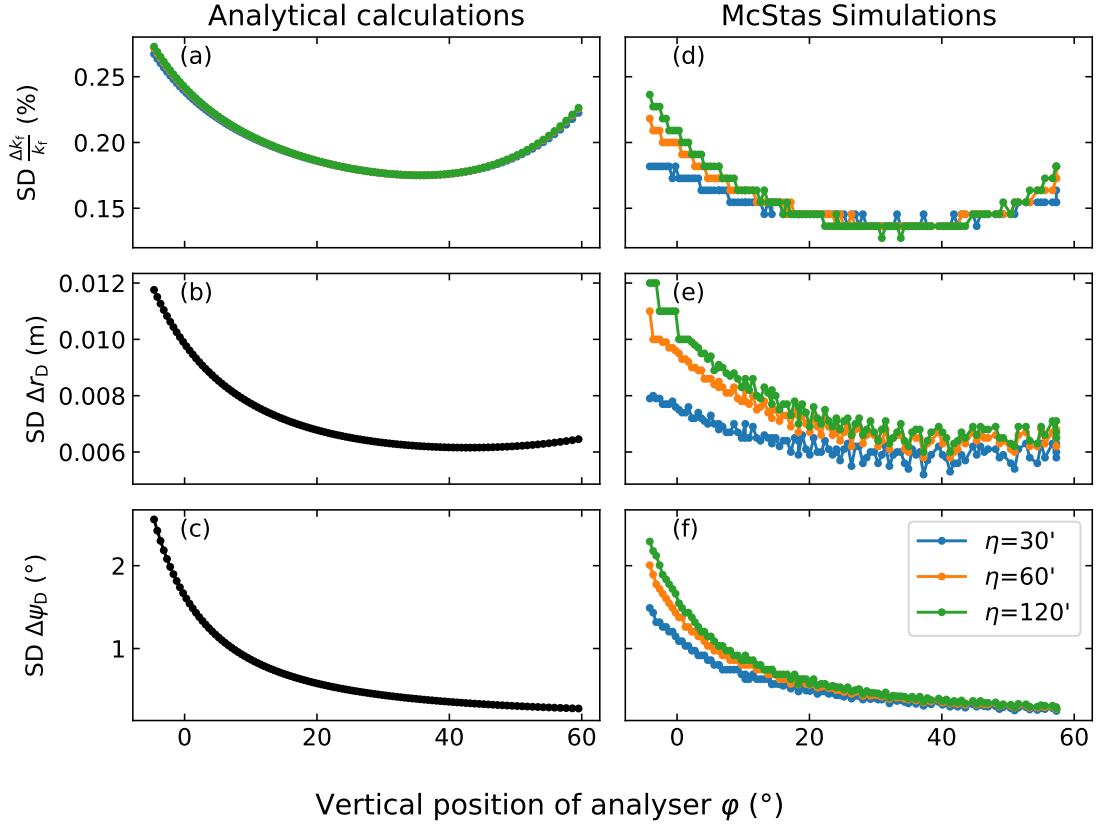


Figure 1.28: Resolutions characterised by SD as a function of the vertical position φ (Sec. 1.3) of the analyser segment where a neutron is reflected, considering $l_S = l_A = l_F = 1$ cm. Panels a-c depict the results from analytical calculations, while panels d - f illustrate the data obtained from McStas simulations. Panels a and d show the k_f -resolution with $k_f = 1.1 \text{ \AA}^{-1}$, panels b and e represent the radial spreads Δr_D on PSDs, and panels c and f signify the angular spreads $\Delta \psi_D$ on PSDs. In the analytical calculations for Δk_f as well as in all simulations, three values of the mosaicity of analyser crystals are considered and labelled with colours: $\eta = 30', 60', 120'$. The black curves in the analytical results of Δr_D and $\Delta \psi_D$ indicate that the respective calculations do not involve mosaicities.

arrive at the detector. Depending on the characteristics of the PSDs, this distance can range from a few centimetres to sub-millimetres. Secondly, the divergence of the beam between the sample position and an analyser segment causes a deviation of $\hat{\mathbf{k}}_f$ from its expected value. Thirdly, signals from neutrons reflected by neighbouring segments of the analyser may overlap on the PSDs. A signal might be erroneously assigned to an incorrect analyser segment in such cases.

Details regarding the analyser calculations of angular resolutions considering these three factors are provided in the appendix (Sec. 5.4). The results for the configuration with $l_S = l_A = l_F = 1$ cm are illustrated in Fig. 1.29, denoted as “Square”, while results for other geometrical sizes are presented in the appendix. The diagrams in Fig. 1.29 demonstrate an uncertainty in the vertical direction of $\Delta\varphi_f \lesssim 0.5^\circ$ with $l_S = l_A = l_F = 1$ cm, while the horizontal spread reaches $\Delta\psi_f \approx 2.5^\circ$ at $\varphi < 0^\circ$ under the same geometry. This results from the decreasing distance L_{AF} at diminishing φ , with $L_{AF} \approx 0.4$ m for the lowest analyser segment. Additionally, the radial position r_D where neutrons arrive at the PSD diminishes with decreasing φ , implying that the same tangential spread in length on the PSD results in a higher spread in angle ψ_f at a lower φ . Consequently, in this design, the $\mathbf{Q}$ -resolution may be compromised in the horizontal plane (Q_x and Q_y), even with small sizes of l_S , l_A , and l_F . One solution is to modify the the analyser segments such that the horizontal size $\frac{1}{2}l_A$ is half of that in the vertical direction (l_A). In this manner, the vertical and horizontal angular spreads can match with each other. Another potential solution is to create a circular stripe for each value of φ , covering the entire ψ range except for the area utilising a beam stop. This could be achieved by bending a large PG crystal using a pair of silicon bases. These possibilities are currently under further investigation. The analytical resolution using this concept is depicted in Fig. 1.29, labelled as “Circular”, for $l_S = l_A = l_F = 1$ cm, while results for other configurations are presented in the appendix (Sec. 5.5).

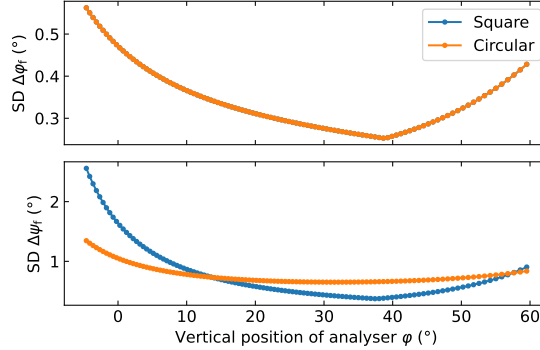


Figure 1.29: Angular resolution of $\mathbf{k}_f$ as a function of the vertical position φ (Sec. 1.3) of the analyser segment where a neutron is reflected, calculated analytically considering $l_S = l_A = l_F = 1$ cm. The SD $\Delta\varphi_f$ signifies the angular spread of $\mathbf{k}_f$ in the vertical direction, while $\Delta\psi_f$ represents the horizontal term.

The angular resolution can also be evaluated by examining the spreads in the radial and angular positions on PSDs, where the radial position r_D follows the same definition as depicted in Fig. 1.15, while the angle ψ_D is defined in the same manner as the horizontal angle ψ of analyser segments. The analytical and simulated

resolution values are presented in Fig. 1.28 considering $l_S = l_A = l_F = 1$ cm with analyser segments in a square shape. Here, the analytical calculations of Δr_D and $\Delta\psi_D$ do not involve mosaicities of analyser crystals.

Simulations The resolution of the secondary spectrometer is analysed using McStas. In the simulation, a neutron source with incident wavelengths $\lambda_i \in (5 \text{ \AA}, 6 \text{ \AA})$ is targeted directly onto an incoherent. Without loss of generality, analyser segments with a constant horizontal angle $\psi = 60^\circ$ were utilised. Each simulation considers an analyser segment employing a flat PG crystal, with its position and orientation provided by a Python script corresponding to the configuration depicted in Fig. 1.15. Additionally, to approximate the opening for the order selector, a slit with a diameter of l_F is used. Alongside a PSD bank, a wavelength monitor is placed at the same position to provide information about the neutron wavelengths upon reaching the PSDs. The simulated resolutions for $l_S, l_A, l_F = 1$ cm are presented in Fig. 1.28 alongside the analytical calculations, while the results for $l_S, l_A, l_F \in \{2 \text{ cm}, 5 \text{ cm}\}$ are detailed in the appendix (Sec. 5.5). The major part of the simulation code is provided in the appendix (Sec. 5.6).

The simulated results and analytical calculations show good agreement for sizes $l_S, l_A, l_F \in \{1 \text{ cm}, 2 \text{ cm}\}$, whereas for components of 5 cm, the simulated results align in the order of magnitude with the analytical calculations but display a distinct trend with uncertainties as functions of φ . This disparity supports our expectation, as discussed in the analytical calculation section. Both analytical and McStas estimations indicate that the configurations with $l_A = l_F = 5$ cm result in less satisfactory resolutions. Since l_A and l_F cannot be adjusted for sample sizes during experiments, it is beneficial to implement configurations with higher resolutions.

Considering the configuration with $l_S, l_A, l_F = 1$ cm, Fig. 1.28 demonstrates excellent agreement between the analytical and simulated outcomes, especially when a relaxed mosaicity ($\eta_A \gtrsim 1^\circ$) is considered. While the analytical calculations do not involve the mosaicity for simplicity, simulations reveal a noticeable enhancement in resolution when accounting for a fine mosaicity $\eta_A = 0.5^\circ$. Consequently, square-shaped analyser segments with a small mosaicity can yield a comparable resolution $\Delta\psi_f$ to that of a circular-shaped configuration, providing an alternative option when high angular resolution is required but a circular design is unavailable.

1.5.2 Primary spectrometer

Since $\hat{\mathbf{x}} \parallel \mathbf{k}_i$, the angles defining the direction of $\mathbf{k}_i$ are $\varphi_i = \psi_i = 0$ in the ideal case. They can be written explicitly in order to take into account the angular

spreads of the wavevector $\mathbf{k}_i$, yielding:

$$\mathbf{k}_i = \begin{pmatrix} k_i \cos \varphi_i \cos \psi_i \\ k_i \cos \varphi_i \sin \psi_i \\ k_i \sin \varphi_i \end{pmatrix}. \quad (1.43)$$

Here, the angles φ_i and ψ_i are defined in the same manner as for $\mathbf{k}_f$ (Fig. 1.10b).

Crystal monochromators

The $\mathbf{k}_i$ -resolution using a monochromator can be determined in the same manner as in the secondary spectrometer with an analyser. The uncertainty of wavenumber k_i is given by:

$$\frac{\Delta k_i}{k_i} = \sqrt{\left(\frac{\Delta d}{d}\right)^2 + (\cot \theta_M \Delta \theta_M)^2}, \quad (1.44)$$

where θ_M represents the scattering angle at the monochromator. The uncertainty of θ_M yields:

$$\Delta \theta_M = \sqrt{\frac{\alpha_{M,i}^2 \alpha_{M,f}^2 + \eta_M^2 \alpha_{M,i}^2 + \eta_M^2 \alpha_{M,f}^2}{4\eta_M^2 + \alpha_{M,i}^2 + \alpha_{M,f}^2}}. \quad (1.45)$$

Without collimators, the divergence $\alpha_{M,i}$ is governed by the divergence of the neutron guide, while $\alpha_{M,f}$ is determined by the monochromator-sample distance L_{SM} (single monochromator) or L_{SM2} (double monochromators). Collimators can be installed both before and after the monochromator to improve the resolution, as discussed by Kalus [47]. Since the angular spreads in the secondary spectrometer are close to 1° , a collimation close to 1° is sufficient. Hence, a mosaicity $\eta_M \approx 1^\circ$ ca be used.

The angular spreads of the primary spectrometer, $\Delta \psi_i$ and $\Delta \varphi_i$, are governed by the beam divergences in the horizontal and vertical dimensions, respectively. Hence, they can be approximated by $\alpha_{M,f} \approx 1^\circ$.

ToF chopper system

The work focuses on the performance of the secondary spectrometer, while the design of the primary spectrometer, which depends on the neutron transport system, is under further development within the collaboration with C. Herb, J. Voigt and R. Georgii [49]. As discussed in Section 1.4.2, the uncertainty of the total ToF is governed by the opening time of the first chopper, expressed as $\Delta t_{\text{tot}} = w_1$, leading to the dependency of Δt_1 on Δt_f . Utilising Eq. 1.12 and 1.40, the time uncertainty attributable to the secondary spectrometer is expressed as:

$$\frac{\Delta t_f}{t_f} = \frac{\Delta k_f}{k_f} = \sqrt{\left(\frac{\Delta d}{d}\right)^2 + (\cot \theta_A \Delta \theta_A)^2}, \quad (1.46)$$

where the expression for t_f is given by:

$$t_f = \frac{L_{SD}m}{k_f\hbar} = \frac{L_{SD}md \sin \theta_A}{\pi\hbar}. \quad (1.47)$$

The time resolution due to the primary spectrometer, as described in Eq. 1.15, is calculated as:

$$\begin{aligned} \Delta t_i &= \sqrt{(\Delta t_{tot})^2 + (\Delta t_f)^2} \\ &= \sqrt{w_1^2 + \left(\left(\frac{\Delta d}{d} \right)^2 + (\cot \theta_A \Delta \theta_A)^2 \right) \left(\frac{L_{SD}md \sin \theta_A}{\pi\hbar} \right)^2}. \end{aligned} \quad (1.48)$$

This demonstrates the dependency of Δt_i on both L_{SD} and t_A , which are contingent on the φ -position of the analyser segment reflecting the neutron beam. However, as depicted in Fig. 1.30, the dependency exhibits a minimal change in $\Delta t_i \in (0.9012 \text{ ms}, 0.9018 \text{ ms})$ across $\varphi \in (-5^\circ, 60^\circ)$, closely resembling $\Delta t_{tot} = w_1 \approx 0.9 \text{ ms}$ (Sec. 1.4.2).

This observation can be attributed to the significantly shorter flight path of the neutron beam in the secondary spectrometer than the primary spectrometer while maintaining a small relative time uncertainty in the secondary spectrometer. Consequently, the k_i -resolution is given by:

$$\frac{\Delta k_i}{k_i} = \frac{\Delta t_i}{t_i}, \quad (1.49)$$

where $\Delta t_i \approx \frac{w_1}{\sqrt{3}}$.

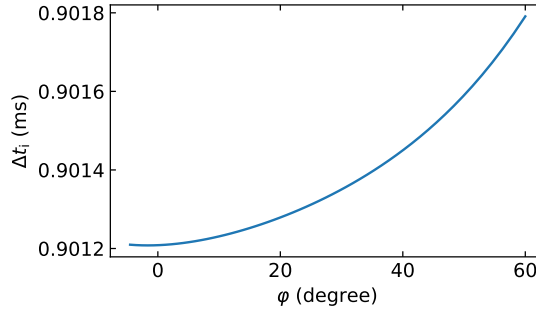


Figure 1.30: Resolution Δt_i as a function of the polar angle φ (Sec. 1.3) of the analyser segment where the neutron beam is reflected.

The angular spreads $\Delta\psi$ and $\Delta\varphi$ are contingent upon the focusing effect induced by the NMO [37] and are subject to variation based on the intricate design of the chopper system. As a rough approximation, the values $\Delta\psi = \Delta\varphi = 2^\circ$ can be considered. Upon matching these parameters, the secondary spectrometer can consider the sizes $l_A = l_F = 1 \text{ cm}$ or 2 cm to offer a similar resolution.

1.5.3 Wavevector transfer

The wavevector transfer, $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$, is defined as:

$$\mathbf{Q} = \begin{pmatrix} k_i \cos \varphi_i \cos \psi_i - k_f \cos \varphi_f \cos \psi_f \\ k_i \cos \varphi_i \sin \psi_i - k_f \cos \varphi_f \sin \psi_f \\ k_i \sin \varphi_i - k_f \sin \varphi_f \end{pmatrix}. \quad (1.50)$$

Hence, the uncertainties, Δk_i , $\Delta \varphi_i$, $\Delta \psi_i$, Δk_f , $\Delta \varphi_f$ and $\Delta \psi_f$, can be utilised following the formula in Eq. 1.39 to derive the $\mathbf{Q}$ -resolution, yielding:

$$\begin{aligned} (\Delta Q_x)^2 &= \cos^2 \varphi_i \cos^2 \psi_i (\Delta k_i)^2 + \cos^2 \varphi_f \cos^2 \psi_f (\Delta k_f)^2 \\ &\quad + k_i^2 \sin^2 \varphi_i \cos^2 \psi_i (\Delta \varphi_i)^2 + k_f^2 \sin^2 \varphi_f \cos^2 \psi_f (\Delta \varphi_f)^2 \\ &\quad + k_i^2 \cos^2 \varphi_i \sin^2 \psi_i (\Delta \psi_i)^2 + k_f^2 \cos^2 \varphi_f \sin^2 \psi_f (\Delta \psi_f)^2 \\ (\Delta Q_y)^2 &= \cos^2 \varphi_i \sin^2 \psi_i (\Delta k_i)^2 + \cos^2 \varphi_f \sin^2 \psi_f (\Delta k_f)^2 \\ &\quad + k_i^2 \sin^2 \varphi_i \sin^2 \psi_i (\Delta \varphi_i)^2 + k_f^2 \sin^2 \varphi_f \sin^2 \psi_f (\Delta \varphi_f)^2 \\ &\quad + k_i^2 \cos^2 \varphi_i \cos^2 \psi_i (\Delta \psi_i)^2 + k_f^2 \cos^2 \varphi_f \cos^2 \psi_f (\Delta \psi_f)^2 \\ (\Delta Q_z)^2 &= \sin^2 \varphi_i (\Delta k_i)^2 + \sin^2 \varphi_f (\Delta k_f)^2 \\ &\quad + k_i^2 \cos^2 \varphi_i (\Delta \varphi_i)^2 + k_f^2 \cos^2 \varphi_f (\Delta \varphi_f)^2 \end{aligned} \quad (1.51)$$

The norm of $\mathbf{Q}$ yields:

$$Q = |\mathbf{Q}| = \sqrt{k_i^2 + k_f^2 - 2k_i k_f (\cos \varphi_i \cos \varphi_f \cos (\psi_i - \psi_f) + \sin \varphi_i \sin \varphi_f)}. \quad (1.52)$$

The resolution of the norm Q is given by:

$$\begin{aligned} (\Delta Q)^2 &= \frac{1}{Q} \left\{ \left[k_i - k_f (\cos \varphi_i \cos \varphi_f \cos (\psi_i - \psi_f) + \sin \varphi_i \sin \varphi_f) \right]^2 (\Delta k_i)^2 \right. \\ &\quad + \left[k_f - k_i (\cos \varphi_i \cos \varphi_f \cos (\psi_i - \psi_f) + \sin \varphi_i \sin \varphi_f) \right]^2 (\Delta k_f)^2 \\ &\quad + k_i^2 k_f^2 \left[(\sin \varphi_i \cos \varphi_f \cos (\psi_i - \psi_f) - \cos \varphi_i \sin \varphi_f)^2 (\Delta \varphi_i)^2 \right. \\ &\quad + (\cos \varphi_i \sin \varphi_f \cos (\psi_i - \psi_f) - \sin \varphi_i \cos \varphi_f)^2 (\Delta \varphi_f)^2 \\ &\quad \left. \left. + \cos^2 \varphi_i \cos^2 \varphi_f \sin^2 (\psi_i - \psi_f) ((\Delta \psi_i)^2 + (\Delta \psi_f)^2) \right] \right\}. \end{aligned} \quad (1.53)$$

Akin to a conventional TAS, the resolution of the Mushroom spectrometer relies on the $(\mathbf{k}_i, \mathbf{k}_f)$ -combinations during a measurement.

1.5.4 Energy transfer

The relationship between energy E and wavenumber k of neutrons is given as:

$$E = \frac{\hbar^2 k^2}{2m}, \quad (1.54)$$

resulting in:

$$\frac{\Delta E}{E} = 2 \frac{\Delta k}{k}. \quad (1.55)$$

For an energy transfer

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m} (k_i^2 - k_f^2), \quad (1.56)$$

the resolution can be determined by:

$$\Delta(\hbar\omega) = \frac{\hbar^2}{m} \sqrt{k_i^2 (\Delta k_i)^2 + k_f^2 (\Delta k_f)^2}. \quad (1.57)$$

The uncertainty Δk_i exhibits a nearly linear dependency on k_i for both monochromator and ToF options. At the same time, Δk_f experiences marginal changes at varying (ψ, φ) -positions of analyser segments, with k_f remaining constant at a defined diffraction order n_A . Consequently, the uncertainty $\Delta(\hbar\omega)$ -increases nearly quadratically with k_i and with approximation linearly with k_f .

1.6 Coverage in momentum and energy

1.6.1 Four dimensional space

The coverage of a Mushroom instrument in the 4D $(\mathbf{Q}, \omega)$ -space influences the planning of measurements with single-crystal samples. For obtaining this coverage, Eq. 1.50 can be rewritten, first without accounting for the lattice structure of the sample:

$$(Q_x - k_i)^2 + Q_y^2 = k_f^2 \cos^2 \varphi = k_f^2 - Q_z^2, \quad (1.58)$$

which utilises the coordinate system illustrated in Fig. 1.10b. It indicates that for each pair of (Q_z, ω) , the variables Q_x and Q_y describe a circle centred at $(Q_x, Q_y) = (k_i, 0)$ with a radius of $k_f \cos \varphi = \sqrt{k_f^2 - Q_z^2}$. Besides, this circle exhibits gaps within $-10^\circ < \psi < 10^\circ$ and $170^\circ < \psi < 190^\circ$ due to a neutron guide and beam stop, as discussed in Sec. 1.3.

Considering the rotation of a sample around the z -axis, the transformation of the scattering vector $\mathbf{Q}$ into the reciprocal lattice space is contingent upon the sample structure. For simplicity, an orthorhombic structure is utilised¹⁰, aligning $\mathbf{a} \parallel \mathbf{x}$, $\mathbf{b} \parallel \mathbf{y}$ and $\mathbf{c} \parallel \mathbf{z}$ before any rotations occur. The anti-clockwise rotation of the sample by the angle α results in the anti-clockwise rotation of the scattering vector by $-\alpha$:

$$\begin{pmatrix} Q_a \\ Q_b \end{pmatrix} = \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} Q_x \\ Q_y \end{pmatrix}. \quad (1.59)$$

¹⁰Structures with lower symmetries work under the same principle, while the mathematical formulae to project $\mathbf{Q}$ into the reciprocal lattice space are distinct.

This transformation yields:

$$(Q_x - k_i \cos \alpha)^2 + (Q_y + k_i \sin \alpha)^2 = k_f^2 \cos^2 \varphi = k_f^2 - Q_z^2, \quad (1.60)$$

which corresponds to an anti-clockwise rotation of the circle, as described in Eq. 1.58, around the origin $(0, 0)$ by an angle of $-\alpha$.

While the specific coverage relies on intricate designs within its primary and secondary spectrometers, Fig. 1.31 exemplifies the incorporation of the ToF chopper primary spectrometer and the PG 004 secondary spectrometer. This particular configuration corresponds to λ_i within the range of $1 \text{ \AA}$ to $10 \text{ \AA}$, equivalent to k_i between $0.63 \text{ \AA}^{-1}$ and $6.28 \text{ \AA}^{-1}$, with $k_f = 2.2 \text{ \AA}^{-1}$. It offers the broadest coverage within the $(\mathbf{Q}, \omega)$ -space among the configurations discussed in previous sections of this chapter.

The impact of rotating the sample by 360° with increments of 36° is depicted in Fig. 1.31. Employing a smaller step size allows for a more detailed spectrum in the measurement.

In practical applications, planning the sample rotation should match the structure and anticipated characteristics of the excitation. A total rotation of 90° , with increments ranging from one to several degrees, is feasible. Furthermore, it can be tailored among the options discussed so far, with the diagrams illustrated in Fig. 5.10, 5.11, and 5.12 in the appendix (Sec. 5.7), to correspond with the intended coverage within the $(\mathbf{Q}, \omega)$ -space.

1.6.2 Two dimensional space

Concerning measurements involving polycrystalline samples, Fig. 1.32 illustrates coverage within the 2D (Q, ω) -space for various options discussed previously. The relationship between Q and $\hbar\omega$ can be derived from Eq. 1.52, resulting in:

$$\begin{aligned} Q^2 &= k_i^2 + k_f^2 - 2k_i k_f \cos \varphi \cos \psi \\ k_i^2 &= k_f^2 + \frac{2m\hbar\omega}{\hbar^2} \end{aligned} \quad (1.61)$$

As k_f remains fixed at a chosen diffraction order of the secondary spectrometer, a given $\hbar\omega$ value determines k_i . Considering the ranges of $-10^\circ < \varphi < 10^\circ$ and $170^\circ < \varphi < 190^\circ$:

$$\begin{aligned} Q_{\min}^2(k_i) &= k_i^2 + k_f^2 - 2k_i k_f \cos 10^\circ = (k_i - k_f)^2 + 2k_i k_f (1 - \cos 10^\circ) \\ Q_{\max}^2(k_i) &= k_i^2 + k_f^2 + 2k_i k_f \cos 10^\circ = (k_i + k_f)^2 + 2k_i k_f (\cos 10^\circ - 1), \end{aligned} \quad (1.62)$$

determining $Q_{\min}$ and $Q_{\max}$ at a given $\hbar\omega$, where the smallest value of $\hbar\omega$ depends on the resolution at $k_i \approx k_f$. The coverage of Mushroom in the 2D (Q, ω) -space

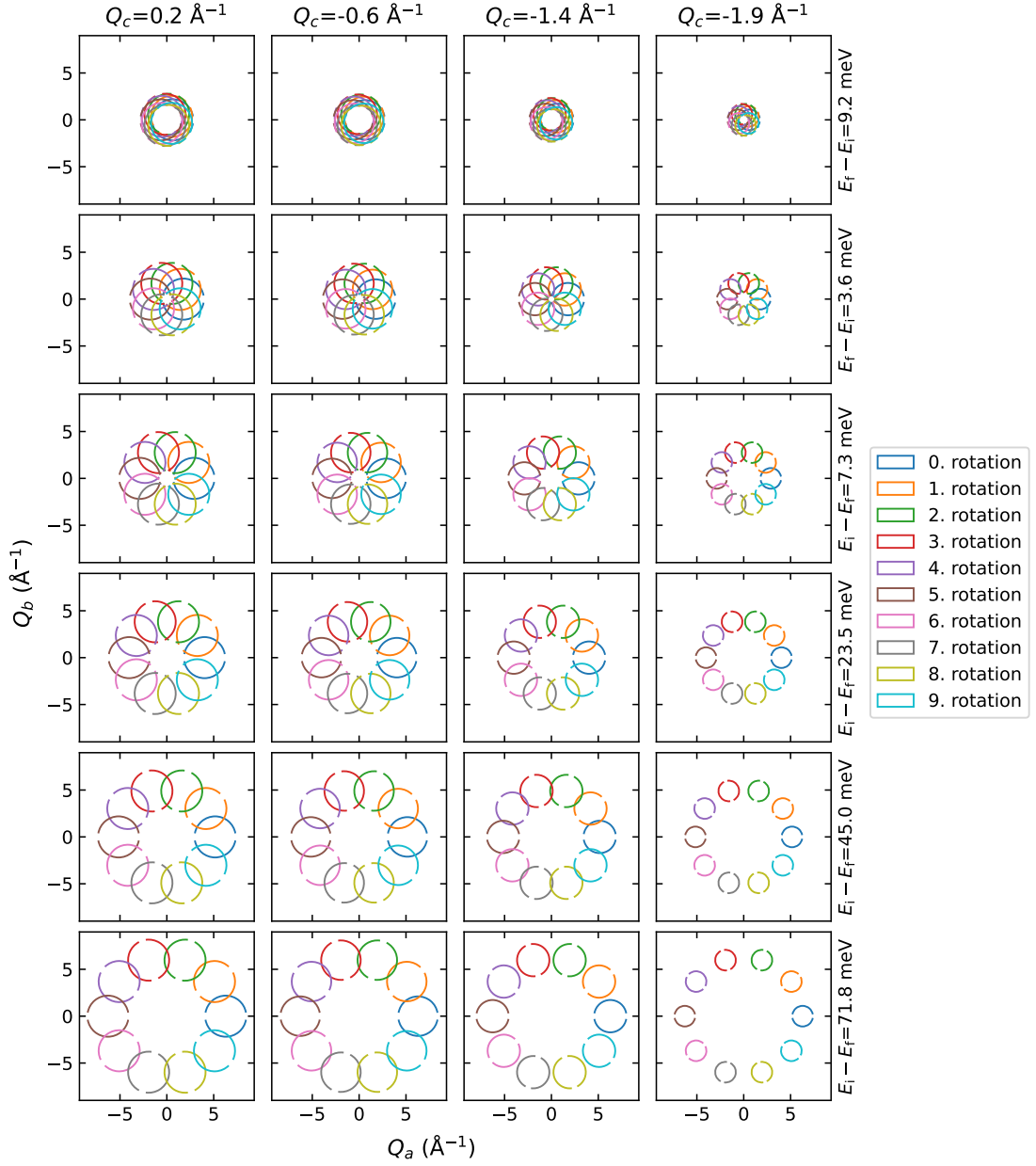


Figure 1.31: Accessible regions of the $(\mathbf{Q}, \omega)$ -space using Mushroom with the ToF primary spectrometer ($\lambda_i \in (1 \text{ \AA}, 10 \text{ \AA})$) and PG 004 secondary spectrometer ($\lambda_f \approx 2.36 \text{ \AA}$). The depiction is mapped onto the $Q_a Q_b$ -plane considering an orthorhombic structure of the sample, using the unit of $\text{\AA}^{-1}$, because the lattice lengths a -, b - and c are not specified for generality. Each column represents a constant Q_c -value displayed at the top, and each row a constant $\hbar\omega$ -value shown on the right-hand side. The calculations consider the rotation of the sample around its c -axis by 36° each step, with the colours depicting the steps.

is depicted in Fig. 1.32. Configurations offering broader coverage, such as the ToF chopper system in the primary spectrometer or the PG 004 order in the secondary spectrometer, entail a trade-off with inferior resolution. Hence, during instrument implementation, this trade-off needs careful consideration in line with specific objectives and applications.

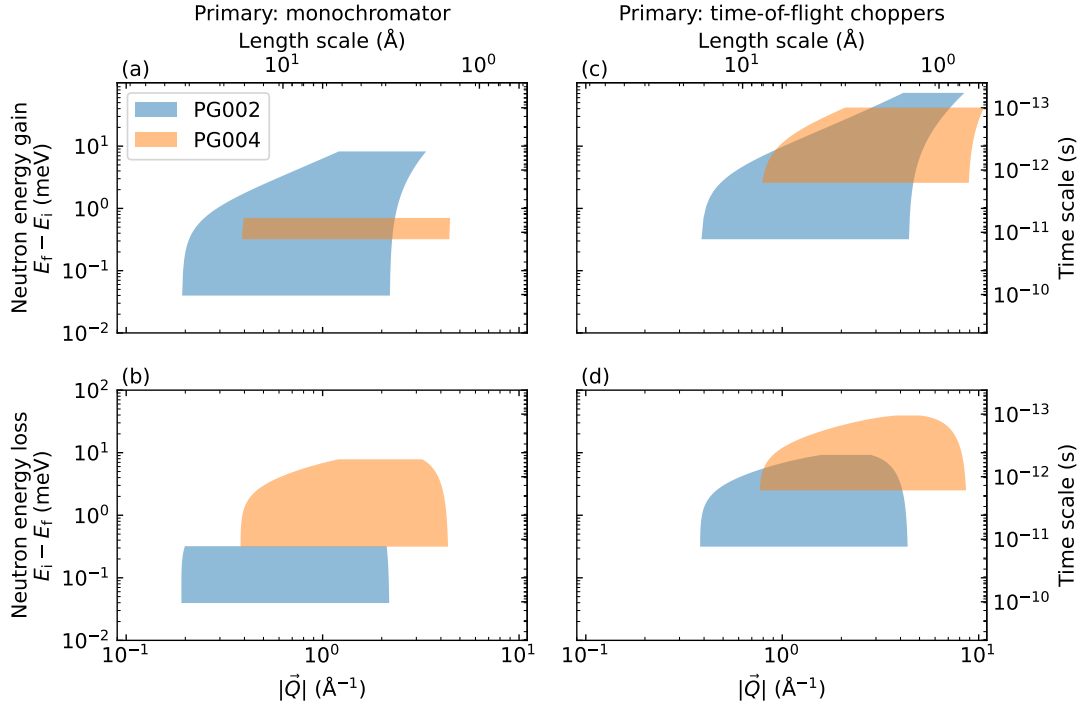


Figure 1.32: Accessible regions in the (Q, ω) -space as described in Eq. 1.61. The primary spectrometer is equipped with either a monochromator system (panels a and b) or a chopper system (panels c and d), and the secondary spectrometer uses either the scattering order PG 002 (blue) or PG 004 (orange). The relations between the length scale and Q as well as between $\hbar\omega$ and t are the same as described in Fig. 1.2.

1.7 Performance

Further aspects of the performance of the instrument have been evaluated and are presented in this section. A mangon excitation is used as an example to examine the performance of Mushroom for an inelastic measurement. In addition, an elastic line of a vanadium sample helps to assess the count rate of the instrument.

1.7.1 Magnon excitation

Analytical calculations and McStas simulations have been carried out to demonstrate measurements using a Mushroom-type spectrometer. Here, we consider a magnon excitation in a system featuring a body-centred cubic (bcc) structure with a lattice parameter $a = 4.5 \text{ \AA}$. For simplicity, we solely consider ferromagnetic interactions among nearest neighbours ($J_1 = 0.3 \text{ meV}$) with the spin of $s = 1$, in the absence of external fields. For this magnon model, the energy transfer of the neutron during the scattering process can be calculated using [50, 51]:

$$\begin{aligned} \hbar\omega_{\mathbf{\kappa}} = 2J_1s \left[4 - \cos\left(\frac{a}{2}(\kappa_x + \kappa_y + \kappa_z)\right) + \cos\left(\frac{a}{2}(\kappa_x + \kappa_y - \kappa_z)\right) \right. \\ \left. + \cos\left(\frac{a}{2}(\kappa_x - \kappa_y + \kappa_z)\right) + \cos\left(\frac{a}{2}(\kappa_x - \kappa_y - \kappa_z)\right) \right], \end{aligned} \quad (1.63)$$

where $\mathbf{\kappa}$ represents a vector in the first Brillouin zone. The double-differential cross-section quantifying the scattering probability can be determined by [50]:

$$\begin{aligned} \frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = (\gamma r_0)^2 \frac{k_f}{k_i} \frac{(2\pi)^3}{v_0} \frac{1}{2} s (1 + \hat{q}_z^2) \left(\frac{1}{2} g F(\mathbf{q}) \right)^2 e^{-2W} \times \\ \sum_{\mathbf{\tau}, \mathbf{\kappa}} [\delta(\mathbf{q} - \mathbf{\tau} - \mathbf{\kappa}) \delta(\hbar\omega_{\mathbf{\kappa}} - \hbar\omega) \langle n_{\mathbf{\kappa}} + 1 \rangle + \\ \delta(\mathbf{q} - \mathbf{\tau} + \mathbf{\kappa}) \delta(\hbar\omega_{\mathbf{\kappa}} + \hbar\omega) \langle n_{\mathbf{\kappa}} \rangle], \end{aligned} \quad (1.64)$$

where $\mathbf{q}$ denotes the wavevector transfer $\mathbf{Q}$ in reciprocal lattice units (r.l.u), $\mathbf{\tau}$ represents the nuclear lattice, and W signifies the Debye-Waller factor. The thermal average of $n_{\mathbf{\kappa}}$ is given by:

$$\langle n_{\mathbf{\kappa}} \rangle = \frac{1}{e^{\hbar\omega_{\mathbf{\kappa}}\beta} - 1}, \quad \beta = \frac{1}{k_B T}, \quad (1.65)$$

where a temperature of $T = 30 \text{ K}$ is considered in our example. The first term in the summation of Eq. 1.64 represents the energy gain of neutrons, and the second term represents the energy loss of neutrons. For calculating the double-differential cross-section, a Dirac delta function $\delta(x)$ of an arbitrary variable x with a small deviation can be approximated by a Gaussian distribution:

$$\delta_{\sigma}(x) \approx \frac{1}{|\sigma| \sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}, \quad (1.66)$$

where σ signifies the SD of the Gaussian distribution that can be derived by considering the resolution of the instrument.

The analytical and simulated results of this magnon model are depicted in Fig. 1.33, where momentum transfers of $\mathbf{Q}_{hkl} = (h, -1.00, -0.12)$ (r.l.u) are considered at a constant energy transfer of $E_i - E_f = 2.80 \text{ meV}$ (corresponding to

$k_i = 1.6 \text{ \AA}^{-1}$ and $k_f = 1.1 \text{ \AA}^{-1}$), using the accessible h -range determined by the secondary spectrometer and sample. The source generates neutrons with wavelength $0.99 * 5.712 \text{ \AA} < \lambda_i < 1.01 * 5.712 \text{ \AA}$. The sample is initially aligned such that its a -, b - and c -axes are parallel to the x -, y - and z -axes of the coordinate system shown in Fig. 1.10, respectively. The sample is rotated around the z -axis anti-clockwise by 90° in total, with an increment of 1° each step. The analyser segments have a rectangular shape with $l_A = 2 \text{ cm}$ vertically and 1 cm horizontally. The sample size and the opening of the focal point of $l_S = l_F = 2 \text{ cm}$ are considered.

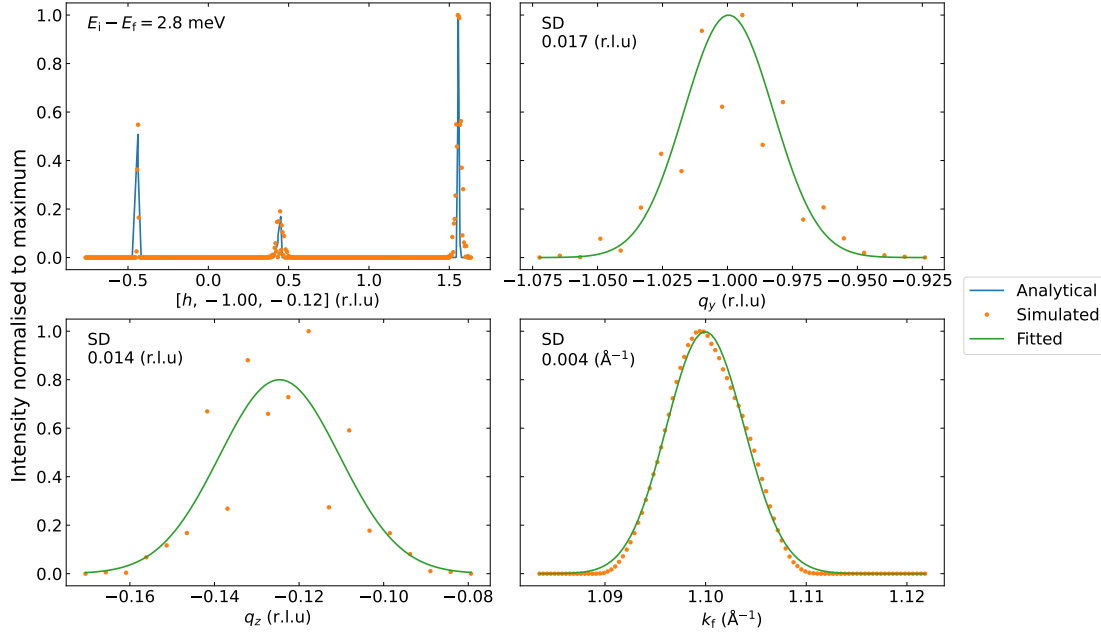


Figure 1.33: Panel a: Intensity normalised to its maximum for the spin-1 magnon excitation (Eq. 1.63 and 1.64) at $\hbar\omega = 2.80 \text{ meV}$ and $\mathbf{Q}_{hkl} = (h, -1.00, -0.12) \text{ (r.l.u.)}$, considering the accessible range of h -values of the Mushroom instrument. Panel a compares the analytical calculations (“Analytical”, in blue) and McStas simulations (“Simulations”, in orange). The sample has a bcc structure with $a = 4.5 \text{ \AA}$, where only the ferromagnetic interactions among the nearest neighbours $J_1 = 0.3 \text{ meV}$ are considered. Panel b, c and d show the values of $q_y \text{ (r.l.u.)}$, $q_z \text{ (r.l.u.)}$ and k_f , respectively. All three diagrams are fitted using a Gaussian distribution, providing the values of the respective SDs.

