



Master Thesis in Physics

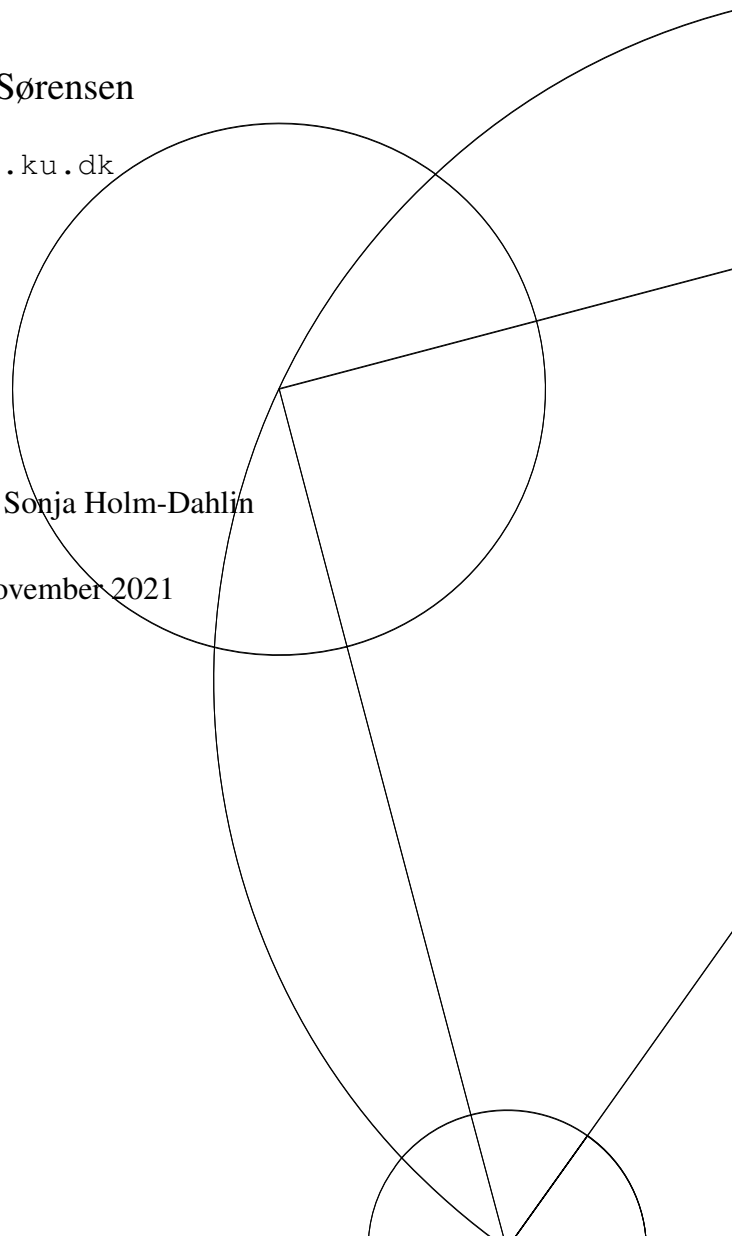
2D Quasi-Elastic Magnetic Scattering in Deuteronium Jarosite

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Abstract

In this master thesis the difference between the 3D long-range ordered frustrated kagomé antiferromagnet potassium jarosite and the disordered spin-glass deuterium jarosite is studied with the goal of gaining insight into why deuterium jarosite does not exhibit long-range 3D order. ^2H MAS NMR and PXRD were used to chemically characterise the samples. The deuterium sample was shown to have $95.1 \pm 1.3\%$ iron occupancy and less than ideal occupancy of the D_3O^+ -site. Susceptibility measurements were performed on deuterium jarosite and showed a spin-glass transition at 14 K. The magnetism of both compounds was examined with neutron scattering. Inelastic measurements were carried out on the Time-of-Flight spectrometer FOCUS at PSI, and neutron diffraction was performed at neutron diffractometer HRPT. Potassium jarosite was found to order magnetically and had a lifted zero-energy mode at ~ 7 meV. Deuterium jarosite showed no indication of magnetic Bragg peaks in data from both FOCUS and HRPT. Instead FOCUS measurements revealed dynamic 2D short range magnetic correlations with correlation length $\xi = 4.8 - 6.7$ Å below ≈ 0.8 meV. The centre of the scattering was found to reside between $Q = 1$ Å and $Q = 1.1$ Å, which is the Q -value of the first 3D magnetic peak in jarosites.

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1 | Introduction

In condensed matter and materials science the distinction between magnetically ordered and disordered materials is made. A special type of magnetic material is the frustrated magnet where the interactions in the system oppose each other in such a way as to prevent the materials from ordering at the temperature where it would otherwise be expected. This makes frustrated magnets interesting in the conversation about disorder, as their existence prompts the idea of low temperature disordered materials.

In this thesis we focus on a specific family of magnetically frustrated compounds: The jarosite minerals. The most common, naturally occurring jarosite has chemical formula $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$. It was first described already in the 19th century where it was found in mines in Baranco Jaroso in Spain. Since then jarosites have been frequently observed to precipitate from acidic, metal loaded waters associated with the mining industry,¹ as it forms in wet, oxidising and acidic environments. In 2004 it even gained mainstream fame as the Martian rover Opportunity discovered it at its landing site.² Recently interest in jarosite has been sparked anew, as it is a candidate material to exhibit magnon edge states.³

In nature the potassium ion in jarosite can be replaced by sodium and hydronium (H_3O^+), and many more types of artificial jarosites have been produced in laboratories all around the world (with for example NH_4^+ , Rb^+ or Ag^+ as the ion). Almost all of these different jarosites order magnetically when the temperature is cooled down to approximately 60 K. Hydronium jarosite, however, although chemically similar to the rest of the jarosites, behaves staggeringly differently; at low temperatures it enters a spin-glass phase, which is not an ordered phase of matter. The reason for this difference has not yet been found, but its solution could provide important insight into just how disorder is created.

This thesis does not answer the question "why is hydronium jarosite a spin-glass?", but it does offer an important contribution in the form of an in-depth analysis of magnetic scattering from a chemically well-characterised deuterium jarosite sample. The magnetic response was found to be quasi-elastic, short-ranged and two-dimensional in nature and emanate from the same position in Q -space where other jarosites show 3D long-range order.

2 | Introduction to Magnetism

On the door to the student library is a joke: Magnets are magnetic because they have little pieces of gravity still stuck inside them. This is of course utterly ridiculous, although humorous. The version I was taught in elementary school was a little better: Iron is magnetic because it has smaller magnets inside that line up next to each other with their poles all in the same direction. I found it rather strange that the explanation for what was, was just a smaller version of the same question. But conceptually it worked, and it neatly avoided the murky depths of quantum mechanics and the nature of the small magnets inside. Today I know the small magnets by a new name: spins, and I know magnetism is an entirely quantum mechanical phenomenon.

2.1 Basic magnetism

The two most basic types of magnetism are diamagnetism and paramagnetism. Diamagnetism is universally present and repulsive, meaning that if a magnetic field is applied, a magnetic moment opposite to the applied will be induced. The effect is usually small.⁴ Paramagnetism is the exact opposite: An applied field lines up the magnetic moments so they lie parallel to the field, making the overall field stronger.

You certainly cannot stick a diamagnet or paramagnet to your fridge. The fridge magnet is another type of magnet: A ferromagnet. The ferromagnet has a magnetic moment even without a magnetic field present; it is a part of its (using an elusive term) nature. The spontaneous moment is only present below a certain temperature; the transition temperature, T_C (C for Curie), where the system goes from a paramagnetic phase through a phase transition to an ordered phase with a net magnetic moment brought about due to the parallel alignment of spins.

A way to understand the quantum mechanical nature of spins and magnetism is to use a microscopic mathematical model; the simplest being the Ising Hamiltonian⁴

$$H = - \sum_{\langle ij \rangle} J_{ij} S_i^z \cdot S_j^z \quad (2.1)$$

The Hamiltonian is used to determine the energy of the system. J_{ij} is the coupling constant between two neighbouring spins i and j (determined by the overlap of the orbitals of spin i and spin j), and $\langle ij \rangle$ indicates that the sum is to be taken only over spins who are nearest neighbours (NN). In simple models J is taken to be the same for all neighbouring spins, and is therefore taken outside the sum. In case of the Ising model, i and j are only allowed to point either up or down (i.e. we are only considering the z -component of the spin). If the spins instead are regarded as three-dimensional vectors ($\mathbf{S}_i$ and $\mathbf{S}_j$) the Hamiltonian is known as the Heisenberg Hamiltonian.⁴

At low temperatures, nature likes to expend the least amount of energy possible. The lowest energy state, the ground state, depends on the sign of J . If $J > 0$ the lowest energy state will be the one where spins are parallel to each other; the ferromagnet (visualised on a square lattice in Figure 2.1a). If $J < 0$ the state with the lowest

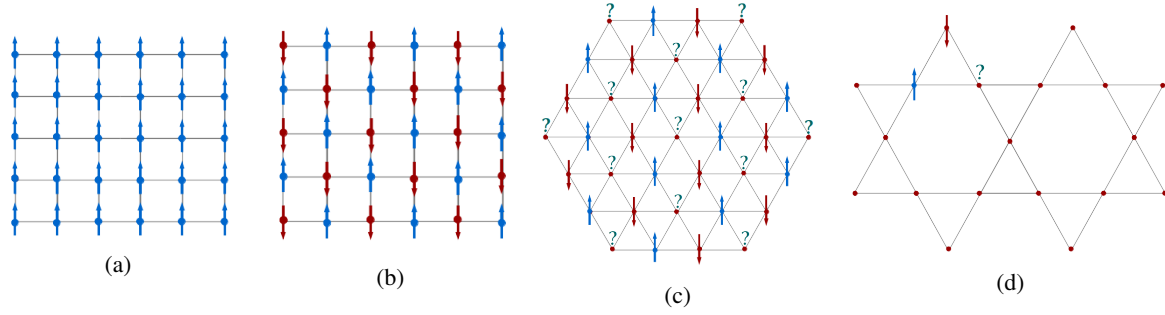


Figure 2.1: **(a)** Ferromagnetism on the square lattice **(b)** Antiferromagnetism on the square lattice **(c)** Wannier's solution on the triangular lattice **(d)** Frustration exemplified by antiferromagnetic coupling on the kagomé lattice. All illustrated spins are Ising spins.

energy will be the one where spins are antiparallel, known as an antiferromagnet (visualised on a square lattice in Figure 2.1b). The antiferromagnet also goes through a phase transition to an ordered phase. In this case it is however conventional to name the temperature T_N (the Néel temperature). By nature of the oppositely oriented spins, an antiferromagnet has no net magnetic moment.

The Hamiltonian can be made to encompass more complex situations by adding on terms from further interactions. If an applied magnetic field ($\mathbf{B}$) is present, the Zeeman term⁵

$$H_Z = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (2.2)$$

is added, where $\boldsymbol{\mu}$ is the magnetic moment of the spin in question. Other interactions relevant for the discussion of jarosites are the next-nearest neighbour (NNN) Heisenberg coupling, single-ion anisotropy (SIA) and the Dzyaloshinsky-Moriya (DM) interaction.

In the Heisenberg Hamiltonian all directions in the spin system (x , y and z) have the same coupling constant J ; the coupling is isotropic. If the coupling is somehow orientation dependent it is referred to as anisotropic. The anisotropy can come about due to crystal field effects, i.e. the surrounding atoms make it energetically favourable for a spin to lie along a particular crystalline direction; this is what is known as a single-ion anisotropy⁴ and the term in the Hamiltonian looks different depending on the system. For potassium jarosite the following two terms are added to the Heisenberg Hamiltonian⁶

$$H_{SIA} = -D \sum_i (S_i^x)^2 - E \sum_i [(S_i^x)^2 - (S_i^y)^2] \quad (2.3)$$

where E and D are anisotropy parameters and x' , y' and z' are axes in the crystal.

The Dzyaloshinsky-Moriya (DM) interaction is an interaction that can happen between two spins S_i and S_j if certain symmetry requirements are met in the crystal structure. It is an antisymmetric coupling and is introduced via the Hamiltonian

$$H_{DM} = \sum_{\langle ij \rangle} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$$

where $\mathbf{D}_{ij}$ is the DM-vector. The above expression was originally developed in 1958 by Dzyaloshinsky,⁷ who was trying to explain why some antiferromagnets (mainly α - Fe_2O_3) had a small ferromagnetic moment despite their

antiferromagnetic interactions. The solution to the mystery had to do with spin canting (spins making a small angle with the plane they are in, thus creating a small net moment), and the DM Hamiltonian above was exactly the term that favoured the canted structure above the antiferromagnetic one. In 1960 Moriya⁸ expanded on the theory by explaining how the interaction occurs and how to calculate $\mathbf{D}_{ij}$. The crystal symmetry is hugely important for the existence (or absence) of the DM interaction, and it furthermore is a deciding factor in the direction of the DM-vector. Moriya put down five rules, now known as Moriya's Rules, from which the main characteristics of the DM-vector can be deduced. In the list A and B are the positions of the two spins, and C is the midpoint of the line, AB , connecting them.

1. If an inversion centre is present in C , $\mathbf{D} = \mathbf{0}$
2. If a mirror plane perpendicular to AB goes through C , either $\mathbf{D} \parallel$ mirror plane, or $\mathbf{D} \perp AB$
3. If a mirror plane that includes A and B is present, $\mathbf{D} \perp$ mirror plane
4. If a twofold rotation axis goes through C and is perpendicular to AB , $\mathbf{D} \perp$ rotation axis
5. If there is an n -fold axis (with $n \geq 2$) along AB , $\mathbf{D} \parallel AB$

From the rules it is clear that if the symmetry of the crystal is very high the DM-interaction is not going to be present. Not having an inversion centre is however not a guarantee that the DM interaction is present in the compound, it just does not exclude the possibility. To be sure one either has to derive the interaction theoretically or observe it experimentally (ideally both).

The strength of the DM interaction is^{8,9}

$$|\mathbf{D}_{ij}| \propto \frac{\lambda t_{ij}^2}{\Delta U} \quad (2.4)$$

where t_{ij} is the intersite hopping, Δ is the crystal field splitting, U is the on-site Coulomb repulsion and λ is the coupling between spin angular momentum ($\mathbf{S}$) and orbital angular momentum ($\mathbf{L}$). $\mathbf{L}$ has its origin in the electrons orbiting the atom (creating an electric field that in turn produces a magnetic field), while $\mathbf{S}$ is the intrinsic spin of the electrons. The magnetic fields arising from the two different magnetic moments interact and give rise to the intrinsic spin-orbit interaction of form $\epsilon \mathbf{S} \cdot \mathbf{L}$, where ϵ is a constant.⁴ We will here not go through the formal theory of angular momentum, but it can be found in any introductory textbook on quantum mechanics (for example Griffiths).¹⁰

2.2 Frustrated magnetism and spin liquids

Spins are anthropomorphic entities; they can be fulfilled or 'frustrated' by their interactions with each other and their surroundings. A frustrated magnet is a system wherein the magnetic interactions make competing contributions to the energy that cannot be simultaneously satisfied.¹¹

One way frustration can come about is due to the interactions in the system being frustrated in and of themselves. The most common example of this type of frustration is spin-glasses, where frustrated interactions are created due to site disorder. Another very common type of frustrated magnetism is geometrically frustrated magnetism wherein the frustration is caused by the structure of the lattice itself;¹⁴ a macroscopic reason rather than a microscopic one. The reason for the frustration in the Ising case is illustrated on the kagomé lattice (Figure 2.1d); if two spins fulfil

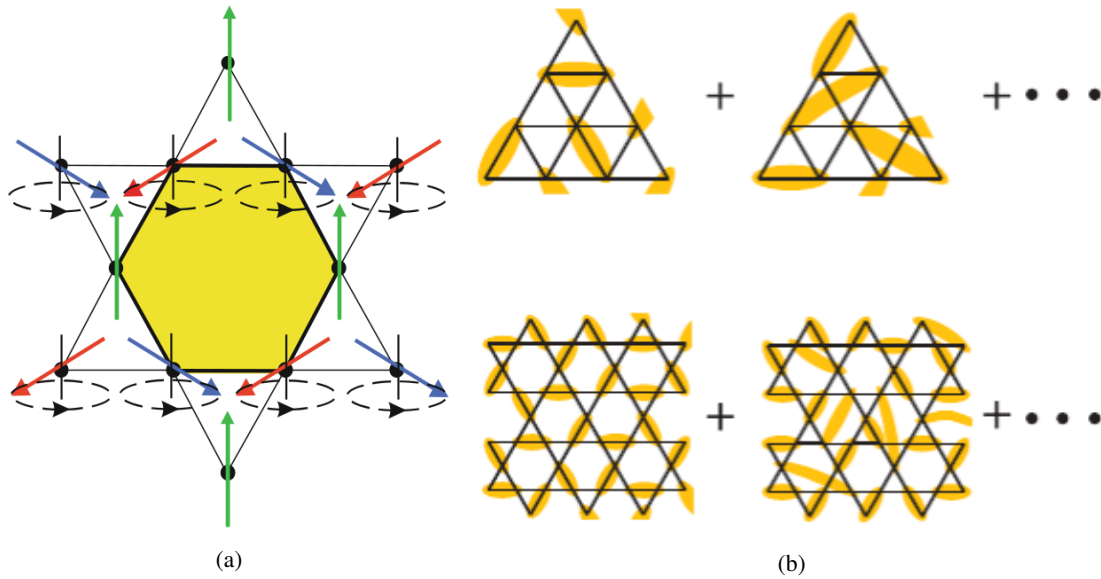


Figure 2.2: **(a)** Classical Heisenberg spins on the kagomé lattice. The red and blue spins can rotate freely around the axis of the green spins giving rise to zero energy excitations. The figure is from Mendels and Wills¹² **(b)** Singlet states (yellow slugs) on the triangular and kagomé lattice. A QSL in the RVB formulation is a linear superposition of all possible singlet states. The figure is adapted from Imai and Lee.¹³

their AFM coupling the last spin is left 'frustrated' about which way to turn. The latter type is the one we will focus on in this section. Spin-glasses will be described in chapter 4.

The prototype for geometric frustration was the Ising antiferromagnet on a triangular lattice (see Figure 2.1c) studied by Wannier in 1950;¹⁵ Wannier discovered that the model had a large ground state degeneracy, was disordered at all temperatures and had a finite entropy at absolute zero. It was later discovered that the model ordered if spins were allowed to be xy -spins instead of Ising spins into a structure with 120° between neighbouring spins.¹⁴ Another two-dimensional lattice that utilises triangular motifs is the kagomé lattice; where the triangular net is edge-sharing, the kagomé lattice is corner-sharing, resulting in fewer nearest-neighbours and more frustration. This creates a highly degenerate ground state as two spins (in the classical picture with Heisenberg spins) can rotate about the axis of the third with no energy cost.¹² These excitations are referred to as zero-energy excitations, or sometimes weathervane modes (in reference to the "spinning motion"). Such modes are visualised in Figure 2.2a. The low-cost excitations suppress T_N , limit the range of magnetic correlations, and may even fully prevent long-range order down to absolute zero.¹² The idea of an ever-fluctuating material has captured the hearts of scientists, and the study of highly frustrated materials have in part been led by the chase of the fabled "quantum spin liquid" (QSL); an elusive material that has quantum correlations and shows no long-range order down to absolute zero. Its existence was proposed by Anderson in 1973 as a "resonating valence bond" (RVB) state and further developed by Anderson and Fazekas in 1974.¹⁶ Anderson described the RVB state (on the triangular lattice) as a "fluid of mobile valence bonds, i.e. pairs of spins correlated together into singlets".¹⁷ The singlet pairs would perpetually break apart and be created anew with different spins included in the pairings; a QSL ground state would thus be a superposition of all possible pairings of singlets on the lattice.¹³ Such states are visualised for the triangular and the kagomé lattice in Figure 2.2b.

It is important for us to have an idea of the behaviour of the ground state and excitations of systems that do not

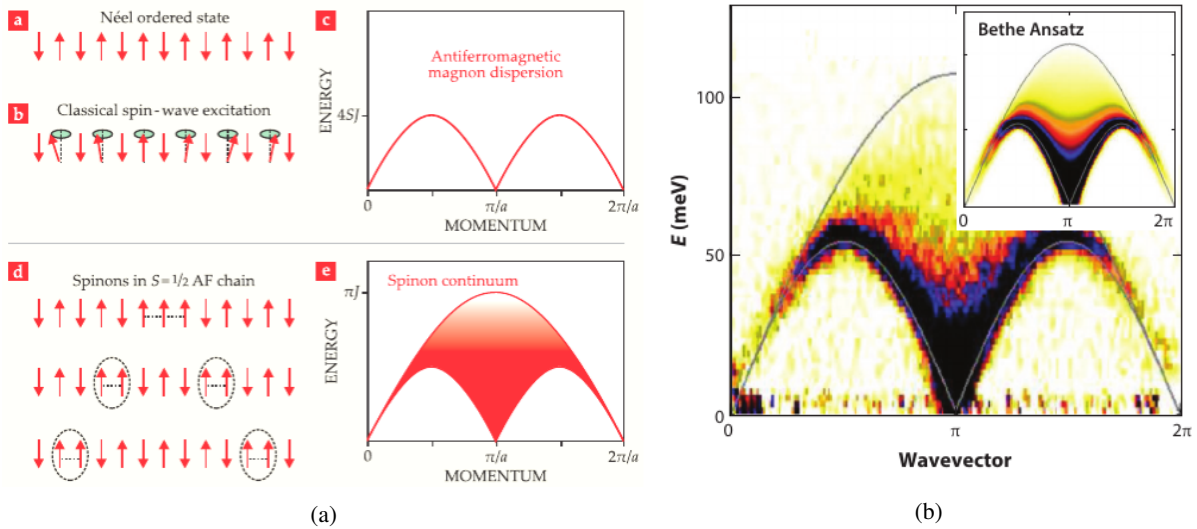


Figure 2.3: **(a)** Panels from Imai and Lee.¹³ The top three panels (a to c) show the ordered structure, low temperature excitations and dispersion relation in a 1D Néel ordered antiferromagnet. The bottom two panels (d and e) show spinons coupling together in singlets and moving around a 1D $S = \frac{1}{2}$ Ising chain and the continuous dispersion that results **(b)** (Almost) experimental realisation of the spinon continuum in $S = \frac{1}{2}$ Heisenberg chain material KCuF_3 compared with the Bethe ansatz. Figure is from Knolle and Moessner,¹⁸ based originally on Lake et al..¹⁹

undergo conventional phase transitions. For this reason we will give a short description of quantum spin liquid characteristics. First we need to iron out some terminology. "Spin liquids" exist both in a classical and a quantum version: The difference is found primarily in the nature of the fluctuations that keep the material from ordering. The classical spin liquid has $S > \frac{1}{2}$ and the fluctuations are thermal in nature and the material will eventually either order or the fluctuations will freeze.¹¹ A quantum spin liquid has $S \sim \frac{1}{2}$ and the fluctuations have a quantum nature; they are entangled (as described by the RVB state) and persist all the way down to $T = 0$ K¹¹ (or at least down to temperatures much smaller than the interaction scale of the system.¹⁸)

Evidence for QSL's is hard to come by as their definition is built on absences. It is possible for us to (indirectly) measure phase transitions, as compounds distinctly change their properties before and after the transition, and as we shall see in section 3.1 phase transitions also show up as sharp features in for example the susceptibility. In the case of QSL's no symmetries are broken, and no phase transition takes place,¹³ so the usual ways of detection cannot be used. QSL's do however have a very distinct property that one can look for by using the method of inelastic neutron scattering (described in detail in section 3.2): Fractionalised excitations. The description of fractionalised excitations we will give here builds heavily on the one in Imai and Lee.¹³ Fractionalised excitations are most easily described on the one-dimensional $S = \frac{1}{2}$ AFM chain, while keeping in mind the way a conventional AFM works.