The diagram in Fig. 1.33a shows an excellent agreement between the analytical and simulated result, demonstrating the good capability of Mushroom for measuring spectra. The panels b, c and d depict the distributions of q_y , q_z and k_f , giving

the SD values $\Delta q_y = 0.017$ (r.l.u), $\Delta q_z = 0.014$ (r.l.u) and $\Delta k_f = 0.004 \text{ \AA}^{-1}$. The values agree with the resolution discussed in Sec. 1.5.

1.7.2 Count rates

The concrete design of the primary spectrometer of Mushroom is currently in development in collaboration with C. Herb, J. Voigt, and R. Georgii [49]. Here, a simplified design of the primary spectrometer has been employed to evaluate the count rate of the ToF-Mushroom compared with the IN5 instrument at ILL [18]. For this purpose, an elastic line at $k_i = k_f = 1.1 \text{ \AA}^{-1}$ ($\lambda_i = \lambda_f = 5.712 \text{ \AA}$) of a vanadium sample is simulated using McStas. The neutron source provided by the IN5 template in McStas has been implemented for both simulations, generating an initial wavelength $5.5 \text{ \AA} < \lambda_i < 5.9 \text{ \AA}$.

For the ToF-Mushroom, the double-chopper configuration mentioned in Sec. 1.4.2 is used, where an extra counter chopper with the same design as chopper C_1 is placed 5 cm behind C_1 . The radius of all choppers is set as 25 cm, while the other parameters are identical to those presented in Fig. 1.24. For simplicity, neutron guides with the same design as IN5 have been used, with the geometrical parameters modified for the geometry of the Mushroom primary spectrometer. For matching the energy resolution of IN5, sizes of sample and opening of the focal point are $l_S = l_F = 2 \text{ cm}$, while the analyser segments are in a rectangular shape, with the horizontal size 1 cm and the vertical size $l_A = 2 \text{ cm}$. Akin to actual measurements, the wavenumber of $k_f = 1.1 \text{ \AA}^{-1}$ is used for analysing the data, while the values of k_i are obtained using the ToF channel and the positional information on the PSD.

For IN5, the maximum rotating speed of the pulse-cutting chopper is used, i.e. 17 000 RPM. Here, $k_i = 1.1 \text{ \AA}^{-1}$ is used for data analysis, while the values of k_f are obtained using the ToF channel and the positional information on the PSD.

The intensity as a function of energy transfer $\hbar\omega = E_i - E_f$ is depicted in Fig. 1.34. Each dataset has been fitted using a Gaussian distribution, providing the average ($\overline{\hbar\omega}$) and SD ($\Delta(\hbar\omega)$) of $\hbar\omega$ as well as the integrated intensity over the peak.

The diagram in Fig. 1.34 shows a nearly identical energy resolution of ToF-Mushroom and IN5, both equal to 0.02 meV, while the ToF-Mushroom offers a slightly higher count rate than IN5. This result indicates a great performance of Mushroom even though the neutron guide used for the primary spectrometer has a simplified version. Upon implementing the NMO system and implementing neutron guides specifically tailored for the primary spectrometer, the count rate at the sample position can likely be further enhanced, improving the overall performance of the instrument.

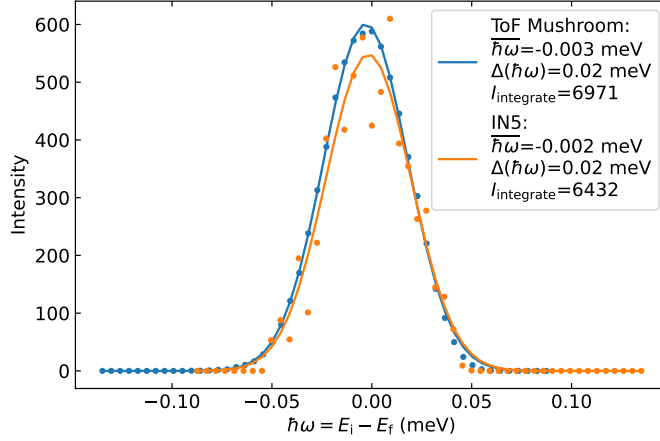


Figure 1.34: Elastic line of a vanadium sample simulated using McStas, comparing ToF Mushroom and IN5. The simulation considers a initial beam with $5.5 \text{ \AA} < \lambda_i < 5.9 \text{ \AA}$ from the source provided by the IN5 template in McStas. The chopper system of IN5 was set to select $\lambda_i = 5.712 \text{ \AA}$ before the sample scatters the incident beam. The analyser of Mushroom selects $\lambda_f = 5.712 \text{ \AA}$ of the scattered beam. The average ($\overline{\hbar\omega}$) and SD ($\Delta(\hbar\omega)$) of the energy transfer $\hbar\omega = E_i - E_f$ are obtained from the Gaussian fit of each curve. The integrated intensities are provided.

1.8 Summary

We have investigated the concept of Mushroom aiming at enhancing the efficiency of measuring a broad area in the $(\mathbf{Q}, \omega)$ -space. A unique secondary spectrometer, featuring a super flat-cone analyser, has been designed to analyse required for a conventional TAS. The analytical calculations and Monte Carlo simulations have demonstrated the excellent resolution of the secondary spectrometer.

The primary spectrometer of the instrument can be equipped with two options, providing considerable flexibility in its realisation: it can be constructed along a neutron guide using two crystal monochromators, or it can be positioned at a dedicated neutron guide using a ToF chopper system. With the crystal monochromators, the ability to control and rotate the two monochromators enables the heavy secondary spectrometer to remain unmoved during measurements. The ToF chopper system allows for the simultaneous measurement of multiple λ_i -values and offers adjustable resolution tailored to the $(\mathbf{Q}, \omega)$ -space of interest.

Due to the small sizes of many modern samples, an advanced optical system like NMO can enhance the focusing effect of Mushroom and further improve the count rate.

In conclusion, we have shown the flexibility, high count rate and great resolution of Mushroom, making it a very promising instrument for measuring modern

systems with smaller sample size and broad spectra. With the work in collaboration with Voigt *et al.* [49], the primary spectrometer can be further tailored to maximise the advantage of the instrument.

Chapter 2

MiniPAD

First introduced in [52], our cylindrical miniaturised polarisation analysis device (MiniPAD) has been designed for spherical neutron polarimetry (SNP) experiments. This chapter begins with a review of the theory of neutron polarisation analysis and a brief comparison among the configurations of polarisation analysis including SNP, followed by an examination of previous devices developed for SNP. Subsequently, the design and principles of the MiniPAD are presented. Finally, recent measurements evaluating its performance are presented. Some more details about the theory of neutron scattering and polarisation analysis can be found in [52].

2.1 Theory of neutron polarisation analysis

The neutron is sensitive to crystal structures through the nuclear force and magnetic features through the dipole moment. When the nuclear and magnetic contributions are independent of each other, the magnetic contribution can be isolated by comparing intensities below and above the temperature of the phase transition [53]. This process is particularly straightforward when the change in nuclear contributions with temperature is absent or negligible. However, in more intricate magnetic systems involving, for example, interference between nuclear and magnetic contributions or contributions from non-centrosymmetric structures (chiral contributions) [54], the magnetic contributions cannot be obtained in this straightforward manner. One solution is neutron polarisation analysis, or polarimetry, which studies the behaviour of neutron polarisation during the scattering process. This section reviews theories on nuclear and magnetic neutron scattering processes relevant to this work, followed by the theory of neutron polarisation analysis, before diving into more specific techniques in the next section.

2.1.1 Neutron scattering from a magnetic system

Double-differential cross section

The quantum-mechanical description of a system during a scattering process is encapsulated by Fermi's golden rule [53, 55–57]. This rule defines the transition rate, denoting the probability of the system changing from an initial state $|\phi_i\rangle$ to a final state $|\phi_f\rangle$ per unit time:

$$W_{\phi_i \rightarrow \phi_f} = \frac{2\pi}{\hbar} \left| \langle \phi_f | \hat{V} | \phi_i \rangle \right|^2 \rho_f(E_f). \quad (2.1)$$

Here, $\hat{V}$ signifies the interaction potential operator, $\hbar = \frac{h}{2\pi}$ denotes the reduced Planck constant, and $\rho_f(E_f)$ represents the density of scattered states per unit energy interval [53]. Fermi's golden rule is rooted in the first-order perturbation theory, applicable to both nuclear and magnetic neutron scattering processes. This is because nuclear forces have a very short range of about 1×10^{-15} m to 1×10^{-14} m, permitting only for s-wave scattering, and the potential for magnetic scattering is exceedingly weak [53].

In order to describe scattering processes quantitatively, the direction of the outgoing neutron beam can be defined by the angles θ and ϕ as in Fig. 2.1. In this direction, the finite divergence of the beam results in a unit solid angle $d\Omega$ corresponding to a unit area dS . With this, the double-differential cross-section is defined as the number of neutrons scattered in unit time into a unit solid angle with a unit interval of E_f [53]:

$$\begin{aligned} \frac{\partial^2 \sigma}{\partial \Omega \partial E_f} &= \sum_{\lambda_i \sigma_i} \sum_{\lambda_f \sigma_f} W_{\mathbf{k}_i \sigma_i \lambda_i \rightarrow \mathbf{k}_f \sigma_f \lambda_f} \frac{m_n^2}{(2\pi\hbar)^3} \frac{k_f}{k_i} \\ &= \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2} \right)^2 \sum_{\lambda_i \sigma_i} \sum_{\lambda_f \sigma_f} p_{\lambda_i} p_{\sigma_i} \left| \langle \mathbf{k}_f \sigma_f \lambda_f | \hat{V} | \mathbf{k}_i \sigma_i \lambda_i \rangle \right|^2 \delta(\hbar\omega + E_{\lambda_i} - E_{\lambda_f}). \end{aligned} \quad (2.2)$$

Here, m_n represents the neutron mass, the initial state of the scatterer is denoted by $|\lambda_i\rangle$, and the state of the incoming neutron beam is characterised by its wavevector $|\mathbf{k}_i\rangle$ and spin $|\sigma_i\rangle$. The subscript “f” refers to the terms after scattering. The probabilities of the scatterer and neutron to be in the states $|\lambda_i\rangle$ and $|\sigma_i\rangle$ are p_{λ_i} and p_{σ_i} , respectively. The expression of the potential $\hat{V}$ depends on the type of interaction. If no spins are considered, the spatial contribution in Eq. 2.2 can be formulated in the reciprocal space as:

$$\langle \mathbf{k}_f | \hat{V}(\mathbf{r}) | \mathbf{k}_i \rangle = \int e^{-i\mathbf{k}_f \cdot \mathbf{r}} \hat{V}(\mathbf{r}) e^{i\mathbf{k}_i \cdot \mathbf{r}} d^3r = \hat{V}(\mathbf{Q}). \quad (2.3)$$

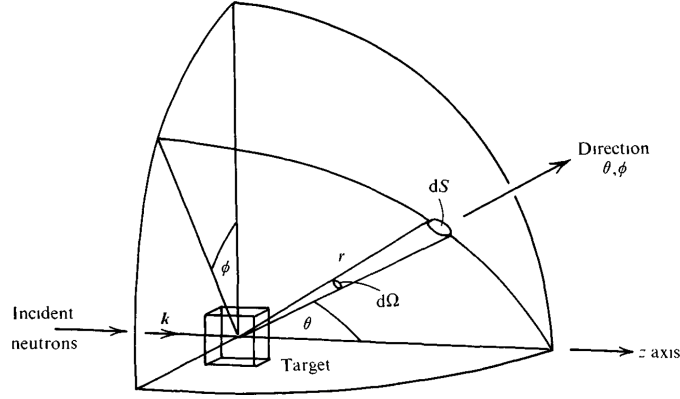


Figure 2.1: Schematic from [50] depicting the geometry of neutron scattering. The wavevector $\mathbf{k}$ denotes an incident neutron beam before scattering. The angles θ and ϕ signify the direction of an outgoing beam after scattering, while the beam divergence determines a unit solid angle $d\Omega$ corresponding to a unit area dS .

Spin contribution

For discussing spin contributions, we first consider the neutron spin associated with the magnetic moment:

$$\boldsymbol{\mu}_n = \gamma_n \mu_B \boldsymbol{\sigma} = \frac{2\gamma_n \mu_B}{\hbar} \mathbf{s}. \quad (2.4)$$

Here, $\gamma_n = -1.832 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$ represents the gyromagnetic ratio of the neutron, μ_B denotes the Bohr magneton, and $\mathbf{s}$ signifies the neutron spin [58]. The polarisation of a single neutron is a unit vector pointing in the spin direction:

$$\mathbf{P}_n = \langle \boldsymbol{\sigma} \rangle = \langle \sigma_n | \boldsymbol{\sigma} | \sigma_n \rangle. \quad (2.5)$$

Here, $\boldsymbol{\sigma}$ is the spin operator, yielding $\mathbf{s} = \frac{\hbar}{2} \boldsymbol{\sigma}$, and $|\sigma_n\rangle$ denotes an arbitrary spin state of the neutron. The state $|\sigma_n\rangle$ can be represented as a linear combination of the spin-up ($|+\rangle$) and spin-down ($|-\rangle$) states:

$$|\sigma_n\rangle = a|+\rangle + b|-\rangle = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (2.6)$$

For a neutron beam, its polarisation is the statistical average over all N neutrons:

$$\begin{aligned} \mathbf{P} &= \frac{1}{N} \sum_{j=1}^N \mathbf{P}_j, \quad j = 1, \dots, N. \\ &= \frac{N^+ - N^-}{N^+ + N^-}, \end{aligned} \quad (2.7)$$

where N^+ and N^- represent the numbers of neutrons in the states $|+\rangle$ and $|-\rangle$, respectively. The spin states before and after the scattering can be denoted as

$$\begin{aligned} |\sigma_i\rangle &= a_i |+\rangle + b_i |-\rangle \\ |\sigma_f\rangle &= a_f |+\rangle + b_f |-\rangle. \end{aligned} \quad (2.8)$$

The transition between these two states is described by a hermitian matrix S as:

$$|\sigma_f\rangle = S |\sigma_i\rangle, \quad (2.9)$$

or

$$\begin{pmatrix} a_f \\ b_f \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} a_i \\ b_i \end{pmatrix}. \quad (2.10)$$

Since the matrix S is hermitian, it can be expressed as:

$$\begin{aligned} S &= \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} \frac{S_{11} + S_{22}}{2} & 0 \\ 0 & \frac{S_{11} - S_{22}}{2} \end{pmatrix} + \begin{pmatrix} \frac{S_{11} - S_{22}}{2} & S_{12} \\ S_{21} & -\frac{S_{11} - S_{22}}{2} \end{pmatrix} \\ &= \begin{pmatrix} \beta & 0 \\ 0 & \beta \end{pmatrix} + \begin{pmatrix} A_z & A_x - iA_y \\ A_x + iA_y & -A_z \end{pmatrix} = \beta \mathbb{1} + \mathbf{A} \cdot \boldsymbol{\sigma}. \end{aligned} \quad (2.11)$$

Here, β is a scalar, $\mathbf{A} = (A_x \ A_y \ A_z)^T$ is a vector, $\mathbb{1}$ is the identity matrix, and $\boldsymbol{\sigma}$ represents the Pauli matrices with:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.12)$$

Analogous to the spatial contribution, the spin contribution in reciprocal space yields:

$$\begin{aligned} \begin{pmatrix} a_f \\ b_f \end{pmatrix} &= \begin{pmatrix} \beta(\mathbf{Q}) + A_z(\mathbf{Q}) & A_x(\mathbf{Q}) - iA_y(\mathbf{Q}) \\ A_x(\mathbf{Q}) + iA_y(\mathbf{Q}) & \beta(\mathbf{Q}) - A_z(\mathbf{Q}) \end{pmatrix} \begin{pmatrix} a_i \\ b_i \end{pmatrix} \\ &= \hat{V}(\mathbf{Q}) \begin{pmatrix} a_i \\ b_i \end{pmatrix}. \end{aligned} \quad (2.13)$$

Considering the incident and outgoing states, each projected onto either the spin-up $|+\rangle$ or spin-down $|-\rangle$ direction, the scattering amplitudes yield:

$$\begin{aligned} \hat{U}^{\pm\pm} &= \beta(\mathbf{Q}) \pm A_z(\mathbf{Q}) \\ \hat{U}^{\pm\mp} &= A_x(\mathbf{Q}) \pm iA_y(\mathbf{Q}), \end{aligned} \quad (2.14)$$

where the first sign in the superscript denotes the spin state of the incident neutron beam, and the second sign is for the outgoing beam.

Combining the spatial and spin factors, the scattering amplitudes can be derived by considering the nuclear and magnetic scattering processes.

Nuclear contribution

The contribution of the nuclear force is described by the Fermi pseudo-potential [59] as:

$$\hat{V}(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} \sum_j \delta(\mathbf{r} - \mathbf{R}_j) (b_j + c_j \mathbf{I}_j \cdot \boldsymbol{\sigma}). \quad (2.15)$$

Here, $\mathbf{R}_j$ denotes the position of the j -th nucleus, $\mathbf{I}_j$ represents its nuclear spin, b_j is the scattering length, and c_j signifies the respective coupling strength. The Dirac delta function reflects the point-like nature of the interaction, given the range of nuclear forces in 10^{-15} m to 10^{-14} m compared to the wavelength of a neutron beam in the order of 10^{-10} m [53]. The Pauli matrices $\boldsymbol{\sigma}$ indicate the dependency of the interaction on the nuclear spin states of the sample. The potential can be written in the form of Eq. 2.14:

$$\begin{aligned} \beta_{\text{nuc}}(\mathbf{Q}) &= N(\mathbf{Q}) = \sum_j b_j e^{i\mathbf{Q} \cdot \mathbf{R}_j} \\ \mathbf{A}_{\text{nuc}}(\mathbf{Q}) &= \sum_j c_j \mathbf{I}_j e^{i\mathbf{Q} \cdot \mathbf{R}_j}. \end{aligned} \quad (2.16)$$

Since the nuclear spin of the sample is randomly distributed in most neutron scattering experiments, the contribution from $\mathbf{I}_j$ is smeared out, yielding $\mathbf{A}_{\text{nuc}} = 0$ [53].

Magnetic contribution

The magnetic contribution is given as [53]:

$$\begin{aligned} \hat{V}(\mathbf{r}) &= -\mu_0 \gamma \mu_N 2\mu_B \boldsymbol{\sigma} \cdot \left(\frac{1}{4\pi} \nabla \times \frac{\mathbf{s} \times \mathbf{r}}{|\mathbf{r}|^3} + \frac{1}{4\pi\hbar} \frac{\mathbf{p} \times \mathbf{r}}{|\mathbf{r}|^3} \right) \\ &= \mathbf{W}_S(\mathbf{r}) + \mathbf{W}_L(\mathbf{r}), \end{aligned} \quad (2.17)$$

with $\mathbf{W}_S(\mathbf{r})$ depending on the electron spins and $\mathbf{W}_L(\mathbf{r})$ due to the orbital motion. The magnetic contribution to the double-differential cross-section yields:

$$\begin{aligned} \beta_{\text{mag}}(\mathbf{Q}) &= 0 \\ \mathbf{A}_{\text{mag}}(\mathbf{Q}) &= \mathbf{M}_\perp(\mathbf{Q}) = \frac{\mathbf{Q} \times (\mathbf{M} \times \mathbf{Q})}{|\mathbf{Q}|^2}, \end{aligned} \quad (2.18)$$

with $\mathbf{M} = -2\mu_B(\mathbf{W}_S + \mathbf{W}_L)$. Due to the cross product $\mathbf{Q} \times (\mathbf{M} \times \mathbf{Q})$, neutron magnetic scattering is only sensitive to the component of $\mathbf{M}$ that is perpendicular to $\mathbf{Q}$. This feature is often referred to as the geometric selection rule.

The double-differential cross-section is essential for obtaining the nuclear and magnetic structure of a sample from an experiment with neutron scattering. It also provides the basis for the theory of neutron polarisation analysis.

2.1.2 Polarisation during scattering processes

Combining the nuclear and magnetic contributions described above, the behaviour of the spin polarisation of the neutron beam during scattering is described by the Blume-Maleyev equation [60, 61]:

$$\begin{aligned} \mathbf{P}_f I = & \mathbf{P}_i (NN^* - \mathbf{M}_\perp \cdot \mathbf{M}_\perp^*) \\ & + \mathbf{M}_\perp (\mathbf{P}_i \cdot \mathbf{M}_\perp^*) + \mathbf{M}_\perp^* (\mathbf{P}_i \cdot \mathbf{M}_\perp) \\ & + \mathbf{M}_\perp N^* + \mathbf{M}_\perp^* N - i\mathbf{P}_i \times (\mathbf{M}_\perp N^* - \mathbf{M}_\perp^* N) \\ & + i(\mathbf{M}_\perp \times \mathbf{M}_\perp^*). \end{aligned} \quad (2.19)$$

Here, $\mathbf{P}_i$ and $\mathbf{P}_f$ are the polarisations before and after scattering, respectively, and

$$I = NN^* + \mathbf{M}_\perp \cdot \mathbf{M}_\perp^* + \mathbf{P}_i \cdot \mathbf{M}_\perp N^* + \mathbf{P}_i \cdot \mathbf{M}_\perp^* N - i\mathbf{P}_i \cdot (\mathbf{M}_\perp \times \mathbf{M}_\perp^*) \quad (2.20)$$

is the total double-differential cross-section (Eq. 2.2). The relation in Eq. 2.19 can be expressed in a tensor form [54]:

$$\begin{aligned} \mathbf{P}_f = & \begin{pmatrix} \frac{N^2 - M_y^2 - M_z^2}{I} & \frac{J_{nz}}{I} & \frac{-J_{ny}}{I} \\ -\frac{J_{nz}}{I} & \frac{N^2 + M_y^2 - M_z^2}{I} & \frac{R_{yz}}{I} \\ \frac{J_{ny}}{I} & \frac{R_{zy}}{I} & \frac{N^2 - M_y^2 + M_z^2}{I} \end{pmatrix} \begin{pmatrix} P_{i,x} \\ P_{i,y} \\ P_{i,z} \end{pmatrix} + \begin{pmatrix} -\frac{J_{yz}}{I} \\ \frac{R_{ny}}{I} \\ \frac{R_{nz}}{I} \end{pmatrix} \\ = & \tilde{P} \mathbf{P}_i + \tilde{\mathbf{P}}, \end{aligned} \quad (2.21)$$

where $\tilde{P}$ is a transformation matrix describing the rotation of polarisation during the scattering process and $\tilde{\mathbf{P}}$ is the polarisation that is created independently of $\mathbf{P}_i$. The detailed terms in Eq. 2.21 are [54]:

$$\begin{aligned} I_x &= M_y^2 + M_z^2 + N^2 + P_{i,x} J_{yz} \\ I_y &= M_y^2 + M_z^2 + N^2 + P_{i,y} R_{ny} \\ I_z &= M_y^2 + M_z^2 + N^2 + P_{i,z} R_{nz} \\ I &= M_y^2 + M_z^2 + N^2 + P_{i,x} J_{yz} + P_{i,y} R_{ny} + P_{i,z} R_{nz}, \end{aligned} \quad (2.22)$$

with

$$\begin{aligned} N^2 &= NN^* & R_{\alpha\beta} &= 2\text{Re}(\mathbf{M}_{\perp\alpha} \mathbf{M}_{\perp\beta}^*) & J_{\alpha\beta} &= 2\text{Im}(\mathbf{M}_{\perp\alpha} \mathbf{M}_{\perp\beta}^*) \\ M^2 &= \mathbf{M}_\perp \cdot \mathbf{M}_\perp^* & R_{n\alpha} &= 2\text{Re}(N \mathbf{M}_{\perp\alpha}^*) & J_{n\alpha} &= 2\text{Im}(N \mathbf{M}_{\perp\alpha}^*), \end{aligned}$$

with $\alpha, \beta \in \{y, z\}$. Using Eq. 2.21, the polarisation matrix can be defined as:

$$\begin{aligned} \mathbb{P}_{\alpha\beta} &= \frac{\tilde{P}_{\alpha\beta} P_{i,\beta} + \tilde{P}_\beta}{|\mathbf{P}_i|} = \frac{P_{f,\beta}}{P_{i,\alpha}} \\ &= \begin{pmatrix} \frac{N^2 - M_y^2 - M_z^2 - J_{yz}}{I_x} & \frac{J_{nz} - J_{yz}}{I_y} & \frac{J_{ny} - J_{yz}}{I_z} \\ \frac{J_{nz} + R_{ny}}{I_x} & \frac{N^2 + M_y^2 - M_z^2 + R_{ny}}{I_y} & \frac{R_{yz} + R_{ny}}{I_z} \\ \frac{J_{ny} + R_{nz}}{I_x} & \frac{R_{zy} + R_{nz}}{I_y} & \frac{N^2 - M_y^2 + M_z^2 + R_{nz}}{I_z} \end{pmatrix}. \end{aligned} \quad (2.23)$$

The polarisation matrix $\mathbb{P}$, often also referred to as the polarisation tensor, can be measured experimentally for combinations of $(P_{i,\alpha}, P_{f,\beta})$, providing nuclear and magnetic information about the sample. In such measurements, the coordinate system during scattering is conventionally chosen such that $\hat{\mathbf{x}} \parallel \mathbf{Q}$. Consequently, there is no M_x -term in Eq. 2.21 and 2.23 due to the geometric selection rule as presented in Eq. 2.18.

2.2 Instrumentation for neutron polarisation analysis

2.2.1 Instrument components

The technique of neutron polarisation analysis involves the usage of a spin polariser polarising the incident neutron beam, and of a spin analyser analysing the polarisation after scattering. Between the spin polariser and analyser, there are instrument components necessary to adjust the polarisation to a desired direction and to protect it from stray fields.

Polariser

The spin of the initial neutron beam from the source is randomly distributed. In order to study the behaviour of spin polarisation in scattering, the initial beam must first be polarised. Various techniques are available for this purpose [62].

One technique involves a polarising crystal monochromator, which polarises and monochromatises the beam simultaneously. The crystal of such a monochromator exhibits constructive nuclear-magnetic interference for one spin state and destructive interference for the opposite one. Typical examples include $\text{Co}_{0.92}\text{Fe}_{0.08}$ and the Heusler alloy Cu_2MnAl , with a polarisation efficiency reaching approximately 95 % [63].

Another technique involves a filter with a polarised atomic spin, causing the absorption cross-section to be much larger for one spin state than for the opposite one. Consequently, the neutron beam with one spin direction is transmitted, while the neutrons with the opposite spin direction are absorbed. An example of polarising filters makes use of ^3He , with an efficiency of up to 80 % [62].

Additionally, an optical polariser based on total reflection can be employed. A common type is a neutron supermirror composed of layers with a gradually increasing d -spacing to fulfil Bragg's law (Eq. 1.4). The critical glancing angle θ_c , at which the neutron hits a surface and undergoes a total reflection, is given by:

$$\theta_c = \lambda \sqrt{\frac{\rho b}{\pi}}, \quad (2.24)$$

where λ represents the neutron wavelength, ρ denotes the number density of nuclei, and b signifies the nuclear scattering length. When the material of a supermirror is magnetic, the critical angle becomes sensitive to the neutron spin polarisation, yielding:

$$\theta_c^\pm = \lambda \sqrt{\frac{\rho(b \pm p)}{\pi}}, \quad (2.25)$$

where p denotes the magnetic scattering length. The term $\theta_c^\pm$ indicates that a ferromagnetic material has two different critical angles for the two spin components. Therefore, a supermirror consists of two materials that exhibit the same θ_c for one spin component, and the sequence is calculated from the contrast of the two materials for the other spin component. Consequently, one spin component is reflected while the opposite one is transmitted. A supermirror polariser provides a polarisation efficiency up to over 99 % for the reflected beam while retaining over 70 % of the intensity of the original beam [62, 64]. Presently, two combinations are commonly used [65]: Fe-SiN_x [66] and Fe₈₉Co₁₁-Si [67], or Co-Ti [68], FeCo-TiZr [69], and Fe₅₀Co₄₈V₂-TiN_x [70]. One example is depicted in Fig. 2.2, showcasing the polarisation efficiency and reflectivity of a Fe-Si supermirror manufactured by SwissNeutronics [71], each as a function of the out-of-plane component Q_z of the scattering vector.

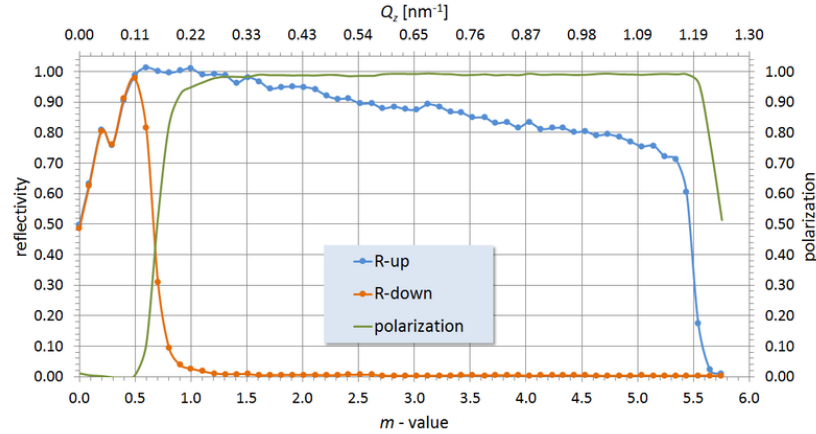


Figure 2.2: Reflectivity and polarisation each as a function of the out-of-plane component Q_z of the scattering vector. The coefficient m measures the critical angle of a supermirror with respect to that of natural nickel: $\theta_c^{\text{SM}} = m\theta_c^{\text{Ni}}$. Figure taken from [64].

Spin analyser

A spin analyser functions essentially as a second polariser, while its name “analyser” indicates its function to analyse the polarisation of the scattered neutron beam. Similar to a polariser, a spin analyser can be either a polarising crystal analyser, which simultaneously selects the wavevector $\mathbf{k}_f$ and polarisation $\mathbf{P}_f$ at the same time, or a stand-alone component. In the latter case, the spin analyser is positioned before the crystal analyser determining E_f , so that the guide field is necessary only until the spin analyser. The polarisation determined by the spin channel of a spin analyser yields:

$$P_f = \frac{I^+ - I^-}{I^+ + I^-}, \quad (2.26)$$

where I^+ denotes the intensity of a neutron beam with the spin parallel to the channel of the spin analyser, and I^- in the opposite direction ¹.

Spin conservation and manipulation

In magnetic fields with a constant orientation that is perfectly aligned, either parallel or anti-parallel, to the polarisation of a neutron beam in an ideal case, the polarisation stays in the same direction as the field. If the field and polarisation are not collinear, the polarisation undergoes Larmor precession around the field with an angular frequency (Larmor frequency):

$$\omega_L = -\gamma_n |\mathbf{B}| = -\gamma_n B, \quad (2.27)$$

where $\gamma_n < 0$ denotes the gyromagnetic ratio of a neutron (Eq. 2.4) and B represents the strength of the magnetic field. Consequently, the precession angle of a neutron travelling through this field along a distance L yields:

$$\phi_L = \omega_L t = -\gamma_n B \frac{L}{v_n}, \quad (2.28)$$

where v_n denotes the velocity of the neutron. When a neutron beam passes through magnetic fields whose directions change, two possible behaviours of the polarisation can occur - adiabatic and non-adiabatic transitions:

- Adiabatic transitions happen when the fields change much more slowly than the Larmor frequency. In this case, the neutron spin will follow the field and precess around the field direction that changes gradually. The angle between the spin and its precession axis remains constant.

¹Here the plus and minus signs do not refer to the states with spin up and down but only to the relation between the spin state of a neutron and the channel of a spin analyser.

- Non-adiabatic transitions happen when the field changes so abruptly that the spin cannot follow it any longer. Instead, the spin precesses around the direction of the new field, resulting in changes of the angle between the spin and its precession axis.

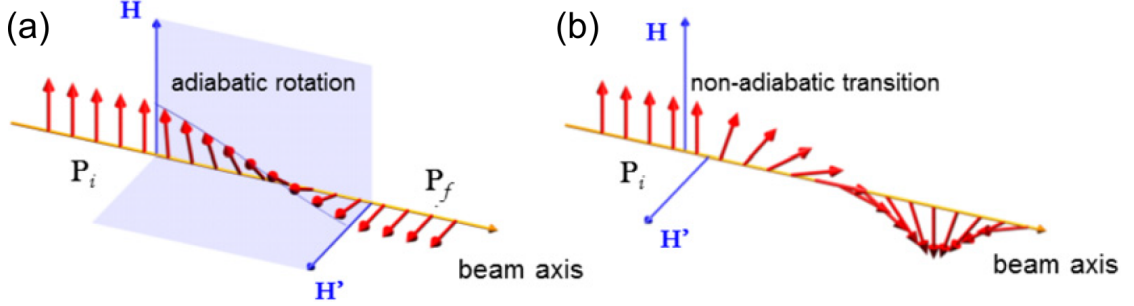


Figure 2.3: Schematic from [72] illustrating the adiabatic (a) and non-adiabatic (b) transitions of the neutron spin during the change of the field from $\mathbf{H}$ to $\mathbf{H}'$. The polarisation is initially perfectly aligned with the field direction. Panel a: The magnetic field changes slowly enough so that the neutron spin always stays in the same direction as the field. Panel b: The magnetic field rotates abruptly by 90° . The neutron spin cannot follow the change and precesses around the direction of the new field $\mathbf{H}'$.

On the one hand, both adiabatic and non-adiabatic transitions can result in a loss of information on the neutron polarisation due to stray fields. Hence, it is necessary to implement guide fields significantly stronger than the expected stray fields ² to preserve the neutron polarisation. On the other hand, both types of transitions can be utilised to manipulate the neutron spin if magnetic fields are well defined. Adiabatic transitions can be conveniently implemented with fields whose direction changes continuously, while non-adiabatic transitions can be employed using coils that generate magnetic fields to turn the spin by desired angles. If the turning angle has a specific value, typically π or $\frac{\pi}{2}$, such a coil is referred to as a spin flipper ³. When a π -flip is performed by the spin flipper, both I^+ and I^- in Eq. 2.26 can be measured by simply turning the flipper off and on without changing the orientation of a spin analyser. Therefore, the intensities are often denoted with respect to the spin flipper rather than the analyser, yielding I^{SF} for the spin π -flip and I^{NSF} for the non-spin-flip (NSF) intensity. By measuring the flipping ratio [58],

$$R = \frac{I^{\text{NSF}}}{I^{\text{SF}}} = \frac{(F_{\text{nuc}} + F_{\text{mag}})^2}{(F_{\text{nuc}} - F_{\text{mag}})^2}, \quad (2.29)$$

²Guide fields are typically $\gtrsim 10$ times the strength of the sum of the other fields.

³A spin flipper is often equipped with an extra coil to compensate the guide field.

the magnetic scattering contributions F_{mag} can be obtained based on the *a priori* knowledge of the nuclear contributions F_{nuc} . This flipping-ratio method enhances the ability to resolve the magnetic contributions, especially when they are much weaker than the nuclear ones [58]. Since this method requires no spin analyser but only a spin polariser and a spin flipper, it is usually not classified as polarisation analysis.

2.2.2 Configurations of polarisation analysis

Polarimetry, or polarisation analysis, measures the dependency of the final $\mathbf{P}_f$ on the incident $\mathbf{P}_i$, providing access to information on magnetic properties as described in Sec. 2.1.2. Polarisation analysis can be implemented very conveniently on a triple-axis spectrometer (TAS), where the spin polariser is installed before the sample, and the spin analyser is positioned between the sample and the detector. The spin polariser and analyser are typically preset to select the same polarisation direction. Because the spin can interact with magnetic fields via Larmor precession, guide fields are implemented between the spin polariser and analyser in order to protect the polarisation from the stray fields, as discussed in Sec. 2.2.1. The guide field before the sample is collinear with the direction of the spin channel of the polariser, while the field after the sample is collinear with the spin direction of the analyser. There are several configurations regarding the vicinity of the sample position, yielding different accessible parts in the polarisation matrix, as summarised in Fig. 2.4.

Longitudinal polarisation analysis

In longitudinal polarisation analysis, the guide field remains in the same direction along the entire neutron trajectory between the spin polariser and analyser (Fig. 2.4a). For a straightforward configuration, the polariser, analyser, and guide field are aligned for the same spin direction. Due to the presence of the guide field near the sample, the neutron beam scattered by the sample senses the field immediately after scattering. If the polarisation deviates from the initial direction due to magnetic scattering, a non-adiabatic transition takes place, where the final polarisation $\mathbf{P}_f$ precesses around the guide field. Consequently, only the component of $\mathbf{P}_f$ that aligns with the guide field will be preserved, while the transverse component $\mathbf{P}_{f,\perp}$ precesses around the field. Thus, the transverse $\mathbf{P}_{f,\perp}$ is averaged to zero by the spin analyser, leading to loss of information. Depending on the polarisation direction set by the instrument, one of the three diagonal elements of the polarisation matrix is accessible without reorienting the sample.

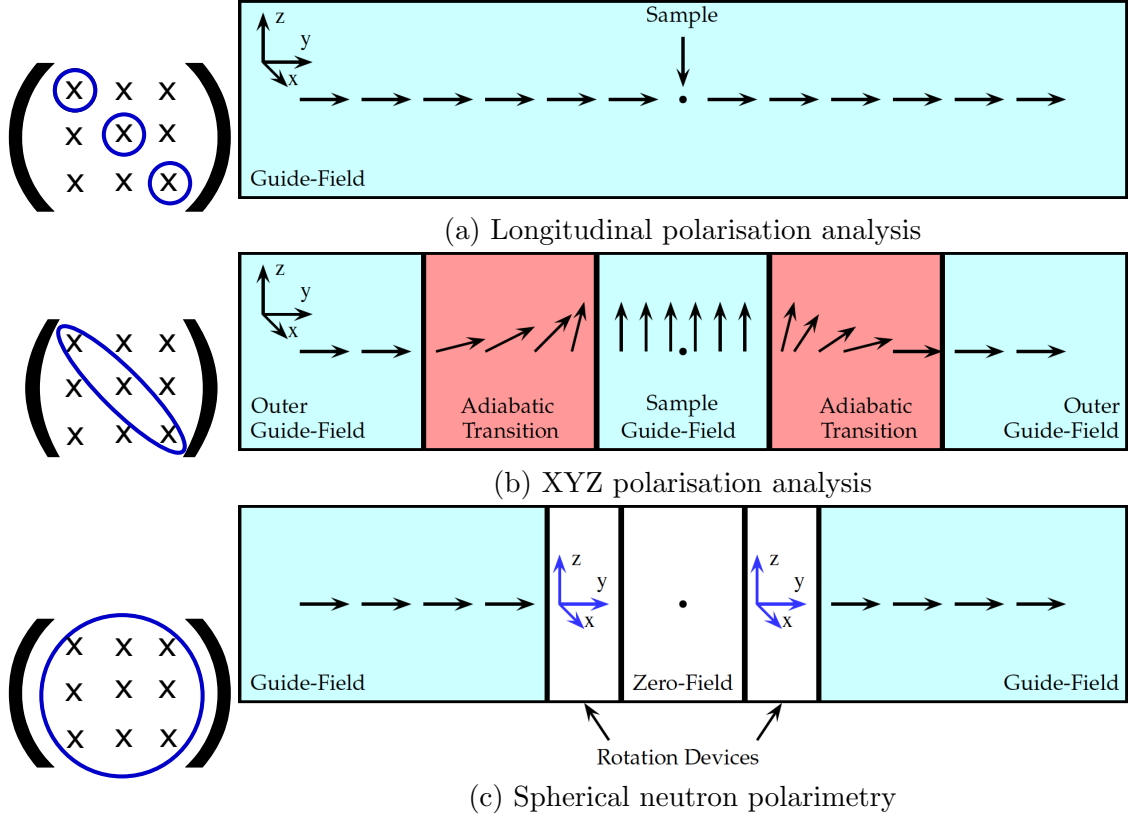


Figure 2.4: Schematic from [73] summarising three most common configurations of neutron polarisation analysis. The available elements in the polarisation matrix $\mathbb{P}$ using respective techniques are highlighted in blue on the left-hand side. Black arrows indicate the polarisation direction of the neutron beam, which moves from the left-hand side to the right-hand side. The outer guide fields in this example align along the neutron flight path (in the schematics denoted by the y -direction).

XYZ polarisation analysis

XYZ polarisation analysis operates on the same principle as longitudinal polarisation analysis, with the distinction being an adiabatic change in the direction of the guide field (Fig. 2.4b). Consequently, the guide field at the sample position can be perpendicular to the directions of the channels of the spin polariser and analyser (Fig. 2.4b). However, owing to the presence of guide fields at the sample position, the polarisation $\mathbf{P}_f$ will still be projected onto the field direction. As a result, one only has access to the same component in $\mathbf{P}_i$ and $\mathbf{P}_f$. Therefore, the off-diagonal elements of the polarisation matrix are still unavailable with this configuration. Its sole advantage over longitudinal polarisation analysis is the ability to access all three diagonal elements through adiabatic transitions due to guide fields without reorienting the sample. For this reason, this method is often referred to indistinctly from the longitudinal polarisation analysis.

Spherical neutron polarimetry

The designation of SNP suggests its advantage in providing access to all nine elements of the polarisation matrix. This accomplishment is realised by eliminating magnetic fields in the sample area, thus decoupling the accessible components of $\mathbf{P}_i$ and $\mathbf{P}_f$. The incident polarisation undergoes rotation by two precession coils from the direction of the guide field into an arbitrary direction $P_{i,\alpha}$ ($\alpha \in \{x, y, z\}$) before reaching the sample (Fig. 2.4c). Subsequently, an arbitrary component $P_{f,\beta}$ ($\beta \in \{x, y, z\}$) is turned back to the direction of the guide field after scattering. Consequently, all combinations of $(P_{i,\alpha}, P_{f,\beta})$ with $\alpha, \beta \in \{x, y, z\}$ become available, providing access to all elements of the polarisation matrix through Eq. 2.23. This technique is particularly potent for elucidating complex magnetic systems, such as those with non-zero nuclear-magnetic interference and chiral contributions.

2.2.3 Devices for spherical neutron polarimetry

CryoPAD

The SNP technique was pioneered by F. Tasset *et al.* in 1988 [74], with its initial objective being the measurement of neutron polarisation rotation in an antiferromagnetic crystal, Cr_2O_3 . The [102]- and [104]-reflections were measured for this purpose over a temperature range of 7 K to 320 K. The device, named cryogenic polarisation analysis device (CryoPAD), incorporates an outer cryostat featuring double neutron-transparent superconducting screens made of niobium (Nb) to employ Meissner effect (Fig. 2.5). This design enables the isolation of different regions of magnetic fields [74–76]. A distinct inner cryostat is employed to establish the desired sample environment, independent of the temperature of the Meissner

shields. Further in-depth discussions on this device can be found in the literature [74–77]. Even today, CryoPAD remains a formidable tool for implementing SNP due to its great resolution of the polarisation matrix. However, it is worth noting that a Meissner shielding alone is insufficient to eliminate stray fields, necessitating the installation of an additional magnetic shielding layer with a high magnetic permeability for an optimal performance.

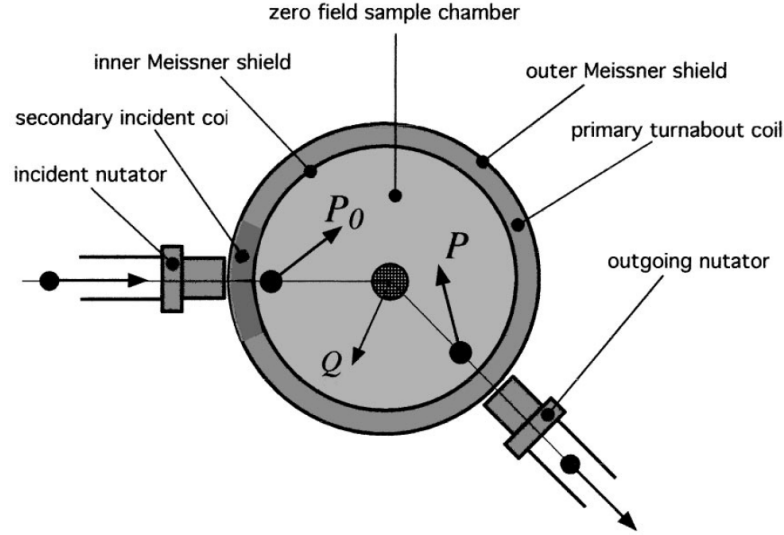


Figure 2.5: Schematic illustration from [76] showcasing the design of the CryoPAD-II, featuring inner and outer Meissner shields to establish the zero-field (ZF) sample chamber. The arrows delineate the trajectory of the neutron beam, while precession coils (nutators) facilitate the adjustment of polarisation before and after the sample position. The vectors $\mathbf{P}_0$ and $\mathbf{P}$ denote the polarisations before and after the scattering, respectively. Their directions emphasise the ability of the CryoPAD to effectively utilise components of $\mathbf{P}$ that remain independent of the incident $\mathbf{P}_0$.

MuPAD

Given the necessity of installing an additional shielding composed of a highly permeable material (e.g. mu-metal) outside the superconducting screen of CryoPAD, another instrument named mu-metal polarisation analysis device (MuPAD) was introduced by M. Janoschek *et al.* [78]. In MuPAD, the ZF region in the vicinity of the sample position is established through a cylindrical mu-metal shielding.

Mu-metal is a soft ferromagnetic alloy composed of approximately 77 % nickel (Ni), 16 % iron (Fe), 5 % copper (Cu), and 2 % chromium (Cr). Due to a low coercivity and an exceptionally high relative permeability $\mu_r \approx 80\,000 - 100\,000$

of mu-metal at the room temperature (RT) [79, 80], a magnetic field passes preferentially through this highly permeable material than elsewhere. This property allows for the implementation of a ZF region without the necessity of cooling down a large shielding area for the Meissner effect.

The schematic design of MuPAD is illustrated in Fig. 2.6. The precision of MuPAD in manipulating polarisation has been achieved with errors not exceeding 5° for the majority of elements of the polarisation matrix and approximately 10° for two elements [77]. The device underwent initial testing with an MnSi-sample at its magnetic satellite reflections around the Bragg reflections [111] and [011] with a propagation vector $\mathbf{k} = [0.017, 0.017, 0.017]$ [77, 78]. Furthermore, it played a crucial role in observing a fluctuation-induced first-order transition associated with Brazovskii scenario, thereby refuting the scenario proposed by Bak and Jensen [81].

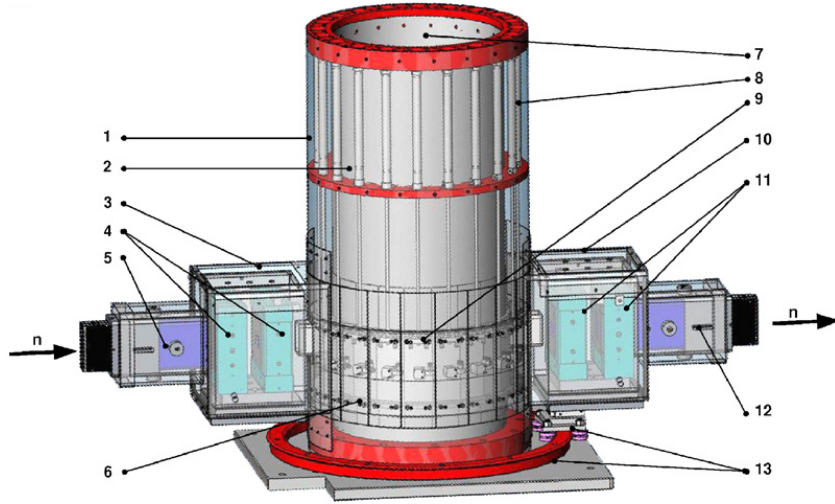


Figure 2.6: Schematic of MuPAD [77], with $\mathbf{n}$ representing the direction of the neutron beam. Key components include (1) outer mu-metal shield; (2) inner mu-metal shield; (4) precession coils; (7) top hole for the insertion of cryostats; (9) sample position. Further detailed notations can be found in [77].

The MuPAD offers a mechanically simpler solution with a trade-off of lower accuracy than that of the CryoPAD. Hence, its handling demands more calibration efforts for good performance. Presently, one MuPAD is available as an add-on feature at the TASP instrument of the neutron source SINQ, Paul Scherrer Institute (PSI), Switzerland [82].

MiniMuPAD

Based on the concepts of CryoPAD and MuPAD, J. Kindervater *et al.* introduced the rectangular miniaturised mu-metal polarisation analysis device (MiniMuPAD)

with a more compact design [73, 83]. Its small size allows a direct insertion into a cryostat with a sample tube having a diameter of 80 mm, the larger one of the two cryostat designs at FRM II. As illustrated in Fig. 2.7, the MiniMuPAD features four rectangular precession coils, with two positioned before and two after the sample position. A mu-metal housing encloses the coils and the sample position, effectively guiding the stray fields and creating a ZF area around the sample position. Due to its geometric configuration, the MiniMuPAD is suitable for experiments with scattering angles 2θ up to 15° [73]. At higher angles, when the neutron beam with a finite size passes through the coil, the difference in flight paths becomes more significant, leading to a larger deviation in the turning angles of neutron polarisation through the coils. This effect causes depolarisation of the beam and inaccuracy of the final polarisation. Additionally, the scattering angle is also constrained by the size of the beam windows and the potential scattering with other components, such as the magnetic shielding made of mu-metal.

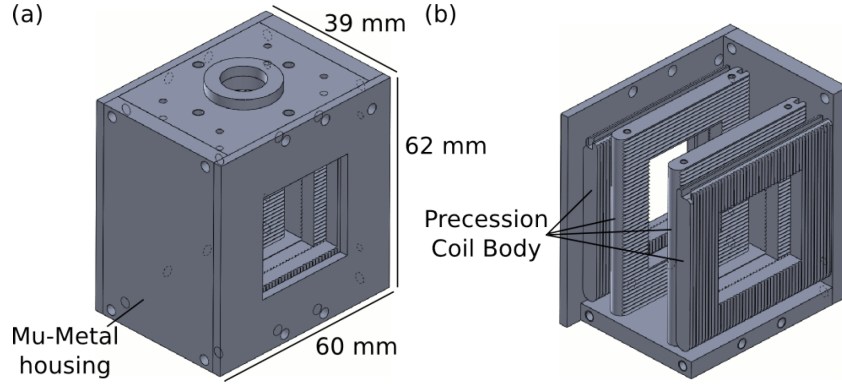


Figure 2.7: Rendered drawing of the second generation of MiniMuPAD [73]. Panel a: The MiniMuPAD with a closed mu-metal housing. The setup is 62 mm high and 60 mm wide. In the beam direction, the mu-metal box extends over 39 mm. Panel b: The bodies of four precession coils where the mu-metal housing is transparent in the figure. The coil bodies are designed, each equipped with a beam window in the middle and with grooves to guide the aluminium wires of coils. With the sample position in the middle, the two coils next to the sample are wound in the horizontal plane, generating magnetic fields in the vertical direction. The two coils further away are wound in the vertical plane, generating fields in the horizontal plane transverse to the beam.

The MiniMuPAD was employed to investigate the evolution of the chiral fraction η during the phase transition of the compound MnSi above the Curie temperature T_c . The chiral fraction is defined as the ratio between the anti-symmetric

and symmetric parts of the magnetic scattering cross-section, given by [73, 83]:

$$\eta(\mathbf{Q}) = \frac{\sigma_{\text{mag}}^{\text{A}}(\mathbf{Q})}{\sigma_{\text{mag}}^{\text{S}}(\mathbf{Q})}. \quad (2.30)$$

The measurements demonstrated a comparable performance of the MiniMuPAD to that of MuPAD, with a maximum deviation of approximately 4% from the expected values in the polarisation matrix [83].

2.3 Design of MiniPAD

The primary limitation of the MiniMuPAD is its constrained scattering angle $2\theta_{\text{S}}$. The concept behind our MiniPAD is to enhance the design of the MiniMuPAD to allow for greater flexibility in scattering experiments. Similar to other devices for SNP, the MiniPAD is comprised of four precession coils - two before and two after the sample position. Each coil is cylindrically shaped, enabling a scattering angle $2\theta_{\text{S}}$ of up to 120° . Moreover, the MiniPAD is designed to be compact enough to fit into a more commonly used type of cryostat whose sample tube has a diameter of 50 mm, contrasting to the 80 mm variant necessary for the MiniMuPAD. A magnetic shielding structure surrounds the coils to eliminate stray fields. The subsequent sections present the design and operational principles of the MiniPAD.

2.3.1 Coil system

The arrangement of the four precession coils around the sample position is vital for manipulating the neutron spin in desired orientations. Fig. 2.8a illustrates a schematic of the coil system, with some details of the coils summarised in Tab. 2.1. Each coil is intricately wound around a core structure designed to support its cylindrical configuration. The core surface features grooves, facilitating the definition of the coil winding and the direction of magnetic fields. For simplicity and cleanliness in design, the cores are crafted from commercially available aluminium. The compact geometry of MiniPAD ensures that the minimal impurities present in aluminium contribute significantly less to scattering processes compared to larger devices like CryoPAD or MuPAD.

Given that a scattering process alters the trajectory of a neutron beam, three coordinate systems (Fig. 2.8b) are essential to describe the behaviour of polarisation between a spin polariser and an analyser: the initial, scattering, and final frames, denoted by the subscripts “i”, “scatt” and “f”, respectively. The z -axes in all frames point in the vertical direction. The x -axes are defined such that $\mathbf{x}_i \parallel \mathbf{k}_i$, $\mathbf{x}_f \parallel \mathbf{k}_f$, and $\mathbf{x}_{\text{scatt}} \parallel \mathbf{Q}$. The y -axes lie in the horizontal plane, completing the respective right-hand systems. The angles δ_i and δ_f describe the relation among

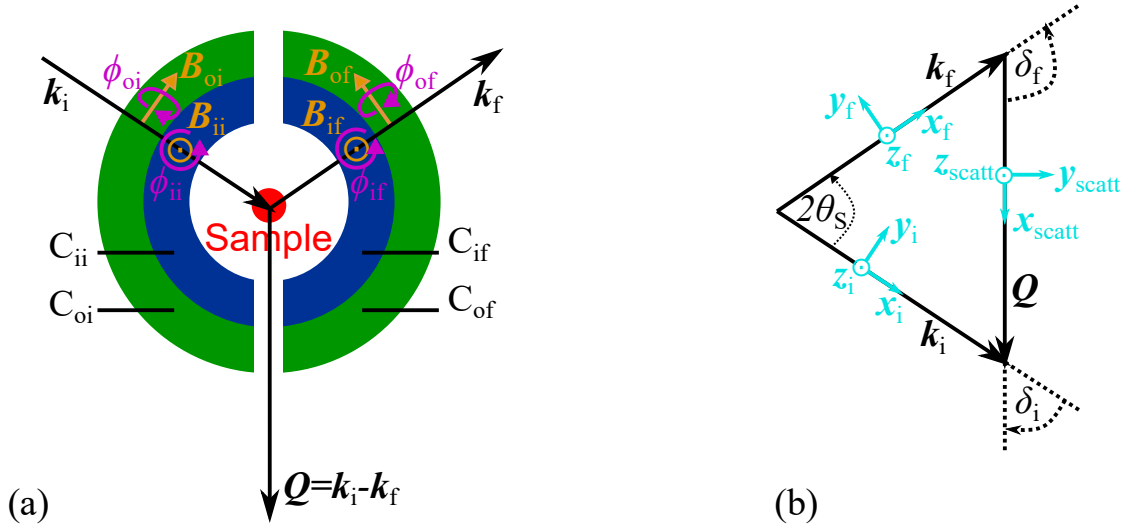


Figure 2.8: The coil system and coordinate systems of MiniPAD. Panel a: Schematic representation of the precession coils (Tab. 2.1) with respect to the sample position and neutron trajectory. The magnetic fields generated by coils are depicted in orange, with the corresponding turning angles of a neutron spin due to these fields shown in magenta. The sample position at the centre of the coil system is marked in red. Panel b: Coordinate systems (cyan) utilised MiniPAD: the incoming, scattering, and final frames denoted by the subscripts “i”, “scatt” and “f” respectively. The x -axes of these frames align with $\mathbf{k}_i$, $\mathbf{k}_f$ and $\mathbf{Q}$, respectively. The z -axes are oriented vertically, while the y -axes lie in the horizontal plane, completing the right-hand rule in the respective systems. The angle δ_i signifies the rotation from $\hat{\mathbf{k}}_i$ to $\hat{\mathbf{Q}}$, and δ_f represents the rotation from $\hat{\mathbf{Q}}$ to $\hat{\mathbf{k}}_f$. As summarised in Tab. 2.1, the directions of magnetic fields are $\mathbf{B}_{oi} \parallel \mathbf{y}_i$, $\mathbf{B}_{ii} \parallel \mathbf{z}_i$, $\mathbf{B}_{if} \parallel \mathbf{z}_f$ and $\mathbf{B}_{of} \parallel \mathbf{y}_f$.

Coil	C_{oi}	C_{ii}	C_{if}	C_{of}
Position	Outer-initial	Inner-initial	Inner-final	Outer-final
Current	I_{oi}	I_{ii}	I_{if}	I_{of}
Magnetic field	$\mathbf{B}_{oi} \parallel \mathbf{y}_i$	$\mathbf{B}_{ii} \parallel \mathbf{z}_i$	$\mathbf{B}_{if} \parallel \mathbf{z}_f$	$\mathbf{B}_{of} \parallel \mathbf{y}_f$
Turning angle	ϕ_{oi}	ϕ_{ii}	ϕ_{if}	ϕ_{of}

Table 2.1: Information about the four precession coils: notation, position, current, magnetic field generated by the coil, and the turning angle of a neutron spin in this field. The sequence of listing the coils corresponds to the neutron trajectory.

these three systems due to scattering, with δ_i representing the rotation from $\hat{\mathbf{k}}_i$ to

$\hat{\mathbf{Q}}$ ⁴, and δ_f signifying the rotation from $\hat{\mathbf{Q}}$ to $\hat{\mathbf{k}}_f$. In an elastic scattering process, the two angles δ_i and δ_f can be determined by the scattering angle θ_s :

$$\delta_i = \frac{\pi}{2} - \theta_s, \quad \delta_f = \pi - \delta_i = \frac{\pi}{2} + \theta_s. \quad (2.31)$$

As presented in Fig. 2.8 and Tab. 2.1, the two precession coils preceding the sample, C_{oi} and C_{ii} , generate magnetic fields in the y_i - and z_i -directions, respectively. The coils C_{if} and C_{of} generate fields in the z_f - and y_f -directions, respectively. The corresponding turning angles of a neutron spin due to Larmor precession in these fields are denoted as ϕ_{oi} , ϕ_{ii} , ϕ_{if} , and ϕ_{of} . Magnetic fields are defined as positive when aligned with the positive directions of the respective axes, resulting in positive values of turning angles when the rotation is anticlockwise around the corresponding axes. As discussed in [52], each of the precession angles of the neutron spin, ϕ_{oi} , ϕ_{of} , ϕ_{ii} and ϕ_{if} , is proportional to the respective magnetic field at a constant velocity of the neutron (Eq. 2.28), while the field strength is proportional to the current in the corresponding coil. Hence, a precession angle exhibits a linear dependency on the current in the respective coil:

$$\phi_\epsilon = f_\epsilon I_\epsilon + \phi_{0,\epsilon}, \quad (2.32)$$

with $\phi_\epsilon \in \{\phi_{oi}, \phi_{of}, \phi_{ii}, \phi_{if}\}$. Each coil has its prefactor f_ϵ and considers a possible phase shift $\phi_{0,\epsilon}$ due to some remanent fields from an imperfect magnetic shielding.

Aligning with $\mathbf{z}_i$, The polarisation of the initial beam after the spin polariser can be defined as $\mathbf{P}_0 = \begin{pmatrix} 0 & 0 & P_0 \end{pmatrix}^\top$. Upon entering the precession coils, the incident beam passes through the fields in the y_i -direction and then in the z_i -direction, with turning angles ϕ_{oi} and ϕ_{ii} , respectively. During the transition from the incident frame to the scattering frame, the coordinate system undergoes a clockwise rotation around $\hat{\mathbf{z}}_i$ by the angle δ_i . This is equivalent to an active anticlockwise rotation of vectors by the angle δ_i . Consequently, the incident polarisation in the scattering frame just before the sample, after passing through the first two precession coils (C_{oi} and C_{ii}), is given by:

$$\mathbf{P}_i^{\text{scatt}} = P_0 \begin{pmatrix} \cos(\delta_i + \phi_{ii}) \sin \phi_{oi} \\ \sin(\delta_i + \phi_{ii}) \sin \phi_{oi} \\ \cos \phi_{oi} \end{pmatrix}. \quad (2.33)$$

Therefore, by setting the turning angles ϕ_{oi} and ϕ_{ii} , the incident polarisation can be turned into one of the three directions, giving $\mathbf{P}_{i,\alpha}^{\text{scatt}} = P_0$ with $\alpha \in \{x, y, z\}$, in order to determine the corresponding elements of the polarisation matrix according to Eq. 2.23. Due to periodic behaviours of trigonometric functions, there can be varying combinations of ϕ_{oi} and ϕ_{ii} to complete this task, with an example summarised in Tab. 2.2a.

⁴A unit vector $\hat{\mathbf{a}}$ denotes the direction of an arbitrary vector $\mathbf{a}$.

α in $\mathbb{P}_{\alpha\beta}$	ϕ_{oi}	ϕ_{ii}
x	$\frac{\pi}{2}$	$-\delta_i$
y	$\frac{\pi}{2}$	$\frac{\pi}{2} - \delta_i$
z	0	0

(a) Before the sample position

β in $\mathbb{P}_{\alpha\beta}$	ϕ_{if}	ϕ_{of}
x	δ_f	$-\frac{\pi}{2}$
y	$\delta_f + \frac{\pi}{2}$	$\frac{\pi}{2}$
z	0	0

(b) After the sample position

Table 2.2: Turning angles (ϕ_{oi} , ϕ_{of} , ϕ_{ii} and ϕ_{of}) for measuring the elements $\mathbb{P}_{\alpha\beta}$ ($\alpha, \beta \in \{x, y, z\}$) of the polarisation matrix (Eq. 2.23). Due to the periodic behaviours of trigonometric functions, other combinations of these angles can also be utilised to measure the same elements.

Denoting the final polarisation in the scattering frame using $\mathbf{P}_f^{\text{scatt}} = (a \ b \ c)^\top$, the final polarisation in the outgoing frame after passing through the last two precession coils (C_{if} and C_{of}) can be derived in the same manner as for the incident polarisation, yielding:

$$\mathbf{P}_f^{\text{out}} = \begin{pmatrix} a \cos \phi_{of} \cos(\phi_{if} - \delta_f) - b \cos \phi_{of} \sin(\phi_{if} - \delta_f) + c \sin \phi_{of} \\ a \sin(\phi_{if} - \delta_f) + b \cos(\phi_{if} - \delta_f) \\ -a \sin \phi_{of} \cos(\phi_{if} - \delta_f) + b \sin \phi_{of} \sin(\phi_{if} - \delta_f) + c \cos \phi_{of} \end{pmatrix}. \quad (2.34)$$

The spin analyser is preset to the same spin channel as the polariser, pointing in the z_f -direction. Therefore, the polarisation of the scattered beam after the precession coils can be determined by:

$$\frac{I^{\text{NSF}} - I^{\text{SF}}}{I^{\text{NSF}} + I^{\text{SF}}} = P_{f,z}^{\text{out}} = -a \sin \phi_{of} \cos(\phi_{if} - \delta_f) + b \sin \phi_{of} \sin(\phi_{if} - \delta_f) + c \cos \phi_{of}. \quad (2.35)$$

Here, I^{NSF} denotes the intensity when the spin flipper is turned off (NSF channel), and I^{SF} is for the case with the spin flipper on (spin-flip (SF) channel). Therefore, by setting the turning angles in the coils C_{if} and C_{of} , the x -, y - or z -component of the final polarisation in the scattering frame $\mathbf{P}_f^{\text{scatt}}$ can be selected and turned into the spin channel of the analyser (z -direction), determining the corresponding elements of the polarisation matrix following Eq. 2.23. An example of ϕ_{if} and ϕ_{of} is summarised in Tab. 2.2b.

Therefore, in measurements, the currents of the precession coils should be set to achieve the turning angles for the required elements $\mathbb{P}_{\alpha\beta}$ of the polarisation matrix $\mathbb{P}$, with the angles summarised in Tab. 2.2. With this, the polarisation $P_{f,z}^{\text{out}}$ can be measured by a spin analyser, determining the elements of the polarisation matrix:

$$\mathbb{P}_{\alpha\beta} = \frac{P_{f,z}^{\text{out}}}{P_0}. \quad (2.36)$$

Aligned with the operational principle of the coil system, its design is illustrated in Fig. 2.9b, featuring an outer diameter of 45 mm. The surrounding constructions, including the magnetic shielding, are described next.

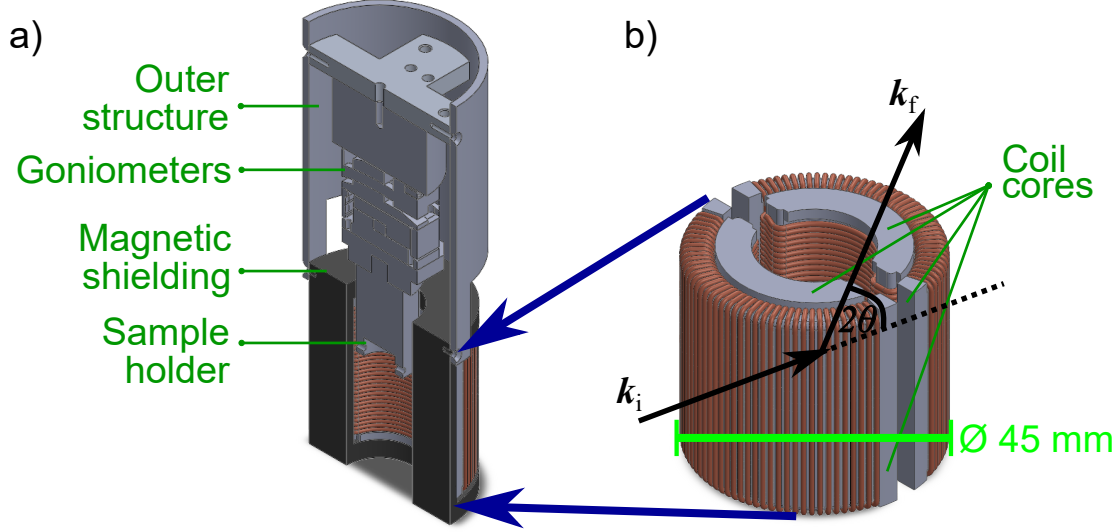


Figure 2.9: Panel a: Schematic of the MiniPAD consisting of four precession coils, a magnetic shielding yoke, a sample holder, three goniometers and an outer structure. Panel b: The enlarged figure of the coil system with its core structures. The arrows of k_i and k_f show the relation between the neutron trajectory and the coils.

2.3.2 Surrounding constructions

In addition to the coil system, surrounding constructions are designed for magnetic shielding and the installation of the coil system. The incorporation of a magnetic shielding structure is essential for SNP in the MiniPAD for providing a zero-field environment in the vicinity of the sample position. This involves the installation of a shielding yoke around the precession coils, as depicted in Fig. 2.9. While mu-metal was utilised for shielding in the designs of MuPAD and MiniMuPAD, it poses challenges due to its high cost and sensitivity to mechanical stresses that can lead to a decrease in permeability by one to several orders of magnitude [84, 85]. In our work, we consider a more cost-effective alternative, employing soft iron for shielding, which also contributes to the name MiniPAD omitting the term “mu”. Soft iron is annealed pure iron, exhibiting a lower coercivity and a higher permeability than hard iron, as well as a lower sensitivity to mechanical stresses than mu-metal [84, 85]. It is crucial, however, to generally avoid mechanical stresses for

optimal functionality of the shielding material.

The magnetic shielding yoke around the coils is installed on an outer structure made of aluminium, allowing the MiniPAD to be mounted onto the sample stick. Additionally, goniometers manufactured by Attocube [86] are utilised to control the sample orientation independently of the coils, which are aligned with the sample stick and cryostat. Three goniometers, including a rotator and two tilting goniometers, are employed. The two tilting goniometers are designed to share the same rotational centre when stacked on top of each other in the correct sequence. This feature enables the keeping the rotational centre within the scattering plane. Moreover, the closed-loop feature of the goniometers allows a sample alignment using neutrons rather than using a visual inspection.

The MiniPAD, consisting of the coil system, goniometers and outer structure (Fig. 2.9b), has been installed on a sample stick. The stick can be inserted into a standard cryostat at FRM II with a sample tube having a diameter of 50 mm [87]. An additional adapter was constructed to connect the setup and the flange of another 50 mm-cryostat, such as “ILL-1” at SINQ [88]. A photo of the implemented design during our recent measurement is presented in Fig. 2.10.

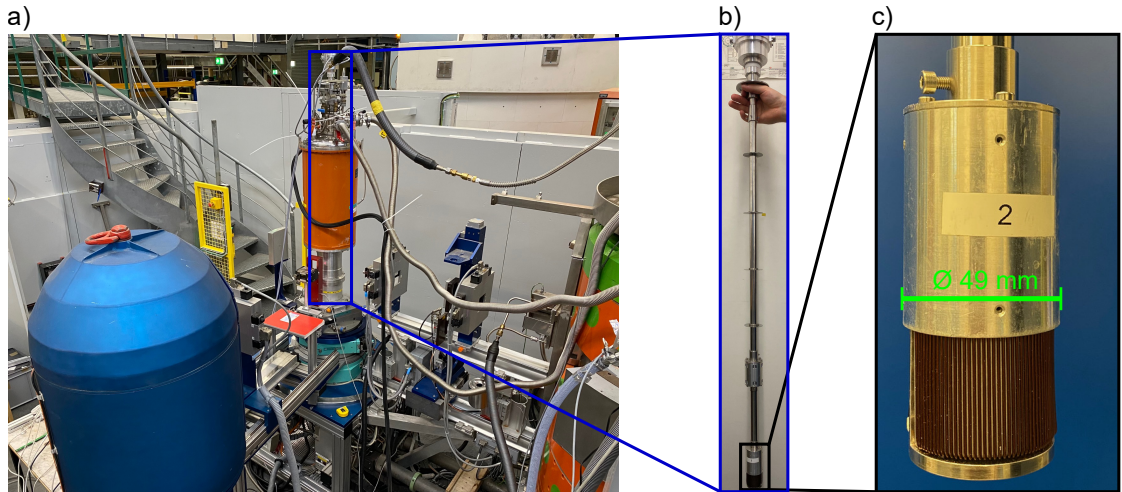


Figure 2.10: Photo of the MiniPAD during the most recent measurement at the MORPHEUS instrument of the Swiss spallation neutron source SINQ, PSI, Villigen, Switzerland. Panel a: The entire setup at MORPHEUS. Panel b: The sample stick that was installed in the “ILL-1” cryostat. Panel c: A photo of the MiniPAD.

2.4 Performance evaluation

The performance of MiniPAD has been assessed using a single-crystalline sample of MnSi at the MORPHEUS instrument of the Swiss spallation neutron source SINQ, PSI, Villigen, Switzerland [89, 90].

2.4.1 Sample: MnSi

The sample employed for the measurement is MnSi, a helimagnet featuring its magnetic phase diagram illustrated in Fig. 2.11a. MnSi is classified under the cubic space group $P2_13$ (No. 198) with the lattice constant $a = 4.558 \text{ \AA}$. As a weak itinerant helimagnet, MnSi possesses a Curie temperature $T_C \approx 29 \text{ K}$ [91, 92]. The non-centrosymmetric magnetic structure introduces an additional term $i\mathbf{b}\mathbf{k} \cdot (\mathbf{S}_k \times \mathbf{S}_k^*)$ when minimising the free energy using the Ginzburg-Landau theory. This term results from interactions between spins of the form $\mathbf{S}_i \times \mathbf{S}_j$ and is known as Dzyaloshinskii-Moriya interaction (DMI) [93]. It elucidates the spiral magnetic structure of MnSi in ZF with a propagation vector $\frac{2\pi}{a}(\zeta, \zeta, \zeta)$, where $\zeta \approx 0.017$, providing a period of approximately $180 \text{ \AA}$ along the $[111]$ -direction [94]. Polarised small-angle neutron scattering (SANS) measurements have confirmed the left-handed nature of the spiral spin structure [95, 96]. This structure differs from regular ones where both right- and left-handed spirals coexist with equal probabilities, as a single-handed spiral scatters only a particular polarisation of the neutrons [97]. Chiral fluctuations above T_C were observed by B. Roessli *et al.* [98]. Using SNP, M. Janoschek *et al.* demonstrated that the chiral terms could be directly obtained from the two off-diagonal components $\mathbb{P}_{yx}$ and $\mathbb{P}_{zx}$ in the polarisation matrix $\mathbb{P}$ [77].

2.4.2 Preparation of measurements

A TAS exhibits varying resolutions at different $(\mathbf{k}_i, \mathbf{k}_f)$ -combinations, as discussed in Sec. 1.2.1. Hence, in addition to the reflections forbidden by the extinction rules based on the crystal lattice of a sample, there may be some reflections that are not resolvable by an instrument. Consequently, the angles A_3 and A_4 (Tab. 1.1) of the sample stage were scanned first in order to identify the nuclear reflection $[011]$ and its magnetic satellite $[-0.0155, 1 - 0.0155, 1 - 0.0155]$. The zero alignment of the angle of A_3 was not performed after the manual installation of the cryostat because the crystal structure of MnSi and the scattering angles for the reflections are known. Instead, a combined scan of the (A_3, A_4) -angles was completed for locating the target reflections. An A_3 -scan presented in Fig. 2.12 has shown the nuclear reflection $[011]$ and the magnetic satellite peak $[-0.0155, 1 - 0.0155, 1 - 0.0155]$.

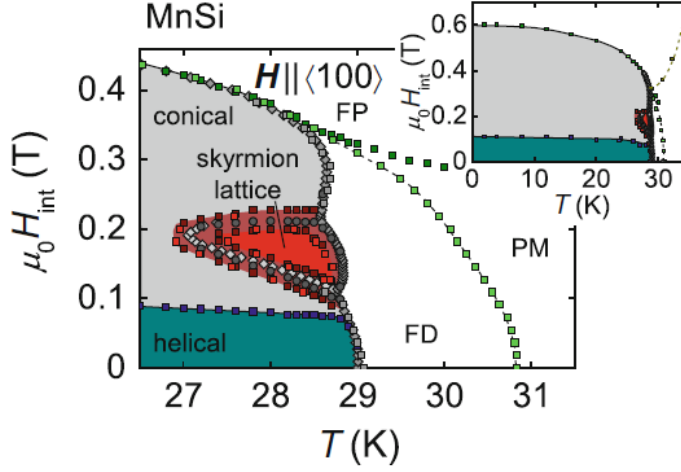


Figure 2.11: Panel a: Magnetic phases of MnSi as a function of temperature and external magnetic field, as determined by ultrasonic studies conducted by A. Bauer *et al.* [99]. Panel b: Photo of a cylindrical MnSi sample mounted on an aluminium sample holder. The red line indicates the [011]-direction aligned using the ORION instrument at the Swiss spallation neutron source SINQ, PSI, Villigen, Switzerland.

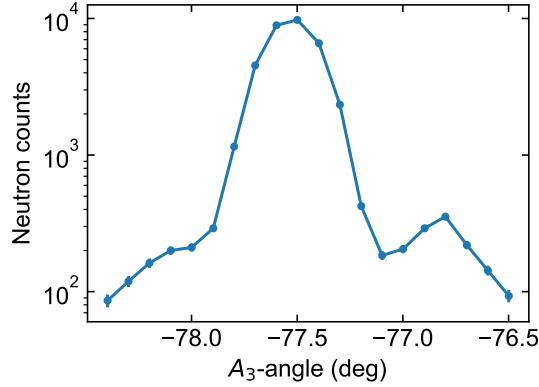


Figure 2.12: An A_3 -scan of the MnSi sample at 25 K, where the main peak corresponds to the nuclear reflection [011] and the peak on its right-hand side depicts its magnetic satellite $[-0.0155, 1 - 0.0155, 1 - 0.0155]$. Given that the intensity of the magnetic reflection is approximately 50 times weaker than the nuclear one, the vertical axis is scaled logarithmically for enhanced visibility. The angle A_3 is correlated with the scattering angle θ_s with a phase shift, as discussed in the text.

The measurements were conducted without a crystal analyser selecting λ_f , while the monochromator was preset for a constant wavelength of $\lambda_i = 4.9 \text{ \AA}$ throughout the entire beamtime. Consequently, only the two angles A_3 and A_4 (Tab. 1.1) were adjusted to measure different reciprocal positions of the sample. The sample stick was inserted into the “ILL-1” cryostat [88] whose sample tube has a diameter of 50 mm. A cylindrical MnSi sample (Fig. 2.11b) with a diameter of 10 mm and a height of 27 mm was mounted onto the Attocube goniometers. The crystal orientation was verified at the instrument ORION of the Swiss spallation neutron source SINQ, PSI, Villigen, Switzerland [100]. The [011]-direction is indicated with a red line (Fig. 2.11b), with the [002]-direction perpendicular to it ⁵.

The spin polariser and analyser that were employed for the measurement are transmission polarisers manufactured by SwissNeutronics [71], consisting of supermirrors and a collimator. As illustrated in Fig. 2.13a, the spin-up ($|+\rangle$) neutrons are reflected by the supermirrors and subsequently absorbed by the collimator, while the spin-down ($|-\rangle$) neutrons are transmitted, remaining in the same trajectory. With both devices from an identical production model, they both select the $|-\rangle$ neutrons. While installing both polarisers, the angular alignment of each device has been scanned, as shown in Fig. 2.13b, exhibiting a scan curve with a similar shape to that presented in Fig. 2.2. The polarisation generated by the spin polariser is denoted as $\mathbf{P}_0 = (0 \ 0 \ -P_0)^\top$, with the initial polarisation determined to be $P_0 \approx 0.749$ with the complete setup installed and all the precession coils of the MiniPAD turned off.

2.4.3 Measurement on a nuclear reflection

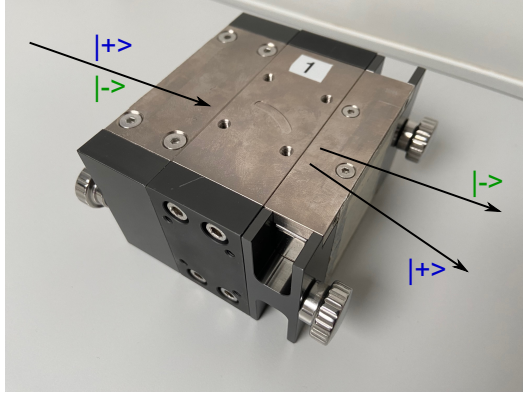
At the nuclear Bragg reflection [011], only the nuclear contributions appear in the polarisation matrix (Eq. 2.23), resulting in:

$$\mathbb{P}_{\alpha\beta} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (2.37)$$

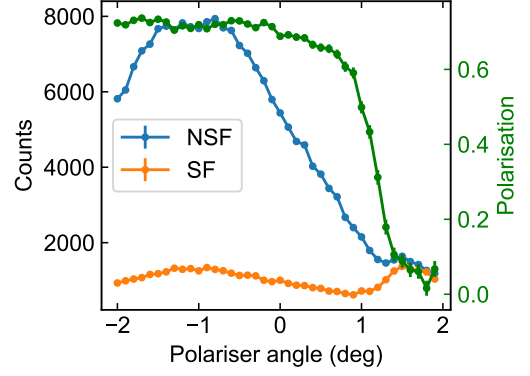
Consequently, the initial and final polarisations are the same in the scattering frame (Fig. 2.8a), i.e. $\mathbf{P}_f^{\text{scatt}} = \mathbf{P}_i^{\text{scatt}}$. Hence, following Eq. 2.33, the final polarisation in the scattering frame yields:

$$\mathbf{P}_f^{\text{scatt}} = \begin{pmatrix} a \\ b \\ c \end{pmatrix} = P_0 \begin{pmatrix} \cos(\delta_i + \phi_{ii}) \sin \phi_{oi} \\ \sin(\delta_i + \phi_{ii}) \sin \phi_{oi} \\ \cos \phi_{oi} \end{pmatrix}. \quad (2.38)$$

⁵The diffraction order [001] is forbidden by the lattice structure of MnSi.



(a) Photo of polariser



(b) Polariser alignment scan

Figure 2.13: Panel a: Photo of the supermirror polariser utilised in the measurement, where neutrons with the spin state $|-\rangle$ are transmitted. Neutrons with $|+\rangle$ spin are reflected by the supermirror layers and consequently deviate from the original trajectory. The spin polariser and analyser employed in the measurement were of an identical model manufactured by [71]. Panel b: Angular scan of the motorised stage of the polariser for alignment.