For a one-dimensional Néel ordered antiferromagnet the ground state is the one where all spins are antiparallel to their neighbours. The low-energy excited states are known as spin-waves and span the entire lattice. One quantum of excitation is denoted a magnon (a boson; i.e. it has an integer value). The ordered Néel state and one side of the spin-wave as well as the magnon dispersion relation is shown in the top panel of Figure 2.3a. The bottom panel of Figure 2.3a shows the situation in the case where singlet states, like in a RVB state, are energetically favourable. This system was shown by Hans Bethe not to have Néel order already in 1931;²⁰ instead it has short-ranged AFM correlations. The low-energy excitations in this case are different; the $S = 1$ of excitation is carried by two $S = \frac{1}{2}$

spinons, and we can think of the magnon as having fractionalised into these spinons. In this situation one flipped spin in the perfect antiparallel state results in two unsatisfied bonds that can propagate freely through the system and act as domain boundaries between short-range ordered AFM regions. For this reason the allowed energies for spinons form a continuum rather than the well-defined modes in the magnon dispersion.¹³ The realisation of this 1D QSL almost exists in the fractionalised $S = \frac{1}{2}$ Heisenberg chain KCuF_3 , whose excitation spectrum is very close to the theoretical Bethe ansatz¹⁹ (see Figure 2.3b). There, however, still exists residual coupling between the chains, which leads to a transition to an ordered 3D magnet.¹⁸

The coupling between chains prevent strict 1D behaviour and is a prime example of how real materials often are much more complex than theoretical predictions can account for; a fact that keeps the search for all sorts of frustrated magnets and spin liquids alive today.

3 | Instrumental Theory

This chapter will serve to introduce the varied instrumental methods that have been used to characterise jarosites in this project. We will cover in some detail both general theory for the method in question as well as the specific instruments used in data acquisition.

3.1 Susceptibility

When we talk about the magnetisation of a compound we do not talk about the individual magnetic moments, we look at the bulk properties. I.e. $\mathbf{M}$ is the magnetic moment per unit volume. If the relation between the applied field $\mathbf{B}$ and the magnetisation is a linear one, we have⁴

$$\mathbf{M} = \chi \mathbf{B} \quad (3.1)$$

where the proportionality constant, χ , is the magnetic susceptibility. The role of the susceptibility is then to tell us how much magnetic moment is induced by a magnetic field (per unit volume). This is a very simple way to distinguish between a paramagnet and a diamagnet: If diamagnetism dominates $\chi < 0$, since diamagnetism gives an induced magnetism opposite to the applied field. If paramagnetism dominates $\chi > 0$.

When the temperature is far from the ordering temperature (i.e. $T \gg T_C$) the susceptibility can be described by the Curie-Weiss law⁴

$$\chi = \frac{C}{T - \theta_{CW}} \quad (3.2)$$

The constant C is the Curie constant; a material dependent parameter. θ_{CW} is the Curie-Weiss temperature. Both are measured in kelvin, such that the susceptibility is a unitless quantity. The namesakes are Pierre Curie and Pierre-Ernest Weiss, and the constants are given by⁴

$$C = \frac{\mu_B g^2 S(S+1)}{3k_B} \quad (3.3)$$

$$\theta_{CW} = 2 \sum_i J_{0,i} \frac{S(S+1)}{3k_B} = \frac{2zJS(S+1)}{3k_B} \quad (3.4)$$

Introducing yet more constants: μ_B is the Bohr magneton, or, the magnetic moment of one electron due to its spin or orbital angular momentum, S is the value of the spin and k_B is the Boltzmann constant. The last equality in Equation 3.4 is a simplification of the sum in the case where only nearest neighbour interactions are considered. The number of nearest neighbours is denoted z .

The magnitude and sign of θ_{CW} can be used to distinguish between different types of magnets. In a paramagnet the magnetic susceptibility is inversely proportional to the temperature and $\theta_{CW} = 0$. This simpler version of the law is known as Curie's law. If $\theta_{CW} > 0$ the material is ferromagnetic and if $\theta_{CW} < 0$ we have an antiferromagnet. The Curie-Weiss temperature is expected to be equal to the unfrustrated ordering temperature, i.e. $+T_C$ or $-T_N$ in the two cases.⁴

Sometimes the Curie-Weiss temperature is far from the actual ordering temperature. The paramagnetic, disordered phase persists at much lower temperatures than would be expected; this is one of the trademarks of frustration. Comparison of the Curie-Weiss temperature and the actual ordering temperature gives us a way to compute the degree of frustration in a system. This measure is due to Ramirez¹⁴

$$f = -\frac{\theta_{CW}}{T_N} \quad (3.5)$$

In statistical mechanics the susceptibility would be represented as the derivative of the magnetisation $\chi = \partial M / \partial B$, where the magnetisation is given by⁴

$$M = -\left(\frac{\partial F}{\partial B}\right)_{T,V} = Nk_B T \left(\frac{\partial \ln Z}{\partial B}\right)_{T,V} \quad (3.6)$$

Here F is the Hemholtz free energy and Z is the partition function (from German Zustandssumme). The subscripts denote the parameters to be kept constant (temperature and volume). This relation is important to keep in mind when we look at phase transitions, a discontinuity or other types of anomalous behaviour in the susceptibility curve can tell us that something is happening in the sample at that temperature. A discontinuity in the susceptibility curve is a discontinuity in the second derivative of the free energy, and is therefore termed a second order phase transition. Similarly a discontinuity in the magnetism gives us knowledge about a first order phase transition.⁴ This method of detecting phase transitions is only indirect, as we cannot tell precisely what is going on inside the sample.

3.1.1 DC and AC susceptibility

Two types of susceptibility measurements that are often met in the experimentalist's world are the DC and AC susceptibilities.

When performing a DC susceptibility measurement M is measured for an applied DC field (B_{DC}). One can change the value of this field to get M as a function of field or keep the field constant to study how the magnetisation at the applied field changes with temperature. The magnetic moment in this type of measurement does not change with time, and the susceptibility is therefore also called the static susceptibility.

When performing an AC susceptibility measurement M is measured in an AC field (B_{AC}), which is frequency dependent. The fluctuating field makes the magnetisation time dependent and makes it possible to investigate the dynamics of the magnetisation. The AC susceptibility is defined as the derivative of the magnetisation with respect to the driving field; $\chi_{AC} = dM/dB_{AC}$ (at a given frequency of the field).

3.2 Neutron Scattering Theory

The following sections are based heavily on the treatment of neutron theory in "Introduction to the Theory of Thermal Neutron Scattering" by G. L. Squires²¹ and the lecture notes for the neutron scattering course at Copenhagen University taught and written by Kim Lefmann.⁵

The neutron is a little, wonderfully useful spin $\frac{1}{2}$ -particle. When used for scattering, it can help us gain insight into both structure and dynamics of many types of samples.

Neutrons have wavelengths similar to inter-atomic distances in solids, which allows for characterisation of the atomic structure; in experiments the most typically used neutrons are "cold" or "thermal" neutrons. This means they have wavelengths $\lambda = 2.4 - 40 \text{ \AA}$ (corresponding to energy $E = 0.05 - 14 \text{ meV}$) and $\lambda = 0.6 - 2.4 \text{ \AA}$ (corresponding to energy $E = 14 - 200 \text{ meV}$).⁵ As an added bonus this energy range is well suited to a study of the elementary excitations in solids and provides us with a way to determine for example the dispersion relations of excitations.⁵

The arguably coolest feature of the neutron is its magnetic moment, $\mu = \gamma\mu_N$, which is coupled antiparallel to its spin. Here $\gamma = -1.913$ is the neutron gyromagnetic ratio and $\mu_N = e\hbar/(2m_p) = 5.051 \cdot 10^{-27} \text{ J/T}$ (m_p is the proton mass) is the nuclear magneton. Due to its magnetic moment, the neutron scatters from magnetic structures in the sample, providing a window into the magnetic ordering (or lack thereof) in the sample under investigation.

In a study such as this, this is very valuable indeed!

3.2.1 General concepts

As all of nature's smallest things, the neutron is affected by quantum mechanics and thus by the particle-wave duality of matter. When neutrons scatter in experiments they behave as waves, and are described by their wavenumber, $k = 2\pi/\lambda$ (where λ is the de-Broglie wavelength) and corresponding wave vector, $\mathbf{k} = m_n\mathbf{v}/\hbar$ (where m_n is the neutron mass and $\mathbf{v}$ is the velocity). A typical setup for a scattering experiment can be found in Figure 3.1a.

The neutron comes into the experiment and hits the sample with wavevector $\mathbf{k}_i$, scatters from the sample with scattering angle 2θ and emerges with scattering vector $\mathbf{k}_f$. Subtracting the final from the initial wavevector yields the scattering vector $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$, visualised in Figure 3.1b.

Scattering can happen either from nuclear or magnetic structures. These concepts will be covered in subsection 3.2.2 and subsection 3.2.3, respectively. In both types of scattering, however, yet another subdivision can be made: Elastic and inelastic scattering. In elastic scattering the neutron does not exchange energy with the sample and $E_i = E_f$. In inelastic scattering energy is exchanged, and the energy change is defined by $\hbar\omega = E_i - E_f$.⁵

Before moving on to nuclear and magnetic scattering we need to introduce another important concept: The neutron scattering cross section, which is a measure of the system's ability to scatter neutrons.⁵ It is the cross section we measure in an actual neutron scattering experiment. For inelastic scattering it is given by the *partial differential cross section*, which takes into account both the energy and angular dependence of the scattered neutrons²¹

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\text{(number of neutrons scattered per second into a small solid angle } d\Omega \text{ in the direction } \theta, \phi \text{ with final energy between } E_f \text{ and } E_f + dE_f)}{\Phi d\Omega dE_f} \quad (3.7)$$

where Φ is the flux of incoming neutrons (neutron rate per area), which is instrument dependent. To get the total cross section the integral is taken over final energies E_f and solid angles $d\Omega$ (see the cone in Figure 3.1a)

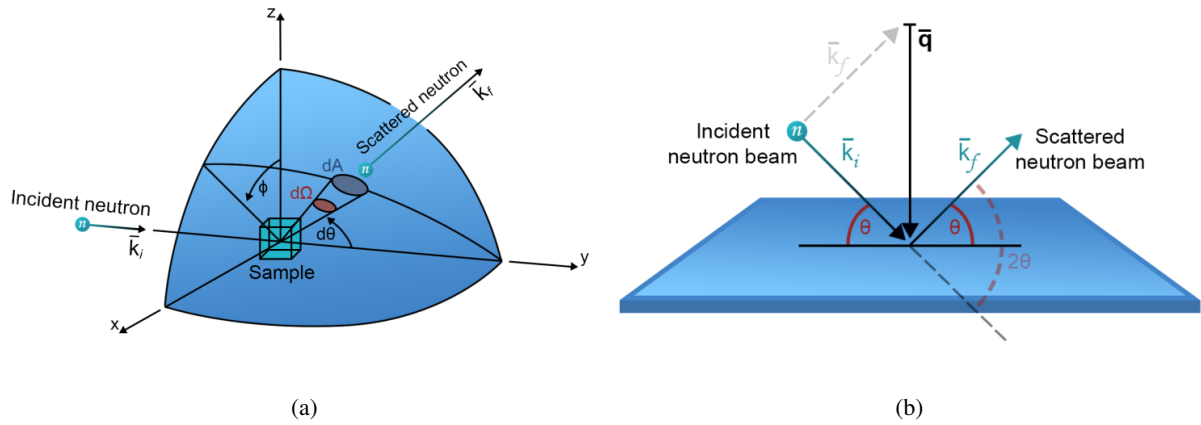


Figure 3.1: **(a)** General neutron scattering experiment. Incident neutrons enter the experiment with $\vec{k}_i$, scatter from the sample into a solid angle $d\Omega$ and emerge with $\vec{k}_f$. **(b)** Definition of the scattering vector $\vec{q}$ from incoming and outgoing neutron momenta. Both figures are from Lefmann.⁵

$$\sigma_{inel} = \int \int \frac{d^2\sigma}{d\Omega dE_f} d\Omega dE_f \quad (3.8)$$

For elastic scattering the spread in final energies need not be considered, and hence we use the *differential cross section*, which only considers the angular dependence of scattered neutrons²¹

$$\frac{d\sigma}{d\Omega} = (\text{number of neutrons scattered per second into } d\Omega \text{ in the direction } \theta, \phi) / \Phi d\Omega \quad (3.9)$$

3.2.2 Nuclear scattering

Nuclear scattering cross section

For the sake of brevity, detailed derivations related to basic neutron scattering theory have been excluded; here we only give an outline of the steps needed as well as important results. The interested reader can find the details in any textbook about neutron scattering. An example can be found in Squires (1978).²¹

The basic equations of nuclear scattering theory can be derived using either semi-classical wave theory or just plain quantum mechanics. The goal is to develop an expression for the cross section mentioned above. In the quantum mechanical treatment the neutron is identified only by its momentum (the wavevector $\vec{k}$) and its appertaining wavefunction, assumed to be a normalised plane wave state, ignoring spin. It interacts with the system, which is described by the parameter λ and corresponding wavefunction, through the potential operator $\hat{V}$ (to be specified). The process is seen as a transition from an initial state $|\vec{k}_i, \lambda_i\rangle$ to a final state $|\vec{k}_f, \lambda_f\rangle$ and the rate can therefore be calculated using Fermi's Golden rule. Using this, and accounting for energy conservation, the partial differential nuclear cross section can be written as

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\lambda_i \rightarrow \lambda_f} = Y^2 \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2} \right)^2 |\langle \vec{k}_f, \lambda_f | \hat{V} | \vec{k}_i, \lambda_i \rangle|^2 \delta(E_{\lambda_i} - E_{\lambda_f} + E_i - E_f) \quad (3.10)$$

E_i and E_f refer to the initial and final energies of the neutron, and E_{λ_i} and E_{λ_f} are the initial and final energies of the system. Y is a normalisation constant that will disappear from the final equation as the matrix element is evaluated. The actual potential for the interaction between neutron and nuclei is complicated and it is therefore customary to use the Fermi pseudopotential, although this is not fully physically correct. For a system of particles the potential is

$$\hat{V} = \frac{2\pi\hbar^2}{m_n} \sum_j b_j \delta(\mathbf{r} - \mathbf{R}_j) \quad (3.11)$$

Here $\mathbf{R}_j$ is the position of the, assumed stationary, j 'th nucleus and $\mathbf{r}$ is the position of the neutron. b_j is an important quantity known as the (nuclear, bound) scattering length, which has a characteristic value for each isotope. Inserting the potential from equation Equation 3.11 into Equation 3.10 and calculating the matrix element gives

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\lambda_i \rightarrow \lambda_f} = \frac{k_f}{k_i} \left| \sum_j b_j \langle \lambda_f | e^{i\mathbf{q} \cdot \mathbf{R}_j} | \lambda_i \rangle \right|^2 \delta(E_{\lambda_i} - E_{\lambda_f} + E_i - E_f) \quad (3.12)$$

In a real experiment we are not looking at a specific transition from state $|\lambda_i\rangle \rightarrow |\lambda_f\rangle$, hence we need to sum over all final states. By furthermore rewriting the δ -function to its corresponding Fourier transformed exponential function and changing to the Heisenberg picture (shifting the time dependence onto the operators) the partial differential cross section can be divided into two parts; The coherent and the incoherent partial differential scattering cross sections

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{coh} = \frac{\sigma_{coh}}{4\pi} \frac{k_f}{k_i} \frac{1}{2\pi\hbar} \sum_{jj'} \int_{-\infty}^{\infty} dt \quad e^{-i\omega t} \langle e^{-i\mathbf{q} \cdot \mathbf{R}_{j'}(0)} e^{-i\mathbf{q} \cdot \mathbf{R}_j(t)} \rangle \quad (3.13)$$

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{inc} = \frac{\sigma_{inc}}{4\pi} \frac{k_f}{k_i} \frac{1}{2\pi\hbar} \sum_j \int_{-\infty}^{\infty} dt \quad e^{-i\omega t} \langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{-i\mathbf{q} \cdot \mathbf{R}_j(t)} \rangle \quad (3.14)$$

$\sigma_{coh} = 4\pi(\bar{b})^2$ (where the bar denotes an average) and $\sigma_{inc} = 4\pi[\bar{b}^2 - (\bar{b})^2]$. The coherent part of the scattering cross section is the part of the scattering signal that deals with the interference effects that provides us with information about the going-ons in our sample. The incoherent scattering contribution, on the other hand, is a scattering in all angles, it is caused by for example spin effects, isotopic mixture or chemical randomness.⁵ Hydrogen is the element with the largest incoherent scattering cross section ($\sigma_{inc} = 80.27 \cdot 10^{-28} \text{ m}^2$). Deuterium has a much smaller incoherent cross section ($\sigma_{inc} = 2.05 \cdot 10^{-28} \text{ m}^2$). For this reason the jarosite samples will be made with deuterium instead of hydrogen.

Nuclear scattering from crystals

The cross sections in the previous section can be calculated in the case where the sample in question is a crystal. For this reason we will have a brief overview of important concepts in crystal theory.

A lattice can be divided up into small repeating motifs denoted unit cells. The dimensions of the unit cell are described by the lattice vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ and the angles α (between $\mathbf{b}$ and $\mathbf{c}$), β (between $\mathbf{c}$ and $\mathbf{a}$) and γ (between $\mathbf{a}$ and $\mathbf{b}$). The lengths of the lattice vectors are known as the lattice constants a , b and c , and the volume of the unit cell can be determined as $V_0 = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$. The position of a lattice point j is described by the real space lattice vector $\mathbf{r}_j = n_j^a \mathbf{a} + n_j^b \mathbf{b} + n_j^c \mathbf{c}$

The reciprocal lattice is described by the reciprocal lattice vectors:

$$\mathbf{a}^* = \frac{2\pi}{V_0} \mathbf{b} \times \mathbf{c} \quad \mathbf{b}^* = \frac{2\pi}{V_0} \mathbf{c} \times \mathbf{a} \quad \mathbf{c}^* = \frac{2\pi}{V_0} \mathbf{a} \times \mathbf{b} \quad (3.15)$$

A general reciprocal lattice point is given by these three vectors along with the Miller indices h, k and l .

$$\boldsymbol{\tau}_{hkl} = h\mathbf{a}^* + l\mathbf{b}^* + l\mathbf{c}^* \quad (3.16)$$

When considering an actual crystal, we can no longer assume the nuclei to be stationary in space. Instead the position of each nucleus is described by its displacement ($\mathbf{u}_j(t)$) from equilibrium, hence the position of nucleus j is

$$\mathbf{R}_j(t) = \mathbf{r}_j + \mathbf{u}_j(t)$$

In a Bravais crystal (one atom per unit cell) the situation is particularly simple; since all atoms are the same and the structure is periodic, only the distance between nuclei plays a role. This allows us to carry out the sum over index j in Equation 3.13 and Equation 3.14 (introduces a factor N). Defining

$$U = -i\mathbf{q} \cdot \mathbf{u}_0(0) \quad \text{and} \quad K = i\mathbf{q} \cdot \mathbf{u}_j(t) \quad \text{and} \quad K_0 = i\mathbf{q} \cdot \mathbf{u}_0(t)$$

allows us to write the coherent and incoherent cross sections for a Bravais crystal as

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{coh} = \frac{\sigma_{coh}}{4\pi} \frac{k_f}{k_i} \frac{N}{2\pi\hbar} e^{\langle U^2 \rangle} \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \int_{-\infty}^{\infty} dt \quad e^{-i\omega t} e^{\langle UK \rangle} \quad (3.17)$$

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{inc} = \frac{\sigma_{inc}}{4\pi} \frac{k_f}{k_i} \frac{N}{2\pi\hbar} e^{\langle U^2 \rangle} \int_{-\infty}^{\infty} dt \quad e^{-i\omega t} e^{\langle UK_0 \rangle} \quad (3.18)$$

Beginning with the coherent cross section, we expand the exponential function in a Taylor expansion

$$e^{\langle UK \rangle} = 1 + \langle UK \rangle + \frac{1}{2!} \langle UK \rangle^2 + \dots + \frac{1}{p!} \langle UK \rangle^p \quad (3.19)$$

This expansion is known as the *phonon expansion* and describes the different possible scattering processes. A crystal containing N atoms have $3N$ vibrational modes (normal modes, described in the idealised case by harmonic oscillators). The oscillators are quantum mechanical in nature, and are hence described by a quantum number each. Depending on how many quantum numbers are changed by the scattering process we have an elastic, one-phonon or multi-phonon process. All multi-phonon processes just add to the incoherent background, and we will therefore not describe them in detail here.

Coherent scattering: Elastic processes - Diffraction

If all quantum numbers for all $3N$ oscillators are unchanged, corresponding to $\exp(\langle UV \rangle) = 1$ in Equation 3.17, the scattering process is an elastic process ($k_i = k_f$). This type of scattering is also called *diffraction*, a process well known from X-ray scattering. Inserting 1 in Equation 3.17 and carrying out the integration over time as well as the integration over final energies yields

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh,el}^{Bravais} = \frac{\sigma_{coh}}{4\pi} N \frac{(2\pi)^3}{V_0} e^{-2W} \sum_{\boldsymbol{\tau}} \delta(\mathbf{q} - \boldsymbol{\tau}) \quad (3.20)$$

where $\exp(-2W) = \exp(-\langle U^2 \rangle)$ is the *Debye-Waller factor*, which has to do with the displacement of nuclei in the system (from the definition of U). Since the displacement $\mathbf{u}_j$ is small but non-zero at low temperature the Debye-Waller factor is always smaller than, but often close to, one. From the δ -function we can conclude that not all values of the scattering vector $\mathbf{q}$ results in scattering. Only when the scattering vector is equal to a reciprocal lattice vector, scattering is observed

$$\mathbf{q} = \boldsymbol{\tau} = \mathbf{k}_i - \mathbf{k}_f \quad (3.21)$$

This formulation of the scattering requirement is known as the *Laue condition*. By observing that $|\mathbf{q}| = 2|k| \sin \theta$ (where $k = k_i = k_f$ in an elastic process) one can show that it is equivalent to the well-known Bragg law

$$n\lambda = 2d \sin(\theta) \quad (3.22)$$

where d is the distance between lattice planes, λ is the wavelength of the neutrons and θ is half the scattering angle. The lattice spacing can be expressed in terms of the Miller indices as

$$d_{hkl} = \frac{2\pi}{|\boldsymbol{\tau}_{hkl}|} \quad (3.23)$$

The scattering requirement still holds for a non-Bravais crystal, but $\sigma_{coh}/(4\pi)$ in the intensity is multiplied by a factor $|F_N(\mathbf{q})|^2$, where $F_N(\mathbf{q})$ is denoted the *nuclear structure factor*. In this more general case the coherent elastic scattering cross section is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh,el}^{Non-Bravais} = N \frac{(2\pi)^3}{V_0} e^{-2W} \sum_{\boldsymbol{\tau}} \delta(\mathbf{q} - \boldsymbol{\tau}) |F_N(\mathbf{q})|^2 \quad (3.24)$$

where

$$F_N(\mathbf{q}) = \sum_i b_i e^{i\mathbf{q} \cdot \mathbf{\Delta}_i} \quad (3.25)$$

and $\mathbf{\Delta}_i$ is the position of atom i in the unit cell. This is the final expression for nuclear scattering from a crystal. The nuclear structure factor has important implications for the final diffraction pattern; sometimes no neutrons are scattered even when the Laue condition is fulfilled, this has to do with certain reflections being 'forbidden' by the structure factor, i.e. for some $\mathbf{q}$, $|F_N(\mathbf{q})|^2 = 0$.