Following Eq. 2.34, the final polarisation in the outgoing frame yields:

$$\begin{aligned}
 \frac{P_{f,z}^{\text{out}}}{P_0} &= -a \sin \phi_{\text{of}} \cos(\phi_{\text{if}} - \delta_f) + b \sin \phi_{\text{of}} \sin(\phi_{\text{if}} - \delta_f) + c \cos \phi_{\text{of}} \\
 &= \sin \phi_{\text{oi}} \sin \phi_{\text{of}} [-\cos(\delta_i + \phi_{\text{ii}}) \cos(\phi_{\text{if}} - \delta_f) + \\
 &\quad \sin(\delta_i + \phi_{\text{ii}}) \sin(\phi_{\text{if}} - \delta_f)] + \cos \phi_{\text{oi}} \cos \phi_{\text{of}} \\
 &= -\sin \phi_{\text{oi}} \sin \phi_{\text{of}} \cos(\phi_{\text{ii}} + \phi_{\text{if}} + \delta_i - \delta_f) + \cos \phi_{\text{oi}} \cos \phi_{\text{of}},
 \end{aligned} \tag{2.39}$$

where $P_{f,z}^{\text{out}}$ can be measured using a spin analyser and a π -flipper. The intensities of NSF and SF channels can be described independently of each other:

$$\begin{aligned}
 I^{\text{NSF}} &= f^{\text{NSF}}(1 + P_{f,z}^{\text{NSF}}) \\
 I^{\text{SF}} &= f^{\text{SF}}(1 - P_{f,z}^{\text{SF}}).
 \end{aligned} \tag{2.40}$$

Here, the prefactors f^{NSF} and f^{SF} indicate the independent characterisations of the two channels. The terms $P_{f,z}^{\text{NSF}}$ and $P_{f,z}^{\text{SF}}$ have the same form as Eq. 2.39 but use their own values of the coil parameters, considering potentially different phase shift due to background noises. In the ideal case, one has $f^{\text{NSF}} = f^{\text{SF}}$ and $P_{f,z}^{\text{NSF}} = P_{f,z}^{\text{SF}}$.

In order to measure the polarisation matrix, the following procedure was originally planned to determine the coefficients f and ϕ_0 for each coil:

1. Each outer coil is scanned separately when all other precession coils are set for the current $I = 0$;
2. The scan results are fitted using Eq. 2.39 to determine the parameters f and ϕ_0 for both outer coils;
3. Both outer coils C_{oi} and C_{of} are set for $\phi_{oi} = 90^\circ$ and $\phi_{of} = -90^\circ$, respectively, using Eq. 2.32;
4. The inner coils C_{ii} and C_{if} are scanned and fitted while the both outer coils are set for $\phi_{oi} = 90^\circ$ and $\phi_{of} = -90^\circ$.

With this procedure, the parameters of all coils can be used to calculate the necessary currents of the coils to turn the polarisation of the neutron beam in order to measure each element of the polarisation matrix following Tab. 2.2. Using these currents, the intensities of the NSF and SF channels can be measured, determining the elements $P_{\alpha\beta}$ according to Eq. 2.35 and 2.36. It is a straightforward procedure for measuring the elements of the polarisation matrix. However, due to some technical issues encountered during our measurements, an alternative approach was employed:

1. The scans of the mentioned procedure were carried out;
2. Further combinations of $(C_{oi}, C_{of}, C_{ii}, C_{if})$ as a mapping among the four coils were measured to achieve better statistics;
3. The polarisation is calculated using the intensities I^{NSF} and I^{SF} at each $(C_{oi}, C_{of}, C_{ii}, C_{if})$ -combination. All polarisations values in dependence of the currents are fitted according to Eq. 2.32 and 2.39. Additionally, the NSF and SF intensities are characterised independently of each other using Eq. 2.32 and 2.40. Through this step, three sets of coil parameters are obtained to characterise the behaviours of $P_{f,z}$, I^{NSF} and I^{SF} .
4. The coil parameters describing $P_{f,z}$ are used to calculate the currents I_{oi} , I_{of} , I_{ii} and I_{if} for each element of the polarisation matrix according to Tab. 2.2. In addition, the coil parameters describing I^{NSF} and I^{SF} are used to predict the intensities at each $(I_{oi}, I_{of}, I_{ii}, I_{if})$ -combination. This approximates a real measurement recording the intensities at these combinations of currents, determining the elements $P_{\alpha\beta}$ ($\alpha, \beta \in \{x, y, z\}$) of the polarisation matrix according to Eq. 2.35 and 2.36.

Although this procedure is less direct and requires more time for measurements, it is an alternative approach that is able to take into consideration that the sinusoidal behaviours of the intensities in the NSF and SF channels can have distinct

phase shifts in the respective sine/cosine functions. Some representative scans are depicted in Fig. 2.14, where one of the four precession coils is scanned while the currents of the other coils remain fixed. The values of currents used in the scans were calculated by fitting the respective coils, contrasting with the procedure in data analysis where all datasets were used to calculate the coil parameters. The corresponding turning angles of the spin when neutrons pass through these coils are calculated using the coil parameters characterising $P_{f,z}$.

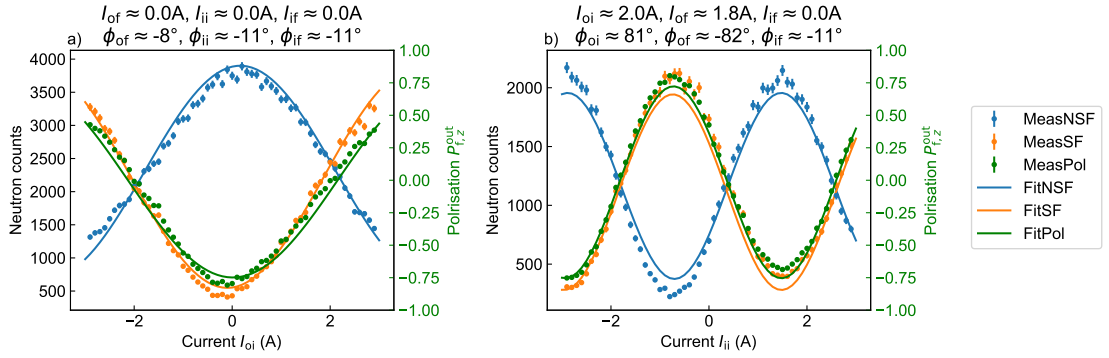


Figure 2.14: Representative results of scanning one of the four precession coils while keeping the currents of the other coils fixed. The fixed currents are provided above the diagrams. The scans are performed using the nuclear reflection [011]. The vertical axis on the left-hand side of each panel depicts the intensity of NSF and SF channels (“MeasNSF” and “MeasSF”), with the fit (“FitNSF” and “FitSF”) of each spin channel performed independently of the other. The polarisation (“MeasPol”) is calculated using the datasets “MeasNSF” and “MeasSF” according to Eq. 2.26, plotted using the vertical axis shown on the right-hand side of each panel. The fitted polarisation (“FitPol”) is obtained by fitting the “MeasPol”-result using Eq. 2.39. The turning angles of the neutron spin passing through each coil with a fixed current are calculated using the “FitPol”-result and are displayed above the diagrams.

The diagrams in Fig. 2.14 give indications of the uncertainties in measurements. In Fig. 2.14a, the maximum of I^{NSF} does not appear at the same current as for the minimum of I^{NSF} when scanning the current of the same coil, indicating small differences of the phase shifts of the sine/cosine functions in the NSF and SF channels. This is likely to be caused by some stray fields causing extra spin precession in addition to the fields generated by the coils. Implementing magnetic shielding made of mu-metal can potentially help to further suppress the stray fields, improving the performance.

With the procedure described above, the polarisation matrix is obtained:

$$\mathbb{P}_{\alpha\beta}P_0 = \begin{pmatrix} 0.717 & -0.027 & -0.121 \\ -0.012 & 0.706 & -0.028 \\ -0.042 & 0.053 & 0.744 \end{pmatrix}. \quad (2.41)$$

The term P_0 indicates that the originally achievable conservation of the spin polarisation has to be also taken into consideration. With $P_0 \approx 0.749$ as mentioned above, the matrix yields:

$$\mathbb{P}_{\alpha\beta} = \begin{pmatrix} 0.958 & -0.036 & -0.162 \\ -0.016 & 0.943 & -0.037 \\ -0.057 & 0.070 & 0.993 \end{pmatrix}. \quad (2.42)$$

Comparing the result to the theoretical value, the diagonal elements could be retrieved with an uncertainty of approx. 5%. Only one off-diagonal element had a larger uncertainty. This measurement has demonstrated the capability of the MiniPAD to control the neutron spin polarisation in order to measure all elements of the polarisation matrix with a good resolution.

2.4.4 Measurement on a magnetic reflection

During the beamtime, measurements were planned for a magnetic satellite reflection of MnSi at $[-0.0155, 1 - 0.0155, 1 - 0.0155]$. However, due to some technical issues, the polarisation matrix could not be obtained. In the following, the procedure to measure the polarisation matrix is summarised.

In the ideal case, there is only the chiral contribution in the polarisation matrix at a magnetic satellite reflection of MnSi, giving the polarisation matrix:

$$\mathbb{P}_{\alpha\beta} = \begin{pmatrix} -\frac{J_{yz}}{I_x} & -\frac{J_{yz}}{I_y} & -\frac{J_{yz}}{I_z} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2.43)$$

Taking the finite resolution of the instrument into consideration, the nuclear and magnetic contributions may be recorded in the measurement besides the chiral term because the magnetic satellite of MnSi is very close to its nuclear peak. This can result in non-zero elements in the polarisation matrix when $\mathbf{P}_f^{\text{scatt}}$ is along the y - or z -direction. In this case, the polarisation matrix yields:

$$\mathbb{P}_{\alpha\beta} = \begin{pmatrix} \frac{N^2 - M_y^2 - M_z^2 - J_{yz}}{I_x} & -\frac{J_{yz}}{I_y} & -\frac{J_{yz}}{I_z} \\ 0 & \frac{N^2 + M_y^2 - M_z^2}{I_y} & 0 \\ 0 & 0 & \frac{N^2 - M_y^2 + M_z^2}{I_z} \end{pmatrix}. \quad (2.44)$$

2.5 Summary

The MiniPAD has been developed as a very compact alternative for implementing SNP. It can be seamlessly integrated as an add-on into a standard 50 mm cryostat, offering outstanding flexibility and ease of use. Its compact design enhances practicality and contributes to its cost-effectiveness. The performance of MiniPAD was evaluated on the MORPHEUS instrument, employing a single-crystal sample of MnSi. The results demonstrate the capability of MiniPAD to measure a polarisation matrix with an uncertainty within 5 % accounting for the maximum achievable polarisation, which is comparable with other devices such as MuPAD and MiniMuPAD. Despite encountering technical challenges leading to incomplete datasets at the magnetic reflection, the results of the nuclear reflection demonstrate the functionality and good performance of the MiniPAD once the technical challenge is resolved. The performance can be further improved by employing mu-metal for the magnetic shielding, which has been demonstrated already by previous devices such as MuPAD [101] and our simulations [52]. Overall, the results confirm the suitability of the MiniPAD for studies on magnetic structure using SNP. Its attributes, including simplicity, versatile design, good resolution, and cost-effectiveness, make it a commendable choice for such investigations.

Chapter 3

Layered perovskite antiferromagnets

Two kinds of frustrated perovskite antiferromagnetic systems have been studied in this thesis: a triangular-lattice antiferromagnet (TLAF) $\text{Ca}_3\text{NiNb}_2\text{O}_9$ with spin $s = 1$ and a frustrated square lattices (FSLs) PbVO_3 with $s = \frac{1}{2}$.

3.1 Triangular-lattice antiferromagnet $\text{Ca}_3\text{NiNb}_2\text{O}_9$

3.1.1 Triangular-lattice antiferromagnets

TLAFs are a typical family of geometrically frustrated systems, where the energies of local interactions cannot be minimised simultaneously, leading to degeneracies of ground states [102–104]. An example is a TLAF with Ising spins, where the geometric frustration among the three spins leads to six ground states rather than two as in the conventional Ising model [102–104]. In the meantime, such degeneracy is not protected by the symmetry and can be lifted by quantum fluctuations, resulting in various unconventional phenomena [104]. Due to the competition between quantum fluctuations and geometric frustrations, TLAFs tend to exhibit either a quantum spin liquid (QSL) [105–108] or a non-collinear 120° -ordered ground state [103, 109–112]. In the latter case, the ordered state tends to undergo a successive two-step transition, evolving into an up-up-down (uud) state and further into an oblique state with an increasing external magnetic field (Fig. 3.1) [113]. Another widely observed phenomenon is a plateau with a $\frac{1}{3}$ -saturation of magnetisation in the high-field region of $\mathbf{M}$ - $\mathbf{H}$ -measurements [114–116]. With much attention attracted to the TLAFs since decades, the association between these features and different spin quantum numbers of systems has been investigated.

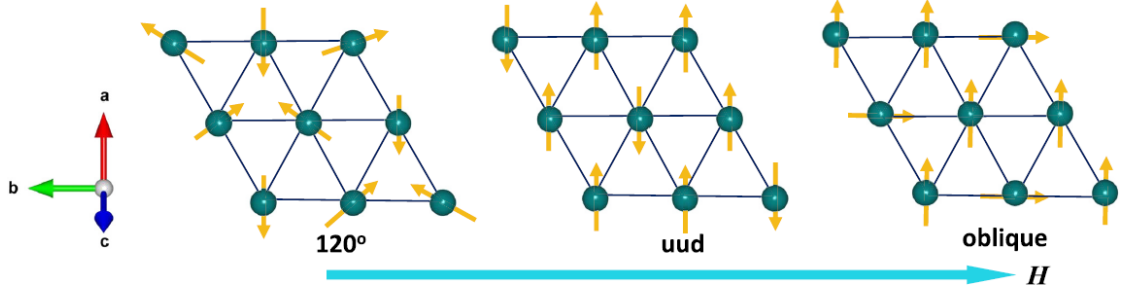


Figure 3.1: A common magnetic ordering of TLAFs shown in the ab -plane (c -direction perpendicular to the plane), where the 120° -ordered ground state undergoes successive transitions into the uud and then oblique states as the increasing external magnetic field H . The direction of the field is associated with the spin quantum number and the anisotropy, as discussed in the text. Figure taken from [113].

In TLAFs, the quantum effect is especially significant with spin $s = \frac{1}{2}$. Both QSL [117–119] and 120° -ordered ground states [114, 120–122] have been observed in those system. Notably, however, strong quantum fluctuations have been observed even in the systems with ordered ground states [123, 124].

In the semi-classical limit with $s > 1$, the interaction among spins becomes dominant. The systems have been found to exhibit the non-collinear 120° -ordered ground state. It has been shown that the phenomenon of plateau with the $\frac{1}{3}$ -saturation of magnetisation is governed by the easy-axis anisotropy [115, 121, 125].

The intermediate situation with $s = 1$ has a less clear tendency due to strong quantum fluctuations. On the one hand, systems such as $\text{Ba}_3\text{NiNb}_2\text{O}_9$ (6H-A phase, space group (SG) $P6_3/mmc$) [126, 127], $\text{Ba}_2\text{La}_2\text{NiTe}_2\text{O}_{12}$ [128] and $\text{Na}_2\text{BaNi}(\text{PO}_4)_2$ [129] exhibit the 120° ground state. On the other hand, in contrast to the case with $s > 1$, some spin-1 systems can have a spin-liquid ground state introduced by quantum fluctuations. One example is the 6H-B phase of $\text{Ba}_3\text{NiNb}_2\text{O}_9$ with SG $P6_3mc$, which is obtained by keeping the 6H-A phase at 600°C under the pressure of 3 GPa for 1 h [130].

The compound $\text{Ca}_3\text{NiNb}_2\text{O}_9$ that is studied in this thesis serves as a further example for a better understanding of the TLAFs with $s = 1$. It is derived from the perovskite system ABO_3 with Ni and Nb ions sharing the B-site positions. Generally, in such a system of type $\text{A}_3\text{M}'\text{M}_2\text{O}_9$, there are two possibilities regarding the magnetic ordering depending on the type of the B-site occupation. The disordered $\text{AM}'_{\frac{1}{3}}\text{M}_{\frac{2}{3}}\text{O}_3$ has a statistical distribution of M' and M ions on the B-site of ABO_3 , resulting in a spin-glass-like ground state, whilst the ordered $\text{A}_3^{2+}\text{M}'^{2+}\text{M}_2^{5+}\text{O}_9$ has a 1 : 2 ordering of M' and M ions. This ordering is called B-site ordering, which is formed through a two-step transition [113].

3.1.2 Previous studies on $\text{Ca}_3\text{NiNb}_2\text{O}_9$

A polycrystalline sample of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ has been previously investigated by Z. Lu *et al.* as part of studies on lattice distortions among the sibling systems $\text{A}_3\text{NiNb}_2\text{O}_9$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$) [131]. The triangular lattices in $\text{Ca}_3\text{NiNb}_2\text{O}_9$ and $\text{Sr}_3\text{NiNb}_2\text{O}_9$ have been found to distort from equilateral, which is the case in $\text{Ba}_3\text{NiNb}_2\text{O}_9$, to isosceles [131]. As a result, $\text{Ca}_3\text{NiNb}_2\text{O}_9$ and $\text{Sr}_3\text{NiNb}_2\text{O}_9$ have both the monoclinic SG $P12_1/c_1$ (No. 14), contrasting to $\text{Ba}_3\text{NiNb}_2\text{O}_9$ with the hexagonal SG $P\bar{3}2/m1$ (No. 164). The $\text{Ca}_3\text{NiNb}_2\text{O}_9$ sample has been measured using neutron powder diffraction. The magnetic peaks were fitted based on the approximated hexagonal SG $P\bar{3}2/m1$, yielding a propagation vector $\mathbf{k} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ [131], as is shown in Fig. 3.2a. The approximated hexagonal structure emphasises the triangular nature of the structure. However, we believe it is more appropriate to describe the magnetic structure based on the true nuclear SG $P12_1/c_1$, because the hexagonal basis would indicate a higher symmetry than the monoclinic structure, given that no structural transition was observed down to 2 K by the authors [131], we. Nonetheless, the temperature dependency of the scattering intensity was studied on the magnetic peak at $\mathbf{Q}_{hkl} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ based on the hexagonal structure (Fig. 3.2b). The data has been fitted to a power law with both single-step and two-step transitions, with the latter one resulting in a better fit [131]. The fit suggests a two-step transition at $T_{N_1} \approx 4.8 \text{ K}$ and $T_{N_2} \approx 4.2 \text{ K}$ [131].

The physical properties of powder samples of the systems $\text{A}_3\text{NiNb}_2\text{O}_9$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$) have been measured by Z. Lu *et al.* as well [131]. The specific heat is measured without applying magnetic fields, and the magnetic susceptibility is measured at 0.1 T (Fig. 3.3). The $\text{Ba}_3\text{NiNb}_2\text{O}_9$ sample exhibits a one-step transition at approx. 4.9 K, while $\text{Sr}_3\text{NiNb}_2\text{O}_9$ shows a very clear two-step transition at $T_{N_1} \approx 5.5 \text{ K}$ and $T_{N_2} \approx 5.1 \text{ K}$ [131]. However, although the data of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ undergoes a general tendency similar to $\text{Sr}_3\text{NiNb}_2\text{O}_9$, there is no clear evidence of a second step of the phase transition. Hence, the two-step transition of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ as is indicated by the neutron data was, in our opinion, not verified unambiguously by the physical-property results that are measured in [131].

The Hamiltonian of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ has been determined by Z. Lu *et al.* [131] based on a quasi-2D XXZ Heisenberg type:

$$H = J \sum_{\langle i,j \rangle}^{\text{intralayer}} (S_i^x S_j^x + S_i^y S_j^y + \Delta S_i^z S_j^z) + J' \sum_{\langle l,m \rangle}^{\text{interlayer}} \mathbf{S}_l \cdot \mathbf{S}_m, \quad (3.1)$$

with an easy-plane exchange anisotropy $\Delta \approx 0.95$ [131].

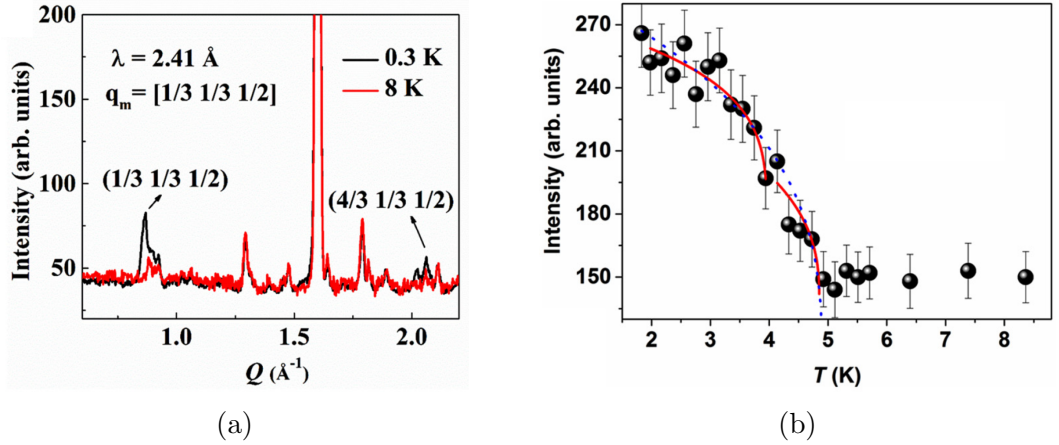


Figure 3.2: The neutron powder diffraction data on $\text{Ca}_3\text{NiNb}_2\text{O}_9$. Panel a: The Q -dependency of the neutron intensity measured at 0.3 K (black) and 8 K (red) with a constant incident wavelength $\lambda = 2.41 \text{ \AA}$, showing magnetic peaks at 0.3 K compared to at 8 K. The fit based on the hexagonal SG $P\bar{3}2/m1$ indicates that the positions of the magnetic peaks at 0.3 K are $(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ and $(\frac{4}{3}, \frac{1}{3}, \frac{1}{2})$, yielding a propagation vector $\mathbf{q}_m = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$. Panel b: The temperature-dependency of the scattering intensity of $\text{Ca}_3\text{NiNb}_2\text{O}_9$. The blue dashed line shows the power-law fit assuming a one-step transition temperature, and the red solid one shows the case with a two-step transition. Both figures taken from [131].

3.1.3 Single crystals of $\text{Ca}_3\text{NiNb}_2\text{O}_9$

The work on the single-crystalline sample of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ has been published together with our collaborators [113], where the work using neutron scattering has been done within the context of this thesis. The single crystals have been grown with different methods by D. Rout and S. Singh using a four-mirror optical float-zone furnace. With the more detailed information available in the publication [113], the abbreviations and some properties of the specimens are shown in Tab. 3.1.

Name	Property
AGO	A s-grown, dark-green and o paque specimen
AGT	A s-grown, pale-green and t ranslucent specimen
AGH	A s-grown specimen with the usage of an after- h heater
AGQ	A s-grown specimen q uenched in the image furnace
ANT	Air- a nnealed, pale-green and t ranslucent specimen

Table 3.1: Name and properties of the $\text{Ca}_3\text{NiNb}_2\text{O}_9$ specimens [113].

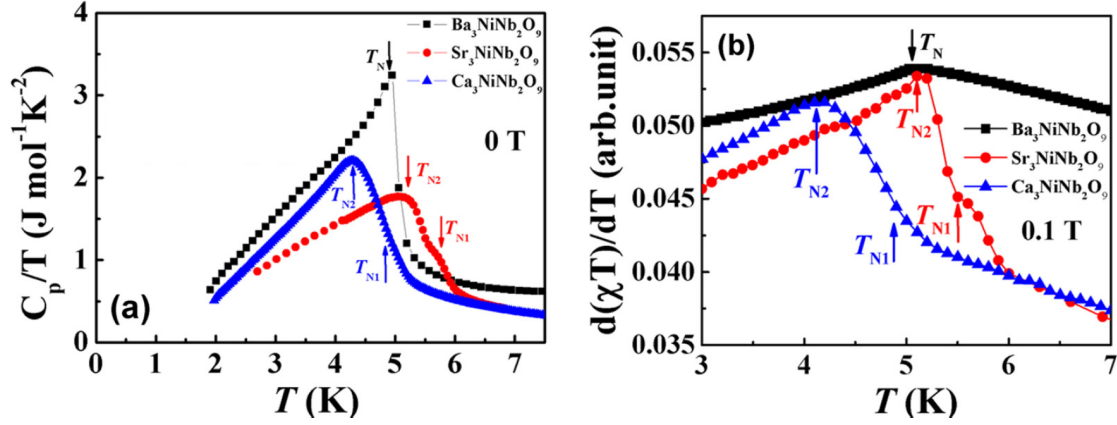


Figure 3.3: Bulk properties of the polycrystalline samples of $\text{A}_3\text{NiNb}_2\text{O}_9$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$) measured at temperatures below 7 K in [131]. Panel a: Specific heat as a function of temperature at zero magnetic field. Panel b: Differential magnetic susceptibility $\frac{d(\chi T)}{dT}$ as a function of temperature measured at low field $B = 0.1$ T. $\text{Ba}_3\text{NiNb}_2\text{O}_9$ exhibits a one-step transition and $\text{Sr}_3\text{NiNb}_2\text{O}_9$ a two-step transition, while $\text{Ca}_3\text{NiNb}_2\text{O}_9$ displays a similar tendency to $\text{Sr}_3\text{NiNb}_2\text{O}_9$ but no clear two-step transition is visible.

The AGO, ANT and AGT specimens of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ have been analysed with more detail in our work [113]. The photos of the AGO and ANT crystals are shown in Fig. 3.4a and 3.4d, respectively. The AGT specimen has a similar visual appearance to ANT [113]. Some results from the characterisation measurements on these three samples are briefly reviewed in the following before the discussion of neutron measurements.

The AGO, ANT and AGT specimens have been characterised by our collaborators [113], with some results shown in Fig. 3.4. The specific heat of the AGO sample exhibits a broad peak at approx. 9 K (Fig. 3.4b), which is in strong contrast to the findings in [131]. The magnetic susceptibility data (Fig. 3.4c) shows a cusp at $T_N \approx 5.5$ K and a bifurcation between the ZFC and FCW data. The high-temperature susceptibility data [113] was fitted using Curie-Weiss law:

$$\chi = \chi_0 + \frac{C}{T - \theta_N}, \quad (3.2)$$

predicting the transition temperature $\theta_N \approx -25$ K. This yields the frustration index $f = \frac{|\theta_N|}{T_N} \approx 5$. These results indicate a spin-glass ground state of the AGO sample [113], which is a new result for the $\text{Ca}_3\text{NiNb}_2\text{O}_9$ compound. The data on specific heat (Fig. 3.4e) shows very clearly a two-step phase transition of the ANT sample at $T_{N1} \approx 4.8$ K and $T_{N2} \approx 4.2$ K at zero field, with the transition temperatures shifting downwards with increasing fields applied parallel to the ab -plane.

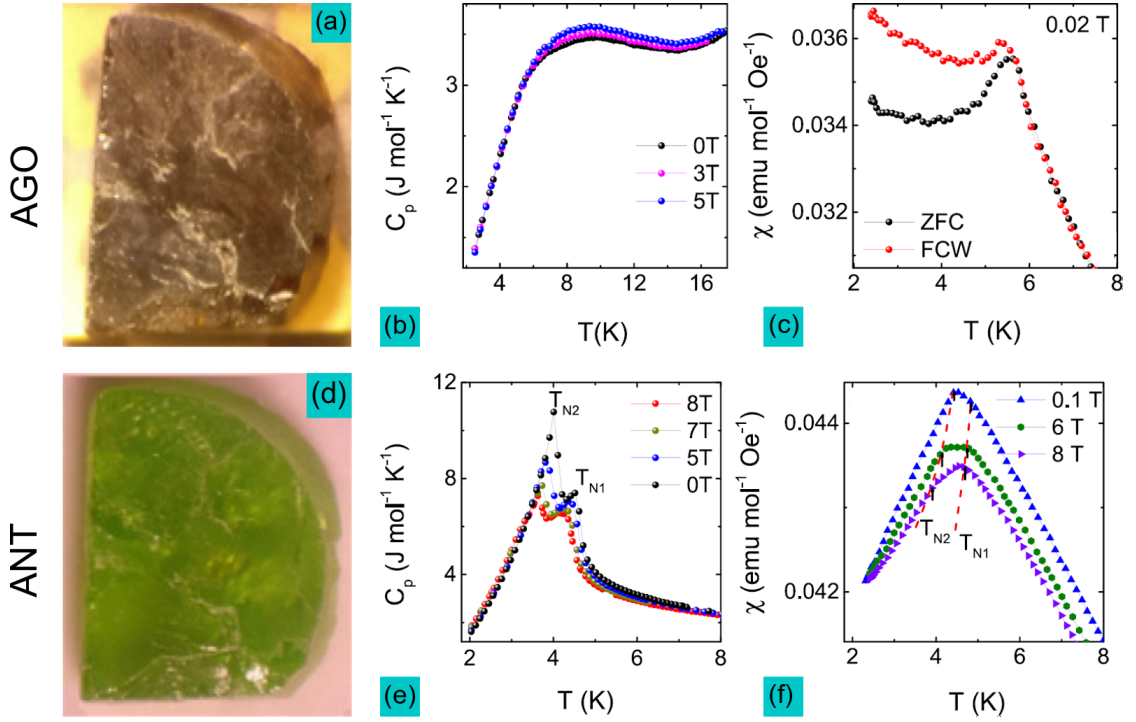


Figure 3.4: Photo, heat capacity C_p and magnetic susceptibility χ of the AGO (panels a - c) and ANT (panels d - f) specimens of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ [113]. The AGO specimen has a dark-green opaque appearance, while the ANT specimen is pale-green and translucent. C_p and χ are measured each as a function of temperature. C_p of the AGO specimen and C_p and χ of the ANT specimen were measured by applying various strengths of the external fields. χ of the AGO specimen is measured at zero-field cooled (ZFC) and field-cooled warming (FCW) conditions with the same field strength 0.02 T. The fields in panel d are parallel to the ab -plane, while the field directions in panels b, c and f were unknown at the time of the measurements.

The susceptibility data of the ANT specimen depicts a peak at approx. 4.4 K (Fig. 3.4f) and there is no ZFC-FCW-bifurcation down to the base temperature of 2 K¹. The results of the ANT specimen agree with the finding in the work by Z. Lu *et al.* [131], with the two-step transition better visible here than in Fig. 3.3. Note that the field directions with respect to the sample were unknown in 3.4b, 3.4c and 3.4f at the time of the measurements [132]. This is mainly due to the difficulties orienting the single crystals with the help of X-ray Laue measurements, resulting from the tendency of the crystal boules to form large cracks while growing under all the

¹The examination of the bifurcation is not depicted here but is discussed in [113]

conditions in the growth experiments [113]. This is evident in the image obtained using an optical microscope (Fig. 3.5), which depicts large cracks traversing the surface [113].

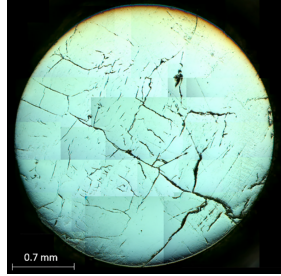


Figure 3.5: Image, obtained with an optical microscope, of an AGT specimen of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ [113]. The image depicts multiple cracks formed during the growth of the specimen [113].

The magnetisation measurements on the AGT specimen show results that are qualitatively almost the same as the ANT sample [113]. Quantitatively, the AGT data has slightly lower transition temperatures than the ANT sample, i.e. at $T_{N_1} \approx 4.6$ K and $T_{N_2} \approx 4.0$ K, and it shows a slightly higher peak intensity, implying a higher degree of the B-site ordering [113]. This phenomenon is also visible in the X-ray diffraction (XRD) data in [113].

The XRD data could be fitted to the orthorhombic SG $Pbnm$ (No. 62) for the AGO sample, and to the monoclinic $P12_1/c_1$ for the ANT and AGT specimens. The lattice parameters of the AGT sample have been determined with the help of synchrotron measurements, yielding $a = 9.6135$ Å, $b = 5.4579$ Å, $c = 16.8413$ Å and $\beta = 125.775^\circ$ at room temperature (RT) and ambient pressure (AP) [113].

3.1.4 Single-crystal neutron diffraction

Since the AGT sample has the highest degree of B-site ordering among the single crystalline specimens from the growth experiments [113], it has been measured with neutron diffraction at Institut Laue-Langevin (ILL), serving as a reference for further investigation on other specimens that are predicted to have more complex structures. It is the first time to measure a single-crystalline sample of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ with neutron scattering.

Neutron Laue diffraction

Neutron Laue diffraction was carried out at the Laue diffractometer CYCLOPS at ILL [133]. The instrument is equipped with a large set of area detectors in

an octagonal geometry, allowing real-time exploration of the reciprocal space and the installation of various sample environments. With the help of the software suite Esmeralda [134], the data has been converted from the octagonal form to a cylindrical one. The sample has been measured at $T = 1.5$ K and 10 K, each with $\omega = 0^\circ$, 30° and 60° , where the angle ω describes the rotation of the sample stage around its vertical axis². Comparing the patterns for $\omega = 0^\circ$ at $T = 1.5$ K and 10 K (Fig. 3.6), the magnetic reflections are visible at the base temperature $T = 1.5$ K in the magnetically ordered phase. The nuclear spots from the 10 K-data have been matched to the patterns generated with the monoclinic SG $P12_1/c_1$ in Esmeralda (Fig. 3.7). This fit does not involve the refinement of lattice parameters. Instead, the lattice parameters from the XRD data (Sec. 3.1.3) have been used to fit the sample orientation to the Laue pattern. The patterns with the three ω -values have been used together to improve the match. Moreover, the broad peaks on the Laue patterns indicate the existence of twinning or the occurrence of multiple grains of the sample. This phenomenon may have its origin in the formation of large cracks in the crystal boules during the growth, as discussed in Sec. 3.1.3.

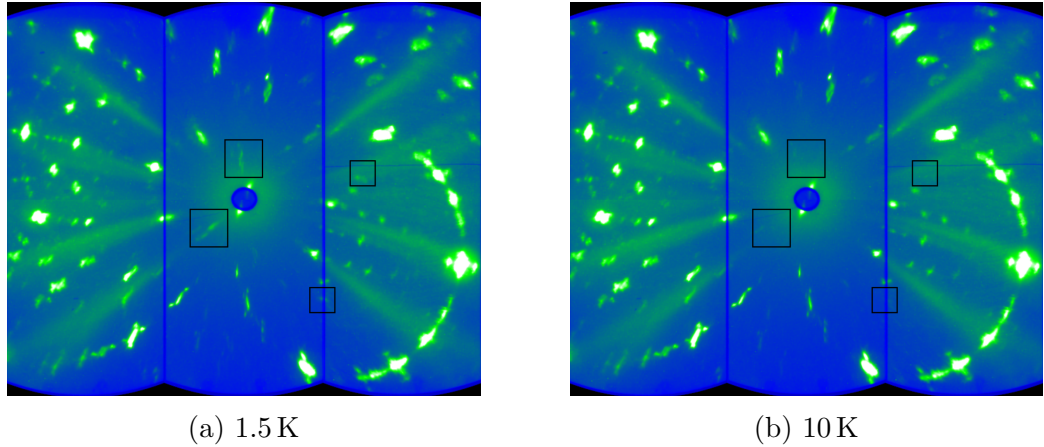
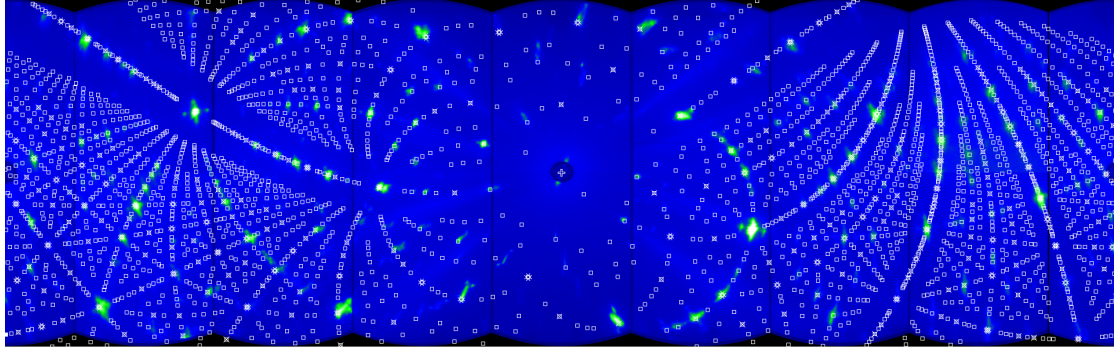
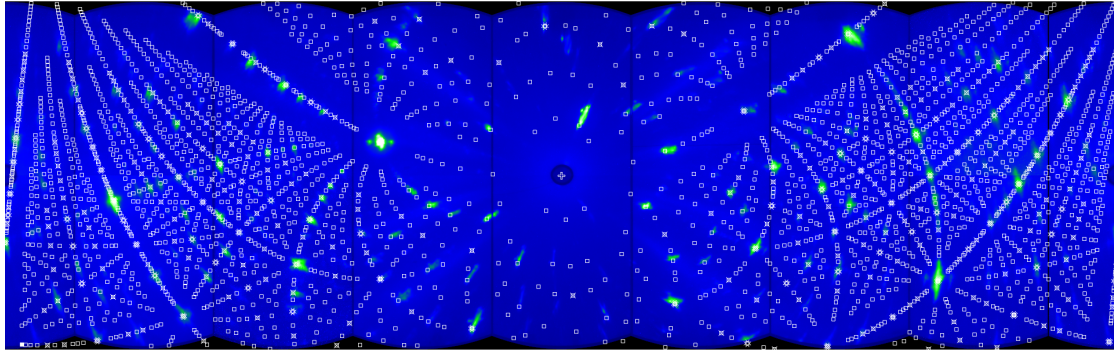


Figure 3.6: Neutron Laue patterns measured at Cyclops, ILL, at 1.5 K (3.6a) and 10 K (3.6b), respectively. The intensity has the colour map from blue (low intensity) to green (high intensity), with the spots with very high intensity being white. The dark blue spot in the centre corresponds to the beam stop for the direct beam. The black space at the top and bottom edges has no intensity due to the conversion of the data from an octagonal shape to a cylindrical one. The black squares guide the eye for the magnetic peaks at 1.5 K (magnetically ordered) compared to at 10 K (paramagnetic).

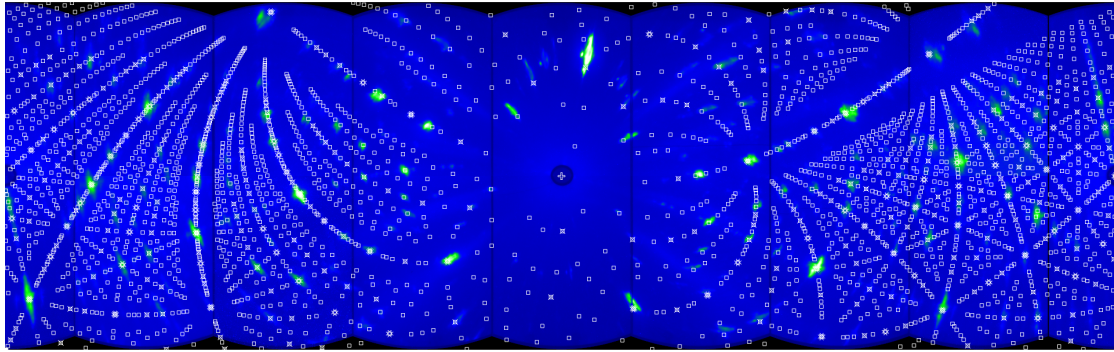
²The sample is not aligned with the sample stage. Instead, the sample orientation is fitted using the Esmeralda software to match the SG.



(a) $\omega = 0$



(b) $\omega = 30^\circ$



(c) $\omega = 60^\circ$

Figure 3.7: Laue patterns measured at Cyclops, ILL, at 10 K with the sample rotation $\omega = 0$ (3.7a), $\omega = 30^\circ$ (3.7b) and $\omega = 60^\circ$ (3.7c), respectively. The white squares show the nuclear reflections generated with the SG $P12_1/c_1$. The crosses in the squares correspond to multiplicity, where the $[h, k, l]$ - and $[nh, nk, nl]$ -reflections ($n = 1, 2, \dots$) appear at the same position.

Single-crystal four-circle neutron diffraction

The AGT sample has been measured at D10, a single-crystal four-circle diffractometer equipped with a four-circle cryostat at ILL [135]. The sample alignment

was first carried out to generate the UB matrix (orientation matrix) [136], which determines the relation between the four angles (ω , χ , ϕ and 2θ) of the diffractometer and the hkl -positions of a sample. Scans in the reciprocal space (hkl -scans) at $T = 2$ K suggest a propagation vector $\mathbf{k} \approx (0.046, 0.34, 0)$ that corresponds to an incommensurate structure very close to the commensurate $\mathbf{k} = (0, \frac{1}{3}, 0)$. However, the following evidences support a commensurate structure:

1. The double peaks appearing irregularly during the hkl -scans give the indication on the twinning that has also been observed in the Laue patterns;
2. The reflections generated with the commensurate $\mathbf{k} = (0, \frac{1}{3}, 0)$ in Esmeralda match the patterns at 1.5 K better than those with the incommensurate $\mathbf{k} = (0.046, 0.34, 0)$ ³, as shown in Fig. 3.8;
3. The commensurate structure agrees with the 120°-ordering that has been observed in various TLAfs.

The temperature dependency of the scattering intensity has been studied between 2 K and 10 K using some strong magnetic peaks (Fig. 3.9). The intensity has been fitted to the power law [137] with a two-step transition:

$$I = \begin{cases} a_2 (T_{N_2} - T)^{2\beta_2} + a_1 (T_{N_1} - T_{N_2})^{2\beta_1} + I_b, & T < T_{N_2} \\ a_1 (T_{N_1} - T)^{2\beta_1} + I_b, & T_{N_2} \leq T < T_{N_1} \\ I_b, & T \geq T_{N_1} \end{cases}, \quad (3.3)$$

where a_1 and a_2 are pre-factors, β_1 and β_2 the critical exponents, $T_{N_1} > T_{N_2}$ the transition temperatures, and I_b the background intensity. Comparing the reduced least-square χ^2 , Akaike information criterion and Bayesian information criterion [138], the two-step transition gives a better result than the single-step model. The fit indicates $T_{N_1} \approx 4.6(1)$ K and $T_{N_2} \approx 4.0(1)$ K, in good agreement with the specific-heat results in Fig. 3.4e.

The results of the ω -scans around various magnetic reflections at the base temperature of $T = 2$ K at D10 are shown in Tab. 3.2, with the angle ω denoting the rotation of the sample stage around its vertical axis.

Some scans in Tab. 3.2 exhibit magnetic peaks (Tab. 3.2a), while some do not depict any signals (Tab. 3.2b). This phenomenon has been analysed according to magnetic extinction rules determining the (h, k, l) -positions where the reflections have no magnetic signals $I_{\text{mag}}(\mathbf{Q}_{hkl}) = |\mathbf{F}_{M\perp}(\mathbf{Q}_{hkl})|^2 = 0$. Here, $\mathbf{F}_M(\mathbf{Q}_{hkl})$ denotes

³Due to the broadening of the Laue spots resulting from the twinning, some peaks in Fig. 3.8 extend to the positions generated with the $\mathbf{k} = (0.046, 0.34, 0)$. This phenomenon explains why the incommensurate $\mathbf{k}$ -value was obtained in the hkl -scans. However, the incommensurate patterns failed to cover some strong magnetic peaks.

the magnetic structure factor at a given (h, k, l) -position, while the term $\mathbf{F}_{M\perp}(\mathbf{Q}) = \frac{\mathbf{Q} \times (\mathbf{F}_M \times \mathbf{Q})}{|\mathbf{Q}|^2}$ indicates that the neutron scattering is only sensitive to the component of $\mathbf{F}_M$ perpendicular to $\mathbf{Q}$. Therefore, a non-zero magnetic intensity has two requirements, i.e. $\mathbf{F}_M$ is not collinear with $\mathbf{Q}$, and $|\mathbf{F}_M| \neq 0$. Denoting the unit cells l at $\mathbf{R}_l = l_a \hat{a} + l_b \hat{b} + l_c \hat{c}$ and the atom j in this unit cell at $\mathbf{r}_j = x_j \hat{a} + y_j \hat{b} + z_j \hat{c}$, the magnetic structure factor $\mathbf{F}_M$ is given as [50]:

$$\mathbf{F}_M(\mathbf{Q}) = p \sum_{j=1}^N f_j(\mathbf{Q}) \mathbf{S}_{\mathbf{k},j} T_j e^{2i\pi \mathbf{Q} \cdot \mathbf{r}_j}, \quad (3.4)$$

where $p = 0.2696 \times 10^{-12} \text{ cm}/\mu_B$ is a constant, T_j denotes the Debye-Waller factor due to thermal effects, and $f_j(\mathbf{Q})$ signifies the magnetic form factor of the atom j . The Fourier component $\mathbf{S}_{\mathbf{k},j}$ of the magnetic moment $\mathbf{m}_{l,j}$ associated with the propagation vector $\mathbf{k}$ yields [50]:

$$\mathbf{m}_{l,j} = \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k},j} e^{-2i\pi \mathbf{k} \cdot \mathbf{R}_l}. \quad (3.5)$$

For the compound $\text{Ca}_3\text{NiNb}_2\text{O}_9$, the magnetic unit cell is depicted in Fig. 3.10, corresponding to the 120° -ordering with $\mathbf{k} = (0, \frac{1}{3}, 0)$. The magnetic ions are at $\mathbf{r}_1 = (0, 0, 0)$, $\mathbf{r}_2 = (\frac{1}{2}, \frac{1}{2}, 0)$, $\mathbf{r}_3 = (\frac{1}{2}, 0, \frac{1}{2})$ and $\mathbf{r}_4 = (0, \frac{1}{2}, \frac{1}{2})$ in reciprocal lattice units (r.l.u). Considering the magnetic moments rotating within the ab -plane, the moment of the j -th ion in the l -th unit cell is

$$\mathbf{m}_{l,j} = m \left(\hat{a} \cos(2\pi \mathbf{k} \cdot \mathbf{R}_l + \phi_j) + \hat{b} \sin(2\pi \mathbf{k} \cdot \mathbf{R}_l + \phi_j) \right), \quad (3.6)$$

with the unit-cell axes $\hat{a}$ and $\hat{b}$. The phase shifts of the four magnetic ions are $\phi_1 = -\frac{\pi}{3}$, $\phi_2 = \pi$, $\phi_3 = \frac{2\pi}{3}$ and $\phi_4 = 2\pi$, respectively. Correspondingly, the Fourier components are

$$\mathbf{S}_{\pm \mathbf{k},j} = \frac{m}{2} \left(\hat{a} \pm i\hat{b} \right) e^{\mp i\phi_j}. \quad (3.7)$$

Therefore, the magnetic structure factor for $\mathbf{Q} = (h, k + \frac{1}{3}, l)$ ($h, k, l \in \mathbb{Z}$), corresponding to $\mathbf{S}_{+\mathbf{k},j}$ with $\mathbf{k} = (0, \frac{1}{3}, 0)$, is

$$\mathbf{F}_M(h, k + \frac{1}{3}, l) \propto \left(\hat{a} + i\hat{b} \right) \left(\sum_{j=1}^{N=4} \mathbf{S}_{+\mathbf{k},j} e^{2i\pi \mathbf{Q} \cdot \mathbf{r}_j} \right) \quad (3.8)$$

$$= \left(\hat{a} + i\hat{b} \right) \left(e^{i\frac{\pi}{3}} - e^{i\pi(h+k+\frac{1}{3})} + e^{-i\frac{2\pi}{3}+i\pi(h+l)} + e^{i\pi(k+l+\frac{1}{3})} \right) \quad (3.9)$$

$$= \left(\hat{a} + i\hat{b} \right) e^{i\frac{\pi}{3}} \left(e^{i\pi k} + e^{i\pi l} \right) \left(\frac{1}{2} \left(e^{i\pi k} + e^{i\pi l} \right) - e^{i\pi h} \right). \quad (3.10)$$

Since $h, k, l \in \mathbb{Z}$, one has

$$e^{i\pi k} + e^{i\pi l} = \begin{cases} 0, & k + l = 2n_1 + 1 \\ 2e^{i\pi k}, & k + l = 2n_1 \end{cases}, \quad (3.11)$$

with $n_1 \in \mathbb{Z}$. In the case of $k + l = 2n_1$, one has

$$\frac{1}{2} (e^{i\pi k} + e^{i\pi l}) - e^{i\pi h} = e^{i\pi k} - e^{i\pi h} = \begin{cases} 0, & k + h = 2n_2 \\ 2e^{i\pi k}, & k + h = 2n_2 + 1 \end{cases}, \quad (3.12)$$

with $n_2 \in \mathbb{Z}$. Therefore, a non-zero $\mathbf{F}_M$ requires simultaneously

$$\begin{aligned} k + l &= 2n_1 \\ h + k &= 2n_2 + 1. \end{aligned} \quad (3.13)$$

The situation with $\mathbf{S}_{-\mathbf{k},j}$ results in the same requirements for $h, k, l \in \mathbb{Z}$. These magnetic extinction rules agree with the results shown in Tab. 3.2a (with magnetic peaks) and 3.2b (no magnetic signals observed). All the positions in Tab. 3.2b have violated at least one of the two requirements described in Eq. 3.13. The 120° -ordered structure agrees with the findings in [131, 140], and it can be transformed into the approximated hexagonal structure that is used by [131, 140] if there were no distortions from the equilateral-triangular lattice. The relation between the two lattice systems is displayed in Fig. 3.10b, where the propagation vector corresponding to the same arrangement of spins would be $\mathbf{k} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ based on the hexagonal SG $P\bar{3}2/m1$, consistent with the result in [131, 140]. However, as already discussed above, the magnetic structure should be described with the correct nuclear basis. Hence, the propagation vector should be $\mathbf{k} = (0, \frac{1}{3}, 0)$ based on the monoclinic nuclear SG $P12_1/c_1$. The hexagonal nuclear structure helps with the visualisation but the monoclinic one is correct for the ordered AGT specimens of $\text{Ca}_3\text{NiNb}_2\text{O}_9$.

Among the magnetic reflections as summarised in Tab. 3.2a, representative scans are depicted in Fig. 3.11, where some scans show a clean single peak like in Fig. 3.11a (peak in the middle) or 3.11b (peak off-centre), while the others have double peaks like in Fig. 3.11c (both peaks visible) or 3.11d (peaks incomplete). Since there is no change of the lattice structure down to 2 K, this irregular appearance of the magnetic peaks is a further indication for twinning, associated with the cracks formed during the growth of samples.

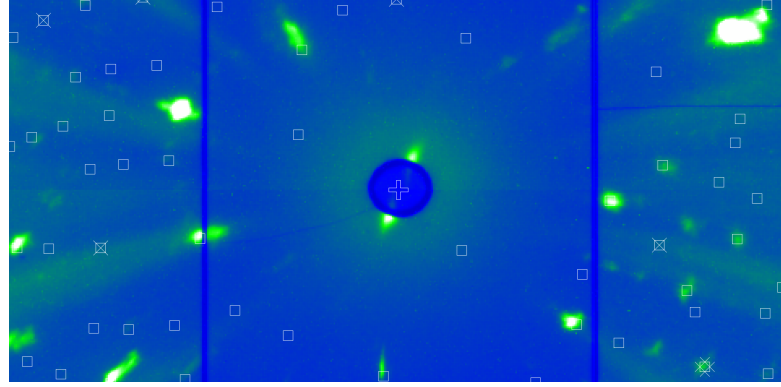
The quantitative analysis of the magnetic moment by calculating the magnetic structure factor (Eq. 3.4) suffers from the deviation of magnetic reflections from the supposed positions (Fig. 3.11) due to the twinning. Besides, the calculations in Eq. 3.10 have the term $(\hat{a} + i\hat{b})$ when assuming the magnetic moments are in the

ab-plane, which implies that the extinction rule does not constraint the plane of the magnetic moment for a 120°-ordering. Nonetheless, the easy-plane anisotropy in spin interactions described in Eq. 3.1 indicates the magnetic moments in the *ab*-plane.

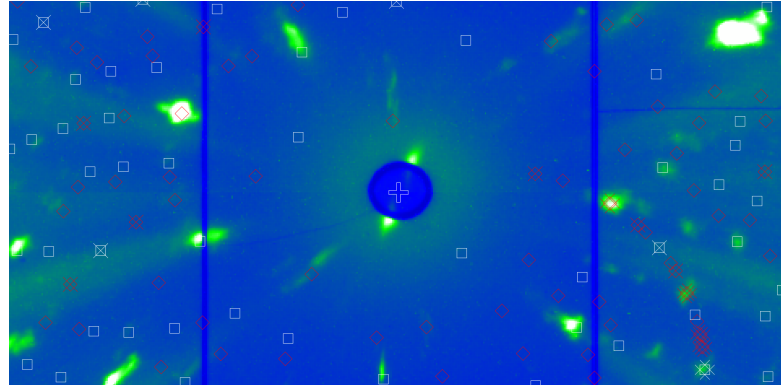
3.1.5 Summary

Our investigations of the single-crystal AGT sample of $\text{Ca}_3\text{NiNb}_2\text{O}_9$ using neutron Laue diffraction and four-circle diffraction confirm the results observed using other methods and give more insights into the magnetic structure of the system. The twinning due to cracks that appear during sample growths has been observed using both diffraction methods. The two-step transition of the ordered ground state of the AGT specimen has been confirmed by our temperature-scan on selected magnetic reflections. The crystal structure determined using XRD has been supported by our neutron results using both diffraction methods, while the magnetic structure has been determined by comparing the measured magnetic reflections and magnetic extinction rules. With this procedure, the correct propagation vector of $\mathbf{k} = (0, \frac{1}{3}, 0)$ based on the monoclinic nuclear SG $P12_1/c_1$, which stays unchanged upon phase transition, has been determined. This result suggests a 120°-ordering of the system with magnetic moments in the *ab* plane.

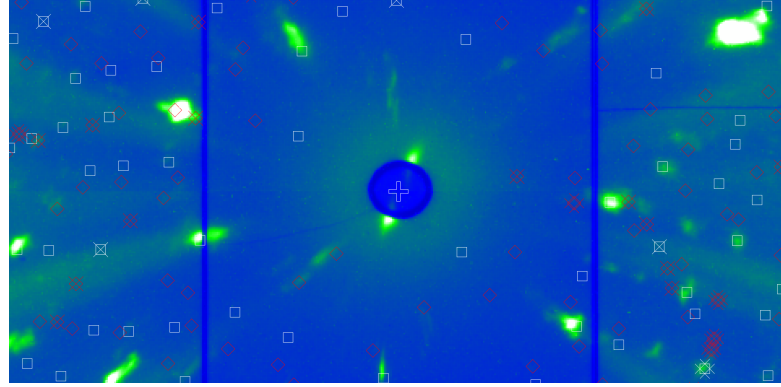
In conclusion, our results have demonstrated the ordered AGT specimen to be a 120°-ordered system in the TLAF family. The investigations on this ordered specimen serve as a solid basis for further studies on the disordered AGO specimen that is expected to exhibit a spin-glass phase, which is so far unique in the TLAFs family.



(a) Pattern at 10 K matched to the nuclear reflections



(b) Pattern at 1.5 K matched to the commensurate magnetic structure



(c) Pattern at 1.5 K matched to the incommensurate magnetic structure

Figure 3.8: Laue patterns measured at CYCLOPS, ILL. 3.8a shows the pattern measured at 10 K. The white squares give the nuclear spots and the red ones the magnetic patterns. The crosses in the squares correspond to multiplicity, where the $[h, k, l]$ - and $[nh, nk, nl]$ -reflections ($n = 1, 2, \dots$) appear at the same position. 3.8b and 3.8c show the same data measured at 1.5 K with the same nuclear spots as 3.8a. The magnetic patterns are generated with $\mathbf{k} = (0, \frac{1}{3}, 0)$ in 3.8b and $\mathbf{k} = (0.05, 0.34, 0.00)$ in 3.8c.

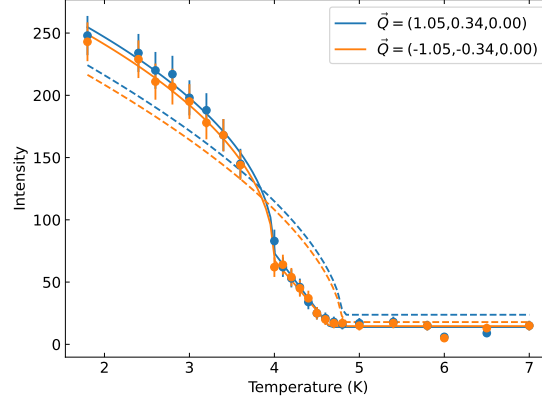


Figure 3.9: Power-law fits of intensities from two magnetic Bragg peaks of the AGT specimen of $\text{Ca}_3\text{NiNb}_2\text{O}_9$, with $\mathbf{Q}_{hkl} = (1.05, 0.34, 0.00)$ in blue and $\mathbf{Q}_{hkl} = (1.05, -0.34, 0.00)$ in orange. The fits with one-step (dashed lines) and two-step (solid lines) transitions are compared.

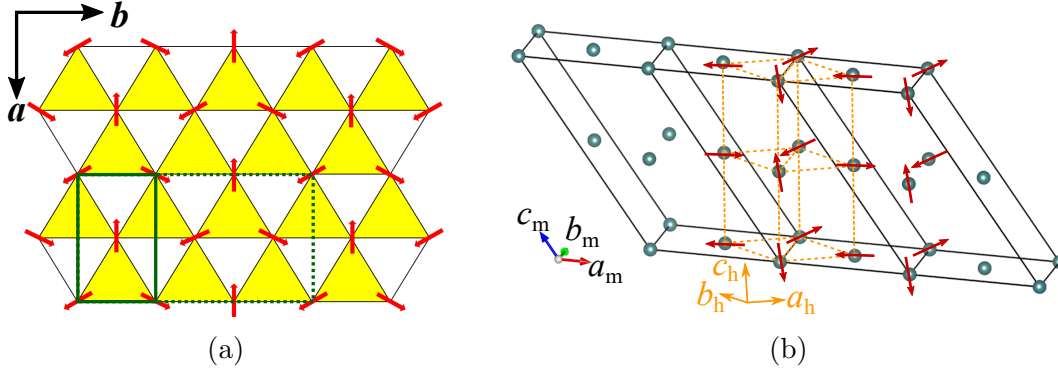


Figure 3.10: Unit cells of $\text{Ca}_3\text{NiNb}_2\text{O}_9$. 3.10a: schematic of the nuclear (solid lines) and magnetic (dashed lines) cells in the ab -plane with the 120° -ordering and $\mathbf{k} = (0, \frac{1}{3}, 0)$ based on the monoclinic SG $P12_1/c_1$. 3.10b: 3D unit cells of $\text{Ca}_3\text{NiNb}_2\text{O}_9$. The black lines depict the crystal unit cells with the monoclinic structure ($P12_1/c_1$) in the coordinate system (a_m, b_m, c_m) . The turquoise spheres represent the Ni^{2+} ions that are relevant for the magnetic structure. The red arrows show the magnetic moments in the ab -plane. The orange dashed lines show the approximated hexagonal magnetic unit cells (based on the SG $P\bar{3}2/m1$) that have been considered in [131, 140], with its coordinate system (a_h, b_h, c_h) displayed in the same orange colour.

Scan centre			Nuclear base			Background	Peak intensity
h	k	l	h	k	l		
-3	0.33	2	-3	0	2	360.764	234.026
-2	-0.67	-1	-2	-1	-1	344.083	290.569
-2	0.67	1	-2	1	1	376.019	326.058
-2	0.67	3	-2	1	3	394.976	183.994
-1	-0.33	-2	-1	0	-2	390.805	427.842
-1	0.33	-2	-1	0	-2	416.431	514.024
-1	-0.33	0	-1	0	0	544.501	611.609
-1	0.33	0	-1	0	0	586.150	653.334
0	-0.67	-3	0	-1	-3	376.663	446.998
0	-0.67	-1	0	-1	-1	533.321	659.897
0	0.67	-3	0	1	-3	438.187	485.408
0	0.67	-1	0	1	-1	571.040	952.734
0	1.33	-1	0	1	-1	420.939	294.668
0	1.33	1	0	1	1	552.553	624.940
0	0.67	1	0	1	1	364.142	547.527
1	0.33	-4	1	0	-4	382.556	400.251
1	-0.33	-4	1	0	-4	450.548	388.393
1	-0.33	-2	1	0	-2	498.694	613.211

(a) Visible magnetic peaks

Scan centre			Base			Scan centre			Base			Scan centre			Base		
h	k	l	h	k	l	h	k	l	h	k	l	h	k	l	h	k	l
-2	-0.67	0	-2	-1	0	-1	1.33	1	-1	1	1	0	1.67	-1	0	2	-1
-2	-0.33	0	-2	0	0	-1	0.67	2	-1	1	2	0	1.67	0	0	2	0
-2	0.33	0	-2	0	0	-1	1.33	2	-1	1	2	0	1.67	1	0	2	1
-2	0.33	2	-2	0	2	-1	1.33	3	-1	1	3	1	-0.67	-4	1	-1	-4
-2	0.67	0	-2	1	0	-1	1.67	1	-1	2	1	1	-0.67	-3	1	-1	-3
-2	0.67	2	-2	1	2	0	-0.67	-4	0	-1	-4	1	-1.33	-3	1	-1	-3
-2	1.33	2	-2	1	2	0	-1.33	-2	0	-1	-2	1	-0.67	-2	1	-1	-2
-1	-0.67	-2	-1	-1	-2	0	-0.67	-2	0	-1	-2	1	-1.33	-2	1	-1	-2
-1	-1.33	-1	-1	-1	-1	0	-0.33	-4	0	0	-4	1	0.67	-4	1	1	-4
-1	-0.67	-1	-1	-1	-1	0	0.33	-4	0	0	-4	1	1.33	-3	1	1	-3
-1	-0.67	0	-1	-1	0	0	-0.33	-2	0	0	-2	1	1.33	-2	1	1	-2
-1	0.67	-2	-1	1	-2	0	0.33	-2	0	0	-2	1	1.33	-1	1	1	-1
-1	0.67	-1	-1	1	-1	0	0.33	0	0	0	0	1	1.33	0	1	1	0
-1	1.33	-1	-1	1	-1	0	0.67	-4	0	1	-4	1	1.33	1	1	1	1
-1	0.67	0	-1	1	0	0	0.67	-2	0	1	-2	1	0.67	1	1	1	1
-1	1.33	0	-1	1	0	0	1.33	-2	0	1	-2	1	1.67	-1	1	2	-1
-1	0.67	1	-1	1	1	0	1.33	2	0	1	2	2	-0.67	-4	2	-1	-4

(b) No magnetic signals

Table 3.2: Centres and nuclear bases of ω -scans for positions of the magnetic peaks that have been derived from the monoclinic SG $P12_1/c_1$ and the propagation vector $\mathbf{k} = (0, \frac{1}{3}, 0)$. 3.2a: scans with visible magnetic peaks, with four representative scans shown in Fig. 3.11. The background and the integrated peak intensity in the table were obtained by fitting using the software Rplot [139]. 3.2b: reflections showing no magnetic peaks, which agrees with the result in Eq. 3.10. The white rows in the table denote the positions where the nuclear base violates the rule $k + l = 2n_1$, the grey ones correspond to the positions violating $h + k = 2n_2 +$ (Eq. 3.13).

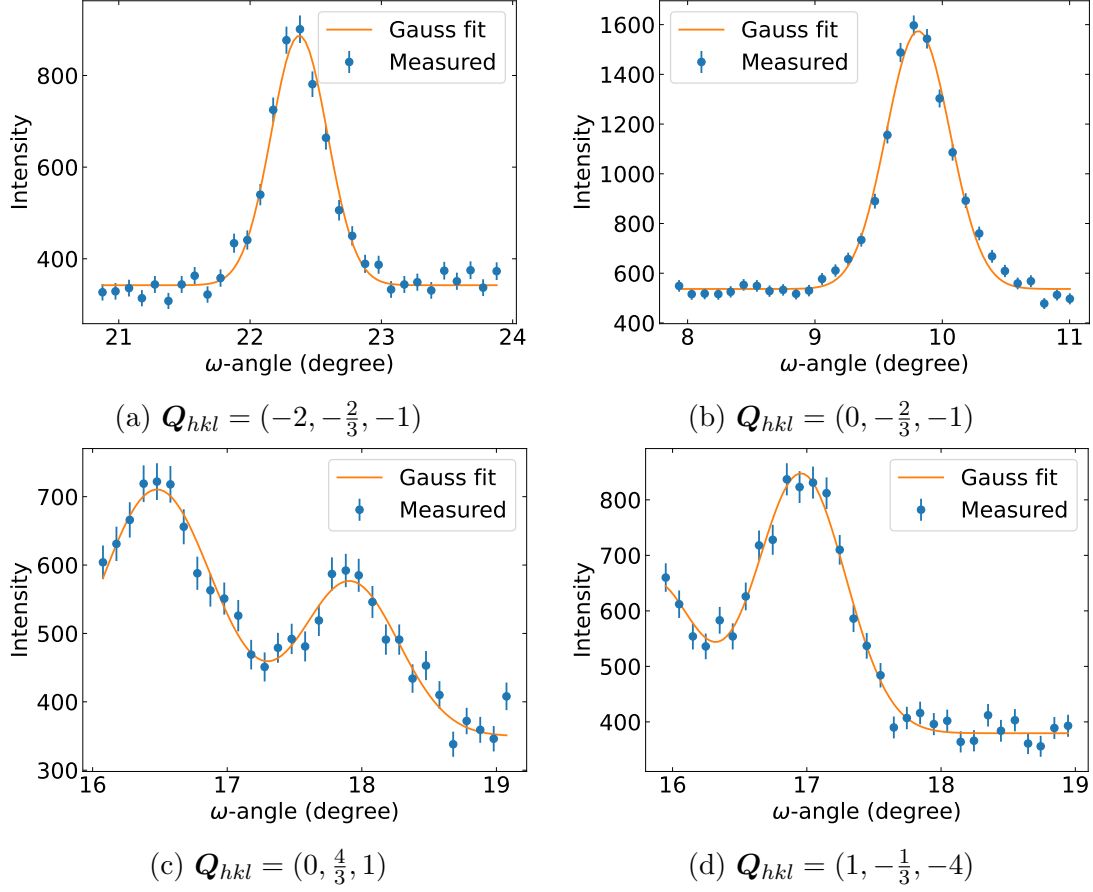


Figure 3.11: Representative ω -scans (Tab. 3.2a) at D10 around magnetic reflections, where the centres of ω correspond to the supposed magnetic peak position with the respective Q_{hkl} -values (in r.l.u). 3.11a depicts the situation where a clear single magnetic peak was at the centre of the scan, 3.11b where the single peak is off-centre, 3.11c where there are double peaks next to each other, and 3.11d where one of the double peaks is at the edge of the scan and this peak was not completely covered.

3.2 Square-lattice antiferromagnet PbVO_3

Over the last decades, considerable attention has been drawn to the square-lattice spin- $\frac{1}{2}$ Heisenberg antiferromagnets, characterised by a Hamiltonian with competing exchange energies:

$$\begin{aligned}\hat{H} &= \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \\ &= J_1 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j.\end{aligned}\tag{3.14}$$

Here, $\langle ij \rangle$ denotes summation over nearest neighbours (NNs), and $\langle\langle ij \rangle\rangle$ over next-nearest neighbours (NNNs), as depicted in Fig. 3.12a. This thesis uses the convention that $J > 0$ indicates an antiferromagnetic exchange whilst $J < 0$ signifies a ferromagnetic exchange. In the case of both the NN term J_1 and the NNN term J_2 being antiferromagnetic, these exchange energies cannot be both minimised simultaneously, leading to frustrated magnetic ordering. Consequently, ground states of square-lattice spin- $\frac{1}{2}$ Heisenberg antiferromagnets are dependent on the ratio $\alpha = \frac{J_2}{J_1}$, as depicted in Fig. 3.12b). For a small α , the system orders as a Néel antiferromagnet (NAF), while a large α leads to a columnar antiferromagnetic (CAF) ordering [141]. In the intermediate region with $\alpha \approx 0.5$, a quantum spin liquid scenario without long-range magnetic order (LRMO) is suggested [142, 143]. The perovskite compound PbVO_3 , with $\alpha = 0.38$ [144], emerges as a promising candidate for this scenario. The following sections review previous works and present our study, including a brief introduction to the muon spin spectroscopy (μSR) technique employed in our research.

3.2.1 Previous studies on PbVO_3

Successful synthesis of polycrystalline PbVO_3 sample was first reported by R. Shpanchenko *et al.* [145]. Their findings revealed the system to exhibit the tetragonal space group $P4mm$ (No. 99), possessing lattice parameters $a = 3.8005 \text{ \AA}$ and $c = 4.6703 \text{ \AA}$ at a temperature of approximately 293 K (Fig. 3.13). Moreover, a separate analysis on another powder sample conducted by A. Belik *et al.* [146] confirmed the same structure at room temperature (RT). The latter work also observed a temperature-dependency of the lattice parameters, where the tetragonality ratio $\frac{c}{a}$ increased between 12 K and 290 K (Fig. 3.14).

Further investigations on PbVO_3 at ambient pressure (AP) have yielded disputed outcomes:

On the one hand, magnetisation measurements at $B = 5 \text{ T}$ conducted by the team of R. Shpanchenko and A. Tsirlin [144] revealed a minimum at $T \approx 50 \text{ K}$,

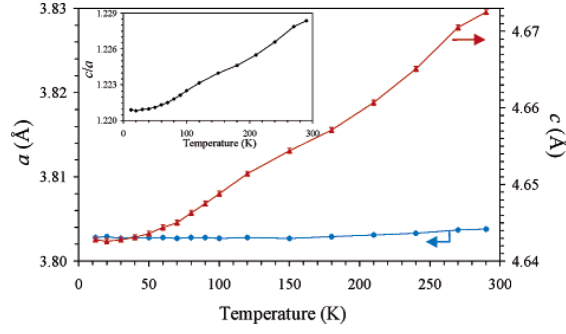


Figure 3.14: Lattice parameters a (in blue, plotted against the left-hand side y -axis) and c (in red, plotted against the right-hand side y -axis) as a function of temperature from 12 K to 290 K. The tetragonality ratio $\frac{c}{a}$ is shown in the inset. Figure taken from [146].

of trapped oxygen undergoing condensation at $T \approx 50$ K hindered an unambiguous identification of this anomaly as intrinsic to PbVO_3 . Moreover, the neutron powder diffraction (NPD) data obtained by the authors at $T = 1.5$ K exhibited neither additional magnetic peaks nor increased intensity on the nuclear reflections when compared to 120 K [145]. Consequently, the authors proposed that PbVO_3 possesses a spin-liquid-like ground state devoid of LRMO [144, 145].

On the other hand, magnetisation measurements on a single-crystal sample at $B = 0.1$ T ⁴ by K. Oka *et al.* [147] exhibited a clear bifurcation between the ZFC and FC datasets below 40 K (Fig. 3.15). Additionally, zero-field (ZF)- μ SR measurements ⁵ on a polycrystalline sample under AP displayed temperature-dependent muon frequencies (Fig. 3.16). These frequencies, corresponding to internal magnetic fields at two muon sites, were fitted using a power law, suggesting a transition at $T \approx 42.5$ K into a magnetically ordered phase. This outcome indicates that the anomaly observed at $T \approx 40$ K in Fig. 3.15 is attributable to an antiferromagnetic ordering rather than a spin-glass-like state.

Beyond the AP investigations, the compound was studied with pressure. By measuring the polycrystalline sample under increasing hydrostatic pressure, A. Belik *et al.* observed a transition from a tetragonal to a cubic structure occurring between $p = 2.0$ GPa and 5.9 GPa at RT [146]. Upon pressure reduction, the tetragonal phase re-emerged around 2.0 GPa, persisting at low pressures and remaining until AP [146]. Theoretical analysis attributes the tetragonal distortion to a non-centrosymmetric pyramidal coordination, where the degeneracy of the three t_{2g} orbitals (d_{xy} , d_{yz} , and d_{zx}) in the cubic structure is lifted [147]. In this dis-

⁴The field direction was not specified, probably due to the lack of alignment of the sample for these measurements.

⁵Further details will be presented along with our μ SR data.

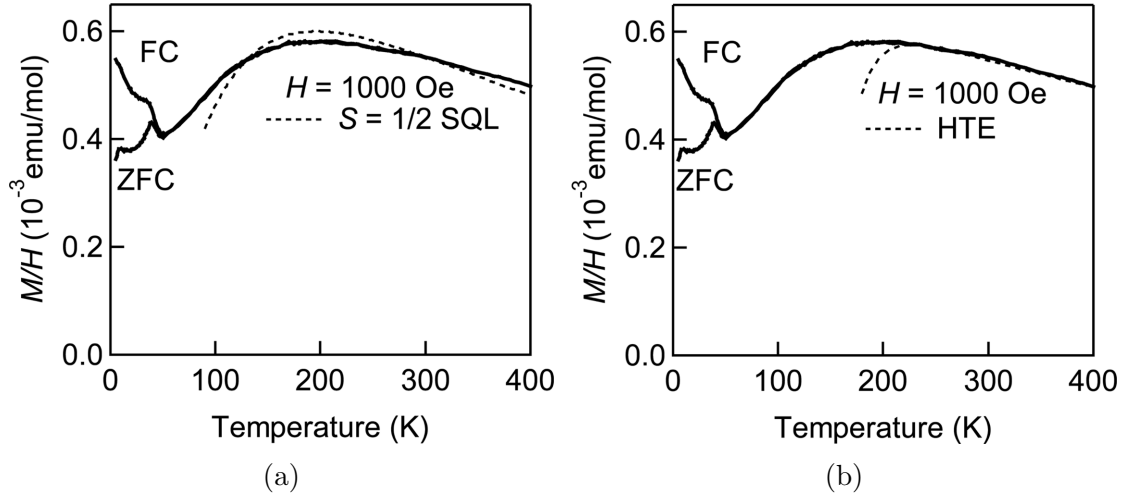


Figure 3.15: Temperature-dependent $\frac{M}{H}$ at $H = 1000$ Oe. Solid lines represent the measured data under ZFC and FC conditions, while dashed lines correspond to fits obtained using either a square lattice model (SQL) with $S = \frac{1}{2}$ in panel a or a high-temperature series expansion (HTE) of the J_1 - J_2 model in panel b. Figure adapted from [147].

tortion, a single d-electron of the V^{4+} ion occupies the non-degenerate d_{xy} orbital with a lower energy than the degenerate d_{yz} , and d_{zx} orbitals [147]. This scenario predicts an insulating property of the tetragonal $PbVO_3$ at AP and a metallic phase of the cubic $PbVO_3$ at high pressure (HP) [147]. The insulating phase has been observed up to 2.3 GPa in both the polycrystalline [148] and single-crystal samples [149]. However, at HP, the metallic phase has only been observed in the single-crystal sample [149] at pressures $\gtrsim 3.2$ GPa, while the insulating phase persisted in the polycrystalline sample up to pressures as high as 11.3 GPa [148]. For the latter observation, there are no theoretical or other experimental evidences supporting this phenomenon, and impurities cannot be ruled out [148]. Consequently, the compound $PbVO_3$ is more likely to exhibit metallic properties at HP, while the existence of a quantum spin liquid (QSL) scenario before the metallic phase is plausible. This scenario echoes the behaviour observed in the compound $BaCdV(PO_4)_2$, where a spin nematic phase could exist before reaching saturation upon an externally applied magnetic field as a tuning parameter [141].

Due to the rather divided findings on $PbVO_3$ so far, we sought to offer more insight on the compound by conducting characterisation of bulk properties as well as neutron scattering and muon measurements. Additionally, the potential QSL scenario has been examined.

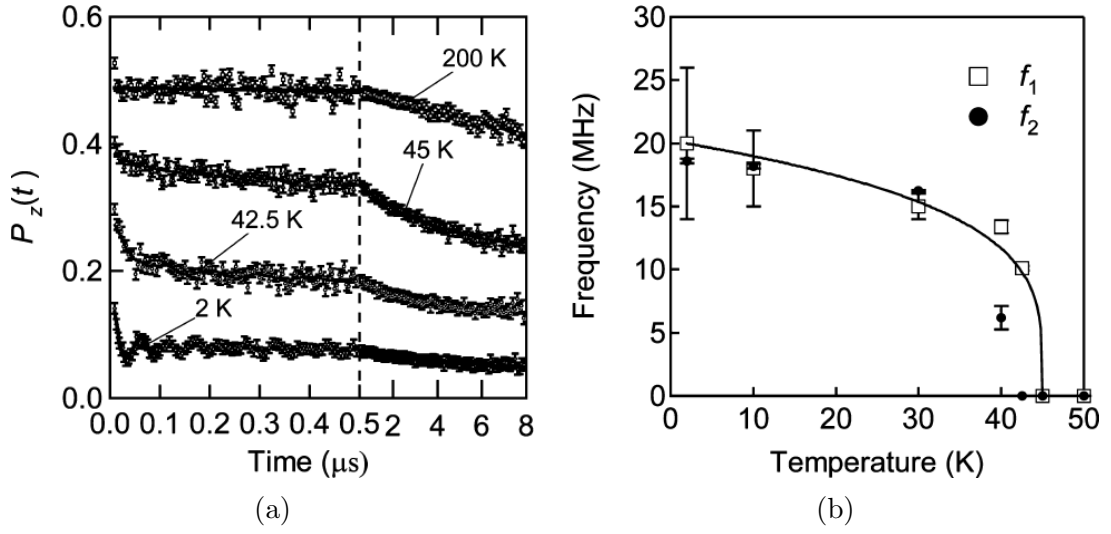


Figure 3.16: Panel a: Time spectra from ZF- μSR measurements conducted on a PbVO_3 powder sample. The x -axis is split into two parts, with time ranging from 0 μs to 0.5 μs on the left-hand side of the dashed line and from 0.5 μs to 8 μs on the right-hand side. Panel b: Temperature dependence of muon spin precession frequencies, determined by fitting the data presented in panel a. Figure adapted from [147].

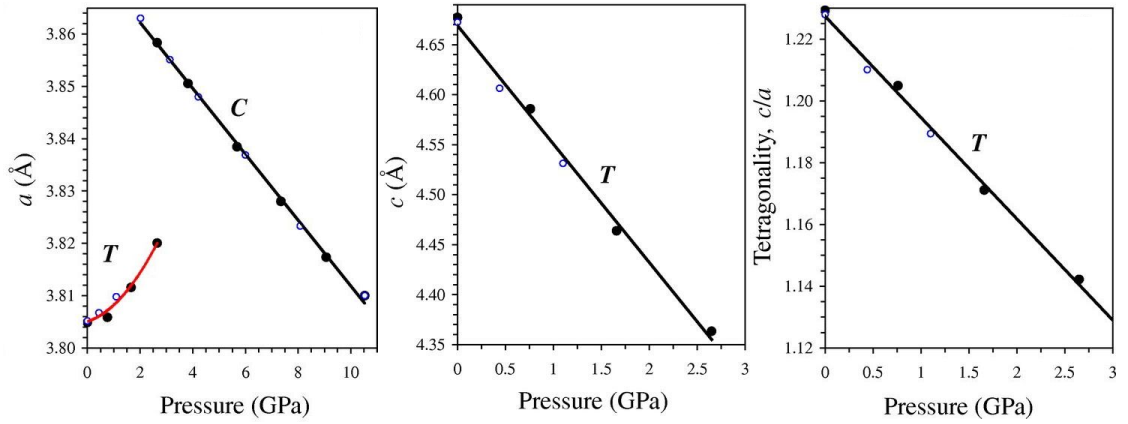


Figure 3.17: Lattice parameters (a and c) and tetragonality ($\frac{c}{a}$) of PbVO_3 as a function of pressure. “T” and “C” denote the tetragonal and cubic phases, respectively, of the system [146]. Data points were obtained at RT during compression (filled circles) and decompression (empty circles). The lines represent the fitting outcomes using the Birch–Murnaghan equation of state [148]. Figure taken from [148].

3.2.2 Synthesis and characterisation

Our powder sample of PbVO_3 was synthesised by our collaborator M. Isobe using a high-pressure-high-temperature (HP-HT) technique at $T = 1400^\circ\text{C}$ and $p = 6\text{ GPa}$, starting with PbO , V_2O_3 , and V_2O_5 contained in a platinum (Pt) capsule [150]. The synthesising experiments were assessed using X-ray diffraction (XRD) and magnetic susceptibility measurements to determine the most suitable starting composition [150]. Three composition options were tested:

Firstly, the purely stoichiometric PbVO_3 composition and compositions with excess oxygen and lead led to an impurity phase $\text{Pb}_3\text{V}_2\text{O}_8$. This compound exhibits multiple phase transitions including one at $T \approx 80\text{ K}$, as reported by J. M. Kiat *et al.* [151]. The formation of $\text{Pb}_3\text{V}_2\text{O}_8$ likely resulted from the reaction of vanadium with the platinum capsule, which could not be replaced by gold (Au) due to the lower melting point of gold at $T \approx 1300^\circ\text{C}$ given $p = 6\text{ GPa}$ [152].

Secondly, an oxygen deficiency induced an impurity $\text{PbV}_6\text{O}_{11}$, which was also observed in other studies [144]. The compound $\text{PbV}_6\text{O}_{11}$ undergoes a transition into a ferromagnetic phase at $T \approx 90\text{ K}$ [153].

Thirdly, the compositions with excess vanadium and oxygen in a ratio of $\text{V} : \text{O} = 1 : 2$ produced an impurity VO_2 . VO_2 undergoes a metal-insulator transition at $T \approx 350\text{ K}$, which is significantly higher than the expected transition temperature $\approx 50\text{ K}$ of PbVO_3 . Additionally, the concentration of VO_2 impurity could be controlled by the vanadium-oxygen ratio, making this option the most viable. Consequently, the starting composition $\text{PbV}_{1.01}\text{O}_{3.02}$ was selected for synthesis, resulting in an impurity of approximately 1 % VO_2 [150].