In a real experiment the peaks are not δ -functions; they are broadened due to instrumental resolution and mosaic spread in the crystal sample. What we actually measure is then the total cross section, i.e. the differential cross section above summed over all directions. For a powdered sample all crystal directions are present in the sample at the same time, hence when a monochromatic beam of neutrons (or X-rays) with wavevector $\mathbf{k}_i$ hits the sample the scattering will happen in a cone of different $\mathbf{k}_f$'s (visualised in Figure 3.2). The famous cone is the Debye-Scherrer cone, and the integrated intensity recorded by a detector a distance r away is given by²¹

$$I = \Phi \frac{d}{2\pi r \sin(\theta)} \frac{N}{V_0} \frac{\lambda^3}{4 \sin(\frac{1}{2}\theta)} e^{-2W} |F_N(\boldsymbol{\tau})|^2 \quad (3.26)$$

Using the emerging diffraction pattern one can elucidate the crystal structure, lattice parameters and atomic posi-

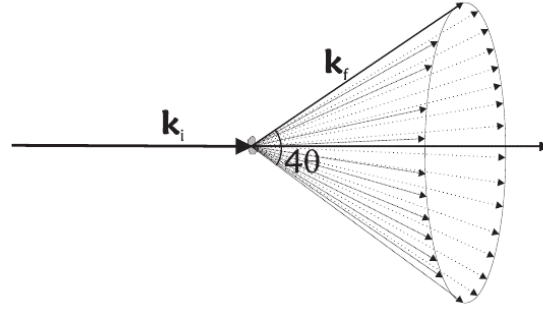


Figure 3.2: Debye-Scherrer cone resulting from a powder diffraction experiment (with either X-rays or neutrons). The figure is from Lefmann.⁵

tions of the compound under scrutiny. For this characterisation the contributions from the different crystal directions need to be separated; a process that can be carried out using the process of Rietveld refinement.

Coherent scattering: One-phonon processes

If all quantum numbers for the $3N$ oscillators are unchanged, except for one that changes its value with ± 1 , corresponding to $\exp(\langle UK \rangle) = \langle UK \rangle$ in Equation 3.17, the scattering process is a one-phonon process. We have now entered the realm of inelastic neutron scattering and the dynamics of lattice vibrations. We will however not be going over the details of the quantum mechanical calculation of the matrix element (details can be found in Squires.²¹) The result of the calculation is

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{coh}^{1pho} = \frac{\sigma_{coh}}{4\pi} \frac{k_f}{k_i} \frac{(2\pi)^3}{V_0} \frac{1}{2M} e^{-2W} \sum_s \sum_{\boldsymbol{\tau}} \frac{(\mathbf{q} \cdot \mathbf{e}_s)^2}{\omega_s} [\langle n_s + 1 \rangle \delta(\omega - \omega_s) \delta(\mathbf{q} - \mathbf{h} - \boldsymbol{\tau}) + \langle n_s \rangle \delta(\omega + \omega_s) \delta(\mathbf{q} + \mathbf{h} - \boldsymbol{\tau})] \quad (3.27)$$

which is a rather lengthy result that needs some unpacking. As mentioned previously the vibrating atoms (of mass M) in a crystal can be envisioned as quantum mechanical harmonic oscillators, the displacement ($\mathbf{u}_j$) of which is described by a sum of normal modes. In the above equation each mode is described by the double index $s = \mathbf{h}, l$, where $\mathbf{h}$ is the wavevector for the mode and l (where $l = 1, 2, 3$) is the polarisation index. ω_s is the angular frequency of mode s , while $\mathbf{e}_s$ is its polarisation vector. n_s is the number of phonons and is present in the expression due to the evaluation of the matrix element using the number operator. The expression has two parts: The phonon emission (first term in square brackets) and the phonon absorption (second term in square brackets) cross section. For phonon emission the frequency should satisfy $\omega = \omega_s$ while $\mathbf{q} = \boldsymbol{\tau} + \mathbf{h}$. From the definition of energy transfer ($\hbar\omega_s = E_i - E_f$) we see that this exactly means that the neutron loses energy corresponding to the energy of a phonon for normal mode s ; thus the neutron has created a phonon. For the absorption part, the neutron absorbs a phonon and uses its energy to increase its own kinetic energy. In both cases momentum is conserved and it is either transferred from the neutron to the phonon (emission) or from the phonon to the neutron (absorption). Just like Bragg scattering, one-phonon processes give rise to a peaked pattern.

Incoherent scattering

The incoherent scattering cross section for a crystal can be treated in the same manner as the coherent cross section. Expanding the exponential $\exp(\langle UK_0 \rangle)$ gives an expansion of the same type as the phonon expansion in Equation 3.19. This means that incoherent scattering also has elastic, one-phonon and multiphonon processes, but in this case all three types of processes lead to continuous scattering in all directions. The expression for the incoherent elastic scattering is very simple and almost isotropic at low temperatures

$$\left(\frac{d\sigma}{d\Omega} \right)_{inc,el} = \frac{\sigma_{inc}}{4\pi} N e^{-2W} \quad (3.28)$$

The one-phonon cross section is almost the same as in the coherent case, apart from the δ -functions limiting the momentum

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{inc}^{1pho} = \frac{\sigma_{inc}}{4\pi} \frac{k_f}{k_i} \frac{1}{2M} e^{-2W} \sum_s \sum_{\mathbf{r}} \frac{(\mathbf{q} \cdot \mathbf{e}_s)^2}{\omega_s} [\langle n_s + 1 \rangle \delta(\omega - \omega_s) + \langle n_s \rangle \delta(\omega + \omega_s)] \quad (3.29)$$

Incoherent scattering provides no information about the structure of our sample, but it can contain a wealth of information regarding the dynamics (see for example subsection 3.2.4).

3.2.3 Magnetic scattering

We mentioned previously that one of the special traits of the neutron is its unique ability to probe the magnetic nature of materials. It is now time to consider this statement in much more detail.

The magnetic dipole moment of the neutron is given by

$$\boldsymbol{\mu} = -\gamma \mu_N \hat{\boldsymbol{\sigma}} \quad (3.30)$$

where $\hat{\boldsymbol{\sigma}}$ are the Pauli matrices containing the information about the direction of the spin. The magnetic dipole moment of the neutron can interact with magnetic moments in a sample. The magnetic moments in the sample are localised on atoms with unpaired electrons (and hence unpaired spins). Denoting the spin of magnetic atom j by $\mathbf{s}_j$, the electron's magnetic dipole moment is given by

$$\boldsymbol{\mu}_e = -g \mu_B \mathbf{s}_j \quad (3.31)$$

where $g = 2.0023$ is the electronic gyromagnetic ratio (or just the g -factor). The dipole of one electron gives rise to a magnetic field ($\mathbf{B}$) that has a component due to spin and a component due to orbital angular momentum. Here we will only focus on the spin part. The full derivation with the orbital part included can be found in Squires.²¹ The interaction between the magnetic moment of the neutron and the magnetic field created by the electrons is described by the Zeeman term in the Hamiltonian (see Equation 2.2).

Magnetic scattering cross section

Just as we did for the nuclear case, we now want to determine the experimentally measurable magnetic scattering cross section. We begin, as we did in the nuclear scattering case, with the partial differential cross section, as determined by Fermi's Golden Rule. This time we also need to keep track of the spin state of the system, which

will be indicated by σ_i and σ_f . The scattering potential is the Zeeman interaction summed up over all sites, where the spins (and hence their dipole moments) are placed on positions $\mathbf{r}_j$

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\sigma_i \rightarrow \sigma_f} = Y^2 \frac{k_f}{k_i} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{m_n}{2\pi\hbar^2} \right)^2 (g\mu_B\gamma\mu_N)^2 \cdot$$

$$|\langle \mathbf{k}_f, \lambda_f, \sigma_f | \sum_j \hat{\boldsymbol{\sigma}} \cdot \nabla \times \left(\frac{\mathbf{s}_j \times (\mathbf{r} - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|^3} \right) | \mathbf{k}_i, \lambda_i, \sigma_i \rangle|^2 \delta(E_{\lambda_i} - E_{\lambda_f} + E_i - E_f) \quad (3.32)$$

where μ_0 is the magnetic permeability in vacuum. This starting expression is already much more complicated than its nuclear counterpart, but luckily the matrix element can be rewritten in a version that is simpler to interpret from a physical standpoint

$$|\langle \mathbf{k}_f, \lambda_f, \sigma_f | \sum_j \hat{\boldsymbol{\sigma}} \cdot \nabla \times \left(\frac{\mathbf{s}_j \times (\mathbf{r} - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|^3} \right) | \mathbf{k}_i, \lambda_i, \sigma_i \rangle|^2 = |\langle \lambda_f, \sigma_f | \sum_j \hat{\boldsymbol{\sigma}} \cdot \mathbf{s}_{j,\perp} e^{i\mathbf{q} \cdot \mathbf{r}_j} | \lambda_i, \sigma_i \rangle|^2 \quad (3.33)$$

where we have used a mathematical identity and defined a new quantity

$$\nabla \times \left(\frac{\mathbf{s} \times \mathbf{r}}{r^3} \right) = \frac{1}{2\pi} \int d^3\mathbf{q}' \quad \hat{\mathbf{q}}' \times (\mathbf{s} \times \hat{\mathbf{q}}') e^{i\mathbf{q}' \cdot \mathbf{r}} \quad \text{and} \quad \hat{\mathbf{q}}' \times (\mathbf{s} \times \hat{\mathbf{q}}') \equiv \mathbf{s}_{j,\perp} \quad (3.34)$$

Here $\hat{\mathbf{q}}'$ is a unit vector in the direction of the scattering vector $\mathbf{q}'$. The rewriting tells us that the magnetic scattering only involves the component of the spin perpendicular to the scattering vector $\mathbf{q}$ (the $\mathbf{s}_{j,\perp}$ component). This component also enters into the definition of the important *magnetic scattering length*

$$b_{m,j} = \frac{g}{2} \gamma r_0 \boldsymbol{\sigma} \cdot \mathbf{s}_{j,\perp} F_m(\mathbf{q}) \quad (3.35)$$

where, $r_0 = e^2\mu_0/(4\pi m_e)$ is the classical electron radius and F_m is the *magnetic form factor* given by

$$F_m(\mathbf{q}) = \int d^3\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \rho_s(\mathbf{r}) \quad (3.36)$$

where $\rho_s(\mathbf{r})$ is the normalised spin density on the unfilled orbitals. From these two equations we can say two things: The magnetic scattering length is dependent on the relative orientations of the nuclear spins (described by the Pauli matrices) and the atomic spin ($\mathbf{s}_j$), and the magnetic scattering length decays as $|\mathbf{q}|$ increases, since the atomic spins are smeared out over their orbitals (as described by the form factor).⁵

To get further with the derivation of the partial differential cross section we need to make some assumptions: We firstly assume that we do not measure the final state λ_f of the system. This means that we can sum up all $|\lambda_f\rangle$. We are also going to perform a thermal average of $|\lambda_i\rangle$. Secondly we assume that the neutrons we are using are not polarised. This step in the derivation is lengthy and the full version can be found in Lefmann.⁵ Here we will make do with the final result, which is

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{mag} = \frac{k_f}{k_i} (\gamma r_0)^2 \left[\frac{g}{2} F_m(q) \right]^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{q}_\alpha \hat{q}_\beta) \sum_{\lambda_i\lambda_f} p_{\lambda_i}$$

$$\sum_{jj'} \langle \lambda_i | e^{-i\mathbf{q} \cdot \mathbf{r}_j} \mathbf{s}_j^\alpha | \lambda_f \rangle \langle \lambda_f | e^{i\mathbf{q} \cdot \mathbf{r}_{j'}} \mathbf{s}_{j'}^\beta | \lambda_i \rangle \delta(E_{\lambda_i} - E_{\lambda_f} + E_i - E_f) \quad (3.37)$$

where $\hat{q}_\alpha$ and $\hat{q}_\beta$ are scalars and the indices α and β run over the Cartesian coordinates x , y and z .

Magnetic scattering from crystals

The cross section in Equation 3.37 can be specialised to the case where we are on a lattice. If Equation 3.37 is shifted to the Heisenberg picture and the energy-conserving delta function is rewritten as an integral over time the equation reads

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{mag} = \frac{k_f}{k_i} \frac{(\gamma r_0)^2}{2\pi\hbar} \left[\frac{g}{2} F_m(q) \right]^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{q}_\alpha \hat{q}_\beta) \sum_{jj'} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle e^{-i\mathbf{q}\cdot\mathbf{R}_j(t)} \mathbf{s}_j^\alpha(0) e^{i\mathbf{q}\cdot\mathbf{R}_{j'}(t)} \mathbf{s}_{j'}^\beta(t) \rangle \quad (3.38)$$

$\mathbf{R}(t)$ (the nuclear position; this is denoted the phonon channel) and $\mathbf{s}(t)$ (the atomic spin; this is denoted the magnetic channel) are now both operators and each give rise to one elastic and one inelastic signal equalling four terms in total. The elastic scattering has to do with the arrangement of electron spins and density distributions of unpaired electrons. The inelastic scattering tells us about the energies of the magnetic excitations.²¹ We have already briefly mentioned the magnetic excitations (spin-waves) in section 2.2 but now we are in a position to describe them more precisely; spin-waves are the coherent excitations in magnetically ordered materials. Spin-waves are quantised and the quantum of energy, $\hbar\omega$, is known as a magnon. Spin-waves disperse in q and it is possible to calculate their dispersion relations for different types of magnetism. One example is seen in Figure 2.3a from section 2.2. Scattering from magnons is in many ways similar to scattering from phonons; spin-waves are able to scatter neutrons in one-magnon and multi-magnon processes; creating and absorbing one or more magnons. Now we will continue with Equation 3.38.

If both the phonon and the magnetic channel give an elastic contribution this is known as magnetic diffraction (elastic magnetic scattering). If the phonon channel gives an elastic contribution and the magnetic channel gives an inelastic contribution we have what we know as "true" inelastic magnetic scattering.⁵ The opposite situation gives magnetovibrational scattering, but we will not treat that here, neither will we treat the case where both channels give an inelastic contribution (see the treatment by Squires).²¹

We keep with the first two terms; to simplify the expression the time-dependent nuclear positions are replaced with their equilibrium positions in the lattice (denoted $\mathbf{r}_j$). Since we then no longer take into account the vibrational motion of the atoms we insert the Debye-Waller factor of paragraph 3.2.2 to compensate. We can then use the translational symmetry of the lattice to carry out one of the sums over j (giving us a factor N representing the amount of unit cells) and get the final partial differential cross section for magnetic scattering.

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{mag,inel} = \frac{k_f}{k_i} \frac{(\gamma r_0)^2 N}{2\pi\hbar} \left[\frac{g}{2} F_m(q) \right]^2 e^{-2W} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{q}_\alpha \hat{q}_\beta) \int_{-\infty}^{+\infty} dt \sum_j e^{-i\omega t} e^{i\mathbf{q}\cdot\mathbf{r}_j} \langle s_0^\alpha(0) s_j^\beta(t) \rangle \quad (3.39)$$

The expression in $\langle \rangle$ is the spin-spin correlation function. This cross section holds both for elastic and inelastic scattering, but simplifies significantly in the case of elastic magnetic scattering from an ordered structure (see Lefmann⁵ for the full derivations)

$$\left(\frac{d\sigma}{d\Omega} \right)_{mag,el} = (\gamma r_0)^2 \left[\frac{g}{2} F_m(q) \right]^2 e^{-2W} \frac{2\pi N}{V_0} |F_M(\mathbf{q})|^2 \sum_{\boldsymbol{\tau}} \delta(\mathbf{q} - \boldsymbol{\tau} - \mathbf{Q}) \quad (3.40)$$

Here $\mathbf{Q}$ is the ordering vector for the magnetic structure in question. This equation is very similar to Equation 3.24

from nuclear diffraction. We see, however, that the nuclear structure factor ($F_N(\mathbf{q})$) has been replaced with the *magnetic structure factor* given by

$$F_M(\mathbf{q}) = \sum_i e^{-i\mathbf{q}\cdot\Delta_i} \langle \mathbf{s}_{i,\perp} \rangle \quad (3.41)$$

where the index i runs over the atoms in the unit cell. Magnetic diffraction thus also gives rise to "Bragg peaks", but the scattering condition is altered so that the scattering vector needs to equal a magnetic ordering vector (modulo a reciprocal lattice vector).⁵ The nuclear and magnetic Bragg scattering need not occur at the same values of the scattering angle (or scattering vector) as the structural and magnetic unit cell of a compound need not be the same. There also exist types of magnetism that give rise to incoherent scattering (i.e. $\mathbf{q}$ -independent). This is for example the case for scattering from a paramagnetic material; every spin in a paramagnet scatter independently of its neighbours and the scattering will therefore be smeared over the entire $\mathbf{q}$ -range, adding to the background.

The dynamical correlation function and the sum rule

The cross section in Equation 3.39 has a part that is due to the experimental setup and one that is due to the sample alone. The part of the scattering that stems from the sample alone is called the *dynamical correlation function* (or sometimes the scattering function). It can be defined for both nuclear and magnetic scattering, but in our case we will only be concerned with the latter. It is given by

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \sum_j e^{-i\omega t} e^{i\mathbf{q}\cdot\mathbf{r}_j} \langle s_0^\alpha(0) s_j^\beta(t) \rangle \quad (3.42)$$

When we are performing a neutron experiment, this is the quantity we are chiefly interested in gaining knowledge about. For magnetic scattering $S^{\alpha\beta}(\mathbf{q}, \omega)$ satisfies the sum rule

$$\sum_{\alpha,\mathbf{q}} \int d\omega S^{\alpha\beta}(\mathbf{q}, \omega) = \frac{N}{2\pi\hbar} S(S+1) \quad (3.43)$$

where S is the spin value for the magnetic ion in the compound. The physical interpretation of the sum rule is that the total amount of magnetic scattering is conserved; if more magnetic scattering appears in an area, another area will see a corresponding decrease in magnetic scattering. Another principle that is important for especially magnetic scattering is the principle of detailed balance, detailed in the next section.

Detailed Balance

Magnetic scattering is often measured at low temperatures (down to 2 K or even lower). At such low temperatures the small amount of thermal energy available in the system introduces an imbalance in the way energy is transferred to and from the sample. Scattering at positive energy transfers (energy is given to the sample) is always stronger than at negative energy transfers (energy is taken away from the sample). This makes intuitive sense, as a system at for example 2 K does not have much energy to be "stolen" by a neutron hitting the sample. This phenomenon is known as the principle of detailed balance⁵

$$S^{\alpha\beta}(-\mathbf{q}, -\omega) = e^{-\hbar\omega/(k_B T)} S^{\alpha\beta}(\mathbf{q}, \omega) \quad (3.44)$$

where the imbalance is given by a Boltzmann factor. The effect of detailed balance on a Lorentzian line shape can

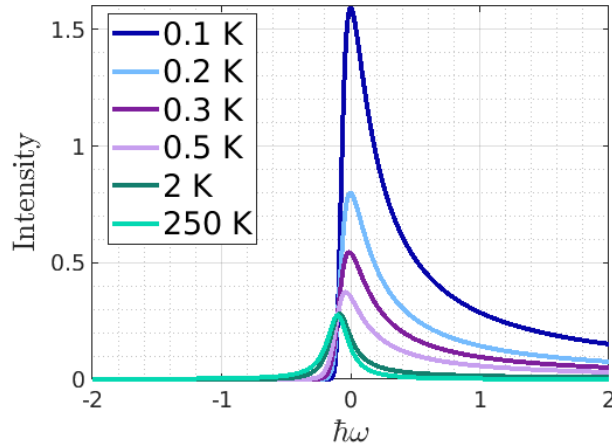


Figure 3.3: Lorentzian lineshape at different temperatures with the detailed balance factor implemented.

be seen in Figure 3.3; the lower the temperature the more the distribution skews toward positive energy transfers. $S^{\alpha\beta}(\mathbf{q}, \omega)$ contains contributions from both elastic and inelastic (dynamical) scattering. Since elastic scattering is not affected by the principle of detailed balance (as no energy is exchanged between sample and neutrons) we only need to include the detailed balance principle when we are dealing with the $\hbar\omega \neq 0$ parts of the dynamical correlation function. We will denote this part $\tilde{S}^{\alpha\beta}(\mathbf{q}, \omega)$. It is shown in Boothroyd²² that the principle of detailed balance then can be implemented as

$$\tilde{S}^{\alpha\beta}(\mathbf{q}, \omega) = [1 + n(\omega)] \frac{1}{\pi} \chi''(\mathbf{q}, \omega) \quad (3.45)$$

where $n(\omega) = [\exp(\hbar\omega/(k_B T)) - 1]^{-1}$ is the Planck distribution function (or Bose number) and $\chi''(\mathbf{q}, \omega)$ is the imaginary part of the generalised susceptibility. For our purposes the generalised susceptibility is a complex quantity defined as²³

$$\chi(\mathbf{q}, \omega) = \chi'(\mathbf{q}, \omega) + i\chi''(\mathbf{q}, \omega) \quad (3.46)$$

where the real and imaginary part are related by the Kramers-Kronig relation²³

$$\chi'(\mathbf{q}, \omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\chi''(\mathbf{q}, \omega')}{\omega - \omega'} \quad (3.47)$$

The real part is the one that is in phase with ω and it is denoted the *reactive* part. The imaginary part is out-of-phase and is denoted the *absorptive* part. The imaginary part governs the dissipation of energy and is the one measured by neutron scattering.²² The link between the susceptibility described in section 3.1 and the generalised one described here is that in the limit of $\mathbf{q} \rightarrow 0$, $\chi'(\mathbf{0}, 0) = \chi_{bulk}$.²³

3.2.4 Quasi-elastic neutron scattering (QENS)

This section leans heavily on the treatment of QENS given in Boothroyd.²² Boothroyd defines QENS as "*a special case of inelastic scattering*" and explains that "*it arises from random rearrangements of the system due to thermal or quantum fluctuations between different configurations with the same energy*".²² To concretise; when energy is transferred to the system via an inelastic process the energy is dissipated rapidly in the system, due to the fluctuations, and the system is left in the same energy state as the one it began in. The neutron scattering response to this process is a peak at the bottom of the elastic signal with a width similar to $1/\tau$, where τ is the characteristic time for the fluctuation.²² As with the other types of neutron scattering we have met so far QENS can be divided into a coherent and an incoherent response; the coherent response can provide information about the correlated motions of the particles in a liquid or a solid, while the incoherent response is linked to the movement of individual particles. We will in this treatment ignore the coherent scattering on account of it being complicated. A simple treatment of coherent QENS in liquids is given in Squires.²¹ Instead we focus on incoherent QENS which is especially concerned with the diffusion of particles, either in liquid form or in materials. In materials it is chiefly the diffusion of hydrogen, due to its large incoherent scattering cross section, that is studied.²²

Single-particle diffusion

The simplest treatment of diffusion is single particle diffusion (also known as self diffusion). We will describe it here to get an understanding of the shape of the quasi-elastic response. The dynamic of a single particle is described by its self-pair correlation function

$$G_s(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_j \int d^3\mathbf{q} \langle e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j} e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j(t)} \rangle e^{-i\mathbf{q} \cdot \mathbf{r}_j} \quad (3.48)$$

where $\hat{\mathbf{r}}_j(t)$ and $\hat{\mathbf{r}}_j$ are (Heisenberg) operators of position that do not commute. $G_s(\mathbf{r}, t)$ is the space and time Fourier transform of the incoherent part of the response function for incoherent scattering (see Equation 3.42)

$$S_i(\mathbf{q}, \omega) = \frac{1}{2\pi\hbar} \int \int d^3\mathbf{r} dt G_s(\mathbf{r}, t) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} \quad (3.49)$$