The magnetisation of the synthesised powder sample was assessed using a vibrating sample magnetometer (VSM) within the PPMS Dynacool device manufactured by Quantum Design [154]. Three conditions were utilised for the measurements:

1. ZFC: The sample was cooled from a high temperature (either 300 K or 400 K) down to base temperature (2 K) without any external magnetic field. Subsequently, measurements were taken while heating the sample.
2. Field-cooled cooling (FCC): The sample was measured while being cooled to 2 K with the application of an external magnetic field.
3. Field-cooled heating (FCH): Measurements were conducted while heating the sample from 2 K upwards, maintaining the same non-zero magnetic field as during the field-cooling process.

The magnetisation measurements are illustrated in Fig. 3.18 at various magnetic field strengths. The metal-insulator transition of the VO_2 impurity at $T \approx 350\text{ K}$ [155] was observed at $B \gtrsim 0.5\text{ T}$. The upturn of signal in all conditions at

$T < 40$ K is attributable to VO_2 , which exhibits a temperature-dependent paramagnetic phase at low temperature [156]. The existence of other impurities are unlikely due to the absence of the transitions of $\text{PbV}_6\text{O}_{11}$ at $T \approx 90$ K or $\text{Pb}_3\text{V}_2\text{O}_8$ at $T \approx 80$ K.

Regarding the compound PbVO_3 , the broad maximum around $T = 200$ K was consistently observed across all field strengths in our magnetisation measurements, agreeing with the experiments by Tsirlin *et al.* [144] and Oka *et al.* [147]. This observation indicates the frustrated 2D nature and antiferromagnetic exchange characteristic of PbVO_3 . Interestingly, our data at low fields ($\lesssim 1$ T) displays a weak FCC-ZFC bifurcation below 50 K, as observed at $B = 0.1$ T by Oka *et al.* [147], yet not corroborated by Tsirlin *et al.* at $B = 5$ T [144]. This phenomenon supports the expected bifurcation of an antiferromagnetic ordering with a transition temperature of $T_N \approx 50$ K, although this bifurcation is potentially overshadowed by the signal strength at higher fields due to a limited resolution. The upturn of the signal in all conditions at $T < 40$ K, attributable to the temperature-dependent paramagnetic behaviour of VO_2 at low temperature [156], has likely also contributed to hindering the identification of the FCC-ZFC bifurcation.

The magnetic susceptibility derived from the magnetisation data is illustrated in Fig. 3.19. The upper bound of the temperature range used for Curie-Weiss (CW) fits is set as 325 K for all applied field strengths, suppressing the influence due to the metal-insulator transition of VO_2 at 350 K. The lower bounds for the fits were adjusted to the magnetic fields, such that each fit includes as much statistics as possible while using only high temperatures ⁶. Specifically, the lower bounds used for the fits are 200 K for $B < 0.5$ T, 225 K for $B = 0.5$ T and 250 K for $B > 0.5$ T. Despite the paramagnetic impurities, the fits suggest a CW temperature of $|\theta_{\text{CW}}| \approx 700$ K. Considering $T_N \approx 50$ K that is indicated by the magnetisation results in Fig. 3.18, the measurements suggest a frustration index $f = \frac{|\theta_{\text{CW}}|}{T_N} \approx 12$, demonstrating a strong frustration of PbVO_3 . Moreover, in the results of CW fits, the higher values of $|\theta_{\text{CW}}|$ at higher fields are attributable to the paramagnetic contributions of VO_2 .

Our measurements of bulk properties have demonstrated of the antiferromagnetic (AFM) ordering of PbVO_3 at $T_N < 50$ K, which is so far the first observation of the AFM ordering using a powder sample. A more quantitative analysis of the magnetic ordering is not carried out using the data of bulk properties due to the contributions of the impurities. Instead, the analysis is conducted using neutron measurements.

⁶The temperature range used for CW fits should be sufficiently distant from the phase transition

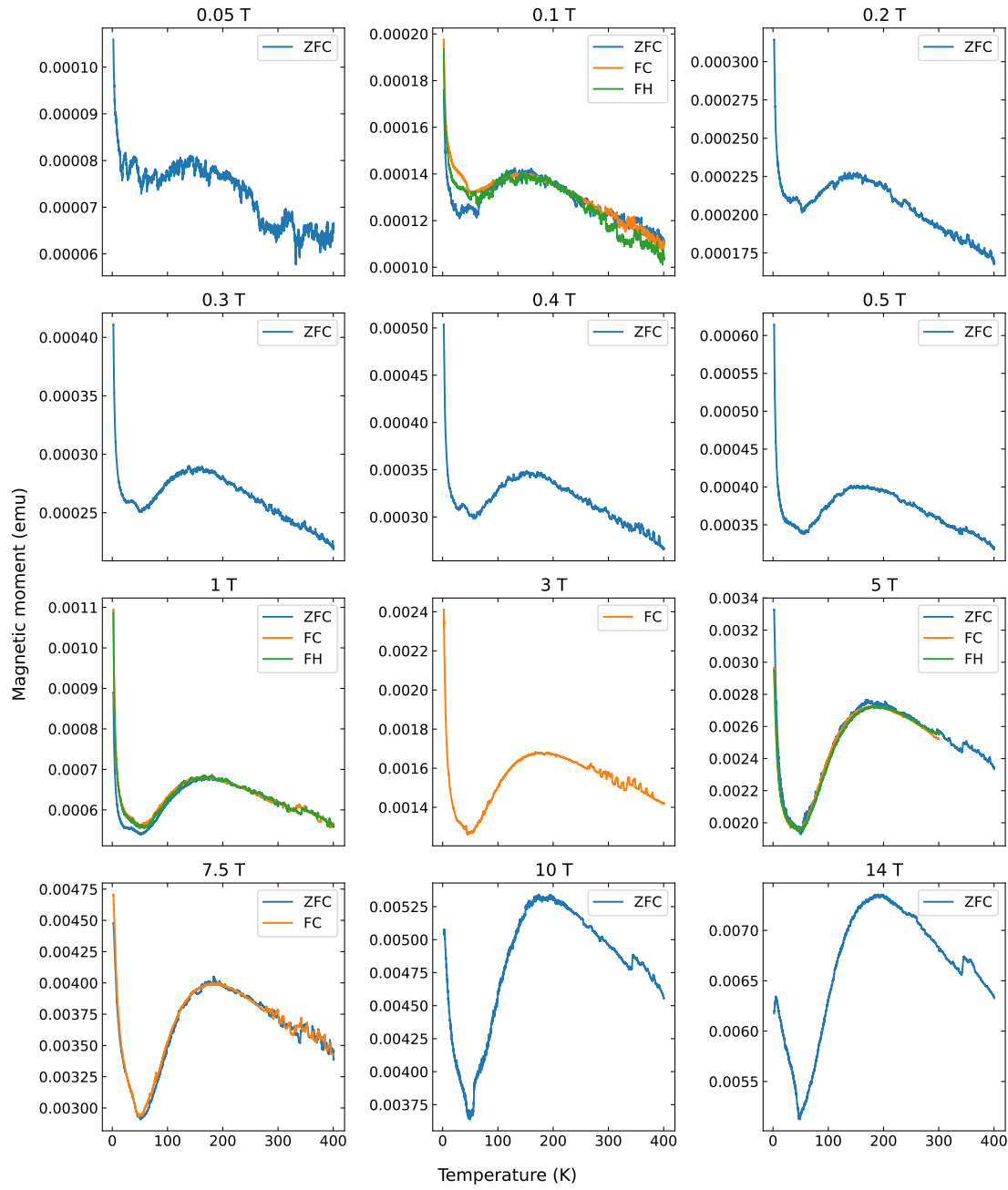


Figure 3.18: Magnetic moment of PbVO_3 plotted against temperature under different magnetic field strengths. Measurements were conducted under zero-field cooling (ZFC), field cooling (FC), and field-cooled heating (FH) conditions. Transition temperatures are estimated for each applied field strength.

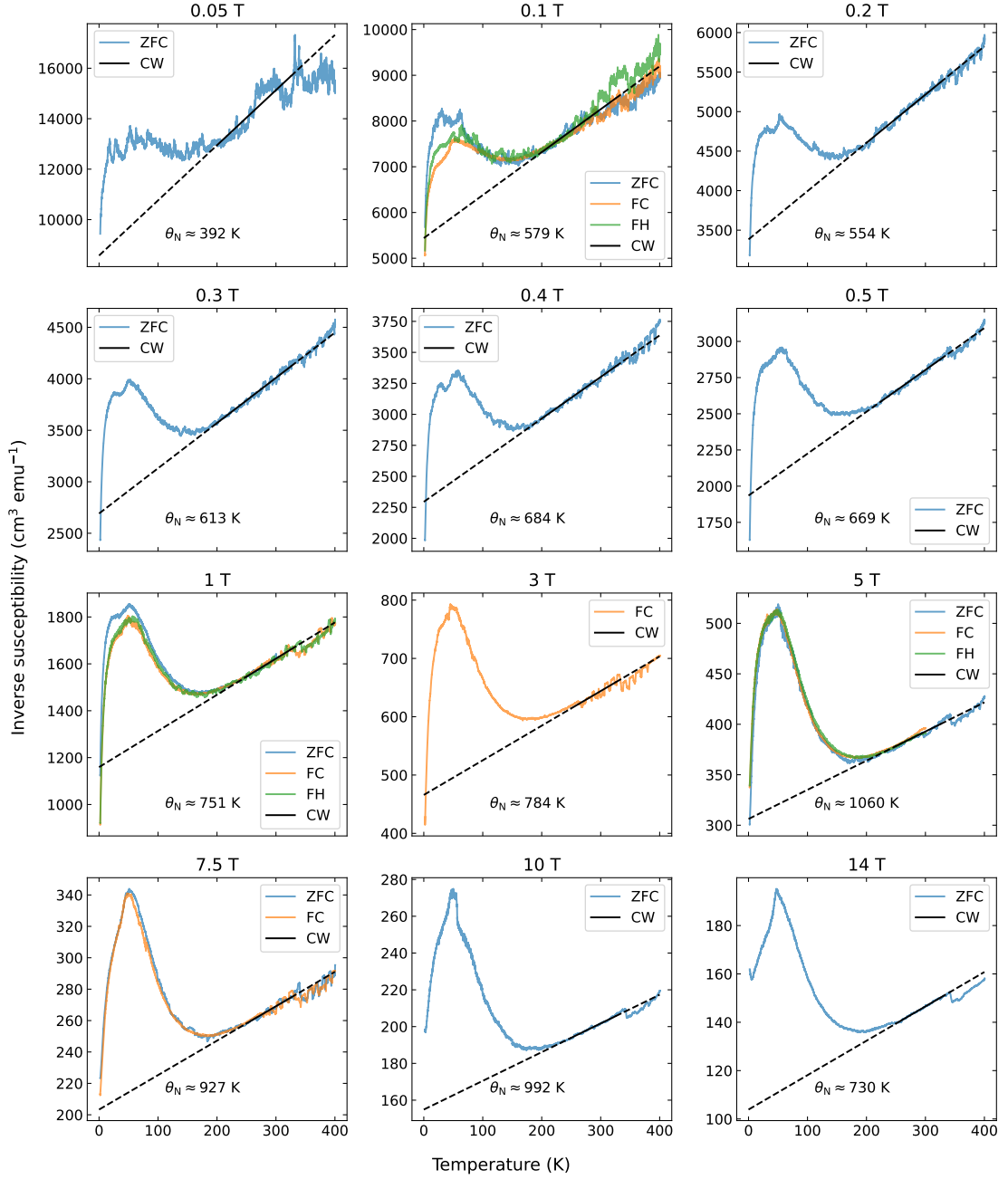


Figure 3.19: Inverse DC magnetic susceptibility of PbVO_3 plotted against temperature for various magnetic fields, derived from the magnetisation (Fig. 3.18). Measurements were conducted under ZFC, FCC, and FCH conditions. For each applied field strength, all datasets are utilised together for a CW fit (black line), where the temperature range used for fitting is indicated by a solid line, with the dashed parts denoting the temperatures not used for fitting. The Néel temperature θ_N indicated by the CW fit is provided in each panel.

3.2.3 Neutron powder diffraction

Further investigation into the magnetic structure of PbVO_3 was conducted by measuring the powder sample using the two-axis neutron diffractometer D20 at ILL [157]. The data was recorded at scattering angles (2θ) up to 153.6° across temperatures ranging from 2 K to 100 K, with an increment of 1 K each step (Fig. 3.20a).

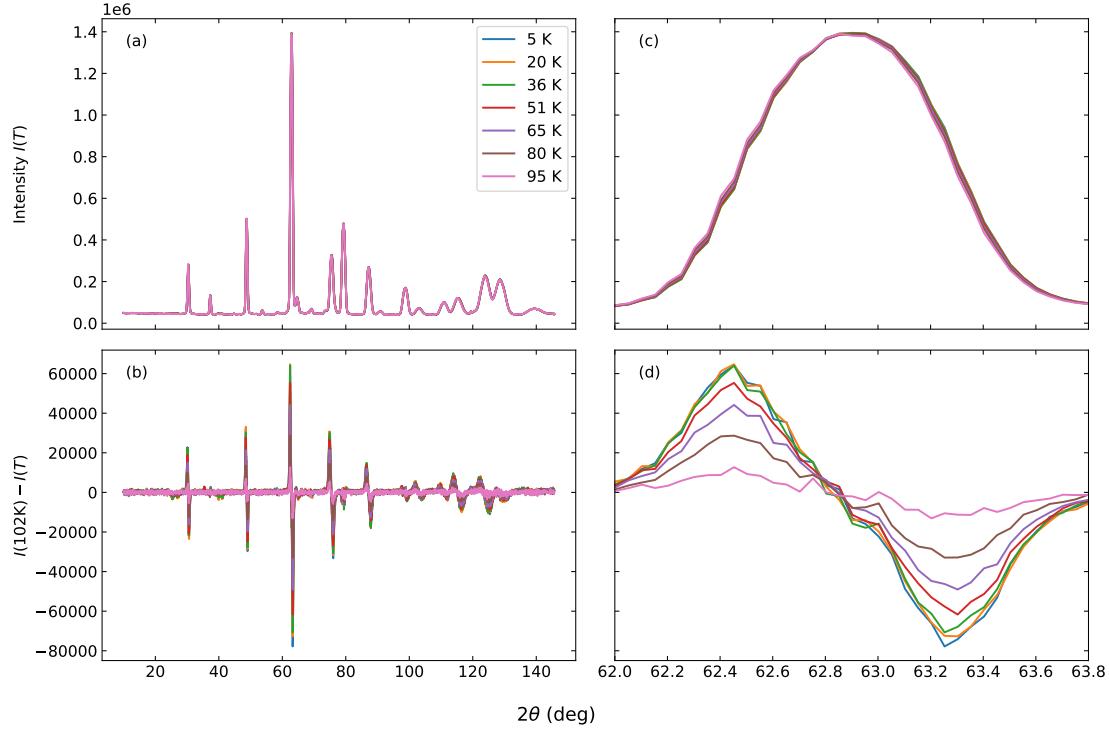


Figure 3.20: Intensity plotted against scattering angle 2θ at various temperatures using neutron powder diffraction for PbVO_3 conducted at the D20 instrument at ILL [157]. Panel a: absolute intensities across the entire 2θ angular range. Panel b: intensity differences, $I(T = 102 \text{ K}) - I(T)$, across the entire 2θ -range. Panels (c) and (d): enlarged views of (a) and (b), respectively, focusing on the strongest reflection, where a peak shift is observed due to the temperature dependency of the lattice parameters.

At $T = 100 \text{ K}$ within the paramagnetic phase, the data was fitted using the Rietveld method within the Fullprof software [158]. Here, the major peaks were attributable to PbVO_3 with the space group (SG) $P4mm$ (No. 99), while the peaks with lower intensities, approximately 1 % of the strongest peak, could be assigned to VO_2 with the SG $P12_1/c1$ (No. 14) [159], supporting the small amount of the VO_2 impurity. Additionally, certain peak positions exhibited evident temperature

dependencies, clearly visible in the enlarged plot of the strongest reflection in the panels b, c and d of Fig. 3.20.

Denoting the scattering vector $\mathbf{Q}$ as (h, k, l) in reciprocal lattice units (r.l.u), the analysis of the reflections from PbVO_3 and VO_2 indicates a shift in the peak positions of PbVO_3 with $l \neq 0$, indicating a decrease in the scattering angle 2θ with increasing temperature. This illustrates an increase of the lattice constant c with rising temperature, consistent with results observed by Belik *et al.* (Fig. 3.14) [146].

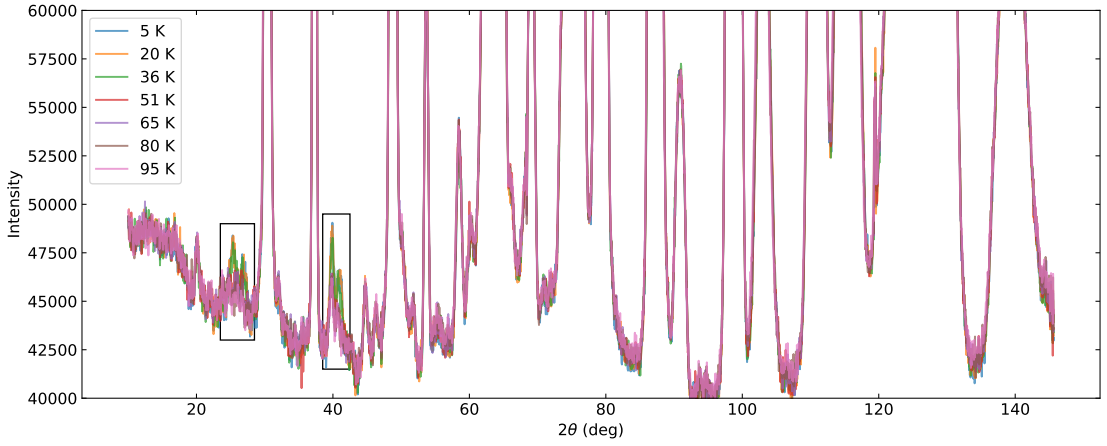


Figure 3.21: Intensity plotted against scattering angle 2θ at various temperatures using neutron powder diffraction for PbVO_3 conducted at the D20 instrument at ILL [157]. Plot is enlarged to focus on the region displaying magnetic signals, as there is no discernible intensity change outside this range. Magnetic peaks are highlighted by black boxes.

Plotting the datasets at various temperatures in Fig. 3.21 reveals magnetic reflections at $T < 50$ K, with two peaks near $2\theta = 26.1^\circ$ and two near 40.3° , respectively. The intensities of these four peaks in dependency of temperature were fitted using a power law, indicating a Néel temperature of $T_N = 45.8 \text{ K} \pm 0.2 \text{ K}$, as depicted in Fig. 3.22. This is so far the first neutron data that could resolve magnetic signals, serving as a crucial evidence of the LRMO in the ground state of PbVO_3 .

Accounting for the temperature dependency of the lattice parameters, the magnetic signals at $T = 2$ K were fitted using the function “k_search” of Fullprof using the nuclear structure at 2 K, suggesting an incommensurate propagation vector of $\mathbf{k} = (0.44, 0.5, 0)$. This finding agrees with the theoretical analysis by I. V. Solovyev [160], which predicts a long-periodic spin-spiral state in PbVO_3 . This structure results from the non-centrosymmetric pyramidal coordination of PbVO_3 ,

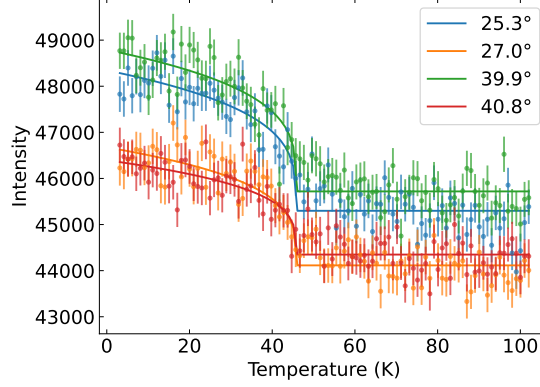


Figure 3.22: Neutron powder diffraction measurements of magnetic reflections in PbVO_3 . Fitted using a power law, where the transition temperature T_N is set as a global parameter for all reflections. The fit yields $T_N = 45.8 \text{ K} \pm 0.2 \text{ K}$.

which can be described with the Hamiltonian [160]:

$$\hat{H} = - \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\langle ij \rangle} \mathbf{d}_{ij} (\mathbf{S}_i \times \mathbf{S}_j) + \sum_i \hat{\tau}_{ii} \mathbf{S}_i \cdot \mathbf{S}_i. \quad (3.15)$$

Here, J_{ij} denotes the isotropic exchange interaction, the vector $\mathbf{d}_{ij}$ signifies the non-centrosymmetric Dzyaloshinskii-Moriya interactions (DMIs) [161, 162], and the tensor $\hat{\tau}_{ii}$ represents the single-ion anisotropy. Due to Kramers' degeneracy theorem [163], the single-ion anisotropy is forbidden in PbVO_3 with a single d electron. Hence, PbVO_3 exhibits an interplay between the isotropic exchange interaction and non-centrosymmetric DMIs, which causes the long-periodic spin-spiral ground state of PbVO_3 , as predicted I. V. by Solovyev [160].

3.2.4 Muon spin relaxation

Considering the spin-spiral ground state of PbVO_3 observed in our NPD measurements and its metallic phase at HPs depicted by Oka [149], our remaining question was its potential spin-liquid phase. For this investigation, a pellet sample was analysed using μSR at the GDP instrument, Swiss Muon Source SpS, Paul Scherrer Institute (PSI), Villigen, Switzerland [164, 165]. Unlike neutron scattering, μSR employs muons as a local probe, distinguishing whether changes in magnetic phases arise from alterations in magnetic volume fraction (MVF) or magnetic moment. Consequently, μSR aids in monitoring the decline of the LRMO in PbVO_3 .

The pallet sample was placed within a pressure cell to investigate the anticipated phase transition induced by applying pressure as an external tuning parameter. This approach draws inspiration from studies on $\text{BaCdVO}(\text{PO}_4)_2$ [166],

where a spin-nematic phase was searched for by employing magnetic fields. In the following, we review key aspects of the μ SR technique and present our experiments.

The μ SR technique

This section summarises primarily from [167], focusing on aspects relevant to our work. Further details can be found in [167]. The muon (μ^-) carries a negative unit charge, whereas the antimuon (μ^+) has a positive charge. In the context of the μ SR technique, the positively charged antimuon (μ^+) is utilised and will hereon be referred to simply as muon.

Akin to a neutron, the spin of a muon undergoes Larmor precession around a magnetic field (as described in Eq. 2.27) with a gyromagnetic ratio of $\gamma_\mu = 2\pi \times 135.538\,817 \text{ MHz T}^{-1}$. The muon is unstable and spontaneously decays into a positron and a neutrino-antineutrino pair, with a mean lifetime of $\tau_\mu \approx 2.197 \text{ }\mu\text{s}$:

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu. \quad (3.16)$$

In this three-body decay, the kinetic energy of a positron, E_{e^+} , can vary from 0 up to a maximum value $E_{e^+, \text{max}}$. The emission of positrons can be described by a differential probability per unit time, energy, and solid angle [167, 168]:

$$\begin{aligned} d\Gamma &= W(\varepsilon, \theta) d\varepsilon d\Omega = \frac{1}{4\pi\tau_\mu} 2\varepsilon^2 (3 - 2\varepsilon) \left(1 + \frac{2\varepsilon - 1}{3 - 2\varepsilon} \cos \theta \right) d\varepsilon d\Omega \\ &= \frac{1}{4\pi\tau_\mu} E(\varepsilon) (1 + a(\varepsilon) \cos \theta) d\varepsilon d\Omega. \end{aligned} \quad (3.17)$$

Here, $\varepsilon = \frac{E_{e^+}}{E_{e^+, \text{max}}} \in [0, 1]$, and $d\Omega = \sin \theta d\theta d\phi$ denotes the solid angle corresponding to a polar angle θ and an azimuthal angle ϕ ⁷. The energy dependent asymmetry term in Eq. 3.17, $a(\varepsilon) = \frac{2\varepsilon - 1}{3 - 2\varepsilon}$, indicates an asymmetric emission of positrons, preferentially in the same direction as the muon spin [167]. Integrating $a(\varepsilon)$ over energy, the average asymmetry yields:

$$\bar{A} = \int_0^1 a(\varepsilon) E(\varepsilon) d\varepsilon = \frac{1}{3}. \quad (3.18)$$

The corresponding angular distribution yields:

$$d\Gamma = W(\theta) d\Omega = \frac{1}{4\pi\tau_\mu} \left(1 + \frac{1}{3} \cos \theta \right) d\Omega. \quad (3.19)$$

⁷We follow the definition used in the cited literature, where the “physics convention” is utilised. This is in contrast to the “mathematics convention” that was used for the Mushroom chapter, where φ denotes a polar angle, while ψ represents an azimuthal angle to differentiate from a scattering angle θ .

The value $\bar{A} = \frac{1}{3}$ corresponds to the ideal scenario where the detector uniformly covers all solid angles and maintains equal efficiency across all positron energies. The experimentally obtained asymmetry typically achieves $A_0 \approx 0.25$ [167].

Experimentally, the number of emitted positrons can be expressed as [167]:

$$N(t) = B + N_0 e^{-\frac{t}{t_p}} (1 + A_0 \mathbf{P}(t) \cdot \hat{\mathbf{n}}), \quad (3.20)$$

with $N_0 = \frac{N_{\mu,0} \Delta \Omega \epsilon}{4\pi \tau_p}$. Hence, measuring the asymmetry of positron emission enables the extraction of information regarding the muon polarisation upon stopping in the sample. This unique characteristic of the muon renders it a potent local probe for studying magnetic properties of materials.

In μ SR experiments, two positron detectors are positioned opposite to each other, with the sample in the centre, to measure the asymmetry. The incident muon beam is polarised ($\mathbf{I}_\mu$), aligning its polarisation collinearly with the trajectories of the positrons. Various μ SR measurement geometries are possible, contingent on the configurations of the external fields applied to the sample concerning the polarisation $\mathbf{I}_\mu$: ZF, longitudinal-field (LF), and transverse-field (TF) geometries, as illustrated in Fig. 3.23.

The ZF geometry is employed within a zero-field environment, allowing the muon polarisation to solely precess around the internal fields of the sample. As depicted in Fig. 3.24, the polarisation affected by a static field $\mathbf{B}$ yields

$$P_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu B t), \quad (3.21)$$

where the z -axis aligns with $\mathbf{I}_\mu$. In reality, magnetic fields have a distribution in value and direction. Firstly, considering a distribution $f(\mathbf{B})$ in direction with a single magnitude of B , the polarisation yields

$$P_z(t) = \int f(\mathbf{B}) [\cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu B t)] d\mathbf{B}, \quad (3.22)$$

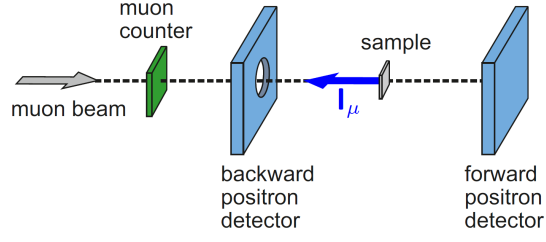
with a non-oscillating term $\cos^2 \theta$ and an oscillating term $\sin^2 \theta \cos(\gamma_\mu B t)$. Given the powder form of our sample, the integration in Eq. 3.22 occurs across the whole space corresponding to a solid angle of 4π sr, yielding

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \cos(\gamma_\mu B t). \quad (3.23)$$

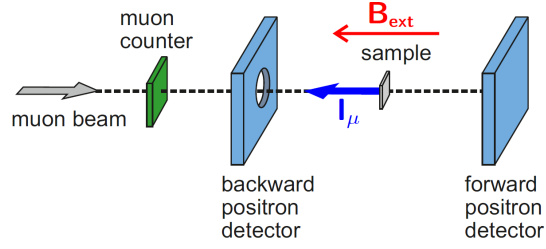
Secondly, considering an imperfect magnetic structure, the field magnitude B can be expressed with a distribution rather than a single value. In the case of a static Gaussian distribution, the polarisation yields the Gaussian Kubo-Toyabe (GKT) function [169]:

$$P_z^{\text{GKT}}(t) = \frac{1}{3} + \frac{2}{3} (1 - \gamma_\mu^2 \sigma^2 t^2) e^{-\frac{\gamma_\mu^2 \sigma^2 t^2}{2}}, \quad (3.24)$$

a) ZF geometry



b) LF geometry



c) TF geometry

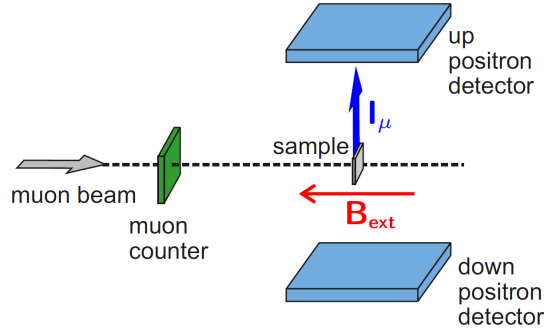


Figure 3.23: μ SR geometries determined by detector positions concerning the field direction: panel a - ZF, panel b - LF, and panel c - TF. $\mathbf{I}_\mu$ represents the polarisation of the incident muon beam, $\mathbf{B}_{\text{ext}}$ signifies the external magnetic field, and the detector pairs are oriented to detect outgoing positrons following trajectories aligned with $\mathbf{I}_\mu$. Figure taken from [167].

where σ represents the standard deviation (SD) of the Gaussian distribution. If the static distribution follows a Lorentzian profile, the polarisation can be described by the Lorentzian Kubo-Toyabe (LKT) function [169]:

$$P_z^{\text{LKT}}(t) = \frac{1}{3} + \frac{2}{3} (1 - \gamma_\mu \Lambda t) e^{-\gamma_\mu \Lambda t}, \quad (3.25)$$

where Λ denotes the half width at half maximum (HWHM) of the Lorentzian distribution. In cases where a distribution of B arises from fluctuations, the LF geometry becomes beneficial. This is because within a ZF measurement, the behaviour of the muon polarisation cannot be differentiated from the impact of static

fields. An instance of this is the extreme motional narrowing limit, denoted by $\gamma \gg \sigma$, where γ signifies the fluctuation rate altering the orientation and magnitude of the local field, and $\sigma^2 = \gamma_{\mu}^2 \sigma_B^2$ corresponds to the Gaussian distribution [167]. In this scenario, the polarisation yields

$$P_{z,\text{dyn}}^{\text{GKT}}(t, \sigma, \gamma) \approx e^{-\frac{2\sigma^2}{\gamma}t}, \quad (3.26)$$

which has the same shape as that of a Gaussian static field scenario (Eq. 3.24). To distinguish between these scenarios, the LF geometry can be employed with the field $\mathbf{B}_{\text{ext}} \parallel \mathbf{I}_{\mu}$. Further insights into LF measurements can be found in [167]. Theoretically, the ZF case may manifest in two possible configurations, with the incident polarisation either aligned with or perpendicular to the trajectory. However, conventionally, the ZF geometry refers to the zero-field limit of the LF geometry [167].

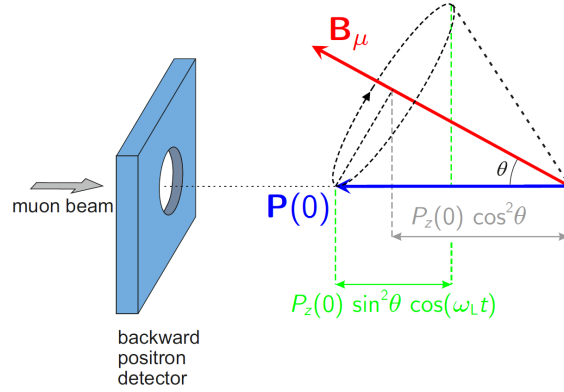


Figure 3.24: Schematic illustrating the muon beam within an internal field, showcasing the angle θ between the initial polarisation and the field. Figure taken from [167].

In the TF geometry, two configurations arise based on the field strength. Firstly, the normal TF geometry involves transverse fields significantly stronger than the internal fields of the sample, causing the predominant effect on the muon polarisation to stem from the external transverse field [167]. Secondly, the weak-transverse-field (wTF) technique utilises a weak transverse field (≈ 50 G), negligible in the presence of internal fields. Consequently, muons stopping at magnetically ordered regions experience predominantly internal fields, while those at non-magnetic areas have a slow spin precession around the weak $\mathbf{B}_{\text{ext}}$. Hence, the wTF geometry serves as a direct means to determine the MVF, quantifying the ratio of magnetically ordered regions within the entire sample:

$$\frac{V_{\text{mag}}}{V_{\text{tot}}} = 1 - \frac{A_{0,\text{wTF}}(T)}{A_0}. \quad (3.27)$$

Here, A_0 is the total asymmetry of the signal, and

$$A_{\text{wTF}}(t, T) = A_{0, \text{wTF}}(T) G(t) \cos(\gamma_{\mu} B_{\text{ext}} t + \phi), \quad (3.28)$$

where ϕ is the initial phase of the muon polarisation. The term $G(t)$ accounts for relaxation resulting from field broadening and the pressure cell:

$$G(t) = e^{-\frac{\sigma_c^2 t^2}{2}} e^{-\lambda_c t}, \quad (3.29)$$

with σ_c and λ_c denoting the Gaussian and exponential relaxation rates encompassing the entire pressure cell (hence the subscript “c”), respectively. Therefore, the asymmetry obtained from a wTF measurement can be described using

$$A_{\text{wTF}}(t, T) = a_0 P_x(t) = a_s \cos(\gamma_{\mu} B_{\text{ext}} t + \phi) e^{-\frac{\sigma_c^2 t^2}{2}} e^{-\lambda_c t}, \quad (3.30)$$

where a_0 represents the initial total asymmetry, $a_s = A_{0, \text{wTF}}(T)$ stands for the oscillating asymmetry, and ϕ denotes the initial phase of the muon polarisation. This unique aspect of the μSR technique aids in distinguishing whether the decrease in the magnetic signal arises from a decline in the magnetic moment of the ions or due to a reduction in the fraction of the magnetically ordered region.

μSR measurements

μSR measurements on polycrystalline PbVO_3 have been carried out during two beamtimes at GDP using a pressure cell. Various pressures were applied to the cell, with the information summarised in Tab. 3.3. At each pressure, both wTF and ZF measurements have been performed at various temperatures.

Beamtimes	Pressures			
First	Ambient	8.20 kbar	15.25 kbar	23.58 kbar
Second	18.50 kbar	19.95 kbar	21.40 kbar	22.90 kbar

Table 3.3: The pressures applied on PbVO_3 in the pressure cell that is used for conducting the μSR measurements during the two beamtimes.

Measurements - weak transverse field

In order to determine the maximum asymmetry and the MVF, wTF measurements were conducted at pressures summarised in Tab. 3.3, across temperatures ranging from 5 K to 100 K. The asymmetry spectra $A_{\text{wTF}}(t, T)$ at each pressure was fitted using Eq. 3.30, determining the parameter $A_{0, \text{wTF}}(T)$ introduced in Eq. 3.27. The

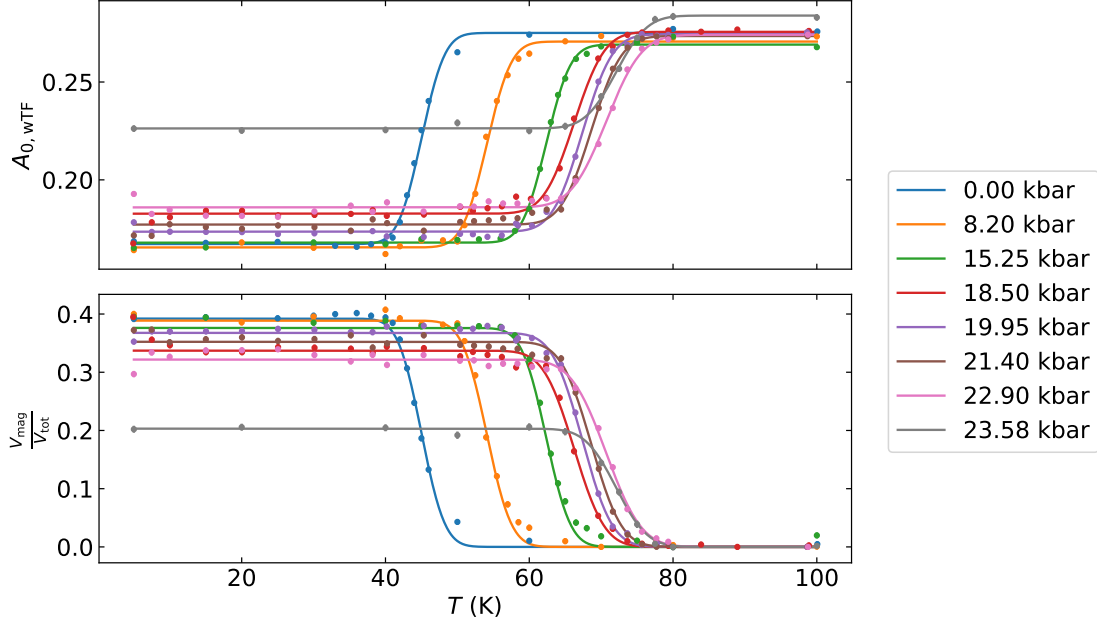


Figure 3.25: Asymmetry and MVF plotted as a function of temperature at various pressures. The raw data was acquired by detecting emitted positrons, providing $A_{wTF}(t, T)$ according to Eq. 3.30, where the small error bars are nearly invisible compared to the point size. The MVF is derived from the asymmetry using Eq. 3.27. The curves are fitted using erf-like functions for determining the transition temperatures [170].

asymmetry $A_{0,wTF}(T)$ is used to derive the MVF through Eq. 3.27, with both parameters in dependence of temperature depicted in Fig. 3.25.

Fig. 3.25 displays a sharp increase of $A_{0,wTF}(T)$ and a decrease of $\frac{V_{mag}}{V_{tot}}$ with temperature, indicating a transition from a paramagnetic phase above the transition temperature T_N into an ordered phase below T_N . Notably, the maximum MVF is significantly smaller at $p = 23.58$ kbar, contrasting to the situation at $p \leq 22.90$ kbar. This indicates a reduced LRMO at temperature below T_N at $p = 23.58$ kbar, which can be attributable to spin fluctuations at HPs. The data were fitted using an erf-like function [170] at each pressure, determining T_N as a function of pressure, as depicted in Fig. 3.26. The analysis indicates an increasing T_N with pressure up to the highest $p = 23.58$ kbar, where the dependency is nearly linear.

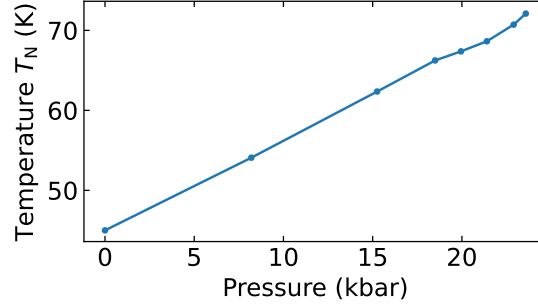


Figure 3.26: Transition temperature T_N plotted as a function of pressure, derived from the erf-like function fits depicted in Fig. 3.25. The fit provides the uncertainties for T_N , with the error bars smaller than the point sizes.

Measurements - zero field

The ZF measurements were conducted to investigate spin fluctuations suggested by the wTF data. Due to time constraints, the measurements in the first beamtime have a better statistics than those in the second beamtime, with a comparison illustrated in Fig. 3.27. The ZF- μ SR asymmetry was fitted considering the presence of two oscillating muon sites:

$$a_0 P_z(t) = a_1 J_0(\omega_1, \phi_1) e^{-\lambda_1 t} + a_2 J_0(\omega_2, \phi_2) e^{-\lambda_2 t} + a_r e^{-\lambda_r t} + a_c P_c(t). \quad (3.31)$$

Here, the first two oscillating terms represent the muon sites, the subscript “r” indicates a non-oscillating relaxation, and the subscript “c” denotes the background signal from the pressure cell. The asymmetry spectra are depicted in Fig. 3.28, where the solid curves depict the fits according to Eq. 3.31. In each fit, the parameter a_0 denotes the maximum asymmetry obtained from the wTF results at each pressure. All other parameters were fitted individually for each pressure, because they can exhibit some changes when the pressure cell was taken out to alter the hydrostatic pressure. These parameters are illustrated in Fig. 3.29, where marginal changes of the parameters associated with the pressure cell could be observed.

The effect of the two oscillating terms on the asymmetry is showcased in Fig. 3.28a with $t < 0.5 \mu\text{s}$. The data at $p = 18.50 \text{ kbar}$, 19.95 kbar , 21.40 kbar and 22.90 kbar from the second beamtime have higher background noises due to the statistics as mentioned in Fig. 3.27. Nonetheless, the fits have values of the reduced χ^2 comparable to the other datasets. The fitted parameters indicate a lower relaxation rate of the first muon site than the second site ($\lambda_1 < \lambda_2$). Given this distinction, the muon site with a larger relaxation rate λ_2 can be attributed to the apical oxygen atom of the oxygen octahedron depicted in Fig. 3.13, while the site with a smaller λ_1 is linked to the in-plane oxygen atom. This result is consistent

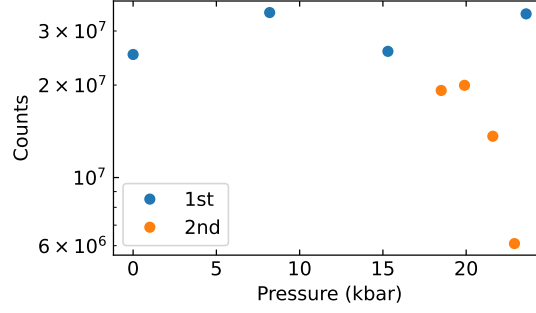
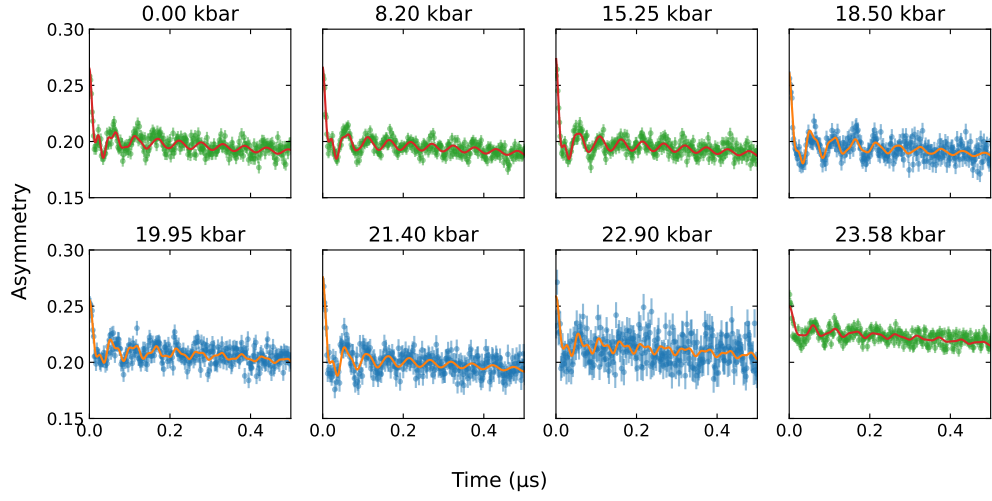


Figure 3.27: The total number of positrons recorded by the forward detector during the ZF measurements at $T = 5$ K and varying pressures, as an indication of the statistics for the experiments performed in the two beamtimes. The labels indicate the 1st or 2nd beamtime.

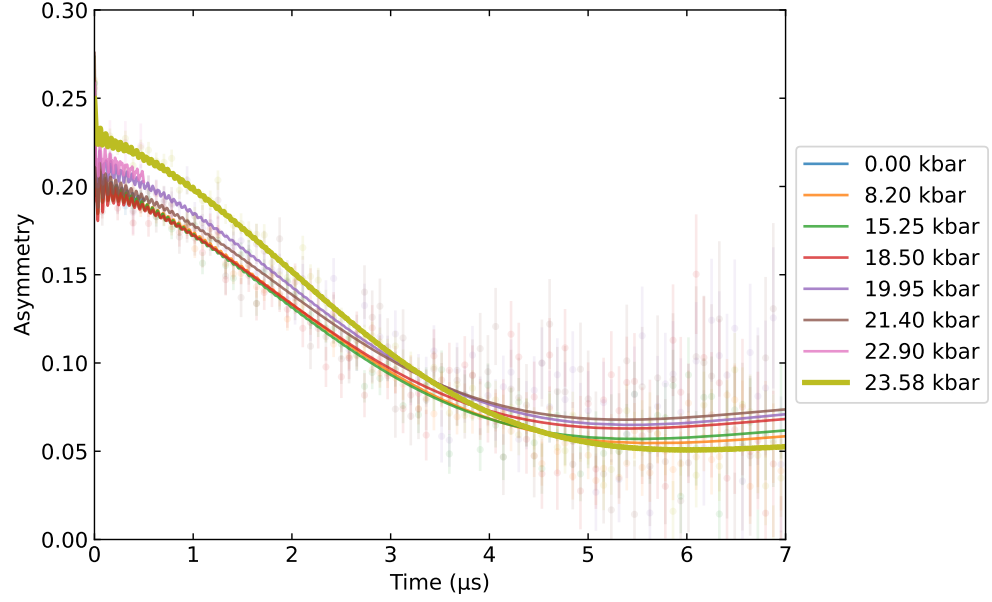
with the findings by K. Oka *et al.* [147]. At low pressures (LPs), both muon sites can be resolved, whereas only one muon site is resolved at $p = 23.58$ kbar. In fact, the fitted results in Fig. 3.29 indicate a power-law-like decay of ω_2 with pressure, while the parameters of the first muon site have a significantly smaller change. The power-law fit of ω_2 implies a critical pressure of $p_c = 23.67 \text{ kbar} \pm 0.11 \text{ kbar}$. Although this fit is based on fit results, it agrees qualitatively with the transition of PbVO_3 from a tetragonal to a cubic phase at increasing pressures [146], where the two distinct environments of muon stopping positions becoming one.

The effect of the non-oscillating relaxation term is illustrated in Fig. 3.28b with $t < 7 \mu\text{s}$. These asymmetry spectra indicate a faster decay of asymmetry at $p = 23.58$ kbar than that at the lower pressures, which is supported by the non-zero non-oscillating relaxation term $\lambda_r = 0.0945 \pm 0.0014$ determined by the fit, as depicted in Fig. 3.29. This agrees with the wTF results that indicated a decrease in the maximum MVF at this pressure, as depicted in Fig. 3.25. Since the maximum MVF is decreased only at 23.58 kbar, and the non-zero relaxation λ_r is only resolvable at 23.58 kbar, the relaxation λ_r should not be attributed to static field distribution but rather to spin fluctuations at HPs, implying a formation of a spin-liquid phase. With data at even higher pressures, this indication can be even better demonstrated.

Our wTF and ZF results using μSR have both indicated a reduction in the LRMO at HPs ($\gtrsim 23$ kbar) with a decrease in the maximum MVF. The observation of a non-oscillating relaxation at $p = 23.58$ kbar in the ZF- μSR asymmetry, attributable to spin fluctuations, suggests the potential presence of a spin-liquid phase. Conducting measurements at even higher pressures would help to confirm this hypothesis.



(a)



(b)

Figure 3.28: Panel a: Asymmetry spectra of PbVO_3 with $t < 0.5 \mu\text{s}$ from the ZF- μSR measurements at different pressure levels. Data from the first beamtime are illustrated in green, and the corresponding fit results are depicted in red. The datasets from the second beamtime are represented in blue and orange. Panel b: Asymmetry spectra with $t < 7 \mu\text{s}$. The measured results are shown with reduced opacity, while the fitted data are presented prominently. The dataset recorded at $p = 23.58 \text{ kbar}$ is highlighted with increased line thickness.

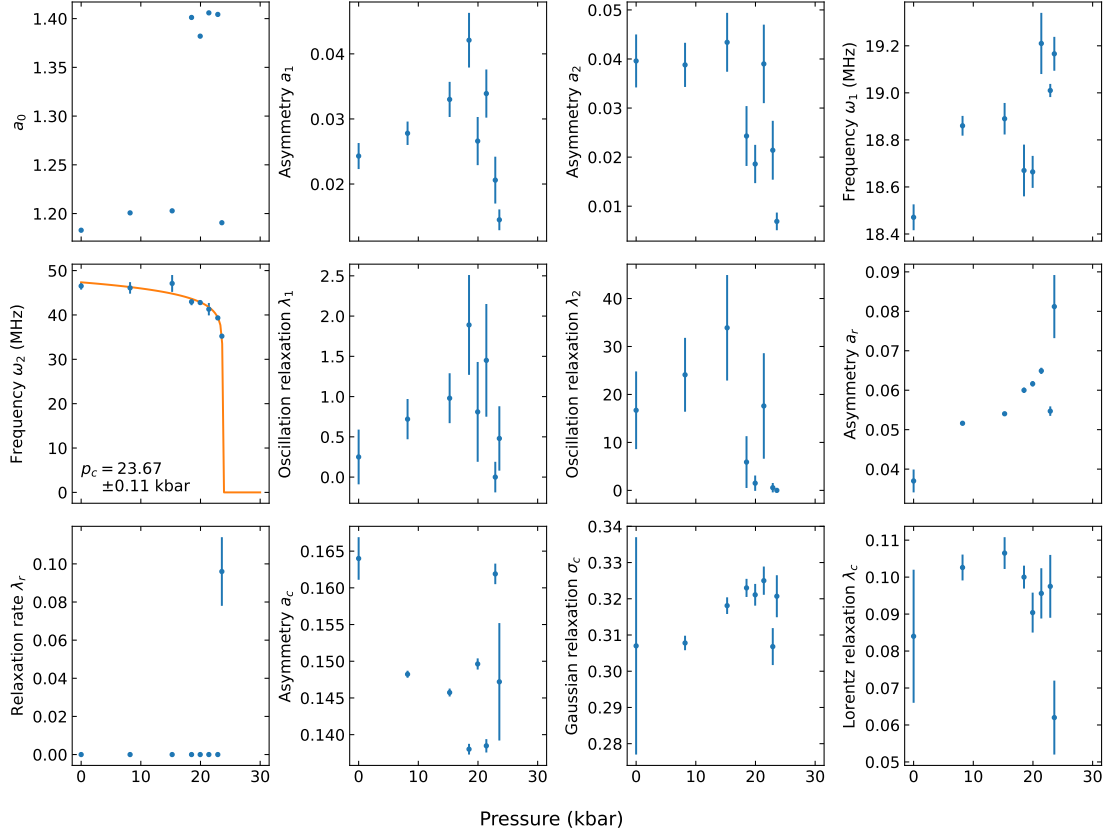


Figure 3.29: The parameters described in Eq. 3.31, fitted using the ZF- μ SR data. The constant a_0 for each pressure is the maximum asymmetry obtained from the wTF results. For $p < 23.58$ kbar, the relaxation rate λ_r was fixed at zero. All parameters, except those held constant, are plotted along with their error bars obtained by analysis using the Musrfit software [171]. The parameter ω_2 has been fitted using a power law, indicating a critical pressure of $p_c = 23.67 \text{ kbar} \pm 0.11 \text{ kbar}$.

3.2.5 Summary

We aimed to investigate the magnetic structural and dynamic properties of the compound PbVO_3 by conducting magnetic property measurements, NPD, and μ SR. All three measurements revealed long-range magnetic ordering at AP and $T \lesssim 50 \text{ K}$. The broad maximum observed in the magnetisation measurement implies a low-dimensional antiferromagnetic ordering in the ground state, consistent with the pyramidal distortion, where a single electron occupies the d_{xy} orbital with a lower energy than the other two t_{2g} orbitals [147]. The presence of a ZFC-FC bifurcation in magnetisation suggests either antiferromagnetic ordering or a spin-glassy ground state, with the former scenario confirmed by our NPD and μ SR

results.

Our NPD findings indicate a propagation vector $\mathbf{k} = (0.44, 0.5, 0)$, corresponding to a long-period spin spiral along the a -direction. It arises from the competition between isotropic exchange interactions and DMIs in the non-centrosymmetric crystal structure. These results agree with the predictions derived from first-principle electronic structure calculations by Solovyev [160].

Furthermore, our wTF- μ SR data exhibited a decline in the MVF at increasing temperature across various pressures up to 23.58 kbar, which further confirms the transitions between a magnetically ordered state and a paramagnetic state at all measured pressures. A substantial reduction in the maximum MVF at $p = 23.58$ kbar suggests an expected spin-liquid state, a feature further supported by our ZF- μ SR data. Once the data at $22.90 \text{ kbar} < p < 23.58 \text{ kbar}$ or $23.58 \text{ kbar} < p < 32 \text{ kbar}$ are obtained, the findings could offer deeper insights into states featuring spin fluctuations before entering the metallic phase at $p \approx 32$ kbar [149].

In conclusion, in face of the divided findings amongst previous studies, our investigations have provided unambiguous evidences for the LRMO of PbVO_3 at AP and $T \lesssim 50 \text{ K}$. The spin-liquid state predicted by other works is indicated by our μ SR data at 23.58 kbar. This indication can be further supported by more data at $23 \text{ kbar} < p < 32 \text{ kbar}$, before PbVO_3 enters a metallic phase.

Chapter 4

Conclusion

In this thesis, we aimed to explore further possibilities in neutron instrumentation by harnessing the unique features of neutron scattering to accommodate the increasingly complex systems that scientists seek to investigate. The concept of a Mushroom-type spectrometer offers significant advantages in terms of the solid angle coverage of the scattered beam, owing to its distinctive analyser configuration. This configuration is particularly well-suited for studying exotic systems with small sample sizes and broad spectra. The design of the secondary spectrometer offers both compact size and high resolution, particularly when compared to conventional time-of-flight direct-geometry spectrometer (ToF-DGS). Depending on the possible location of the instrument, the primary spectrometer can be equipped with a time-of-flight indirect-geometry spectrometer (ToF-IGS) with a chopper system or double crystal monochromators, offering excellent flexibility in its realisation.

In addition, we have advanced in developing the cylindrical miniaturised polarisation analysis device (MiniPAD) for spherical neutron polarimetry (SNP). SNP is a powerful technique for investigating complex magnetic systems, particularly those involving nuclear-magnetic interferences and chiral terms. The design of the MiniPAD offers a much more compact alternative to the other available devices like the cryogenic polarisation analysis device (CryoPAD), because it can be inserted into a standard cryostat. Test measurements have demonstrated a polarisation accuracy comparable to a mu-metal polarisation analysis device (MuPAD). With its advantages and great performance, the MiniPAD can be implemented across various instruments, including triple-axis spectrometers (TASs), thus broadening the accessibility of SNP measurements.

Moreover, we have investigated the layered perovskite-related systems, i.e. $\text{Ca}_3\text{NiNb}_2\text{O}_9$ and PbVO_3 . We have conducted neutron scattering experiments on a single-crystalline sample of the AGT specimen of $\text{Ca}_3\text{NiNb}_2\text{O}_9$. The findings confirm a two-step 120° -ordering of the AGT specimen, with a propagation vector

$\mathbf{k} = (0, \frac{1}{3}, 0)$ with respect to its monoclinic nuclear space group (SG) $P12_1/c_1$. Further analysis suggests magnetic moments within the ab -plane. The neutron powder diffraction (NPD) measurements of PbVO_3 have revealed its long-range magnetic order (LRMO) occurring below 50 K, suggesting a spin spiral structure with a propagation vector of $\mathbf{k} = (0.44, 0.5, 0)$. This structure results from the competition between isotropic exchange interactions and Dzyaloshinskii-Moriya interactions (DMIs) in its non-centrosymmetric crystal structure. The LRMO has been further confirmed by the muon spin spectroscopy (μSR) measurements using weak-transverse-field (wTF) and zero-field (ZF) configurations. Furthermore, the ZF measurements have suggested the presence of spin fluctuations, potentially a spin-liquid phase above 23 kbar. Data at higher pressures can help to examine this scenario.

In summary, this thesis has presented two advancements in neutron instrumentation and investigations of two perovskite systems conducted using neutron scattering techniques. These investigations have provided further knowledge on the systems $\text{Ca}_3\text{NiNb}_2\text{O}_9$ and PbVO_3 and have demonstrated the valuable insights of neutron scattering, complementing findings obtained through other analytical methodologies.

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Chapter 5

Appendix

5.1 Removal of frame overlaps

For an arbitrary combination of n_1 and n_2 , the time window where neutrons can pass the chopper system is defined by Eq. 1.24 and 1.27, which is a parallelogram in the t_S - τ diagram, as shown in Fig. 5.1. The four boundaries of the parallelogram yield:

$$\begin{aligned}t_{S,1}(\tau) &= \tau L_{1S} + n_1 T_1 - w_1 \\t_{S,2}(\tau) &= \tau L_{1S} + n_1 T_1 + w_1 \\t_{S,3}(\tau) &= \tau_0 L_{12} + \tau (L_{1S} - L_{12}) + n_2 T_2 - w_2 \\t_{S,4}(\tau) &= \tau_0 L_{12} + \tau (L_{1S} - L_{12}) + n_2 T_2 + w_2.\end{aligned}\tag{5.1}$$

Each corner of the parallelogram can be determined through the intersection of two lines:

$$\begin{aligned}t_{S,2}(P_1) &= \tau L_{1S} + n_1 T_1 + w_1 \\&= \tau_0 L_{12} + \tau (L_{1S} - L_{12}) + n_2 T_2 - w_2 = t_{S,3}(P_1) \\t_{S,1}(P_2) &= \tau L_{1S} + n_1 T_1 - w_1 \\&= \tau_0 L_{12} + \tau (L_{1S} - L_{12}) + n_2 T_2 - w_2 = t_{S,3}(P_2) \\t_{S,2}(P_3) &= \tau L_{1S} + n_1 T_1 + w_1 \\&= \tau_0 L_{12} + \tau (L_{1S} - L_{12}) + n_2 T_2 + w_2 = t_{S,4}(P_3) \\t_{S,1}(P_4) &= \tau L_{1S} + n_1 T_1 - w_1 \\&= \tau_0 L_{12} + \tau (L_{1S} - L_{12}) + n_2 T_2 + w_2 = t_{S,4}(P_4).\end{aligned}\tag{5.2}$$

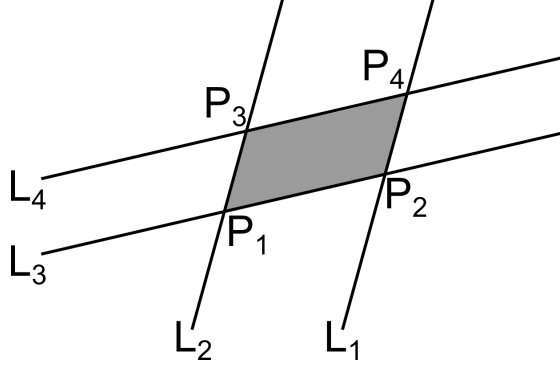


Figure 5.1: t_S - τ -diagram at a given (n_1, n_2) -combination. The grey parallelogram gives the parameters of the neutrons accepted by the chopper system.

This gives the τ - and t_S -values of the corners:

$$\begin{aligned}
 \tau(P_1) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 - w_1 - w_2}{L_{12}} \\
 \tau(P_2) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 + w_1 - w_2}{L_{12}} \\
 \tau(P_3) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 - w_1 + w_2}{L_{12}} \\
 \tau(P_4) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 + w_1 + w_2}{L_{12}} \\
 t_S(P_1) &= \tau_0 L_{1S} + \frac{L_{1S}}{L_{12}} (n_2 T_2 - n_1 T_1 - w_1 - w_2) + n_1 T_1 + w_1 \\
 t_S(P_2) &= \tau_0 L_{1S} + \frac{L_{1S}}{L_{12}} (n_2 T_2 - n_1 T_1 + w_1 - w_2) + n_1 T_1 - w_1 \\
 t_S(P_3) &= \tau_0 L_{1S} + \frac{L_{1S}}{L_{12}} (n_2 T_2 - n_1 T_1 - w_1 + w_2) + n_1 T_1 + w_1 \\
 t_S(P_4) &= \tau_0 L_{1S} + \frac{L_{1S}}{L_{12}} (n_2 T_2 - n_1 T_1 + w_1 + w_2) + n_1 T_1 - w_1.
 \end{aligned} \tag{5.3}$$

The removal of frame overlaps requires:

$$t_S(P_4; n_1, n_2) \leq t_S(P_1; n_1 - 1, n_2) \tag{5.4}$$

$$t_S(P_4; n_{1,\min}, n_2) \leq t_S(P_1; n_{1,\max}, n_2 + 1), \tag{5.5}$$

where $n_{1,\min}$ is the smallest n_1 (largest τ) at a given n_2 with the corresponding wavelength $\lambda \in (1 \text{ \AA}, 10 \text{ \AA})$, and $n_{1,\max}$ the largest n_1 (smallest τ) under this

condition. Inserting the parameters into Eq. 5.4, one has:

$$\begin{aligned} \tau_0 L_{1S} + \frac{L_{1S}}{L_{12}} (n_2 T_2 - n_1 T_1 + w_1 + w_2) + n_1 T_1 - w_1 \leq \\ \tau_0 L_{1S} + \frac{L_{1S}}{L_{12}} (n_2 T_2 - (n_1 - 1) T_1 - w_1 - w_2) + (n_1 - 1) T_1 + w_1, \end{aligned} \quad (5.6)$$

giving the first restriction:

$$2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) \leq T_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right). \quad (5.7)$$

For the coefficients $n_{1,\min}$ and $n_{1,\max}$, one considers the middle value $\tau = \tau_0 + \frac{n_2 T_2 - n_1 T_1}{L_{12}}$ of a passing window as shown in the parallelogram in 5.1, because the time-of-flight (ToF)-resolution requires $w_i \ll T_i$ ($i = 1, 2$). Denoting $\tau_{\min}$ and $\tau_{\max}$ as the minimal and maximal inverse velocities corresponding to $\lambda_{\min} = 1 \text{ \AA}$ and $\lambda_{\max} = 10 \text{ \AA}$, respectively, the coefficient $n_{1,\max}$ can be determined by:

$$\begin{aligned} \tau_{\min} &= \tau_0 + \frac{n_2 T_2 - n_{1,\max} T_1}{L_{12}} \\ n_{1,\max} &= \left\lceil \frac{n_2 T_2 - L_{12} (\tau_{\min} - \tau_0)}{T_1} \right\rceil. \end{aligned} \quad (5.8)$$

For a white beam, one can define $\tau_0 = \tau_{\min}$ and $n_1, n_2 \in \mathbb{N}$. Hence, this can be rewritten as:

$$n_{1,\max} = \left\lceil \frac{n_2 T_2}{T_1} \right\rceil. \quad (5.9)$$

Similarly, one has:

$$n_{1,\min} = \left\lceil \frac{n_2 T_2 - L_{12} (\tau_{\max} - \tau_{\min})}{T_1} \right\rceil. \quad (5.10)$$

For approximation, $n_{1,\min}(n_2) = \frac{n_2 T_2 - L_{12} (\tau_{\max} - \tau_{\min})}{T_1}$ and $n_{1,\max}(n_2) = \frac{n_2 T_2}{T_1}$ can be plugged into Eq. 5.5, giving:

$$\begin{aligned} \tau_{\min} L_{1S} + \frac{L_{1S}}{L_{12}} \left(n_2 T_2 - \frac{n_2 T_2 - L_{12} (\tau_{\max} - \tau_{\min})}{T_1} T_1 + w_1 + w_2 \right) \\ + \frac{n_2 T_2 - L_{12} (\tau_{\max} - \tau_{\min})}{T_1} T_1 - w_1 \leq \\ \tau_{\min} L_{1S} + \frac{L_{1S}}{L_{12}} \left((n_2 + 1) T_2 - \frac{(n_2 + 1) T_2}{T_1} T_1 - w_1 - w_2 \right) \\ + \frac{(n_2 + 1) T_2}{T_1} T_1 + w_1, \end{aligned} \quad (5.11)$$

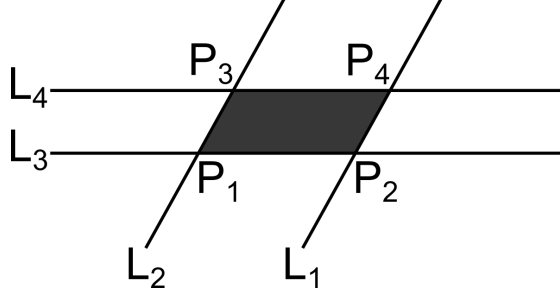


Figure 5.2: t_2 - τ -diagram at a given (n_1, n_2) -combination. The grey parallelogram gives the parameters of the neutrons accepted by the chopper system.

resulting in the second restriction:

$$2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) \leq T_2 - (\tau_{\max} - \tau_{\min})(L_{1S} - L_{12}). \quad (5.12)$$

5.2 Transmission rate and chopper parameters

The transmission rate R of the chopper system is determined by the ratio of the neutrons passing all choppers from those arriving at C_1 . The calculations here take the approximation where the factors like beam size and divergence are not explicitly used in the calculation, but only the contribution from the chopper opening. The t_2 - τ diagram is very suitable for examining the frame overlap. The rate R can be calculated by dividing the sum of all accepted chopper opening time windows by the whole (t_2, τ) -area, which is analogue to the diagram in Fig. 1.21. Each accepted area at a (n_1, n_2) -combination is determined by:

$$\tau L_{12} + n_1 T_1 - w_1 \leq t_2 \leq \tau L_{12} + n_1 T_1 + w_1 \quad (5.13)$$

$$\tau_0 L_{12} + n_2 T_2 - w_2 \leq t_2 \leq \tau_0 L_{12} + n_2 T_2 + w_2. \quad (5.14)$$

The four corners in Fig. 5.1 are:

$$\begin{aligned} t_{2,1}(\tau) &= \tau L_{12} + n_1 T_1 - w_1 \\ t_{2,2}(\tau) &= \tau L_{12} + n_1 T_1 + w_1 \\ t_{2,3}(\tau) &= \tau_0 L_{12} + n_2 T_2 - w_2 \\ t_{2,4}(\tau) &= \tau_0 L_{12} + n_2 T_2 + w_2. \end{aligned} \quad (5.15)$$

The four corners are determined as:

$$\begin{aligned} t_{2,2}(P_1) &= \tau L_{12} + n_1 T_1 + w_1 = \tau_0 L_{12} + n_2 T_2 - w_2 = t_{2,3}(P_1) \\ t_{2,1}(P_2) &= \tau L_{12} + n_1 T_1 - w_1 = \tau_0 L_{12} + n_2 T_2 - w_2 = t_{2,3}(P_2) \\ t_{2,2}(P_3) &= \tau L_{12} + n_1 T_1 + w_1 = \tau_0 L_{12} + n_2 T_2 + w_2 = t_{2,4}(P_3) \\ t_{2,1}(P_4) &= \tau L_{12} + n_1 T_1 - w_1 = \tau_0 L_{12} + n_2 T_2 + w_2 = t_{2,4}(P_4), \end{aligned} \quad (5.16)$$

yielding:

$$\begin{aligned}
\tau(P_1) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 - w_1 - w_2}{L_{12}} \\
\tau(P_2) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 + w_1 - w_2}{L_{12}} \\
\tau(P_3) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 - w_1 + w_2}{L_{12}} \\
\tau(P_4) &= \tau_0 + \frac{n_2 T_2 - n_1 T_1 + w_1 + w_2}{L_{12}}.
\end{aligned} \tag{5.17}$$

These four corners are the same as in Fig. 5.1. This determines:

$$|P_1 P_2| = \frac{2w_1}{L_{12}}. \tag{5.18}$$

The distance between L_3 and L_4 is $2w_2$, giving the area of an acceptance window at a given set of (n_1, n_2) is $2w_1 \cdot 2w_2 / L_{12}$. At a given value of n_2 , the transmission rate can be determined by:

$$R = N_{n_1} \frac{2w_1 2w_2 / L_{12}}{(\tau_{\max} - \tau_{\min}) T_2}, \tag{5.19}$$

where N_{n_1} denotes the number of n_1 -values accepted at a given n_2 . From Eq. 5.9 and 5.10, one has:

$$N_{n_1} \approx \frac{L_{12} (\tau_{\max} - \tau_{\min})}{T_1}, \tag{5.20}$$

resulting in:

$$R \approx \frac{2w_1 2w_2}{T_1 T_2}. \tag{5.21}$$

This theoretical approximation predicts the order of magnitude, whilst one can approximate the rate numerically by:

$$R = \frac{N_{(n_1, n_2)}}{N_{n_2}} \frac{2w_1 2w_2 / L_{12}}{(\tau_{\max} - \tau_{\min}) T_2}, \tag{5.22}$$

where $N_{(n_1, n_2)}$ denotes the number of (n_1, n_2) -sets that are accepted when N_{n_2} is the number of n_2 -values considered in the simulation.

With the restrictions given in Eq. 1.29, the transmission rate given by Eq. 1.30 can be written as a function of $2w_2$, whilst $2w_1$ is determined by the time resolution. For this purpose, the restrictions can be rewritten as:

$$\begin{aligned}
T_1 &\geq \left(2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) \right) / \left(\frac{L_{1S}}{L_{12}} - 1 \right) \\
T_2 &\geq 2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) + \Delta\tau (L_{1S} - L_{12}),
\end{aligned} \tag{5.23}$$

with $\Delta\tau = (\tau_{\max} - \tau_{\min})$. This gives:

$$\begin{aligned}
R &\approx \frac{2w_1 2w_2}{T_1 T_2} \\
&\leq \frac{2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) 2w_2}{2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right)} \\
&\quad \cdot \frac{1}{2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) + \Delta\tau (L_{1S} - L_{12})} \\
&= f(2w_2).
\end{aligned} \tag{5.24}$$

Hence:

$$\begin{aligned}
\frac{df}{d(2w_2)} &= \frac{(2w_1)^2 \left(\frac{L_{1S}}{L_{12}} - 1 \right)^2}{\left(2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) \right)^2} \\
&\quad \cdot \frac{2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) + \Delta\tau (L_{1S} - L_{12})}{\left(2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) + \Delta\tau (L_{1S} - L_{12}) \right)^2} \\
&> 0
\end{aligned} \tag{5.25}$$

This means that the transmission rate $R(2w_2)$ at a given $2w_1$ reaches the maximum when:

$$\begin{aligned}
T_1 &= \left(2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) \right) / \left(\frac{L_{1S}}{L_{12}} - 1 \right) \\
T_2 &= 2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) + \Delta\tau (L_{1S} - L_{12}).
\end{aligned} \tag{5.26}$$

The corresponding transmission rate yields:

$$\begin{aligned}
R_{\max} &= f(2w_2) \\
&= \frac{2w_1 2w_2}{T_1 T_2} \\
&\leq \frac{2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) 2w_2}{2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right)} \\
&\quad \cdot \frac{1}{2w_2 \frac{L_{1S}}{L_{12}} + 2w_1 \left(\frac{L_{1S}}{L_{12}} - 1 \right) + \Delta\tau (L_{1S} - L_{12})}.
\end{aligned} \tag{5.27}$$

The restrictions for removing the frame overlaps can be rewritten as:

$$\begin{aligned}
\frac{\phi_2}{2\pi f_2} \frac{L_{1S}}{L_{12}} + \frac{\phi_1}{2\pi f_1} \frac{L_{1S} - L_{12}}{L_{12}} &\leq \frac{1}{N_1 f_1} \frac{L_{1S} - L_{12}}{L_{12}} \\
\frac{\phi_2}{2\pi f_2} \frac{L_{1S}}{L_{12}} + \frac{\phi_1}{2\pi f_1} \frac{L_{1S} - L_{12}}{L_{12}} &\leq \frac{1}{N_2 f_2} - (\tau_{\max} - \tau_{\min}) (L_{1S} - L_{12}).
\end{aligned} \tag{5.28}$$

This gives:

$$\frac{1}{f_2} \geq \frac{N_2 (L_{1S} - L_{12})}{f_1} \frac{\phi_1 + 2\pi f_1 L_{12} (\tau_{\max} - \tau_{\min})}{2\pi L_{12} - N_2 \phi_2 L_{1S}}, \tag{5.29}$$

yielding:

$$f_1 \leq \left(\frac{2\pi}{\phi_2 N_1 N_2 L_{1S}} - \frac{1}{N_1 L_{12}} - \frac{\phi_1}{\phi_2 N_2 L_{1S}} \right) / (\tau_{\max} - \tau_{\min}). \tag{5.30}$$

With the relative time uncertainty $u_r = \frac{\phi_1}{2\pi f_1} \frac{v}{L_{1S}} = \frac{\phi_1}{f_1} \frac{\hbar}{m\lambda L_{1S}}$, the highest possible resolution (smallest uncertainty) determines the opening time at C_1 as:

$$2w_1 = \frac{\varphi_1}{2\pi f_1} = \frac{m_n \lambda_{\min} L_{1S} u_r}{2\pi \hbar}. \tag{5.31}$$

5.3 Spread of the scattering angle at analyser

The angular spread yields [19, 47]:

$$\Delta\theta_A = \sqrt{\frac{\alpha_{A,i}^2 \alpha_{A,f}^2 + \eta_A^2 \alpha_{A,i}^2 + \eta_A^2 \alpha_{A,f}^2}{4\eta_A^2 + \alpha_{A,i}^2 + \alpha_{A,f}^2}}, \tag{5.32}$$

where η_A is the mosaicity of the analyser crystals. The incoming $\alpha_{A,i}$ and outgoing divergences $\alpha_{A,f}$ concerning the analyser yield:

$$\begin{aligned}\alpha_{A,i} &= \sqrt{\sum_{\xi=x,y,z} f_{\xi,A}^2 (\Delta\xi_A)^2 + \sum_{\xi=x,y,z} f_{\xi,S}^2 (\Delta\xi_S)^2} \\ \alpha_{A,f} &= \sqrt{\sum_{\xi=x,y,z} g_{\xi,A}^2 (\Delta\xi_A)^2 + \sum_{\xi=x,y,z} g_{\xi,F}^2 (\Delta\xi_F)^2}.\end{aligned}\tag{5.33}$$

Here, the parameters are

$$\begin{aligned}|f_{x,A}| &= |f_{\zeta,S}| = \frac{(\zeta_A - \zeta_S)(z_A - z_S)}{|\vec{AS}|^2 r_{AS}}, \quad \zeta = x, y \\ |f_{z,A}| &= |f_{z,S}| = \frac{r_{AS}}{|\vec{AS}|^2} \\ |g_{\zeta,A}| &= |g_{\zeta,F}| = \frac{(\zeta_A - \zeta_S)(z_A - z_F)}{|\vec{AF}|^2 r_{AF}}, \quad \zeta = x, y \\ |g_{z,A}| &= |g_{z,F}| = \frac{r_{AF}}{|\vec{AF}|^2}.\end{aligned}\tag{5.34}$$

Here, $|\vec{A\epsilon}| = \sqrt{\sum_{\xi=x,y,z} (\xi_A - \xi_\epsilon)^2}$ and $r_{A\epsilon} = \sqrt{\sum_{\xi=x,y} (\xi_A - \xi_\epsilon)^2}$ for $\epsilon = F, S$. For each segment of the analyser in the same vertical sectional view, the condition varies with the vertical position φ of segment, while the secondary spectrometer is circular symmetric.

5.4 Angular spreads of wavevector of the scattered beam

For studying these two spreads, the position on the position-sensitive detectors (PSDs), (x_D, y_D) , has to be calculated. Given a preset height (the position along z -axis) of PSD, i.e. z_D , with the subscript “D”, the (x_D, y_D) -position of a neutron that passed by the analyser (“A”), at position (x_A, y_A, z_A) , and the focal point (“F”), at position (x_F, y_F, z_F) , yields:

$$\begin{aligned}x_D &= \frac{x_A(z_F - z_D) + x_F(z_D - z_A)}{z_F - z_A} \\ y_D &= \frac{y_A(z_F - z_D) + y_F(z_D - z_A)}{z_F - z_A}\end{aligned}\tag{5.35}$$

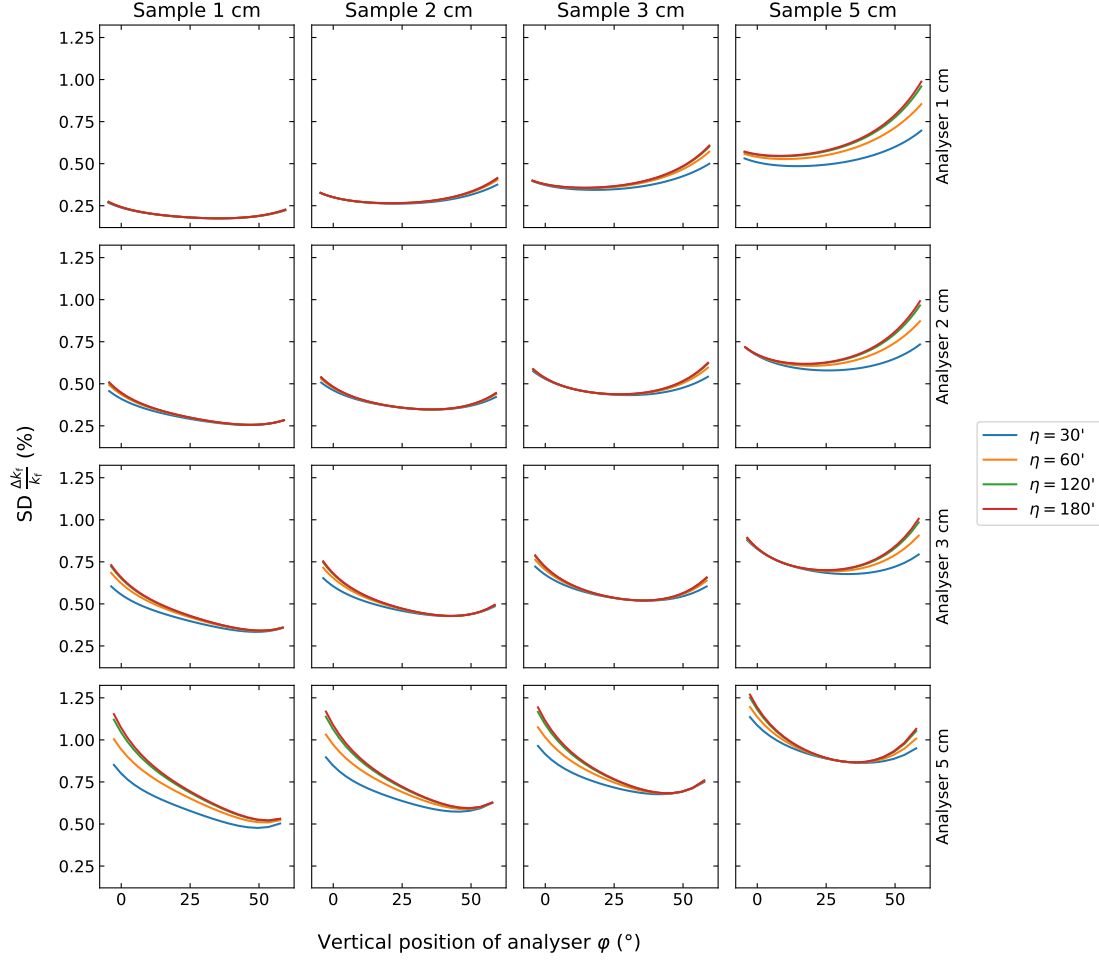


Figure 5.3: Resolution $\frac{\Delta k_f}{k_f}$ as a function of the vertical position φ (Sec. 1.3) of the analyser segment where a neutron is reflected, considering various sizes of a sample (same size in all three dimensions), analyser segments (a square shape), and openings at the other focal point (the same size of radial opening as the analyser). Four mosaic values of the PG crystals for the analyser are considered and labelled with colours. All panels in the same column consider the same sample size (labelled on the top), while all panels in the same row consider the same size of analyser segments (labelled on the right).