If we ignore the quantum nature of the self-pair correlation function (i.e. let the operators commute) it is possible to ascribe physical meaning to it; $G_s(\mathbf{r}, t) d^3\mathbf{r}$ represents the probability of finding a particle at time t in the volume $d^3\mathbf{r}$ at a displacement $\mathbf{r}$ away from a point occupied by the same particle at $t = 0$.²²

If we assume the particles to be moving continuously we can describe the diffusion using Fick's laws:

$$\mathbf{j}(\mathbf{r}, t) = -D \nabla n(\mathbf{r}, t) \quad \text{Fick's first law} \quad (3.50)$$

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \nabla^2 n(\mathbf{r}, t) \quad \text{Fick's second law} \quad (3.51)$$

Here $n(\mathbf{r}, t)$ is the number of atoms per unit volume (the concentration), $\mathbf{j}(\mathbf{r}, t)$ is the flux of particles and D is the diffusion constant (assumed to be independent of concentration). It is shown in Boothroyd²² that the solution to Fick's second law (when $n(\mathbf{r}, 0) = \delta(\mathbf{r})$) is exactly the classical approximation of the self-pair correlation function. For an isotropic system it can be written as

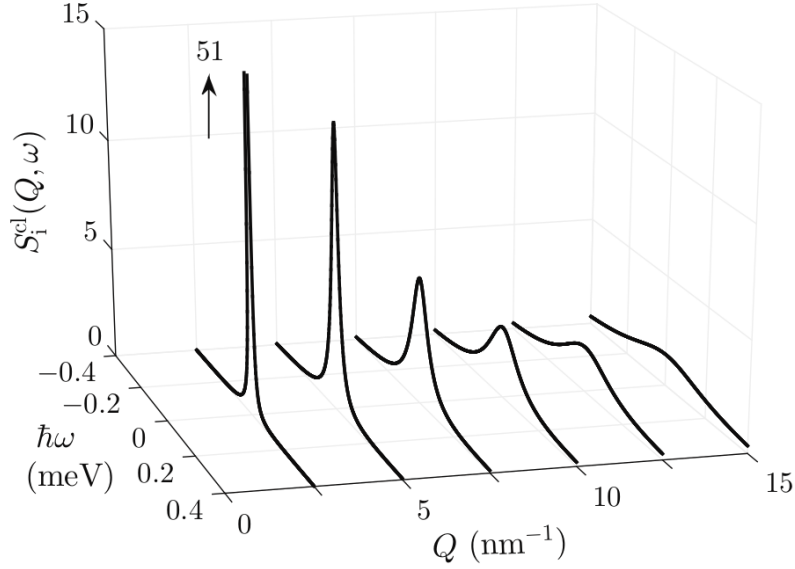


Figure 3.4: Shape of the quasi-elastic incoherent response for single-particle diffusion for $D = 1.5 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$. Q on the figure is synonymous with our q . The figure is from Boothroyd.²²

$$G_s^{cl}(r, t) = \left(\frac{1}{4\pi D|t|} \right)^{\frac{3}{2}} e^{-\frac{r^2 D |t|}{4}} \quad (3.52)$$

If we Fourier transform this result in space and time we get that the incoherent response function (i.e. the shape of the quasi-elastic scattering) is given by a Lorentzian line shape

$$S_i^{cl}(q, \omega) = \frac{1}{\pi} \frac{\hbar \Gamma(q)}{(\hbar \omega)^2 + [\hbar \Gamma(q)]^2} \quad \Gamma(q) = Dq^2 \quad (3.53)$$

This Lorentzian is centred at zero energy transfer and the HWHM depends on the diffusion constant and the scattering vector ($HWHM = \hbar \Gamma(q)$). The Lorentzian broadens when q is increased, as shown in Figure 3.4. We notice that the Lorentzian in Equation 3.53 does not depend on the direction of the scattering vector (q is now a scalar). It is possible to reintroduce the directional dependence of $\Gamma(q)$ by using the jump diffusion model of Chudley and Elliott, where diffusion is assumed to happen as a series of random jump between sites (see Boothroyd²² for the derivation). The resulting equation for the incoherent response is identical to Equation 3.53 but with q replaced by $\mathbf{q}$.

3.2.5 FOCUS and Time-of-Flight neutron scattering

When performing a neutron scattering experiment it is crucial to know the energy and wavelength of both incoming and outgoing neutrons. One way to determine the wavelength of incoming/outgoing neutrons is by utilising a monochromator (a crystal) and the famous Bragg law described earlier in Equation 3.22. A different method is to measure the speed of the neutrons and calculate the wavelength in a Time-of-Flight (ToF) analysis. We will go through such an analysis here for the case where E_i is monochromatised and therefore constant. A ToF spectrometer with this setup is denoted a direct geometry ToF spectrometer. In the next section we will describe the specific instrument used in this thesis (Figure 3.5).

The neutron speed is connected to its wavelength and energy through a series of equations. If we denote the neutron flight time by t and the (known) distance it travels by L , the velocity is expressed as $v = L/t$, which is related to the neutron momentum through $\hbar k = m_n v$. Since the kinetic energy ($E = (\hbar^2 k^2)/(2m_n)$) can be calculated from k and the wavelength can be calculated from the energy we get the following relation for the flight time

$$t = \frac{L}{v} = \frac{m_n}{2\pi\hbar} L\lambda = \alpha L\lambda \quad (3.54)$$

Where we defined $\alpha = m_n/(2\pi\hbar)$. The uncertainty on the calculated wavelength/energy is determined by the neutron pulse width, τ ,⁵

$$\frac{\delta\lambda}{\lambda} = \frac{\tau}{\alpha L\lambda} \quad (3.55)$$

The best resolution in wavelength for a ToF spectrometer is then obtained with large L , short, well-defined pulse lengths and/or long wavelengths.

When performing a ToF experiment the detected spectrum thus end up depending on the flight time. This fact is of course important for proper modelling, and subsequent subtraction, of the background signal from the neutron scattering data. The following calculation of the ToF cross section is based on the one in Berrod et al..²⁴

The ToF spectrum is the distribution of neutron arrival times (in the detectors) in units of solid angle $d\Omega$. If we ignore coherent and incoherent cross sections and just use the total cross section, σ_t , we have (from Squires²¹)

$$\frac{d^2\sigma}{d\Omega d\omega} = N \frac{k_f}{k_i} \frac{\sigma_t}{4\pi} S(Q, \omega) \quad (3.56)$$

To get the dependence on time of flight we use the chain rule to write

$$\frac{d^2\sigma}{d\Omega dt} = \frac{d\omega}{dt} \frac{d^2\sigma}{d\Omega d\omega} \quad (3.57)$$

We get an expression for ω by isolating it in the definition for the energy transfer.

$$\omega = \frac{1}{\hbar} (E_i - E_f)$$

The final energy can be rewritten using the final velocity of the neutrons.

$$E_f = \frac{1}{2} m_n v_f^2 = \frac{1}{2} m_n \left(\frac{L}{t} \right)^2 \quad (3.58)$$

where L is the distance the neutron travels from the sample to the detector. Inserting and differentiating we obtain

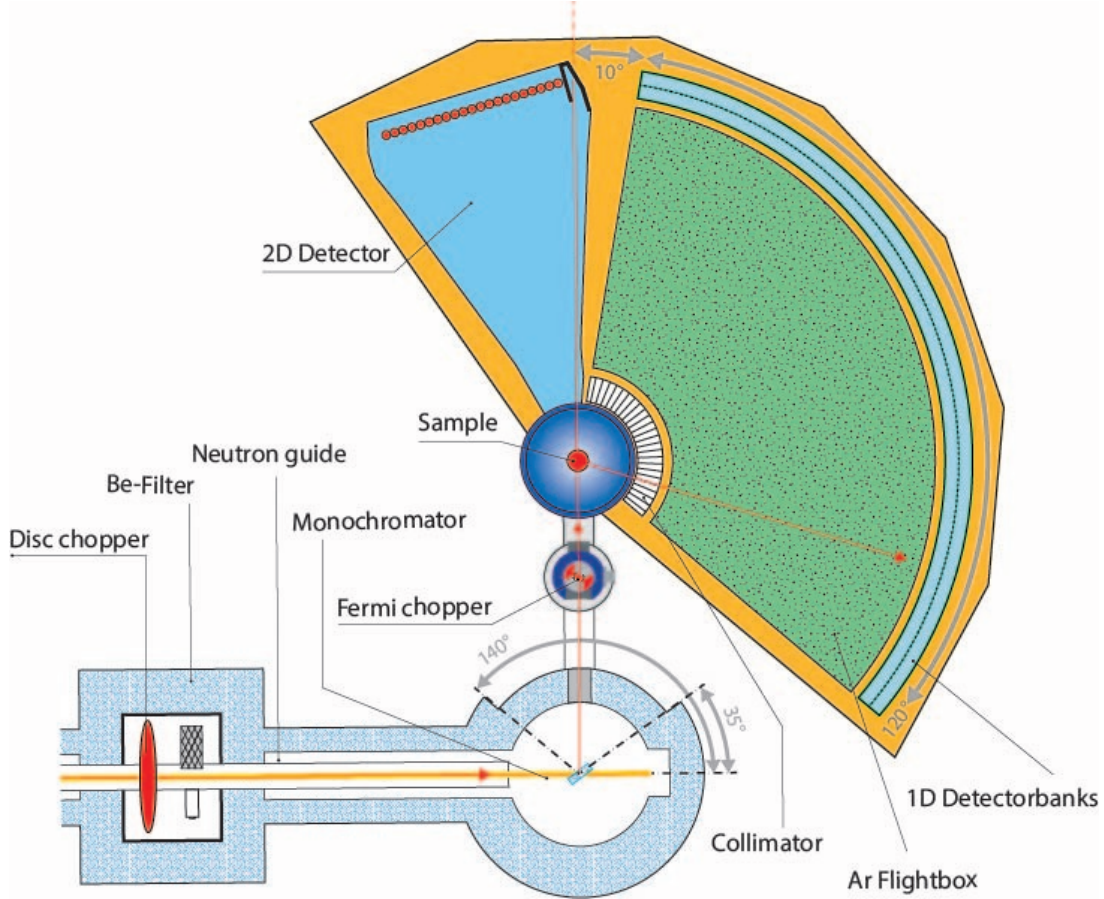


Figure 3.5: Layout of TOF spectrometer FOCUS located at the Paul Scherrer institute in Switzerland. Graphic is downloaded from the PSI homepage.²⁵

$$\frac{d\omega}{dt} = \frac{m_n L^2}{\hbar t^3} \quad (3.59)$$

We can express the k_i/k_f fraction by using the neutron kinetic energy mentioned above, then

$$\frac{k_f}{k_i} = \frac{\sqrt{(E_f \hbar^2)/(2m_n)}}{\sqrt{(E_i \hbar^2)/(2m_n)}} = \sqrt{\frac{E_f}{E_i}} = \sqrt{\frac{m_n}{2E_i}} v_f = \sqrt{\frac{m_n}{2E_i}} \frac{L}{t} \quad (3.60)$$

Now inserting both equations we obtain the final expression

$$\frac{d^2\sigma}{d\Omega dt} = \frac{N\sigma_t}{h} \left(\frac{m_n}{2}\right)^{\frac{3}{2}} \frac{L^3}{t^4} \quad (3.61)$$

The raw data is therefore "deformed" by a factor t^{-4} . This must be corrected in the data, which is measured in intensity as a function of solid scattering angle and time ($I(d\Omega, t)$), before the connection between the cross section and the dynamical correlation function can be seen.

FOCUS

The following section is modelled heavily after the information available on FOCUS at the PSI homepage,²⁵ as well as the two experimental papers by Mesot et al.(1996)²⁶ and Janssen et al. (1997).²⁷

Neutron scattering experiments on the jarosite powder samples were carried out at the direct geometry ToF hybrid spectrometer FOCUS (Focussing Crystal University Spectrometer) located at the Swiss spallation induced continuous neutron source SINQ at the Paul Scherrer institute (PSI). The spectrometer is designed for cold neutrons,²⁵ i.e. neutrons with energy between 0.05 meV and 14 meV, corresponding to wavelengths 2.4-40 Å.⁵ The layout of the spectrometer can be found in Figure 3.5.

Starting in the lower left of the diagram, the neutrons are transported to the instrument via a curved and vertically converging neutron guide (fittingly denoted an "anti-trumpet"). It is coated with Ni-Ti and has $m = 2$, which means that it allows 4 times higher acceptance of incoming solid angle of neutrons to pass through, compared to just Ni coating.²⁶ The guide thus serves a multitude of purposes: Transporting the neutrons, keeping the instrument away from the line of sight of the neutron source (curved nature of guide) as well as reducing the vertical dimension of the beam (converging nature of guide).

After emerging from the end of the guide the neutron beam is chopped by a pre-selector disc chopper. A disc chopper is a wheel-shaped device made up of neutron absorbing material with slits that alternately block and allow passage of neutrons. This monochromatises the incident beam and sets the initial energy/wavelength of the neutrons. It furthermore prevents fast neutrons from previous pulses from overtaking slow neutrons from current pulses (known as frame overlap), as this would muddle the initial times and prevent effective ToF-analysis,⁵ as well as preventing higher order contamination (from higher n in Bragg's law).²⁶

The beam then meets the monochromator that in this case works as another focussing device; it focusses the beam onto the sample through a Fermi chopper, hereby increasing the intensity at the sample position. The monochromator at FOCUS consists of several pieces of single crystals that can be rotated, giving the monochromator variable curvature both horizontally and vertically. The monochromator angle θ_m can be varied from 17.5° to 70°.²⁵ A Beryllium filter can be inserted within the monochromator shielding. It is used when incident wavelengths are larger than 4 Å.²⁵ The filter eliminates certain parts of the wavelength spectrum, since Bragg scattering will take place only for neutron wavelengths smaller than twice the largest lattice spacing in the material. Long-wavelength neutrons are hence transmitted without scattering. It is therefore useful in preventing higher orders from getting through and limiting background.⁵ The Fermi-chopper is a rotating device made up of sheets of neutron absorbing material. The spaces between sheets allow neutrons to pass through in short bursts when alignment between chopper and beam is consistent.⁵

When the beam hits the sample, neutrons scatter to different final energies. The speed with which they reach the detectors depend on how they interacted with the sample. The slowest neutrons will be those that lost kinetic energy to the sample, hereafter follows the elastically scattered neutrons that did not change their energy, while the fastest will be the neutrons that gained kinetic energy from the sample.

ToF analysis is performed to get the final energies from the velocities. The scattered neutrons pass through a radial collimator (thin neutron absorbing sheets, suppress background neutrons) and an Argon filled box (prevents scattering from air) before they are detected in the rectangular ³He counter tubes. The 1D detectors cover scattering angles in range 10° to 130° and the 2D detector covers -1.4° to -24°.²⁵

The distance from neutron guide to monochromator (L_{gm}) and from monochromator to sample (L_{ms}) can be varied, which enables the instrument to be run in two different modes; Time-Focussing (TF) mode (suitable for quasi-elastic scattering) and Monochromatic Focussing (MF) mode (suitable for inelastic scattering). Both modes attempt

to minimise the delay, ΔT , between the first and last neutrons passing through the Fermi-chopper.

$$\Delta T = \frac{\gamma_1}{2\pi\nu} \quad (3.62)$$

where γ_1 is the beam divergence after the monochromator and ν is the Fermi-chopper frequency. In TF mode the resolution is good over a small energy interval.²⁶ In the MF mode a good resolution can be obtained over a wide range of energy transfers. We performed two experiments on FOCUS during this project; both with the instrument in the TF mode. The range of available momentum transfers (Q) as a function of energy (E) for various wavelength are visualised in Figure 3.6.

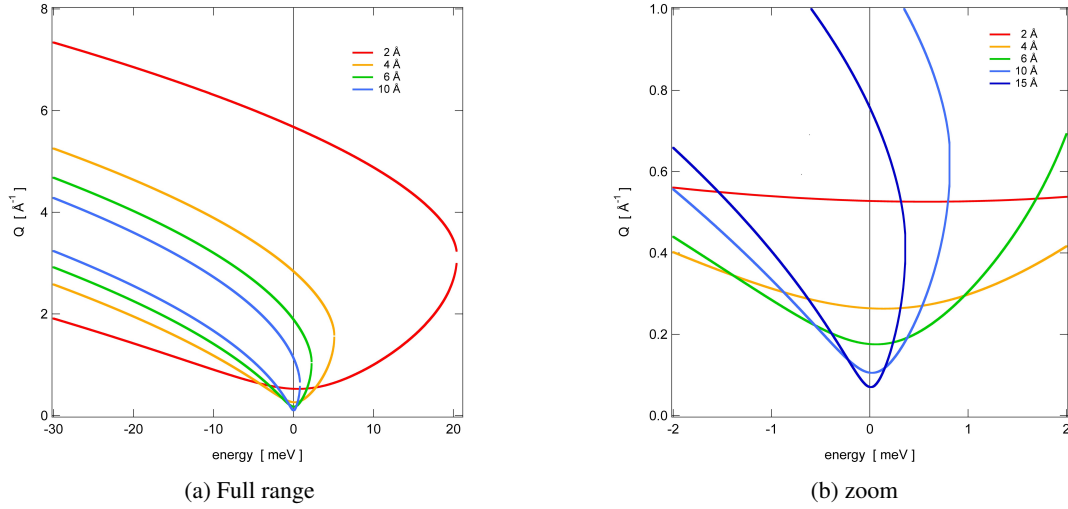


Figure 3.6: $Q - E$ range of FOCUS at various wavelengths. Graphics are downloaded from the PSI homepage.²⁵

3.3 NMR Theory

When performing any type of measurement and subsequent data analysis on a synthesised compound, the first step is to know your compound. Without knowledge about the structure, both the overall and the local, and the purity, conclusions are made while halfway blind. A first step to knowing your compound is to perform X-ray diffraction. With X-rays the overall structure of the compound can be obtained, but the method also has its shortcomings: Hydrogen is difficult to localise with X-rays, as the atom has a very small electron density, and often the position of H and the occupancy of the different atomic sites are not reported. The information about occupancy and local defects can be vital for the understanding of magnetism in materials; especially in the case of jarosites where the magnetism is so very dependent on the local chemical composition. Nuclear Magnetic Resonance (NMR) spectroscopy is ideal for exactly this purpose, as it allows for quantification of different chemical environments present in a sample.

3.3.1 General concepts

To perform magnetic resonance spectroscopy we need a system with a magnetic moment as well as an angular momentum. In Nuclear Magnetic Resonance the angular momentum belongs, of course, to the nucleus.²⁸ The total magnetic moment of the nucleus is denoted μ_N and it is proportional to (caused by) the total angular momentum $\mathbf{J} = \hbar \mathbf{I}$, where $\mathbf{I}$ is the intrinsic nuclear spin angular momentum, i.e.

$$\mu_N = \gamma \hbar \mathbf{I} \quad (3.63)$$

The proportionality constant is the gyromagnetic ratio, which has vastly different values for different nuclei (for example $\gamma/(2\pi) = 42.6$ MHz/T for hydrogen and $\gamma/(2\pi) = 6.5$ MHz/T for deuterium).²⁹

Having established the "N" in NMR, we move on to the M. If we add a magnetic field, B_z , along the z -direction to our system, the interaction energy will be given by the usual Zeeman Hamiltonian (Equation 2.2) with eigenenergies

$$E = -\gamma \hbar B_z I_z \quad (3.64)$$

We know that I_z can only change in integer values $\Delta I_z = 0, \pm 1$ ²⁹ (from $+I$ to $-I$). This will give us $2I + 1$ quantised energy levels with $\gamma \hbar B_z$ separating them. To cause a transition from one level to another one needs an interaction that can supply exactly the right amount of energy. The magnetic moment of the nucleus acts as a lever that a magnetic field can grab hold of and turn to its liking. A magnetic field B_1 (perpendicular to the static field B_z) with energy $\hbar \omega_0 = \Delta E = \gamma \hbar B_z$ and hence frequency $\omega_0 = \gamma B_z$ is therefore ideal. The frequency ω_0 is known as the *Resonance frequency*. This also brings with it the meaning of our last letter, "R". Classically, the nuclear moment inside the sample acts as a vector that precess in the xy -plane with an angle to the z -axis due to B_z . The frequency of this precession is exactly the resonance frequency (which in the classical case is often denoted the Larmor frequency), and it is the spectrum of ω_0 's we want to determine in an NMR experiment.

Free Induction Decay and relaxation

The sample in an NMR experiment is placed inside a probe which again is placed inside a static magnetic field (the B_z field). The alternating, perpendicular field B_1 that induces the transitions in the sample is produced by

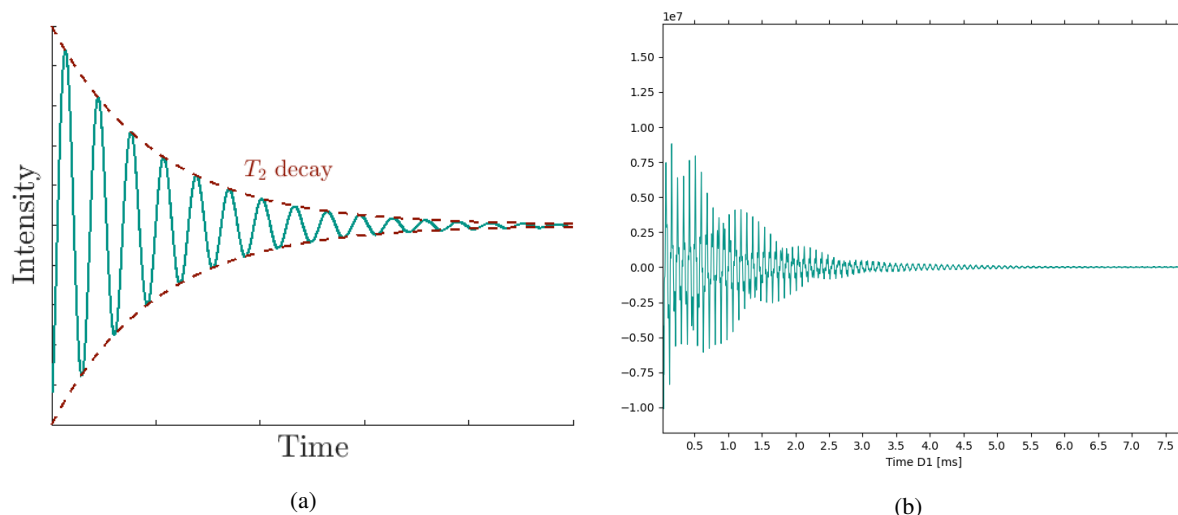


Figure 3.7: **(a)** Shape of FID for a general NMR experiment. The exponential T_2 decay of the signal is indicated with yellow dashed lines. **(b)** Example of FID from a Hahn Echo experiment. The experiment was performed on $D_3OFe_3(OD)_6(SO_4)_2$ at a spinning speed of 34 kHz by Professor Ulla Gro Nielsen.

an AC current in a coil that surrounds the probe. By adjusting the time this field is on and off pulses can be created that push the moments to be perpendicular to B_z and precess with the resonance frequency. Such pulses tilt the moments 90° and are called $\pi/2$ pulses. The precessing magnetic moments create an alternating flux in the surrounding coil as the magnetisation changes direction with respect to B_z . The alternating flux can be observed as an electromotive force (emf) and the signal is called the Free Induction Decay (FID). An example can be seen in Figure 3.7a. The decay in solid-state NMR comes primarily from two processes; the first is a dephasing of the spins, i.e. a spread in the precession frequencies due to inhomogeneities in the field.²⁸ The second is the interaction of the nuclei with their neighbours that results in a relaxation process with time constant T_2 (this is often called transverse relaxation as it happens to the components of the spin in the xy -plane). It is this second process that gives the FID its exponentially decaying shape. The decay from the first process can be eliminated by using the technique of spin echoes (or Hahn echoes after its discoverer Erwin Hahn). Hahn discovered in 1950 that if we apply a second pulse, which is twice as long as the first pulse (a π pulse), a time τ after the first pulse we will get a second FID after a time 2τ with the same shape as the first. This echo appears because the spins, after dephasing, have been rephased due to the second pulse. In the language of relaxation; in the first τ interval the components of the spin in the xy -plane decay exponentially with T_2 , while a z -component develops exponentially with T_1 . T_1 is the longitudinal relaxation time (the time it takes for the magnetisation to regain its thermal equilibrium value after a pulse).²⁹ When the second pulse is applied the z -component is flipped and the dephasing is reversed, while the relaxation due to T_2 continues as before.²⁸ An example of a FID for a Hahn Echo experiment is present in Figure 3.7b. T_1 and T_2 are both time constants linked to the time dependence of the magnetisation, which can be described by the Bloch equations²⁸

$$\frac{dM_x}{dt} = \gamma(\mathbf{M} + \mathbf{B})_x - \frac{M_x}{T_2} \quad (3.65)$$

$$\frac{dM_y}{dt} = \gamma(\mathbf{M} + \mathbf{B})_y - \frac{M_y}{T_2} \quad (3.66)$$

$$\frac{dM_z}{dt} = \gamma(\mathbf{M} + \mathbf{B})_z + \frac{M_0 - M_z}{T_1} \quad (3.67)$$

where $\mathbf{B}$ is the applied field and M_0 is the magnetisation in thermal equilibrium mentioned above. We are now going to focus on the processes linked to T_2 - namely the surrounding nuclei.