Considering the finite sizes of analyser ($\Delta x_A, \Delta y_A, \Delta z_A$) and focal point ($\Delta x_F, \Delta y_F, \Delta z_F$), the spreading on the PSD yields:

$$\begin{aligned}\Delta x_D &= \sqrt{\left(\frac{\partial x_D}{\partial x_A}\right)^2 (\Delta x_A)^2 + \left(\frac{\partial x_D}{\partial z_A}\right)^2 (\Delta z_A)^2 + \left(\frac{\partial x_D}{\partial x_F}\right)^2 (\Delta x_F)^2} \\ \Delta y_D &= \sqrt{\left(\frac{\partial y_D}{\partial y_A}\right)^2 (\Delta y_A)^2 + \left(\frac{\partial y_D}{\partial z_A}\right)^2 (\Delta z_A)^2 + \left(\frac{\partial y_D}{\partial y_F}\right)^2 (\Delta y_F)^2},\end{aligned}\tag{5.36}$$

where the partial derivatives are determined using Eq. 5.35:

$$\begin{aligned}\left|\frac{\partial x_D}{\partial x_A}\right| &= \left|\frac{\partial y_D}{\partial y_A}\right| = \frac{z_F - z_D}{z_F - z_A}, & \left|\frac{\partial x_D}{\partial z_A}\right| &= \frac{(z_F - z_D)(x_F - x_A)}{(z_F - z_A)^2}, \\ \left|\frac{\partial x_D}{\partial x_F}\right| &= \left|\frac{\partial y_D}{\partial y_F}\right| = \frac{z_D - z_A}{z_F - z_A}, & \left|\frac{\partial y_D}{\partial z_A}\right| &= \frac{(z_F - z_D)(y_F - y_A)}{(z_F - z_A)^2}.\end{aligned}\tag{5.37}$$

Here, only the absolute values of the partial derivatives have to be considered, for their contributions in Eq. 5.35 are quadratic. Due to the symmetric geometry of the secondary spectrometer, the radial and angular positions of the neutrons detected by the PSDs are more interesting, which yield:

$$r_D = \sqrt{x_D^2 + y_D^2}, \quad \tan \psi_D = \frac{y_D}{x_D}.\tag{5.38}$$

This results in the radial and angular spreads on the PSDs:

$$\begin{aligned}\Delta r_D &= \sqrt{\frac{x_D^2 (\Delta x_D)^2 + y_D^2 (\Delta y_D)^2}{x_D^2 + y_D^2}} \\ \Delta \psi_D &= \frac{\sqrt{y_D^2 (\Delta x_D)^2 + x_D^2 (\Delta y_D)^2}}{x_D^2 + y_D^2}.\end{aligned}\tag{5.39}$$

Note that the calculations consider the largest possible divergence of the beam coming from the analyser and arriving at the detector, giving a rough estimation of the spreads on the detector. In the case with larger l_S and/or l_A , the detector spreads exhibit higher impact of the beam divergence between sample and analyser and of the analyser mosaicity.

The resolutions in the angles ψ and φ are determined by two factors: Firstly, the signals of neutrons coming from neighbouring segments of the analyser, and the spreads of signals on the PSDs. These two factors result in two situations for determining the resolution: Firstly, if the spreads on the PSDs are smaller than the theoretical positions of neutrons coming from the nearest-neighbour segments of analyser, the resolution is determined by the position difference due to the nearest-neighbour segments. Secondly, if the spreads result in overlaps among signals from

neighbouring segments of analyser, the resolution is determined by the spreads. This yields:

$$\Delta\zeta = \max\left(\Delta\zeta_D, \frac{|\zeta_i - \zeta_{i+1}|}{2}\right), \quad (5.40)$$

where ζ is an arbitrary parameter whose resolution is to be determined, $\Delta\zeta_D$ is the uncertainty due to the spreads on PSDs, and ζ_i is the parameter of the i -th analyser segment.

The angular spreads calculated analytically are depicted in Fig. 5.4 for square-shaped analyser segments and in Fig. 5.5 for circular-shaped analyser stripes, respectively. The Radial Δr_D and angular $\Delta\psi_D$ spreads on PSDs with these two configurations are illustrated in 5.6.

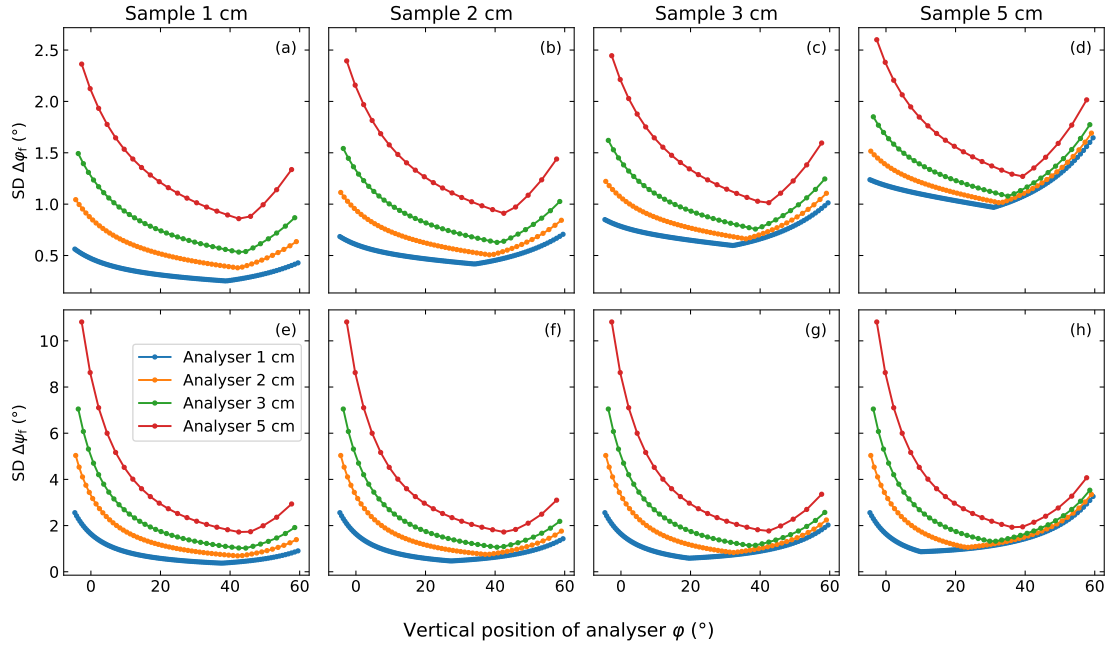


Figure 5.4: Resolutions $\Delta\varphi_f$ (panels a - d) and $\Delta\psi_f$ (panels e - h) as a function of the vertical position φ (Sec. 1.3) of the analyser segment where a neutron is reflected, considering various sizes of a sample (same size in all three dimensions), analyser segments (a square shape), and openings at the other focal point (the same size of radial opening as the analyser). All panels in the same column consider the same sample size (labelled on the top), while the sizes of analyser segments are signified with colours.

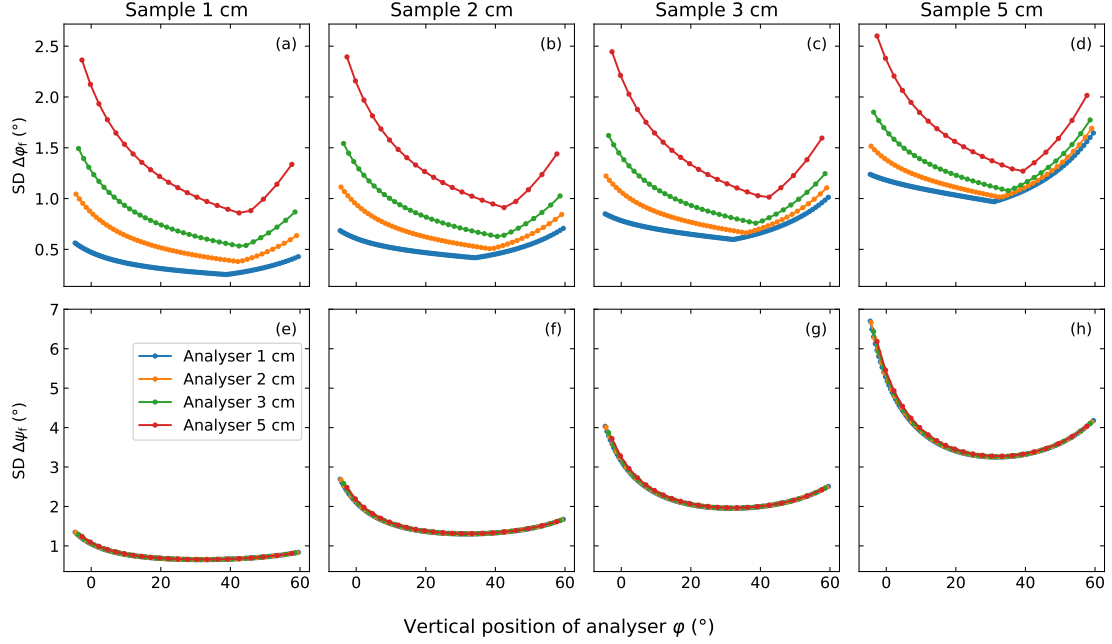


Figure 5.5: Resolution $\Delta\varphi_f$ (panels a - d) and $\Delta\psi_f$ (panels e - h) as a function of the vertical position φ (Sec. 1.3) of the analyser segment where a neutron is reflected, considering various sizes of a sample (same size in all three dimensions), analyser stripes (circular around the sample), and openings at the other focal point (the same size of radial opening as the analyser). All panels in the same column consider the same sample size (labelled on the top), while the sizes of analyser segments are signified with colours.

5.5 Simulated resolution of the secondary spectrometer

The resolutions of the secondary spectrometer simulated using McStas considering varying sizes of the sample, square-shaped analyser segments and the opening at the focal point in values of 1 cm, 2 cm and 5 cm. At each geometrical configuration, the mosaicities $\eta_A = 30', 60', 120'$ of analyser crystals are considered. The resolution of the wavenumber k_f is obtained using an “L_monitor” component, with the result shown in Fig. 5.7. The spreads on the PSD are converted from a Cartesian coordinate system into a polar system, with the spreads in radial (r_D) and angular (ψ_D) positions depicted in Fig. 5.8 and 5.9.

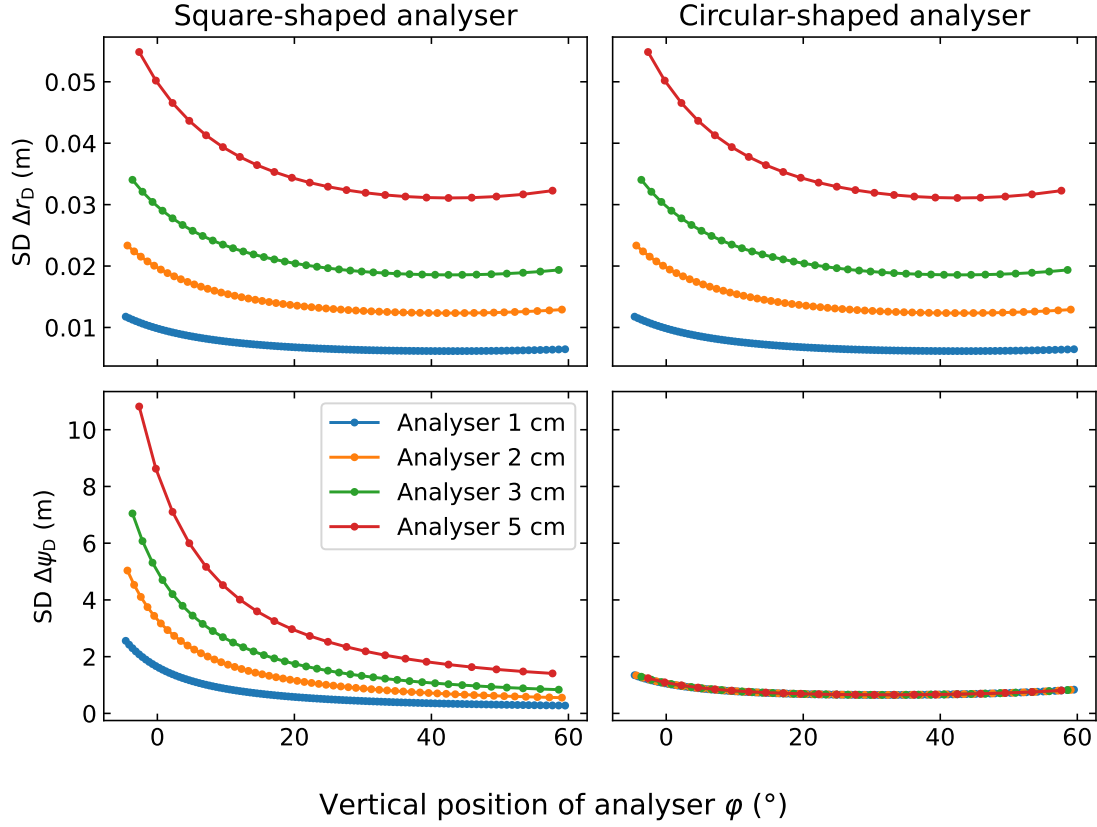


Figure 5.6: Radial Δr_D and angular $\Delta \psi_D$ spreads on the detector as a function of the vertical position φ (Sec. 1.3) of the analyser segment where a neutron is reflected, considering various sizes of a sample (same size in all three dimensions), analyser segments (a square shape) or rings (circular around the sample), and openings at the other focal point (the same size of radial opening as the analyser). The sizes of analyser segments are signified with colours in all panels.

5.6 McStas code for simulations

Following is the McStas code utilised for simulating the resolution of the Mushroom secondary spectrometer. A simulation was run for each segment of the analyser at the horizontal position ψ , where the other parameters for the simulation are generated by a Python program.

```

/*****
*
* Instrument: Mushroom.Secondary
*

```

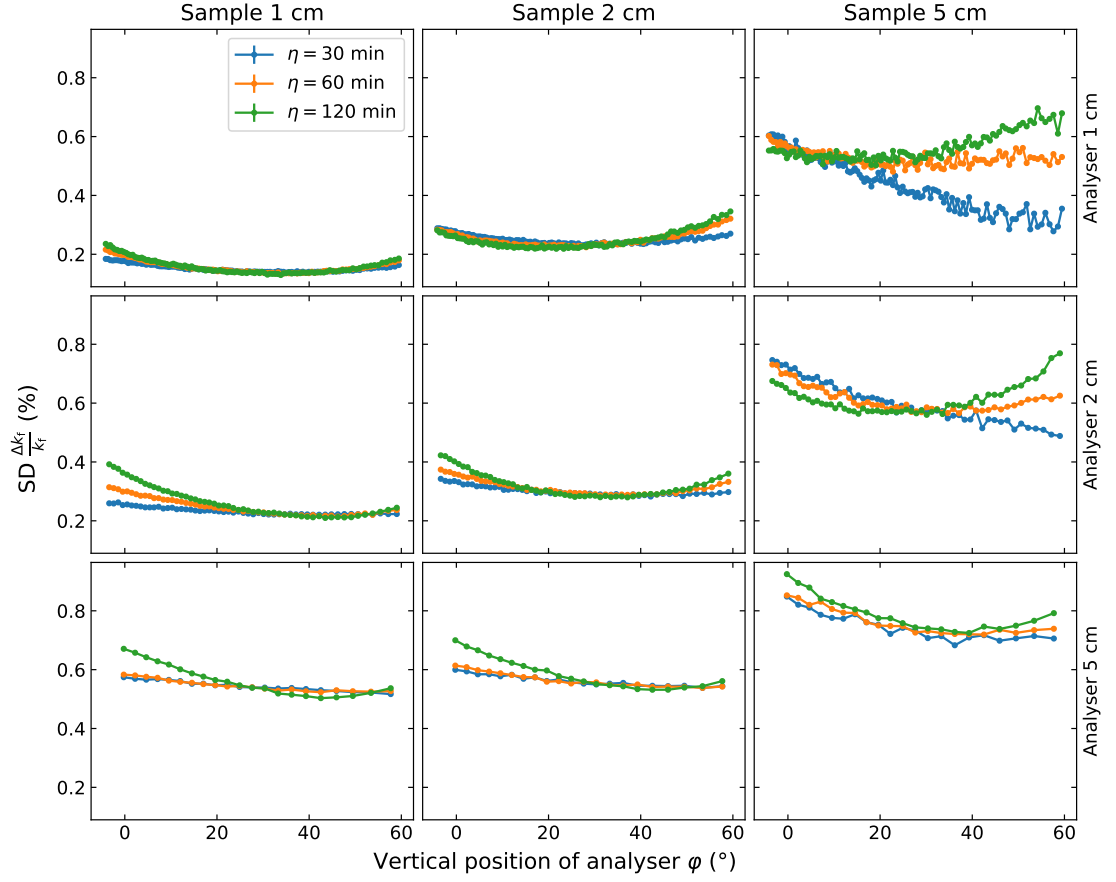


Figure 5.7: Resolution $\frac{\Delta k_f}{k_f}$ (equal to $\frac{\Delta \lambda_f}{\lambda_f}$) as a function of the vertical position φ of an analyser segment, simulated using McStas, considering the sample size $l_s = 1 \text{ cm}, 2 \text{ cm}, 5 \text{ cm}$ (labelled on the top), analyser size $l_A = l_F = 1 \text{ cm}, 2 \text{ cm}, 5 \text{ cm}$ (labelled on the right) and mosaicity of the analyser crystal $\eta_A = 30 \text{ min}, 60 \text{ min}, 120 \text{ min}$ (labelled in the legend).

* %Identification

* Written by: Ran Tang

* Date: Jan 2024

* Origin: FRM II

*

* %Parameters

* r_sa: [m] radius of sample

* A4: [deg] azimuthal angular position of the analyser segment

* AV: [deg] vertical angular position of the analyser segment

* mosaic: [min] mosaicity of the analyser

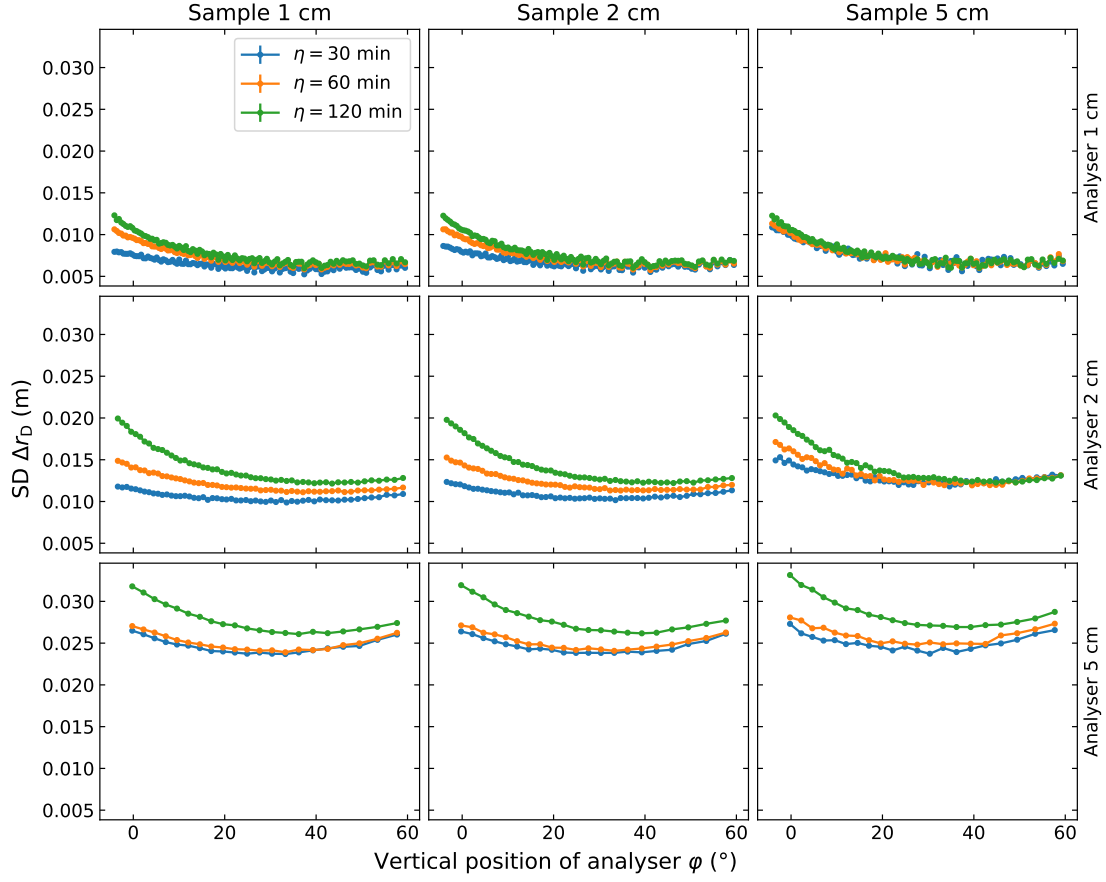


Figure 5.8: Resolution $\frac{\Delta k_f}{k_f}$ (equal to $\frac{\Delta \lambda_f}{\lambda_f}$) as a function of the vertical position φ of an analyser segment, simulated using McStas, considering the sample size $l_s = 1 \text{ cm}, 2 \text{ cm}, 5 \text{ cm}$ (labelled on the top), analyser size $l_A = l_F = 1 \text{ cm}, 2 \text{ cm}, 5 \text{ cm}$ (labelled on the right) and mosaicity of the analyser crystal $\eta_A = 30 \text{ min}, 60 \text{ min}, 120 \text{ min}$ (labelled in the legend).

* an.size: [m] size of analyser segment

* x, y, z: [m] coordinates of an analyser segment with regard to the arm

* a1, a2, a3: [deg] rotation angles of the segment

*****/

```
DEFINE INSTRUMENT Mushroom.Secondary(r_sa=0.005, A4=60, AV=60, mo-
saic=60, an.size=0.01, x=0.0, y=0.0, z=0.0, a1=0.0, a2=0.0, a3=0.0)
```

```
DECLARE
```

```
%{
```

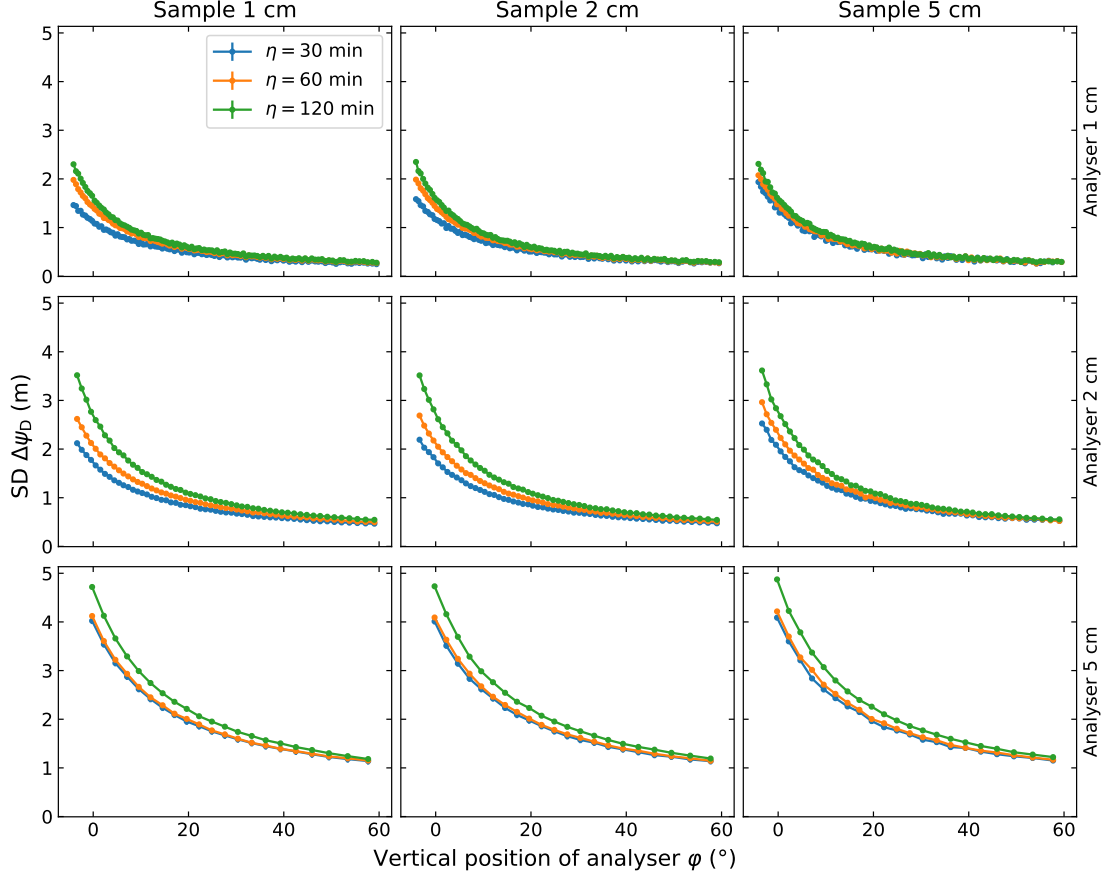


Figure 5.9: Resolution $\frac{\Delta k_f}{k_f}$ (equal to $\frac{\Delta \lambda_f}{\lambda_f}$) as a function of the vertical position φ of an analyser segment, simulated using McStas, considering the sample size $l_s = 1 \text{ cm}, 2 \text{ cm}, 5 \text{ cm}$ (labelled on the top), analyser size $l_A = l_F = 1 \text{ cm}, 2 \text{ cm}, 5 \text{ cm}$ (labelled on the right) and mosaicity of the analyser crystal $\eta_A = 30 \text{ min}, 60 \text{ min}, 120 \text{ min}$ (labelled in the legend).

```

const double h.d=1.24, r.d=1.35;
const double LATTICE_DISTANCE_PG002 = 3.355; // angstrom, the lattice distance of PG002
int nd; // number of bins in the flat PSD
double tx, ty, tz; // x, y and z components of the target
double ang-an; // angle for focusing onto the target
const double kf = 1.1; // wavenumber selected by the analyser
const double lambda=5.7, dlambda=1.0; // mean and half width of initial wavelength considered by the source
%}

```

```

INITIALIZE
%{
nd = r_d * 200;
tx = 1 * cos(DEG2RAD*AV) * sin(DEG2RAD*A4);
ty = 1 * sin(DEG2RAD*AV);
tz = 1 * cos(DEG2RAD*AV) * cos(DEG2RAD*A4);
ang_an = atan(an_size * 0.5 / (x*x+z*z)) * 2;
ang_an = RAD2DEG * ang_an;

printf("tx=%f, ty=%f, tz=%f, ang_an=%f
n",tx, ty, tz, ang_an);
printf("nd=%d
n", nd);
%}

```

TRACE

```

REMOVABLE COMPONENT arm = Progress_bar()
AT (0,0,0) ABSOLUTE
COMPONENT source_frm2_cold = Source_gen(
dist=10,
focus_xw=r_sa*2,
focus_yh=r_sa*2,
lambda0=lambda,
dlambda=dlambda,
T1=35.0, I1=9.38e12,
T2=547.5, I2=2.23e12,
T3=195.4, I3=1.26e13)
AT (0, 0, 0) RELATIVE arm

```

```

COMPONENT arm_sample_position = Arm()
AT (0, 0, 10) RELATIVE source_frm2_cold

```

```

COMPONENT incoherent = Incoherent(
radius=r_sa, yheight=0,
target_x=tx, target_y=ty, target_z=tz,
focus_aw=ang_an, focus_ah=ang_an)
AT (0, 0, 0) RELATIVE arm_sample_position
EXTEND %

```



```

if (!SCATTERED) ABSORB;
%

COMPONENT arm_sa = Arm()
AT (0, 0, 0) RELATIVE arm_sample_position
ROTATED (0, A4, 0) RELATIVE arm_sample_position

COMPONENT pg_an = Monochromator_flat(zwidth=an_size, yheight=an_size,
mosaich = mosaic, mosaicv = mosaic, DM = 3.355)
AT (x, y, z) RELATIVE arm_sa
ROTATED (a1, a2, a3) RELATIVE arm_sa

COMPONENT arm_flat = Arm()
AT (0, 0, 0) RELATIVE arm_sample_position
ROTATED (-90, 0, 0) RELATIVE arm_sample_position

COMPONENT arm_slit = Arm()
AT (0, 0, 0) RELATIVE arm_sa
ROTATED (-90, 0, 0) RELATIVE arm_sa

COMPONENT beamstop = Beamstop(
radius=0.8-an_size*0.5)
AT (0, 0, -0.4) RELATIVE arm_flat

COMPONENT slit = Slit(
radius=an_size*0.5)
AT (0, -0.8, -0.4) RELATIVE arm_slit

COMPONENT psd_flat = PSD_monitor(
nx=nd, ny=nd,
filename="psd_flat",
xwidth=r_d*2, yheight=r_d*2)
AT (0, 0, -h_d) RELATIVE arm_flat
ROTATED (0, 0, -90) RELATIVE arm_flat

COMPONENT l_flat = L_monitor(
nL=300, filename="l_flat",
xwidth=r_d*2, yheight=r_d*2,
Lmin=5.6, Lmax=5.8)
AT (0, 0, -h_d-1E-6) RELATIVE arm_flat

```

FINALLY

%{
%}

END

5.7 Coverage of Mushroom in momentum and energy space

The coverage in momentum and energy space at Mushroom is shown with varying options at primary and secondary spectrometers. The option with monochromator giving $k_i \in (1.03 \text{ \AA}^{-1}, 2.28 \text{ \AA}^{-1})$ is shown in Fig. 5.11 and 5.12, with the analyser orders pyrolytic graphite (PG) 002 and PG 004 in operation, respectively. The ToF option with $k_i \in (0.63 \text{ \AA}^{-1}, 6.28 \text{ \AA}^{-1})$, i.e. $\lambda_i \in (1 \text{ \AA}, 10 \text{ \AA})$, is shown in Fig. 5.10 and 1.31. The coordinate system corresponds to Fig. 1.10. The sample regardless of the orientation is rotated around the z-axis by 90° with 1° each step.

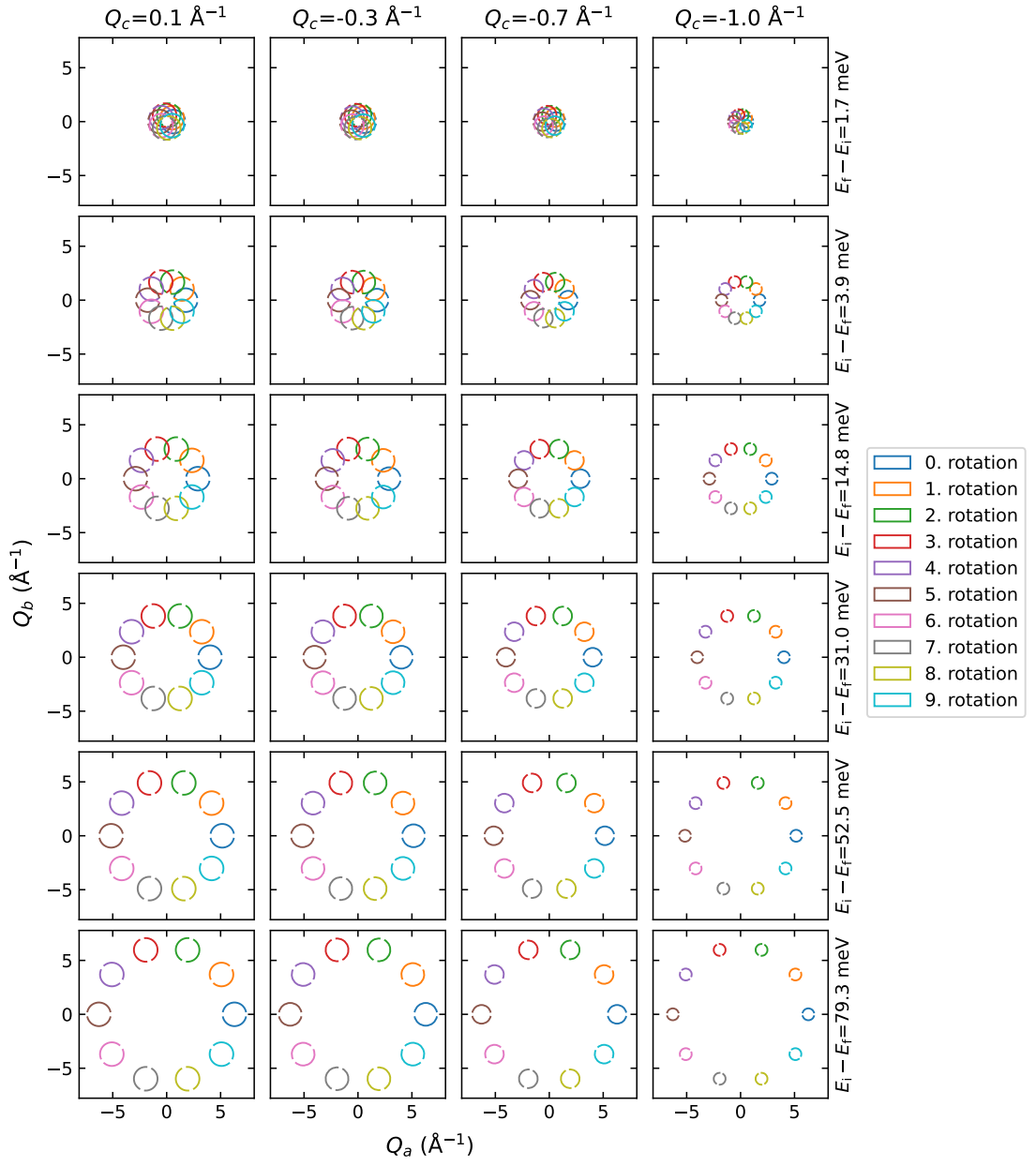


Figure 5.10: Accessible region in 4D ($\mathbf{Q}$, $\hbar\omega$) space where the primary spectrometer is equipped with the ToF option and the analyser has PG 002 order, i.e. $k_f = 1.1 \text{ \AA}^{-1}$.

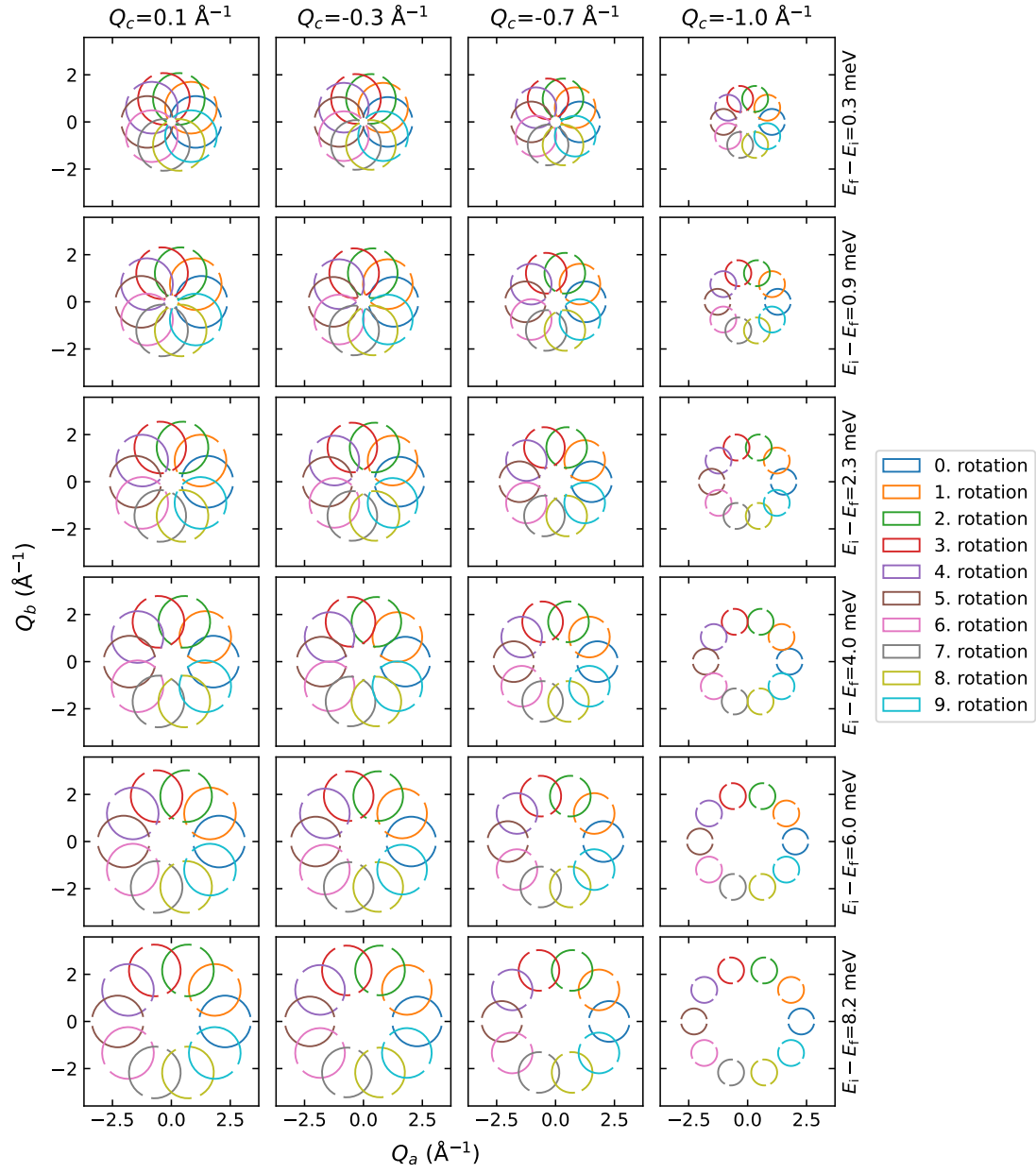


Figure 5.11: Accessible region in 4D ($\mathbf{Q}$, $\hbar\omega$) space where the primary spectrometer is equipped with the monochromator option and the analyser has PG 002 order, i.e. $k_f = 1.1 \text{ \AA}^{-1}$.

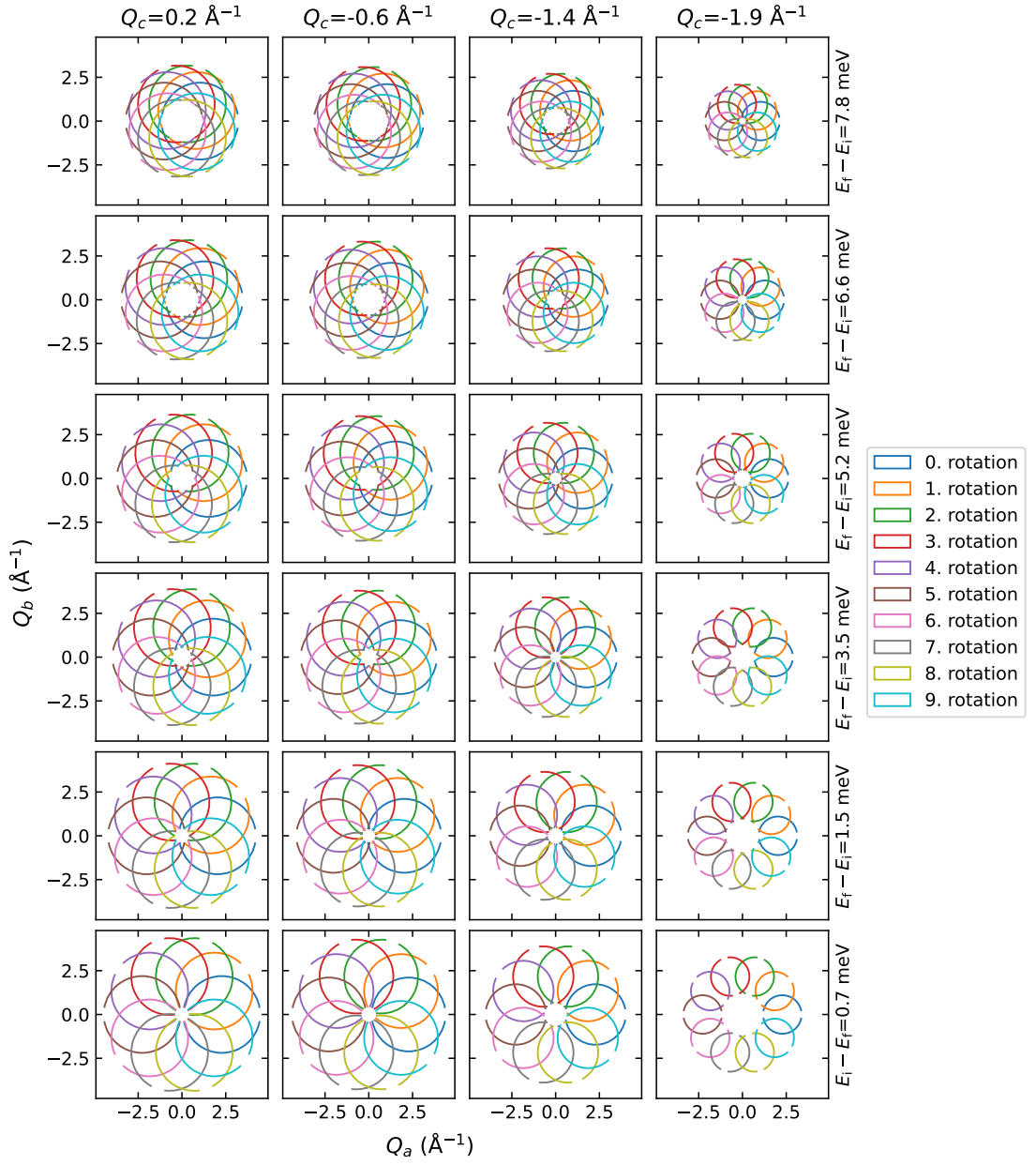


Figure 5.12: Accessible region in 4D ($\mathbf{Q}$, $\hbar\omega$) space where the primary spectrometer is equipped with the monochromator option and the analyser has PG 004 order, i.e. $k_f = 2.2 \text{ \AA}^{-1}$.

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