Chemical shift

The resonance frequency we have mentioned so far is for an isolated nucleus, but nuclei in materials are surrounded by other nuclei and electrons. Nuclei in a material therefore feel different local magnetic fields depending on their chemical surroundings. This means that the nucleus feels an effective field, which is different from the one we apply. The resonance frequency will accordingly be changed to²⁸

$$\omega = \gamma(B_0 + \Delta B) \quad (3.68)$$

Where the applied field has the subscript 0. The extra field ΔB is proportional to the applied field such that $\Delta B = \sigma B_0$. The proportionality constant is denoted the shielding constant and it can be both positive and negative, depending on whether the local environment requires us to use a smaller or larger applied magnetic field to get the "naked" resonance frequency.²⁸ Due to the presence of now several resonance frequencies in the same sample the one resonance will split into as many resonances as there are different environments; it is exactly this that allows us to use NMR as a tool for assessing chemical purity. The shift in resonance frequency is due to σ but we do not talk about σ in an experiment. We do not know exactly what the field inside the sample is, and therefore we need a measure that is relative to a known reference molecule. This measure is known as the chemical shift δ , which is related to the shielding constant by³⁰

$$\delta \approx -(\sigma - \sigma^{ref}) \cdot 10^6 \quad (3.69)$$

where the factor 10^6 is due to the convention of giving δ in parts per million (ppm) and σ^{ref} is the known shielding constant.³⁰

3.3.2 Broadening and shifting of the resonance

Several interactions in materials work to broaden and shift the position of the resonance. Broadening is linked to lower values of T_2 (faster relaxation).²⁹ In the following sections we describe briefly the interactions that shift and broaden the resonance in ^2H NMR, as this is the method we will use to probe the chemical environments in our samples. In the case of jarosites these are paramagnetic, dipolar and quadrupolar effects.

Paramagnetic effects

This section is modelled heavily after the information on paramagnetic NMR in the review by Grey and Dupré.³¹

In paramagnetic materials (such as jarosite) the chemical shifts are much larger than observed for similar diamagnetic materials. This is due to the interactions between nuclear and electronic spins. The electronic spins have magnetic moments μ_e and spin component S_z along the applied magnetic field (assumed to be in the z -direction). In NMR experiments the nuclear spins do not couple directly to the electronic spins, instead they couple to the time averaged value $\langle S_z \rangle$. This is due to a difference in time scales: The electronic spin states relax on a timescale T_{1e} which is much faster than the timescale probed by NMR. The time averaged value of the spin is given by,

$$\langle S_z \rangle = -\frac{B_z \chi_M}{\mu_0 g N_A \mu_B} \quad (3.70)$$

where N_A is Avogadro's number and χ_M is the magnetic susceptibility. The constant that measures the size of the electron-nuclear interaction is the hyperfine coupling constant A/h (given in units of Hz). The hyperfine coupling constant can be very large (many MHz) and depends on how close the NMR nucleus is to the paramagnetic electrons; a large quantity of spin density on the nucleus will give rise to a large hyperfine coupling constant.

There are two ways in which the nuclear spins can interact with the (time averaged) electronic spins. The first is a through-bonds interaction, known as the Fermi contact interaction, and the second is the dipolar (through-space) interaction.

Fermi contact interaction

The Fermi contact interaction gives rise to a shift of the resonance position due to a transfer of unpaired electron spin density from the magnetic ion onto the NMR nucleus.³² It is directly proportional to the time averaged value of the electronic spins

$$\frac{\omega}{\omega_0} = \frac{A}{\omega_0 h} \langle S_z \rangle \quad (3.71)$$

The hyperfine coupling constant determines the direction and size of the shift and is given by³¹

$$A/h = \frac{1}{3} g \mu_B \mu_N \gamma_N \mu_0 \rho(r=0) S \quad (3.72)$$

Here μ_N and γ_N are the magnetic moment and gyromagnetic ratio of the NMR nucleus, S is the value of the spin and $\rho(r=0)$ is the electron spin density at the position of the nucleus. We need only consider electron spin density that is transferred to s orbitals, as these are the only orbitals with a non-zero probability of having an electron being found at the nucleus. The expression holds only in the case where the electronic relaxation rate is sufficiently small such that $|A/h| \ll 1/T_{1e}$. If T_{1e} is lengthened such that $1/T_{1e}$ is similar in size to the electron-nuclear interaction it can lead to substantial broadening of the resonance. Since the interaction happens through bonds it provides information about the pathways of electron transfer and connectivity between the orbitals of the NMR nucleus and the orbitals with unpaired electrons.

Electron-nucleus dipolar interaction

The dipolar electron-nucleus interaction happens between the magnetic moments of the NMR nucleus and the time averaged magnetic moment of the electrons $\bar{\mu}_e = \mu_B g \langle S_z \rangle$. The term in the Hamiltonian is given by

$$H_{Ie} = \frac{\mu_0}{4\pi} \bar{\mu}_e \tilde{D}_{Ie} \mu_N \quad (3.73)$$

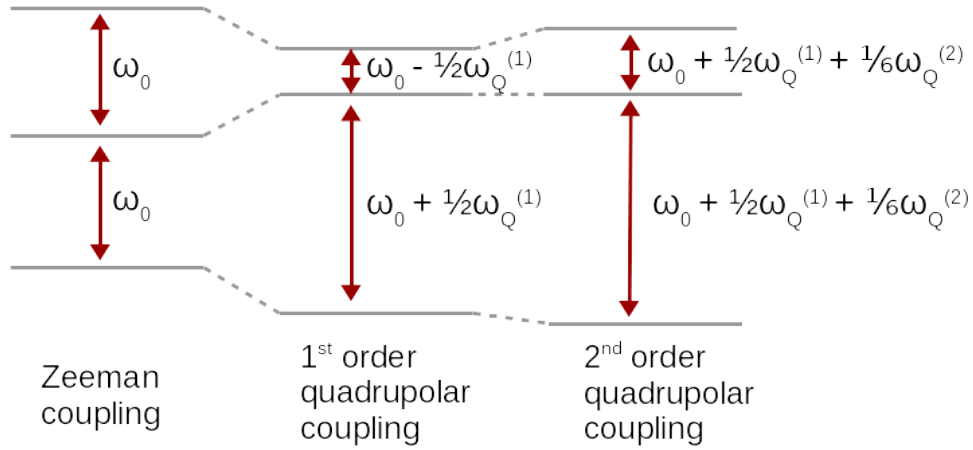


Figure 3.8: Effect of Zeeman splitting and first- and second order quadrupolar coupling on the energy levels of an $I = 1$ nucleus like deuterium. The figure is adapted from Laws et al. (2002).³³

where I is the nuclear spin and $\tilde{D}_{Ie}$ is the dipolar coupling tensor, which describes the coupling between the nucleus and the unpaired electrons. The tensor is a so called "second rank" tensor, which means (among other things) that the matrix elements inside it will depend on second degree spherical harmonic functions Y_{lm} with $l = 2$. Such functions have orientation dependent terms proportional to $1 - 3\cos^2\theta$,²⁸ and we shall see in subsection 3.3.3 why this is important. The orientation dependence of the shift leads to a very broad signal if our sample is a powder sample as all orientations will be present at the same time.

This coupling has the same shape as the chemical shift anisotropy (CSA) has for other nuclei. CSA is an interaction caused by atoms and molecules not having spherically symmetric charge distributions, which leads to a large variation of chemical shifts depending on the orientation of the charge distribution relative to the applied field. For a small atom such as ^2H the CSA is however negligible,³⁷ and we will not discuss it further.

Dipolar effects exist not only between electrons and nuclei, but also between magnetic moments of different nuclei (known as heteronuclear dipolar coupling) and nuclei of the same type (known as homonuclear dipolar coupling). In the final spectra in this project we are not going to be able to see the effects of these couplings, as they are going to be averaged out by MAS (see subsection 3.3.3), and hence we will not go through them here. A description can be found in the review by Laws et al..³³

Quadrupolar interaction

Nuclei with spin $> \frac{1}{2}$ belong to the group of quadrupolar nuclei.³³ Deuterium has $I = 1$ and therefore fall into this category. Such nuclei have non-spherically symmetric charge distributions and as a result interact with the electric field gradient produced by the surrounding charges.³⁴ The interaction naturally affects the transitions visible in an NMR experiment.³³ The strength with which the nucleus couples to the electric field gradient is described by Q ; the nuclear electric quadrupole moment. To first order the quadrupolar coupling is given by

$$\omega_Q^{(1)} = \frac{3e^2qQ}{2I(2I-1)\hbar} \quad (3.74)$$

where $eq = V_{zz}$ is the z -component of the electric field felt at the nucleus. $\eta = (V_{yy} - V_{xx})/V_{zz}$ describes the asymmetry of the electric field gradient.³⁴ Deuterium only has a small value of the first order coupling (deuterium

has $Q = 3.10 \cdot 10^{-31} \text{ m}^2$,³³ so the second order is not very relevant for deuterium NMR. For completeness we mention that it is given by³³

$$\omega_Q^{(2)} = \frac{(\omega_Q^{(1)})^2}{2\omega_0} \quad (3.75)$$

The effect of $\omega_Q^{(1)}$ is to shift all energy levels by the same amount. This means that the central transition (i.e. the isotropic chemical shift) is not affected and stays sharp. Any other transitions (satellite transitions) are displaced outwards with $n = \pm 1, 2, \dots$ times the quadrupolar frequency (Ω_Q) and broadened,³⁴ where

$$\Omega_Q = \frac{\omega_Q^{(1)}}{2} 3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos^2 \alpha \quad (3.76)$$

Here α and β are angles relating the electric field to the external field. If the second order coupling is considered the central transition will shift and broaden as well. This is summarised in Figure 3.8.

The quadrupolar coupling is not only a complication we have to live with in an NMR experiment, it is actually a sensitive probe of internal molecular motion. The quadrupolar coupling depends crucially on the molecular orientation with respect to the magnetic field. If the molecule changes its orientation the width and shape of the ^2H static line will be affected. Mobility of the molecule also works to narrow the linewidth.³³ This has been observed in for example the mobile methyl group in polymers³⁵ and for the hydronium molecule in hydronium jarosites.^{32,36,37}

3.3.3 Motional narrowing and Magic Angle Spinning (MAS)

In liquid NMR the molecules are tumbling rapidly, thus sampling the full range of possible molecular orientations. This has rather miraculous effects, as (almost) all orientation dependencies are averaged out over time leaving us with narrow resonances. This is referred to as motional narrowing. We have just learned that interactions such as the dipolar interaction between electron and nuclei and the quadrupolar coupling broaden the resonance lines, making interpretation of powder spectra difficult. It was inevitable that someone would put two and two together and simply spin the sample during the experiment. It had been shown by experiments of line widths on benzene that the average over time of the angular factor in the (heteronuclear) dipolar coupling could be written²⁸

$$(1 - 3 \cos^2(\theta_{jk}))_{\text{avg}} = (1 - 3 \cos^2(\theta')) \left(\frac{3 \cos^2(\gamma_{jk}) - 1}{2} \right) \quad (3.77)$$

here θ_{jk} is the angle between the static applied field $\mathbf{B}$ and the internuclear vector between moments i and j , γ_{jk} is the angle between the internuclear vector and the rotation axis and θ' is the angle between $\mathbf{B}$ and the rotation axis. If we spin the sample (practically by packing the powder in a rotor) θ' is the same for all pairs of nuclei. If we then choose

$$1 - 3 \cos^2(\theta') = 0 \Rightarrow \theta' = 54.74^\circ \quad (3.78)$$

the (heteronuclear) dipolar coupling "magically" disappears (and the line broadening with it). The above defined angle is therefore referred to as the magic angle, and the method of line narrowing is known as Magic Angle Spinning (MAS). As mentioned above more couplings than just the dipolar one are guilty of broadening the lines. It turns out that also CSA, electron-nuclear dipolar couplings and first order quadrupole couplings can be made to disappear using this method. The common denominator is that the angular factors describing the relationship

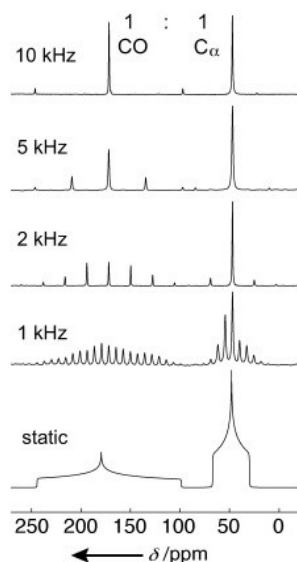


Figure 3.9: Dependence of solid-state ^{13}C NMR on different spinning frequencies (given on the figure). The sample is a glycine powder sample. The figure is from Laws et al..³³

between crystal axes and external field in all these couplings are proportional to $(3\cos^2(\theta) - 1)$ ²⁸ (which we have seen first hand in the preceding sections). The second order quadrupolar coupling cannot be removed by MAS, as it has another angular dependence as well, and it is not possible to choose one angle to make both zero at the same time.³⁴ More advanced methods utilising several spinning angles can average out the second order quadrupolar coupling. The reader is referred to the review by Laws et al.³³ for an overview of the more advanced techniques.

It is important to note that the broadening will only be completely removed if the sample is spun with a frequency that is greater than the static powder width. If it is possible to spin the sample fast enough only the isotropic resonances, as seen in liquid NMR, will be present. Usually the broadening from electron-nucleus dipolar coupling is so large that the sample physically cannot be spun fast enough for the broadening to be completely removed.³¹ In such cases spinning side bands (ssb) will appear at integer multiples of the spinning speed.³⁴ The central line in a MAS spectrum is the isotropic shift. It is the only line that does not move when the frequency of rotation is changed.²⁸ To get the full intensity of the resonances the intensity of the ssb and the isotropic peak must be added. For a slow spinning sample the pattern of the ssb envelope will resemble the static powder pattern,³³ as illustrated in Figure 3.9.

4 | Spin-glasses

So far we have been introduced to diamagnets, paramagnets, ferromagnets and antiferromagnets. Yet more types of magnets exist and one that is very different from the previously discussed is the spin-glass, the theoretical understanding of which awarded Giorgio Parisi the Nobel price this year (2021). In this chapter we will focus on the experimental characteristics of spin-glasses and stay clear of the mathematical theory under the guise of it being outside the scope of this thesis (for a review of the mean field approach to spin-glass theory see the review by Castellani and Cavagna.³⁸) This section leans heavily on the book "Spin Glasses: An experimental introduction" by J. A. Mydosh³⁹ (a rather old book, but spin-glasses is also a rather old topic, and the fundamental behaviour has not changed. For a newer review of the experimental characteristics see Vincent and Dupuis.⁴⁰) Mydosh defines a spin-glass as *"a random, mixed-interacting, magnetic system characterised by a random, yet co-operative, freezing of spins at a well-defined temperature, T_f , below which a highly irreversible, metastable frozen state occurs without the usual long-range spatial magnetic order"*. This definition carries in it all the ingredients needed to create a spin-glass. The first ingredient is randomness. In a conventional, aptly named, site-disordered spin-glass the randomness comes from the random occupation of sites in the lattice, creating a distribution of distances between the magnetic ions. Another possibility is bond randomness, where the NN coupling changes sign from FM to AFM and back. Another necessary ingredient is that of frustration, due to its creation of a degenerate manifold of ground states. Note that in this case the frustration is caused by the mixed interactions and not by the geometry of the lattice. Lastly anisotropy, usually in the form of the Dzyaloshinsky-Moriya interaction or a single-ion anisotropy, plays a role.⁴

The canonical spin-glasses are metallic and their physics is governed by the electron-mediated RKKY interaction. Insulating and semi-conducting spin-glasses often only have antiferromagnetic exchange as their interaction. As we shall see in section 5.4, the spin-glass we are dealing with in this project is of the insulating type and it is therefore not canonical, nor is it conventional.

To understand some of the physics of spin-glasses we will describe here what Mydosh terms the experimentalist's view of the freezing transition. This is a very qualitative description that does not touch on any of the complexity in theoretical treatments, but it is sufficient in the case of being able to understand superficially what is happening in a spin-glass experiment. It goes as follows: When $T \gg T_f$ the system is in the paramagnetic regime and spins are reorienting rapidly in the presence of large amounts of thermal energy ($k_B T$). As $T \rightarrow T_f$ the spins start building themselves into locally correlated, magnetic clusters that can rotate as a whole. The competition in the system is between the short-range exchange (J) between spins and the disordering effect of thermal energy. When $J > k_B T$ a cluster can be formed. The spins within a cluster can still be oriented in a wealth of directions and each cluster therefore still only has a small magnetic moment on average. Spins that are not part of clusters help communicate interactions between the larger clusters. The nearer we get to T_f , the larger the average communication distance between the spins, and the size of the clusters, get. The 'communication distance' is termed the correlation length,

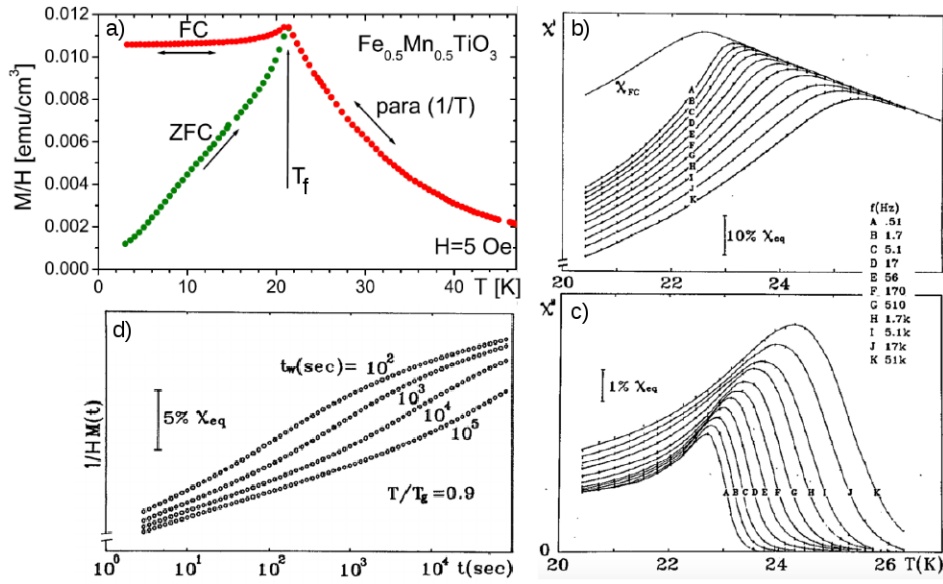


Figure 4.1: (a) FC and ZFC susceptibilities for a single crystal of $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{TiO}_3$. The freezing temperature is marked with an arrow. Figure from Dupuis (2002)⁴¹ (b) χ' for amorphous metallic spin-glass $(\text{Fe}_x\text{Ni}_{1-x})\text{B}_{16}\text{P}_6\text{Al}_3$ at different frequencies of the AC field. The frequencies are marked with capital letters. FC susceptibility at an applied field of 50 mOe is also plotted. 10% of the equilibrium susceptibility is indicated with a vertical line (c) χ'' as previous. 1% of the equilibrium susceptibility is indicated with a vertical line (d) Example of aging dynamics in spin-glass $(\text{Fe}_x\text{Ni}_{1-x})\text{B}_{16}\text{P}_6\text{Al}_3$. ZFC susceptibility and corresponding relaxation rate at different wait times. Figures (b) to (d) are from Svedlindh (1987).⁴²

ξ , and defined via the spin-spin correlation function³⁹

$$\langle S_i S_j \rangle_t^2 \approx e^{-|\mathbf{R}_i - \mathbf{R}_j|/\xi} \quad (4.1)$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are the positions of spins S_i and S_j . The subscript t indicates that the average is taken over a (long) time interval. At T_f the spins freeze into one of the many degenerate ground states. Even in the frozen state we still have some isolated spins rotating freely. The frozen state is only a metastable state and given enough time we would be able to go to other local minima. The freezing process is thus very unlike a standard phase transition where the shift from a SRO state with finite ξ to a LRO state with infinite correlation length happens over a short interval of temperature.³⁹ The freezing transition happens over longer temperature intervals and the correlation lengths are distributed due to the differing sizes of the formed clusters. The distribution progressively broadens while the average shifts to slower values when the temperature is lowered, as bigger clusters have slower dynamics than the rapidly reorienting free spins.

4.1 Experimental characteristics

4.1.1 Susceptibilities

Susceptibility measurements are prevalent whenever we enter a field of magnetism and spin-glasses are no exception to this. In case of conventional spin-glasses the DC susceptibility (χ_{DC}) is linear in T in the high-temperature regime until a point where it deviates from the Curie-Weiss behaviour (as described in section 3.1). If the spin-glass

is cooled down to below the transition temperature in the presence of a field while the magnetisation is measured it is called Field-Cooled (FC) susceptibility. If the sample is cooled down to below T_f in zero field and then heated to above T_f with a field turned on while the magnetisation is measured it is called Zero-Field Cooled (ZFC) susceptibility. For a spin-glass the two susceptibilities diverge from one another when we hit T_f . This is due to the irreversibility of the magnetic response below T_f . The FC susceptibility shows a plateau after the transition and is reversible, while the ZFC curve breaks at the transition temperature and is irreversible. The magnetisation in a spin-glass will only saturate in a high enough field, as the field has to turn *all* the randomly frozen clusters of spins in the same direction to make this happen.³⁹ The magnitude of the ZFC magnetisation will depend on how long the experiment spends at each temperature. This dependence on waiting times, t_w (how long we wait at $T < T_f$ before turning the field on in ZFC measurements) is typical for spin-glasses and many experiments have been performed, where it is shown that the longer we wait, the slower the relaxation will be.⁴⁰ This phenomenon is referred to as aging and an example is given in Figure 4.1 where also the behaviour of the FC and ZFC susceptibility can be found.

AC susceptibility is an important technique for probing the near T_f behaviour. The AC susceptibility has a sharp peak at T_f that shifts to higher temperatures when the driving frequency (ω) of the AC field is increased (and to lower temperatures when ω is decreased). See Figure 4.1. The peak is broadened substantially when a field is applied. The amount of shift is very different between different types of spin-glasses with the canonical RKKY spin-glasses showing only a shift of a few percent.³⁹ Both the real, $\chi'(\omega)$ (related to dispersion), and the imaginary part, $\chi''(\omega)$ (related to absorption) of the AC susceptibility show the shift in temperature with ω . $\chi''(\omega)$ is zero until we reach the freezing temperature from above, whereupon it increases fast. The shifting can be understood in terms of the freezing out of clusters at different temperatures depending on the frequency of the driving field.⁴³

4.1.2 Specific heat

The magnetic specific heat (C_m) as a function of temperature shows a rounded peak near T_f . T_f is therefore not well-defined from specific heat measurements alone. The behaviour is furthermore very field dependent and the peaks is smeared out quickly when a field is applied. Much of the magnetic entropy is already frozen out far above T_f and applying a field shifts more of it from the low temperature part of C_m to the high temperature part.³⁹ A feature that is often highlighted as a characteristic of spin-glass behaviour is that C_m is linear as a function of T in the frozen regime.

4.1.3 Neutron scattering

In a neutron scattering experiment on a magnet we usually look for magnetic Bragg peaks in the elastic signal and signs of propagating spin-waves in the inelastic signal. Since there is no LRO in spin-glasses neither of these features are found. Spin-glasses are however not devoid of inelastic scattering, and broad scattering features have been found, indicating short-ranged order in the materials.

Any process that is slower than the neutron experiment time scale (for example the relaxation time of a particularly large cluster) will be lumped into the elastic or static part of the dynamical correlation function (see paragraph 3.2.3). The truly dynamical part of the correlation function therefore comes from the faster processes which show up as quasi-elastic scattering. When the paramagnetic state is destroyed by the spin-spin correlations that appear upon cooling the quasi-elastic contribution will gradually be converted to elastic scattering, because

the cluster formation creates a distribution of relaxation times linked to the size of the clusters.³⁹

5 | Jarosite literature study

Jarosites have been a field of study for many decades, and the pile of papers with jarosites mentioned is ever-growing. Before diving into the data for this project we therefore sorely need a solid overview of what has been happening in the field. The first part of this chapter will describe the chemical composition and structure of jarosites and the second part will tackle the different synthesis methods. The third part will walk through (some of) the research done on the structure and magnetism of potassium jarosite, which is the most widely studied of the jarosites. The fourth and final part will go through the research done on hydronium and deuterium jarosite as well as collecting the variety of theories regarding the lack of order in this very special jarosite.

5.1 Chemical and crystallographic structure of jarosite materials

The jarosite family of minerals encompasses compounds with structure formula $AB_3(OH)_6(SO_4)_2$, where A^+ is a monovalent cation (for example $A^+ = K^+, H_3O^+, NH_4^+, Rb^+$ and Na^+) and B^{3+} is a trivalent ion (usually $B^{3+} = Fe^{3+}, Cr^{3+}$ or V^{3+}). The jarosites are isostructural with the diamagnetic sister compound alunite ($B = Al^{3+}$ in the structure formula).

The jarosite structure is shown from two angles in Figure 5.1a. The magnetic ions (in this case iron) are placed on the kagomé lattice, which lay in the ab -plane of the structure. The Fe ions are surrounded by tilted octahedra of oxygen. There are four (locally) horizontal bonds going out from the iron atom. These are slightly shorter than the two (locally) vertical bonds. They are referred to as the equatorial and the apical oxygens/bonds, respectively. The equatorial bonds connect to other magnetic ions through a hydroxide group (referred to as the bridging hydroxide group, as it bridges the two octahedra). The apical oxygens connect to the tetrahedral/pyramidal sulfate groups (the capping groups) that are placed alternately above and below the kagomé layers; in between the layers reside the cations. In all jarosites there are possibilities for hydrogen bonds from the apical oxygen atoms to the bridging hydroxide hydrogens. In hydronium jarosite there are extra opportunities for hydrogen bonding; each proton in H_3O^+ can be hydrogen bonded to two sulfate oxygen atoms (bond length 2.562 Å) and to the oxygen in the bridging hydroxide group (bond length 1.948 Å).⁴⁵

Bond angles and lengths are remarkably similar across all the different jarosites (vanadium, iron, chromium), only the interlayer distance fluctuates with the size of the cation.⁴⁶ Unit cell parameters for some jarosites are shown in Table 5.1.

The primitive unit cell of jarosites (marked on Figure 5.1a) is the rhombohedral one and has lattice vectors⁵¹

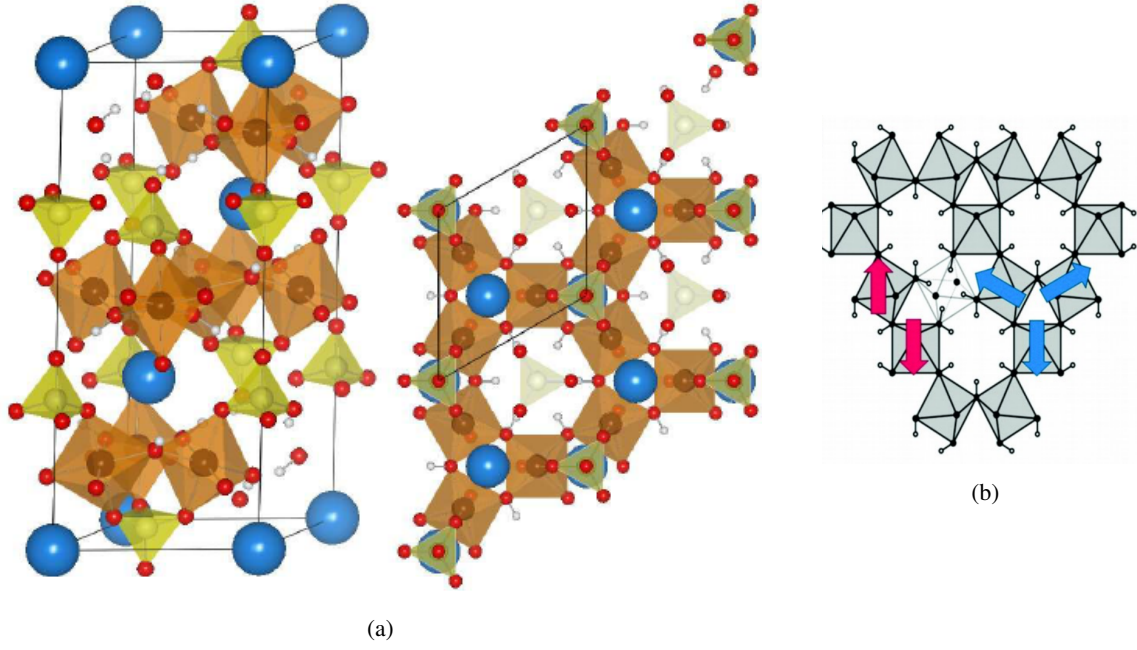


Figure 5.1: **(a)** left picture: View of the jarosite structure perpendicular to the c -axis and inside the conventional unit cell. Larger dark red spheres are iron ions, smaller red spheres are oxygen, white spheres are hydrogen, blue spheres are potassium and yellow/grey spheres are sulphur. The octahedra are highlighted in dark orange and the pyramidal structure of the capping group is highlighted in yellow/grey. Right picture: View of the structure along the c -axis. The primitive unit cell is marked with solid lines and the kagomé structure is visible. Figure is from de Vries et al.⁴⁴ **(b)** Jarosite structure with an iron vacancy. The blue arrows indicate the direction of the frustrated (iron) spins. The red arrows show the local antiferromagnetic coupling happening near a vacancy. Figure from Nielsen et al..³⁶

$$\mathbf{a}_1 = \frac{a}{2}\hat{i} + \frac{\sqrt{3}a}{3}\hat{j} + \frac{c}{3}\hat{k} \quad (5.1)$$

$$\mathbf{a}_2 = -\frac{a}{2}\hat{i} + \frac{\sqrt{3}a}{6}\hat{j} + \frac{c}{3}\hat{k} \quad (5.2)$$

$$\mathbf{a}_3 = -\frac{\sqrt{3}a}{3}\hat{j} + \frac{c}{3}\hat{k} \quad (5.3)$$

The kagomé layers are stacked along the c -direction in a staggered manner; i.e. every time we add a kagomé plane to the structure along the c -axis, it is displaced with $a/2\hat{i}$. We need three kagomé layers to return to the first position and hence the conventional unit cell has three kagomé layers stacked on top of each other (visualised in Figure 5.1a). The height of the conventional unit cell is c and the structure crystallises in the space group $R\bar{3}m$ (ITC 166).⁴⁶

Compound	a [Å]	c [Å]	Reference
$\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$	7.3044(7)	17.185(2)	Grohol et al. (2003) ⁴⁷
$(\text{H}_3\text{O})\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$	7.32457 (12)	16.9153 (4)	Wills and Harrison (1996) ⁴⁵
$(\text{DH}_4)\text{Fe}_3(\text{OD})_6(\text{SO}_4)_2$	7.32877(32)	17.3024(8)	Wills et al. (2000) ⁴⁸
$\text{KCr}_3(\text{OH})_6(\text{SO}_4)_2$	7.2215(1)	17.2343(2)	Janas et. al. (2020) ⁴⁹
$\text{KV}_3(\text{OH})_6(\text{SO}_4)_2$	7.2737(7)	17.399(2)	Grohol and Nocera (2002) ⁵⁰

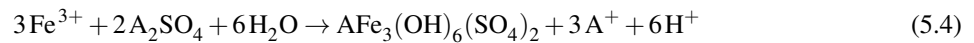
Table 5.1: Unit cell parameters for a variety of jarosites. The unit cell has $a = b$.

5.2 On the synthesis of jarosites

5.2.1 The conventional hydrothermal method and its shortcomings

Historically jarosites have been prepared via conventional hydrothermal synthesis. The description is almost in the name; a hydrothermal synthesis is a synthesis that happens in aqueous solution above the boiling point of water. The point to doing it this way is that it can be carried out at much lower temperatures than in the solid state, as transport of reactants is easier in liquid. The synthesis happens inside a sealed autoclave, and as the water heats up, the inside of the container becomes pressurised, allowing the temperature of the water to rise above the boiling point.⁵²

A typical conventional hydrothermal synthesis of iron jarosite, $\text{AFe}_3(\text{OH})_6(\text{SO}_4)_2$, uses sulfates as the reactants ($\text{Fe}_2(\text{SO}_4)_3$ and A_2SO_4), dissolves them in water, seals the mixture in an autoclave and leaves it in an oven for a given amount of time. A picture of a small autoclave can be found in Figure 5.2a. In order for the jarosites to precipitate the pH value of the solution must be below 2.⁵³ The temperatures and oven times vary, typically from 140° to 200° and between 24 h and 56 h (see for example Inami et al.⁶ or Frunzke et al..⁵⁴) The overall reaction therefore all happens in one step



Afterwards the precipitated jarosite is washed with water and dried either in air or in the oven at a lower temperature. The resulting crystallites are typically small ($5\text{-}20\ \mu\text{m}$),⁵⁵ and it has, to our knowledge, not been possible to prepare a larger single crystal using this method. The method does not always produce stoichiometrically pure jarosites. The most frequent changes to the ideal structure are vacancies on the Fe site (unoccupied sites in the kagomé lattice) and exchange of the monovalent cations (A^+) for hydronium ions (H_3O^+). The magnetic properties of jarosites are very dependent on the exact chemical composition, as iron vacancies can lift the geometric frustration. If $\sim 30\%$ of the iron sites are unoccupied, each triangle will only host two spins on average, which will make it possible for the system to easily fulfil the antiferromagnetic nearest neighbour coupling it so longs to fulfil (see Figure 5.1b); the ordered state and ordering temperature will reflect the changed chemistry.^{46,49,54} Unstoichiometry has mostly been a problem for jarosites that do not host hydronium as the A-site ion, as hydronium jarosites usually have a high M and A-site occupancy.⁴⁵

Jarosites prepared using the conventional hydrothermal method often show two phase transitions in susceptibility measurements,^{48,54,56} the reason for this phenomenon was explained by Grohol and Nocera.⁵⁶ The initial reac-

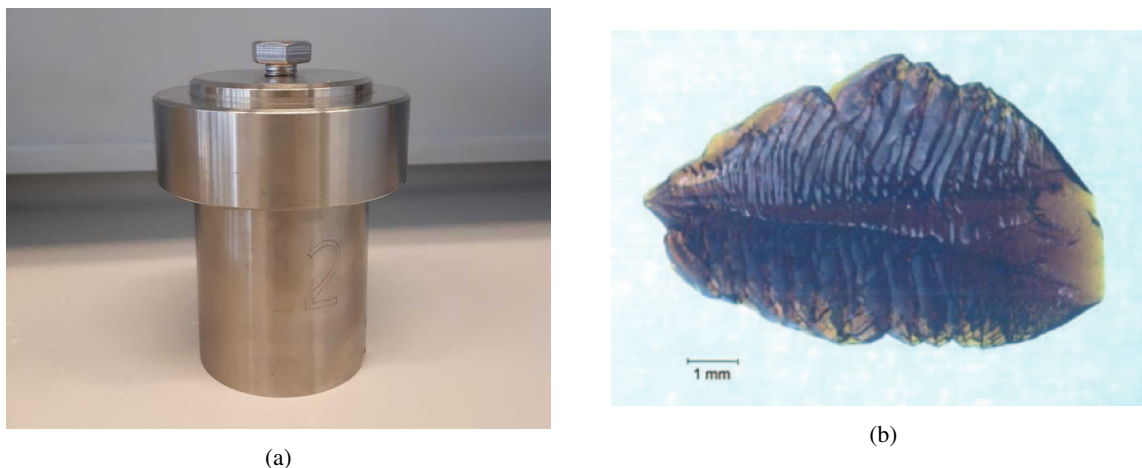
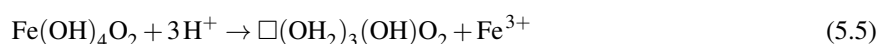


Figure 5.2: **(a)** Example of autoclave used for hydrothermal synthesis. The autoclave in the picture has a Teflon container with a lid inside and belongs to Professor Ulla Gro Nielsen from University of Southern Denmark **(b)** Single crystal weighing 48 mg synthesised by Grohol et al. The crystal is approximately 1 cm in length.⁵⁷

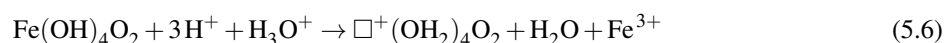
tion solution is very rich in alkali ion with very little hydronium ion present. As the jarosite precipitates the ratio of the two ions in the solution shifts; alkali ion is used and hydronium ion is built up (as according to Equation 5.4 both water and protons are present). The jarosite that precipitates later in the reaction will therefore have more hydronium ions incorporated than the earlier precipitate, creating a product that has alkali-rich islands and hydronium-rich islands. The different parts of the sample will then naturally show up as having two different transitions.

5.2.2 The defect mechanism in jarosite

The mechanism by which defects are introduced into the structure has been studied in great detail for both jarosite and alunite by Nielsen et al.,^{32,58} and since the compounds are isostructural the same mechanism is applicable to both. Let us first consider the effect of a vacancy at the Fe-site^{32,58}



$\text{Fe}(\text{OH})_4\text{O}_2$ in the formula above is the stoichiometric jarosite octahedron with its four bridging hydroxide groups and its two apical oxygens connecting to capping sulfate groups. Removing one Fe^{3+} -ion creates a vacancy ($\square$ symbol), which leads to a charge imbalance of +3, as well as four terminal groups of $\text{Fe}-\text{OH}$ (instead of the normal Fe_2-OH). The charge imbalance is compensated by the binding of three additional H^+ to three of the bridging hydroxide groups, creating $3\text{H}_2\text{O}$. The last hydroxide group above is left alone, but it is possible that this group is protonated as well, even though it will give a net charge of +1. The extra charge can be compensated by a vacancy at the A-site or by a hydronium ion on the A-site giving up a proton in the following manner^{32,58}



Nielsen et al.⁵⁸ found that this was indeed what happened in alunites, and the same thing is true for jarosites.^{32,37}

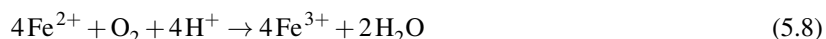
5.2.3 The redox hydrothermal method

The issues with the conventional hydrothermal method was solved by Grohol and Nocera, who invented the redox hydrothermal method of synthesis. The method was used firstly to synthesise a series of single-crystalline and stoichiometrically pure vanadium jarosites⁵⁰ that were subsequently magnetically characterised.⁵⁹ The applicability of the method to other jarosites was quickly proven and the vanadium work was followed up by synthesis and characterisation of iron^{47,60} and chromium jarosites.⁴⁶ In a slightly modified version the method also produced a large single crystal (Figure 5.2b) suitable for neutron scattering experiments.^{57,61}

Grohol and Nocera found that the main issue with the conventional method was the speed with which the synthesis happened. They slowed down the synthesis by inserting a controlling step; instead of having the iron ions readily available in the solution from the beginning of the synthesis, they are generated during the synthesis by oxidation of solid iron metal (in the form of a lump of iron or a piece of iron wire), first by protons in the reaction solution



Following the first oxidation, the iron(II) ions are oxidised a second time to iron(III). This oxidation happens using the oxygen in the air and allows for very slow and controlled introduction of iron(III) to the solution



The precipitation of jarosites then happen according to equation (5.4). When the redox hydrothermal method was used to produce large single crystals (up to 10 mm and 48 mg), a Teflon disc floating on top of the solution was used to slow down the uptake of oxygen.⁵⁷ Another study limited the oxygen uptake by using a glass container with a small hole.⁴⁴

Bisson and Wills (2007)⁵³ proposed that the reason this synthesis method works so well is because it creates a charge neutral intermediate, Szomolnokite ($\text{Fe}^{2+}\text{SO}_4 \cdot \text{H}_2\text{O}$), which they identified by powder X-ray diffraction. It reduces the need for charge compensation of iron vacancies and the stoichiometry of the resulting jarosites is then a direct result of the stoichiometry of the intermediate. The intermediate is not seen in the conventional synthesis method, as it grows on the solid iron metal. It is worth pointing out that the synthesis in this study was carried out at lower temperatures than is common for redox hydrothermal syntheses.

5.3 Potassium jarosite

Potassium jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$) is a naturally occurring mineral and is for this reason seen in many different fields of science. For our purposes we narrow our field of vision to research dealing with the magnetic structure and behaviour of the mineral. Our starting point is therefore the 1986 paper by Townsend et al.,⁶² as this was the first paper to investigate the magnetic ground state of the mineral with neutron scattering. They were also the first to synthesise the synthetic Cr-analogue of jarosite. They found a doubling of the magnetic unit cell as compared to the structural. The proposed magnetic structure was however not entirely correct, as was pointed out by Inami et al. in 2000.⁶ The doubling of the magnetic unit cell was confirmed, but the structure was the so called $q = 0$, 120° spin structure, where the spins are located in the ab -plane (kagomé plane), as visualised in Figure 5.3d. The $q = 0$ structure has two chiralities ($\kappa = \pm 1$) that are degenerate with respect to energy if only nearest neighbour Heisenberg interactions are considered. The chirality is given by

$$\kappa = \left(\frac{2}{3\sqrt{3}} \right) (\mathbf{S}_1 \times \mathbf{S}_2 + \mathbf{S}_2 \times \mathbf{S}_3 + \mathbf{S}_3 \times \mathbf{S}_1) \quad (5.9)$$

The chirality is defined for one triangle in the kagomé lattice at a time (the indices refer to the three spins). A triangle with positive chirality has the spins going 120° in the clockwise direction around the triangle, and a triangle with negative chirality has the spins going around the triangle with 120° between them in the counter clockwise direction. Three long range ordered Néel states are usually proposed as possible ground states at this

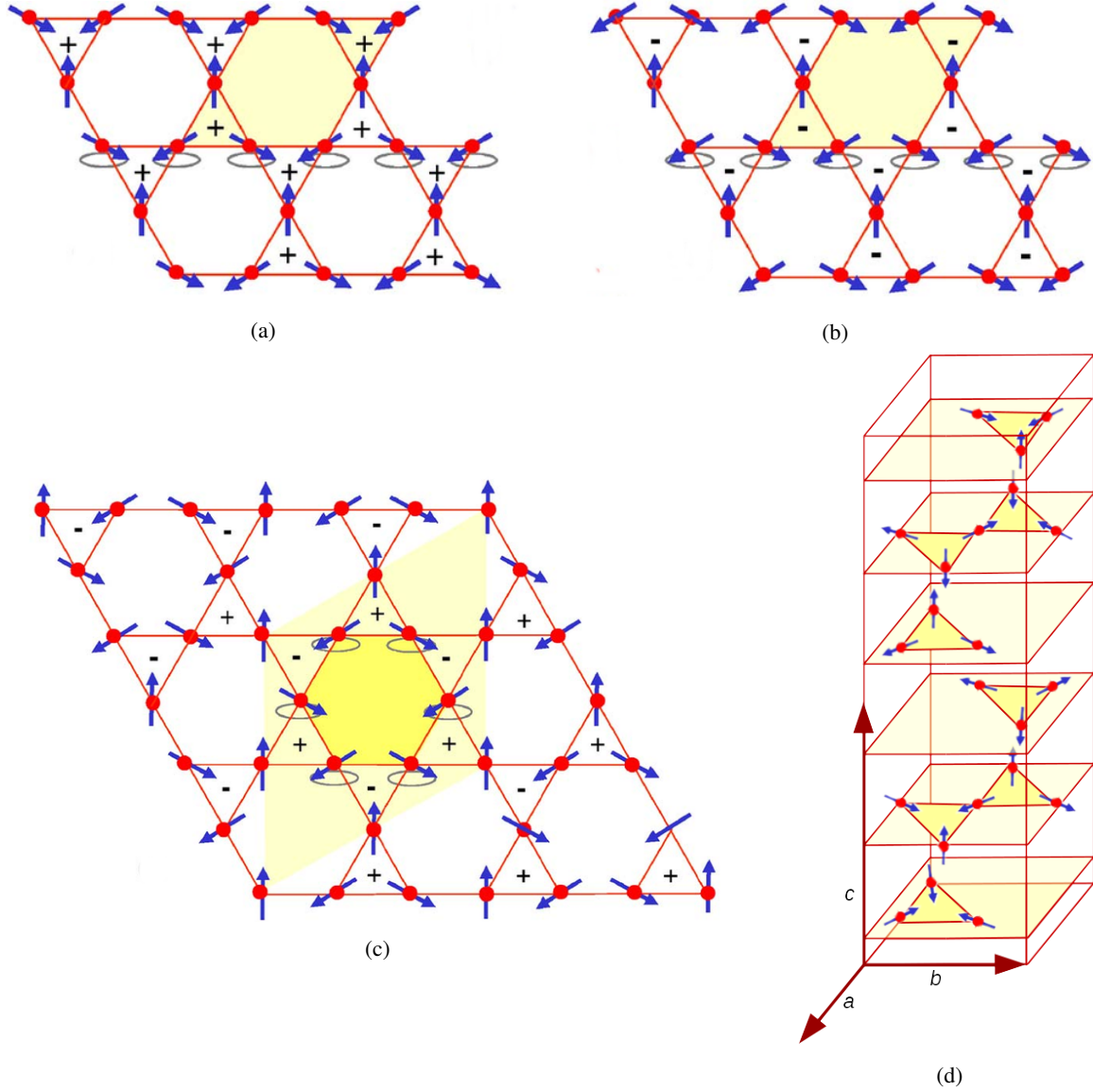


Figure 5.3: **(a)** $q = 0$ ordered state with positive chirality **(b)** $q = 0$ ordered state with negative chirality **(c)** $\sqrt{3} \times \sqrt{3}$ structure with mixed chirality **(d)** $q = 0$, 120° spin configuration with positive chirality. The doubling of the c -axis compared to the structural unit cell is visualised. The light yellow areas on figures (a) to (c) indicate the unit cells and the plus and minus signs indicate the chirality. The small circles indicate ways in which the spins can rotate without any energy cost. Figures (a)-(c) are from Yildirim and Harris (2006).⁵¹ Figure (d) is adapted from Nishiyama et al. (2003).⁵⁵

point: The $q = 0$ structure with all triangles having $\kappa = +1$ (Figure 5.3a), the $q = 0$ structure with all triangles having $\kappa = -1$ (Figure 5.3b) and the $\sqrt{3} \times \sqrt{3}$ structure with mixed chirality (Figure 5.3c). Inami et al. found only the positive chirality experimentally. Naturally the question then arises; what causes the selection of the ground state with the positive chirality over the one with negative chirality? Since the two chiralities are degenerate with respect to the NN Heisenberg interaction there must be another interaction present.

Inami et al. proposed that the interaction in question was a single-ion crystal field (CF) type anisotropy, and that in order to partly satisfy this interaction the spins on a triangle cant slightly out of the plane (often denoted an umbrella structure). A small ferromagnetic moment therefore develops on each kagomé plane, but the layers stack antiferromagnetically, thus preventing an overall ferromagnetic moment.

On the other hand, in 2002, a theoretical paper by Elhajal et al.⁹ proposed that the DM interaction could be the cause of the symmetry breaking, canting and subsequent ordering in the jarosites. The paper was supported by another similar paper by Ballou et al.⁶⁵ in 2003 (includes all authors from the 2002 paper). Using Moriya's rules (previous section) on the kagomé lattice yields two important facts about the DM interaction

- 1 The midpoint between two magnetic ions placed on the kagomé lattice is not an inversion centre, and therefore the DM interaction is allowed by the lattice symmetry.
- 2 The kagomé plane is a mirror plane. Referring to the third rule, this then means that the DM-vector is perpendicular to the kagomé plane.

The symmetry in jarosite is however lower than in the idealised kagomé material. The octahedra surrounding

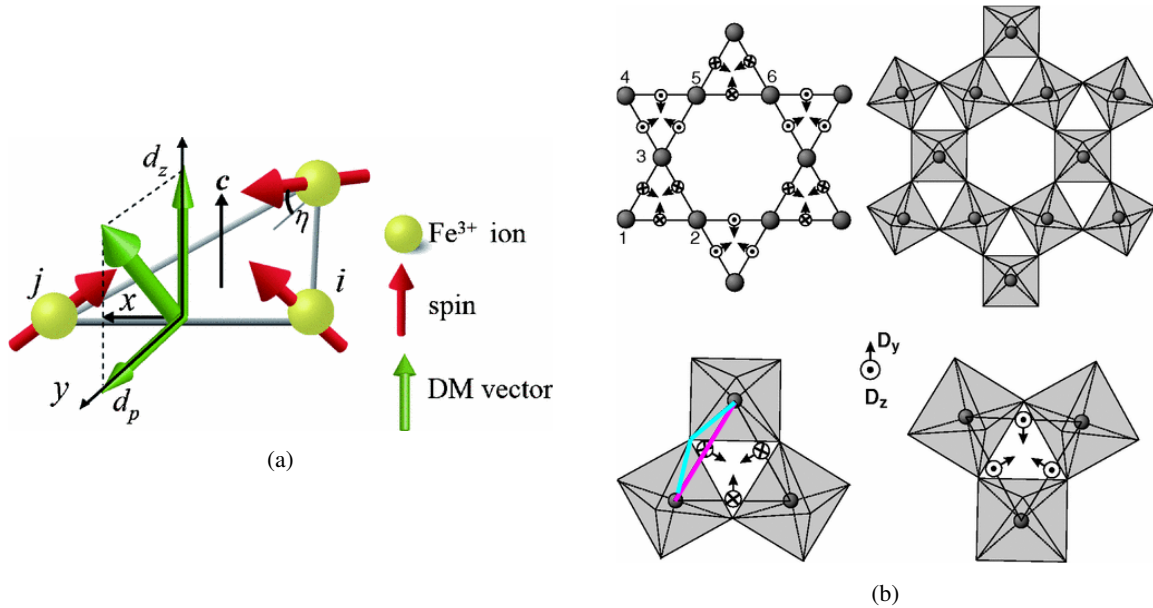


Figure 5.4: **(a)** Direction of the DM-vector (fat green arrow) on one triangle of the kagomé lattice. The in-plane (d_p) and out-of-plane (d_z) contributions are visualised as slim green arrows. The spins are shown in the canted configuration. The figure is from Fujita et al. (2012)⁶³ **(b)** Orientation of the DM-vectors in the jarosite structure seen from many different angles. The pink line in the bottom left picture represents the bond ij mentioned in the text. The two blue lines are the bonds to the OH oxygen. The mirror plane in jarosites is the plane containing the triangle made up of the three bonds. The DM-vector is perpendicular to this plane. The circles with a cross indicates that the vector is pointing slightly into the paper while the dot in a circle indicates the vector is pointing slightly out of the paper. The figure is adapted from Matan et al. (2011).⁶⁴

the magnetic ions are tilted such that their local axes are no longer perpendicular to the kagomé plane, and this prevents the kagomé plane from being a mirror plane from the perspective of the non-magnetic ions. Even though we are talking about magnetism we cannot neglect the non-magnetic ions, as they take part in the superexchange interactions between the magnetic ions and are responsible for the crystal field. The second fact is therefore altered in jarosites

- 2 In jarosites the mirror plane is the plane containing the bond between spin i and spin j . The DM-vector is perpendicular to this plane and not to the kagomé plane itself. The mirror plane and the bond is visualised in Figure 5.4b.

The DM-vector in jarosites has an out-of-plane component (D_z) and an in-plane component (denoted as either D_y or D_p in the literature). The components are shown in Figure 5.4a. D_z changes direction when we move up or down one kagomé layer, following the changing octahedral tilt. It points alternately directly up along the crystalline c -direction (as in Figure 5.4a and as shown by the circles with dots in Figure 5.4b) or opposite to the crystalline c -direction (as shown by the circles with crosses in Figure 5.4b). The in-plane component always points towards the centre of the triangle⁶⁴ (as such there is a discrepancy in Figure 5.4a: The in-plane component of the DM-vector (and the DM-vector) should actually be turned towards the centre of the triangle if Matan et al. is correct). An overview of the directions of the DM-vectors in the jarosite structure from different angles can be found in figure 5.4b.

Using Monte Carlo simulations Elhajal et al.⁹ showed that as soon as the DM interaction is turned on, the kagomé system orders, indicating that the low temperature behaviour of jarosites is dominated by the DM interaction.⁹ Furthermore, the SIA crystal field effects should actually be weaker than the DM effects, as SIA is second order in the spin-orbit coupling⁵⁵ while DM is first order.⁶⁵ Experimental support for the DM hypothesis as the cause of the canted spin structure and resulting weak ferromagnetic moment was found by Grohol et al.⁴⁷ in their study of the magnetism of stoichiometrically pure iron jarosites synthesised via the redox hydrothermal method. Grohol et al. furthermore beat down and subsequently buried the theory that the three-dimensional order in potassium jarosites was due to unstoichiometry in the samples that hitherto had been synthesised using the conventional method and not been reliably chemically characterised.

A picture of the static magnetic structure of potassium jarosite is emerging and solidifying, but the spin dynamics had yet to be properly studied. Theoretically, spin-waves were expected on the basis of an ordered structure.^{65,66} The first to probe the spin dynamics experimentally were Nishiyama et al. in 2003⁵⁵ (same group of people who took part in the Inami et al. 2000 paper that initially clarified the static structure). They confirmed the $q = 0$, positive chirality structure with powder ^1H NMR and found evidence for the presence of spin-waves by modelling the spin-lattice relaxation rate in the NMR experiment below the ordering temperature as a two-magnon process. NMR is however not the most straightforward way to probe magnetic structure and dynamics; inelastic neutron scattering was bound to make its entrance, and in 2005 it did.

The first inelastic neutron scattering study was performed by Grohol et al.⁵⁷ on a ~ 1 cm, 48 mg single crystal synthesised via the redox hydrothermal method (Figure 5.2b). The behaviour of the spins was probed right above (70 K) the ordering temperature (65 K) in the $L = 0$ plane in reciprocal space. No correlations between the kagomé layers were found at this temperature, as 3D order has yet to set in, however 2D (within each kagomé layer) spin fluctuations created rods of scattering along the L direction (Figure 5.5). The rods disappeared upon cooling below the ordering temperature, where magnetic Bragg scattering took their place. This indicated that a type of short range order was present before the transition to the long range ordered state. The placement of the scattering and

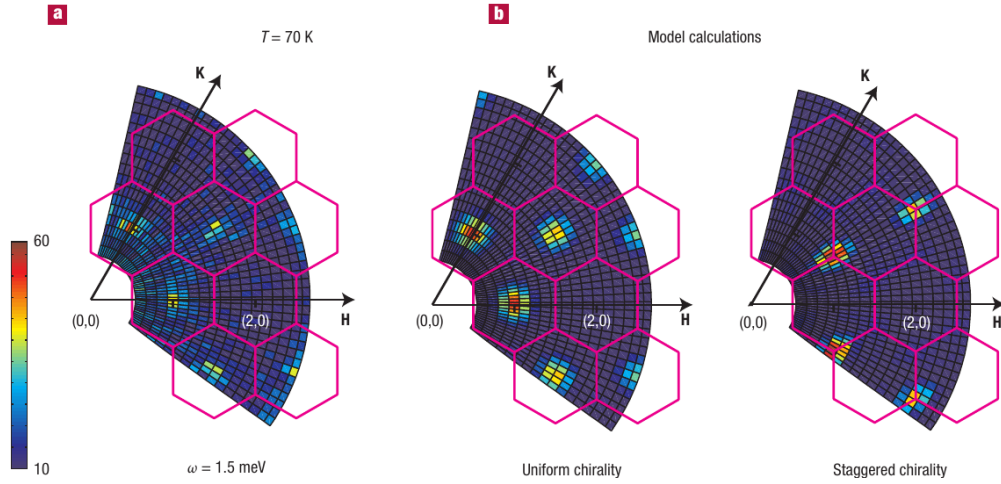


Figure 5.5: Inelastic neutron scattering results from Grohol et al.⁵⁷ taken at 70 K, above the ordering temperature. The red outlines are the structural Brillouin zones. **(a)** Scattering from low energy spin fluctuations ($\omega = 1.5$ meV) **(b)** Model calculations for uniform chirality ($q = 0$, positive chirality) and staggered chirality $\sqrt{3} \times \sqrt{3}$.

modelling of the scattering intensity clarified that the SRO correlations had the $q = 0$ structure and uniform, positive chirality, just as the LRO state. It was furthermore found that a field of around $H_C = 12$ T at 55 K (defined as the point where dM/dH is at maximum and denoted the critical field) applied parallel to the c -axis could overwhelm the antiferromagnetic coupling between the layers and rotate the spins on alternate kagomé layers 180° to give a stronger ferromagnetic response. To describe the transition further, the authors introduced yet another chirality; the scalar chirality

$$K_S = \mathbf{S}_1 \cdot (\mathbf{S}_2 \times \mathbf{S}_3) \quad (5.10)$$

This chirality is also defined for one triangle at a time, and can be non-zero only if the spins cant out of the plane. When the system undergoes the field-induced transition to a ferromagnetically coupled state, the net scalar chirality goes from $K_S = 0$ to $K_S \neq 0$. The field-induced transition on the same crystal sample was investigated further by Matan et al. in 2011,⁶⁴ and therefore we now take a look at the extended results. The original Matan et al. study only postulated that the 180° rotation took place, but the new study found direct evidence through elastic neutron scattering. When the spins rotate, the magnetic unit cell will return to being the same size as the structural unit cell (only three kagomé layers), while, if the spins simply flip the magnetic unit cell will stay the same and require 6 kagomé layers. The unit cells before and after the transition are shown in Figure 5.6a

The critical field is dependent on temperature and increases when the temperature is lowered. This allowed approximations of the interplane coupling strength to be made, and it was found to be $\sim$ hundred times smaller than the intraplane (NN) couplings.^{57,64} The jarosites therefore presented themselves as being highly two-dimensional in nature (the journal as well as the concept). A polarised neutron scattering experiment by Matan et al. (2009)⁶⁷ supported the two-dimensionality by showing that the spin fluctuations in spinspace above the ordering temperature are mainly happening in the kagomé plane. Having now explored the multitude of Matan et al. studies we return to the chronological order of things.

The spin-wave dispersion relations were first calculated by Nishiyama et al.⁵⁵ who assumed SIA as the relevant interaction for ordering. In their derivation they however neglected the spin canting angle out of the kagomé

plane, and this turned out to be not entirely appropriate. In 2006 Yildirim and Harris⁵¹ included the canting in their very thorough derivation of the spin-wave dispersion relations for potassium jarosite. The symmetry analysis was carried out using irreducible representations, which, the authors claimed, is much more fundamental than the hitherto used chiralities, as the ordered structures differentiated by their chiralities (Figure 5.3a, Figure 5.3b and Figure 5.3c) are "just" some of the irreducible representations possible. Yildirim and Harris neglected the interplane coupling and looked at the system as truly two-dimensional. The approximation is a good one, based on the small interplane coupling found by Grohol et al.⁵⁷ (described just above). The theoretical dispersion relations were fit to the experimental dispersion relations measured on a large single crystal by inelastic neutron scattering by Matan et al. (similarly in 2006).⁶¹ Collectively the two papers provided the final answer to the spin-dynamics in potassium jarosite, which we will go through now

The experimental results from Matan et al. (2006) revealed the following spin-wave modes

- An almost flat mode that disperses weakly from ~ 7 meV up to ~ 9 meV. This is the zero-energy mode of the kagomé lattice that has been lifted up from 0 meV due to the anisotropy. The small dispersion of the mode is due to weak NNN interactions, and without this interaction it is not possible to reproduce the weak dispersion; the mode will turn out completely flat. The mode is also seen very clearly in inelastic neutron scattering on powders (Figure 5.6b).
- An in-plane mode with a gap at 1.7 meV
- An out-of-plane mode with a gap at 7 meV

The polarized inelastic neutron scattering study by Matan et al. (2009)⁶⁷ confirmed that the 1.7 meV mode was predominantly in-plane in spinspace, while the 7 meV modes (flat and dispersive) were predominantly out-of-plane in spinspace.

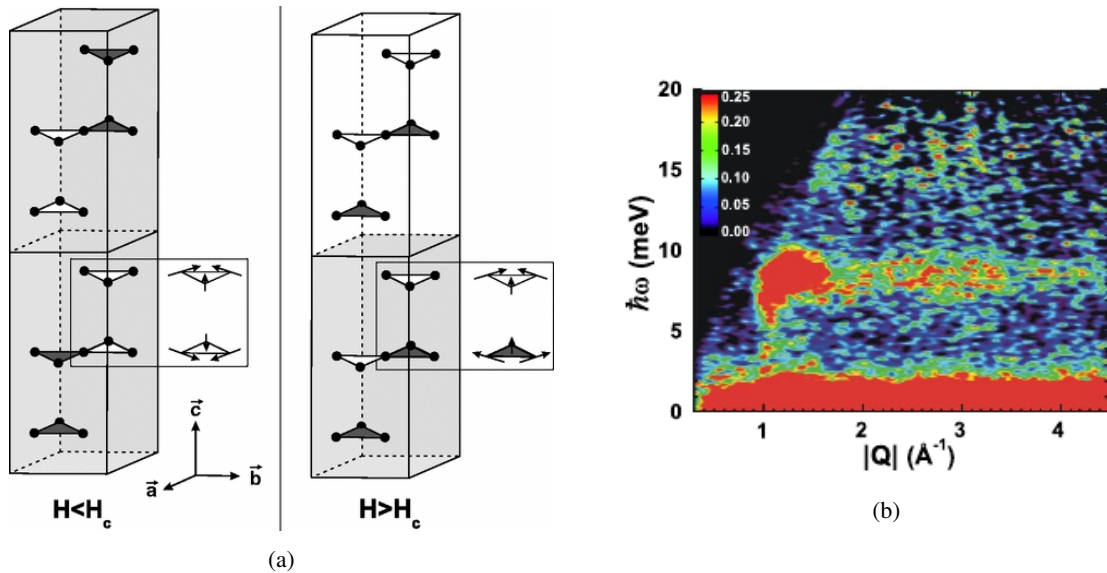


Figure 5.6: (a) Orientation of spins on the kagomé lattice in jarosite before and after the field-induced transition with the size of the magnetic unit cell highlighted. Figure from Matan et al.⁶⁴ (b) Contour map of inelastic scattering at $T = 4$ K. Data was taken on the Time-of-Flight spectrometer DCS (NIST) with an incoming wavelength of 1.8 $\text{\AA}$. Figure is from Matan et al. (2006).⁶¹

Parameter	Fitted value	Mode	Theoretical expression
J_1	3.18(5) meV	ω_0	$\sqrt{12} D_y $
J_2	0.11(1) meV	$\omega_{\pm}$	$[3D_y^2 + 18D_z^2 - 6\sqrt{3}(J_1 + J_2)D_z]^{1/2} \pm 2D_y D_z / (J_1 + J_2)$
$ D_y $	0.197(2) meV		
D_z	-0.196(4) meV		

Table 5.2: Relevant coupling parameters for the DM-model, their fitted values and the calculated expressions for the spin-wave modes in terms of the parameters. $\omega_{\pm}$ is the in-plane and out-of plane mode mentioned in the text. Values and table is reproduced from Matan et al.⁶¹

In order to determine once and for all which anisotropy was the relevant one, Yildirim and Harris fitted both a DM-model and a CF SIA model to the data from Matan et al (2006). The Hamiltonian used for this purpose was a rather general one that included nearest neighbour (J_1), next-nearest neighbour (J_2), single-ion anisotropy (D and E) as well as the DM interaction ($\mathbf{D}_{ij} = [0, D_y(i, j), D_z(i, j)]$ for bond ij).

$$H = \sum_{nn} [J_1 \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)] + \sum_{nnn} J_2 \mathbf{S}_k \cdot \mathbf{S}_l + D \sum_i (S_i^{y'})^2 - E \sum_i [(S_i^{z'})^2 - (S_i^{x'})^2] \quad (5.11)$$

The single-ion anisotropy terms and the axes x' , y' and z' (locally rotated to fit the tilted octahedra) are the ones used by Nishiyama et al.⁵⁵ In case of the DM model, the fitted parameters were J_1 , J_2 , D_y and D_z . For the crystal field model the relevant parameters were J_1 , J_2 , D and E . The best fit to the models are shown in Figure 5.7a (DM) and Figure 5.7b (CF). The largest difference in the fits were found at the high symmetry points of the reciprocal lattice (Γ , X and Y) and especially the spin gaps were affected. The spin gaps are particularly sensitive to the spin canting angle; the fit to the DM model gave a canting angle of 2.09° while the CF model fit gave a much smaller angle of 0.77° . The canting angle was calculated based on experimental measurements of the ordered moment to be $0.65(6)^\circ$ at $T = 50$ K (in a field close to H_C), which is much closer to the CF estimate than the DM estimate. The value is however expected to increase upon cooling when the magnetisation reaches its low temperature value.⁵⁷ A later experiment carried out below 30 K found a canting angle of $1.3(2)^\circ$.⁶⁴ Despite the lack of agreement between the experimentally and theoretically determined canting angles the DM model still

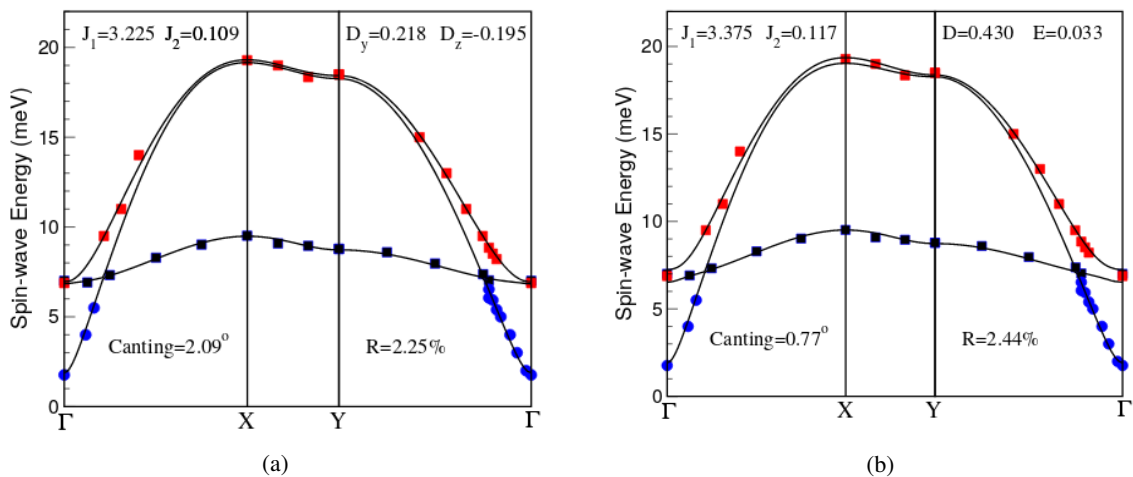


Figure 5.7: (a) Fit to the DM model (b) Fit to the CF model. Figures from Yildirim and Harris.⁵¹

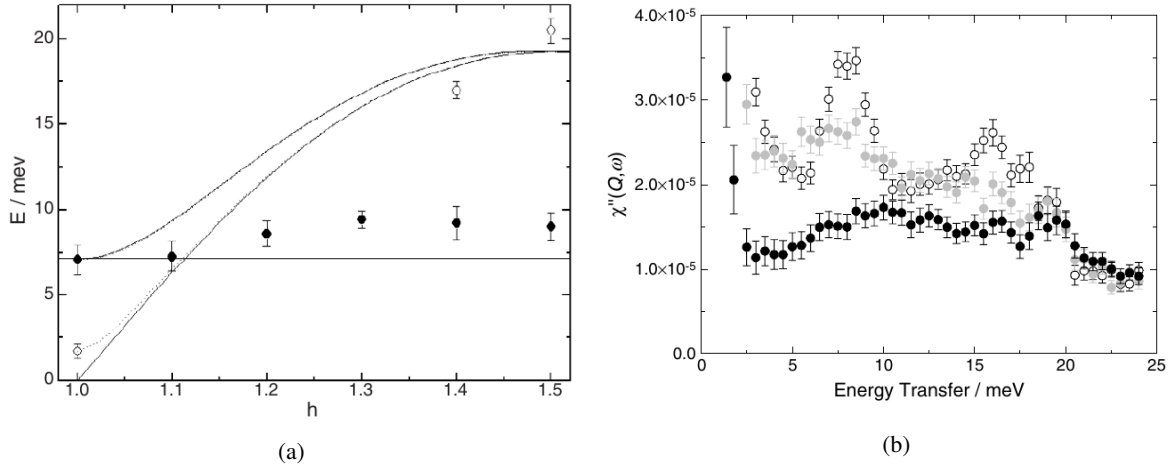


Figure 5.8: **(a)** Dispersion of spin-waves in a natural jarosite crystal. Direction is along $\mathbf{Q} = (h h 1.5)$ and the temperature is 5 K. The solid circles belong to the weakly dispersive mode, the open circles to the more strongly dispersive modes. The solid and dotted lines are fits to a DM and CF model. **(b)** $\chi''(\mathbf{q}, \omega)$ for deuterated potassium jarosite along $q = 1.75 \text{ \AA}^{-1}$. ("Q" on the plot axis is synonymous with our q). Data is taken at 1.5 K (open circles), 57.5 K (grey circles) and 150 K (black circles). All results are from Coomer et al..⁶⁸

provided the best description of the data and in the end it was concluded by Yildirim and Harris⁵¹ and Matan et al.⁶¹ that DM interaction was in fact the correct anisotropy to reproduce the experimental spin-wave dispersion relations for jarosite. An ESR study by Fujita et al. provided further support for this claim.⁶³ The fitted parameters as well as the theoretically calculated expressions for the mode energies have been reproduced in Table 5.2.

The effect of the different DM components on the behaviour of the spin-wave dispersions is complicated. The main dependencies for D_y and D_z are roughly summarised below

D_y : Breaks the rotational symmetry around the c axis and creates a small anisotropy with respect to the in-plane interactions. This is the cause of the in-plane spin gap (1.7 meV, proportional to $|D_y|$). The ordering in the plane affect the canting of the spins, and thus D_y causes the spins to cant out of the plane, giving the famous umbrella structure. The direction of the canting is decided by the sign of D_y .

D_z : Pushes the spins into the ab -plane and thereby functions as an easy-plane anisotropy. It furthermore breaks the symmetry between the negative and positive chirality and chooses the chirality ($D_z > 0 \rightarrow$ positive chirality and $D_z < 0 \rightarrow$ negative chirality). It is lastly responsible for lifting the the zero-energy mode to finite energy.

Simultaneously with Matan et al. (2006) and Yildirim and Harris, Coomer et al.⁶⁸ were performing inelastic neutron scattering measurements on a natural single crystal jarosite sample and a deuterated powder sample. We will describe their results next. Due to incoherent scattering from hydrogen in the natural sample the data quality of the single crystal measurements was poor. The weakly dispersive mode observed by Matan et al. (2006) was clearly visible in Coomer et al. data; the more strongly dispersive modes less so (the results are copied into Figure 5.8a). Both types of modes were fit to a CF and DM model but with inconclusive results as to which was better. The powder data are reproduced in Figure 5.9. In the spectra the flat mode was observed along $E \sim 7 \text{ meV}$, and it furthermore had a large dependence on the momentum transfer. The maxima in intensity were found at $q = 1 \text{ \AA}^{-1}$ and $q = 3 \text{ \AA}^{-1}$. Furthermore two dispersive branches were observed to appear from the $q = 1 \text{ \AA}^{-1}$ point and

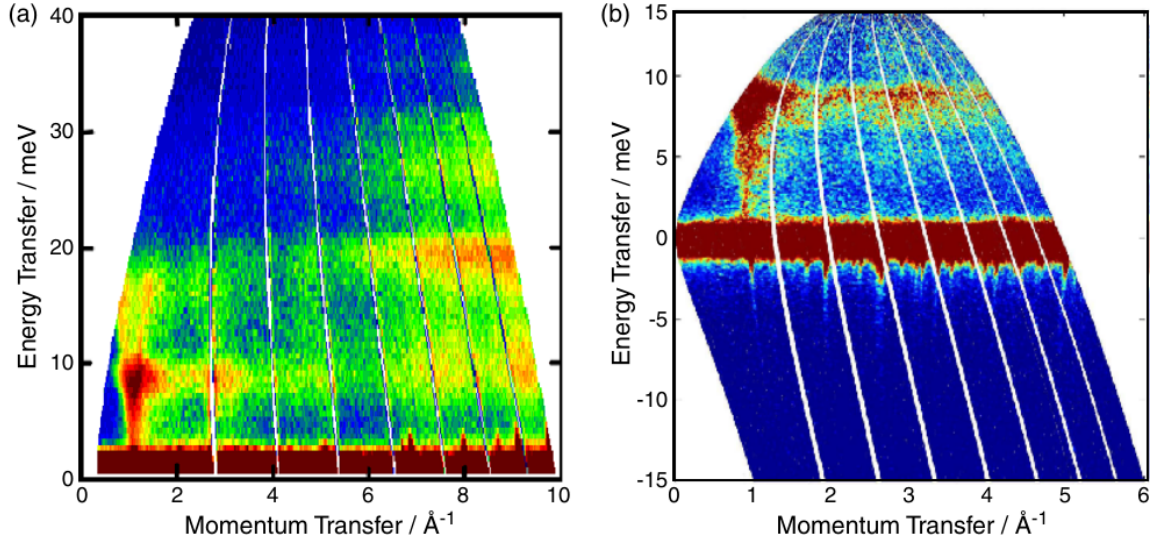


Figure 5.9: **(a)** Inelastic neutron scattering results from an experiment on a deuterated powder of potassium jarosite. Experiment was carried out at MARI at 5 K with incident energy 60 meV. **(b)** Same sample and instrument, but with the incident energy changed to 15 meV. Both figures are from Coomer et al..⁶⁸

separate out with an energy gap of 1.7 meV (corresponding to the in-plane spin gap from Yildirim and Harris). All features were observed to disappear upon warming to above the ordering temperature, as shown in Figure 5.8b.

The last piece to the potassium iron jarosite puzzle lies in the question: Where does the anisotropy even come from, chemically? It is very clearly there, as proven a multitude of times by various different people, but iron jarosites have $S = 5/2$ and the electrons occupy half filled $3d$ orbitals. This gives the charge distribution a spherical shape, as long as the system is in the high spin $3d^5$ configuration.⁴⁴ This means there is no orbital angular momentum ($L = 0$), and as the DM interaction (and SIA) arises due to the spin orbit coupling, $L \cdot S$, how is the interaction present in the first place? This question was attempted answered by de Vries et al. in 2009.⁴⁴ They postulated that the origin of the orbital angular momentum was charge (electron) transfer onto the Fe^{3+} from the surrounding oxygens. This means that a Fe^{2+} -state mixes into the Fe^{3+} -state and changes the shape of the charge distribution, allowing $\langle L \rangle > 0$. The authors showed that this did indeed happen by use of X-ray absorption spectroscopy. They found strong hybridisation between the $3d$ (iron) and $2p$ (oxygen) orbitals and determined that the transfer of electrons was present, although very weak: only ~ 0.4 extra electrons were found in each $3d$ orbital, corresponding to $\langle L \rangle = 0.008(3)$.

With this, we have almost concluded the journey through the potassium jarosite research. A map of the route was provided by Matan et al. in 2011.⁶⁴ They collected much of the magnetisation and field as well as some neutron scattering data to create the phase diagram shown in Figure 5.10. At zero field the ordering happens as we have described; by way of the DM-interaction and the interlayer coupling, and the scalar chirality is zero. As the magnetic field is turned on competition between the $K_S = 0$ and $K_S \neq 0$ (favoured by the field) begins. As the temperature is lowered, H_C needs to increase. Below H_C the 3D ordered state is the one with antiferromagnetic couplings between the planes and no net magnetic moment (in Figure 5.10 this is the phase in the bottom left). Above H_C the spins turn 180° and the coupling between layers becomes ferromagnetic giving rise to a net magnetic moment (in Figure 5.10 this is the phase in the top of the diagram). The last phase in the diagram is the paramagnetic

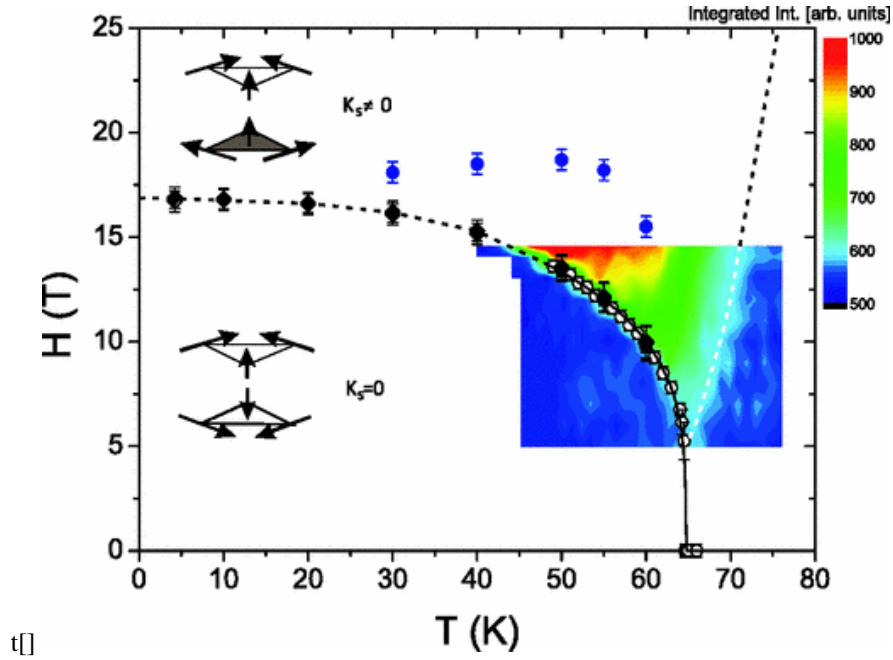


Figure 5.10: Phase diagram for potassium jarosite as a function of field and temperature. White circles on the colour map are magnetisation data from Grohol et al.(2005).⁵⁷ Filled black diamond symbols are the critical fields (H_C , kink in magnetisation curve) obtained from pulsed field measurements for increasing field (unfilled diamond symbols lay almost exactly below the filled ones and represent pulsed field measurements with decreasing field). Blue circles indicate fields where an extra (smaller) kink in the magnetisation was observed. The colour plot shows the intensity of the (1, 1, 0) magnetic peak. The data are from diffractometer E4 at BENSC with $E_i = 2.45 \text{ \AA}$. The black solid line is a power law fit with critical exponent $\beta = 0.25$. The dashed white and black lines are guides to the eye. Kagomé triangles filled in with grey indicate that all spins cant outwards, away from each other, white (empty) triangles indicate that all spins cant inwards, towards one another. Figure and data unless otherwise noted are from Matan et al. (2011).⁶⁴

phase above T_N , where the spins are oriented randomly and the magnetic moment therefore averages to zero (in Figure 5.10 this is the phase along the right edge). The phase becomes "slimmer" towards higher values of the field, indicating that the reorientation transition (and also the magnetic ordering) happens at higher temperatures. We can therefore also conclude that the field has an impact on the ordering temperature in jarosites. With this map in hand, we are at the end of our potassium jarosite journey.

5.4 Hydronium and deuteronium jarosite

Hydronium jarosite is a much more mysterious compound than potassium jarosite. Researchers have speculated for decades, but all the mysteries surrounding its properties have yet to be definitively solved. It was known from early on that hydronium jarosite was special. It had already been demonstrated by Mössbauer spectroscopy in 1974⁷¹ that this particular jarosite does not order like the other jarosites. Instead it was shown to exhibit a freezing

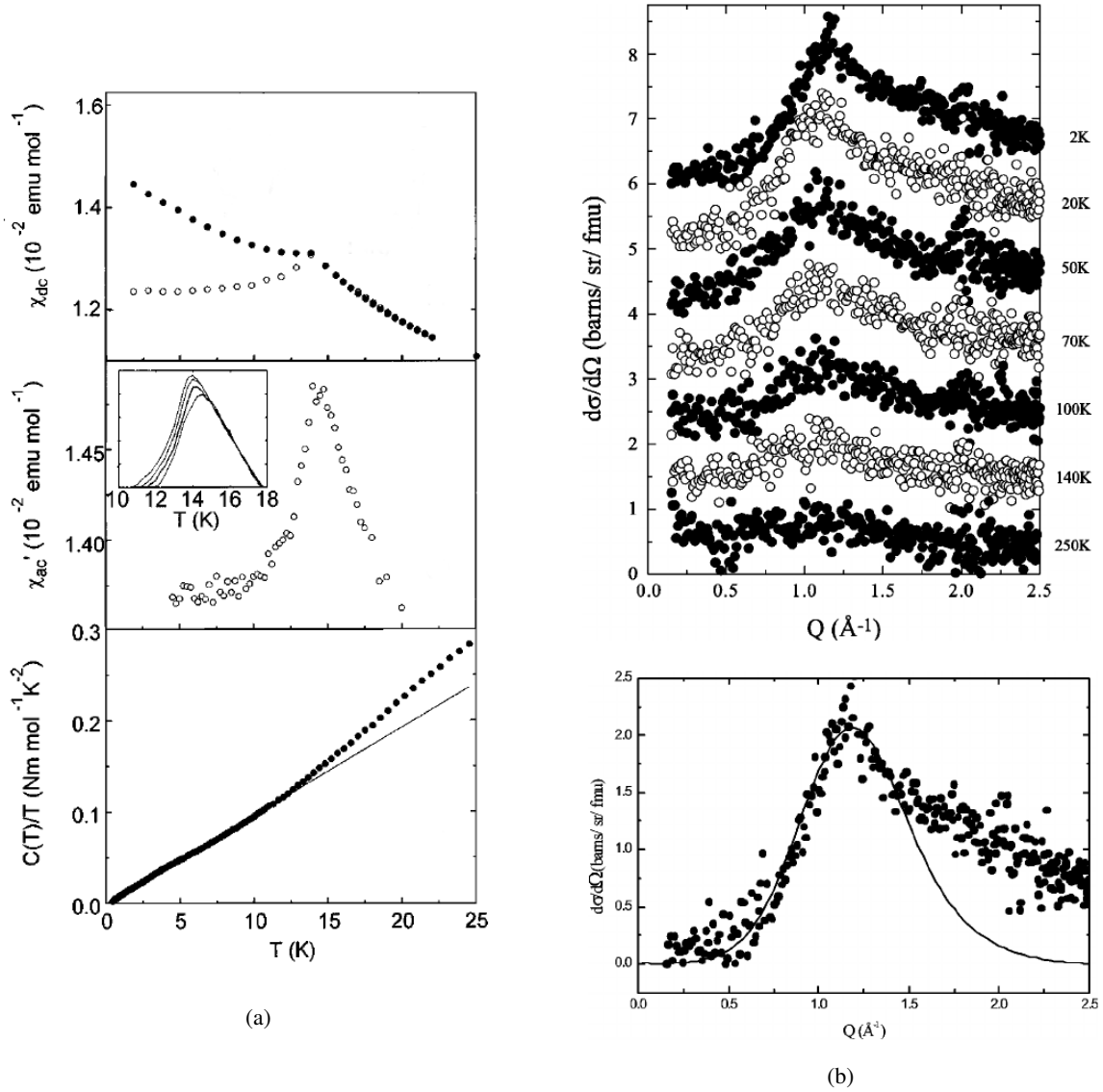


Figure 5.11: (a) top: χ_{dc} for hydronium jarosite. White circles are the ZFC susceptibility and black circles are the FC susceptibility. The FC and ZFC susceptibilities deviate from each other at T_f . Middle: Real part of χ_{ac} measured at frequency $\omega = 1157$ Hz. The inset is measured with frequencies $\omega = 1.157$ to $\omega = 1157$. The highest T_f corresponds to the highest driving frequency. Bottom: T^2 dependence of low temperature specific heat. The solid line highlights the dependence. Figure adapted from Wills et al.(1998)⁶⁹ (b) top: Temperature dependence of magnetic diffraction for hydronium jarosite. The different data sets are offset for clarity. Bottom: 1.5 K data set fit to a modified Warren peak shape (defined in Equation 5.12). Figures are from Wills et al. (2001).⁷⁰

of the spins at $T = 17.5$ K.

The first researchers to determine the entire structure of hydronium jarosite were Wills and Harrison in 1996,⁴⁵ two authors that are met continuously when entering the hydronium jarosite rabbit hole. They found a spin-glass like transition and no LRO down to 1.5 K, in good agreement with the Mössbauer study, as well as a broad inflection in the high temperature part of the susceptibility, indicating the presence of short range correlations. The transition temperature was however not constant across different samples, ranging from 12-18 K and the authors speculated that this had to do with slight differences in the occupancy of the magnetic sites. They furthermore proposed that the lack of order in hydronium jarosite had to do with the lattice coverage being almost perfect compared to other jarosite types. This proposition seemed perfectly sensible at the time, and studies performed in the following years showed that dilution of the magnetic lattice ($\approx 10\%$ vacancies) did indeed cause LRO to appear where it hitherto had been absent^{48,72,73} as well as raise the freezing temperature.⁴⁸ We however already know this to be false due to the experiments on stoichiometric jarosites by Nocera et al.⁴⁶ and Grohol et al.⁴⁷ discussed previously; if full lattice coverage was indeed the cause of the disorder, potassium jarosite with full lattice coverage should not order, but we already know that it does.

The spin-glass transition was examined further in a follow-up study by Wills et al. in 1998.⁶⁹ They found that the ac susceptibility was dependent on frequency, as expected for a conventional spin-glass, but that the magnetic contribution to the specific heat, $C_m(T)$, showed a temperature dependence going as T^2 below the transition temperature, and not the expected linear dependence (Figure 5.11a). This T^2 dependence is more commonly associated with 2D long range order in conventional antiferromagnets. To distinguish the unconventional spin-glass behaviour of hydronium jarosite, and other compounds behaving in a similar manner, from conventional site disordered spin-glasses, the new phase was termed a topological spin-glass phase.

Even though hydronium jarosite shows no long range magnetic order, it does not mean that it is devoid of magnetic scattering features. In fact it exhibits diffuse magnetic scattering, which was the topic of several neutron scattering studies, both regular⁶⁹ and polarised,^{70,74} from the late 1990s to the early 2000s. The studies obtained similarly looking peaks, and examples are shown in Figure 5.11b. The peak was found to be broad and asymmetrical with a maximum around $q \approx 1.2 \text{ \AA}^{-1}$ that became sharper as the temperature was lowered. Since q is a vector in reciprocal space, the broadness of the observed peak indicates short-ranged correlations, and the shape of the peak is specifically indicative of SRO within a plane, but not between planes.⁷⁰ Above $q \approx 1.3 \text{ \AA}^{-1}$ additional scattering, attributed to higher order scattering components⁷⁴ or strongly fluctuating spins⁷⁰ was observed. Fitting a (modified) Warren peak shape to the scattering profile before $q \approx 1.3 \text{ \AA}^{-1}$ allowed estimates of the spin-spin correlation length, ξ , to be made. The Warren function⁷⁵ was developed to describe the structure factor for diffuse diffraction of x-rays from amorphous graphite. It can be modified to describe magnetic scattering by adding the magnetic form factor $F_m(q)$, in which case the peak shape is given by⁷⁰

$$F_W(q) = Km \frac{F_{hk}^2 \left[1 - 2 \left(\frac{\lambda q}{4\pi} \right)^2 + 2 \left(\frac{\lambda q}{4\pi} \right)^4 \right]}{\left(\frac{\lambda q}{4\pi} \right)^{3/2}} \left(\frac{\xi}{\lambda \sqrt{\pi}} \right)^{1/2} F_m(q)^2 F(a) \quad (5.12)$$

Here K is a scaling constant, m is the multiplicity of the reflection and F_{hk}^2 is the structure factor in two dimensions for a Bragg reflection located at (hk) . $F(a)$ is given by

$$F(a) = \int_0^\infty dx e^{-(x^2-a)^2} \quad \text{with} \quad a = \frac{\xi \sqrt{\pi}}{2\pi} (q - q_0) \quad (5.13)$$

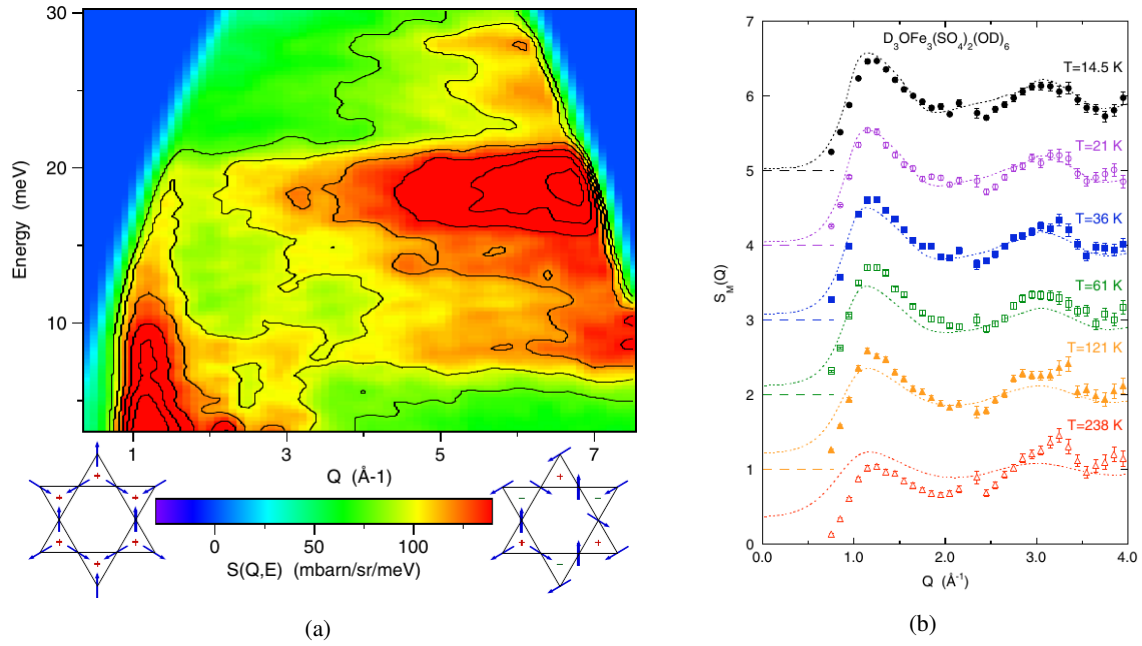


Figure 5.12: **(a)** $S(q, \omega)$ of deuterium jarosite taken at ToF spectrometer MARI (ISIS) at $T = 14.5$ K (below the spin-glass transition temperature) with $E_i = 40$ meV. The structures next to the colour bar are the $q = 0$ and $\sqrt{3} \times \sqrt{3}$ chiralities **(b)** Wave-vector dependence of the magnetic diffraction $S_M(q)$ at different temperatures. The broken lines are Monte Carlo simulations. Both figures are from Fåk et al. (2008)⁷⁶

where q_0 is the centre of the peak. The reported spin-spin correlation lengths that were obtained by fitting Equation 5.12 were very far removed from each other with one study claiming $\xi = 19 \pm 2$ Å (regular neutron scattering),⁶⁹ corresponding to the distance from one end of a kagomé star to the other, and another claiming $\xi \sim 10$ Å (polarised neutron scattering).⁷⁰ A thing that was agreed upon was that the freezing of the spins begun much earlier than the actual spin-glass transition, agreement was however not reached on the temperature at which this happened; one study claimed there were significant short-range spin-spin correlations already at 250 K,⁷⁰ while a μ SR study took the more moderate opinion that the freezing set in around $3T_f$ (~ 50 K).

An inelastic (powder) neutron scattering study performed by Fåk et al. in 2008⁷⁶ shed further light on the magnetic scattering landscape (Figure 5.12a); magnetic scattering dominated for $q < 3.5$ Å⁻¹ while phonon scattering dominated for $q > 4$ Å⁻¹. The peak positions were similar to those found by the older scattering studies (Figure 5.11) with the most intensity placed along $q = 1.1$ Å⁻¹ and a weaker signal along $q = 2.8$ Å⁻¹. A fit to the $q = 1.1$ Å⁻¹ signal yielded $\xi = 11.7(3)$ Å, which is closest to the value determined by Wills et al. (2001).⁷⁰ The magnetic scattering features were only weakly temperature dependent (Figure 5.12b). Fåk et al. stated that this result was indicative of instantaneous spin-spin correlations that only die out slowly with T , which to them was characteristic of the spin-liquid state.

The diffuse scattering observed by all studies so far is not specific to hydronium jarosite. Oakley et al.⁷⁴ showed that this type of diffuse scattering was also present in potassium jarosite above the ordering temperature, and it has furthermore been observed in sodium jarosite and argento jarosite, in all cases without as much additional scattering at $q > 1.3$ Å⁻¹.⁴⁸ This is in line with the $q = 0$ SRO observed in potassium jarosite before the ordering temperature by Grohol et al. (2005).⁵⁷ The peak positions and shapes obtained by Fåk et al. are also evocative of the potassium jarosite powder results from Coomer et al..⁶⁸ The diffuse scattering due to SRO in the planes

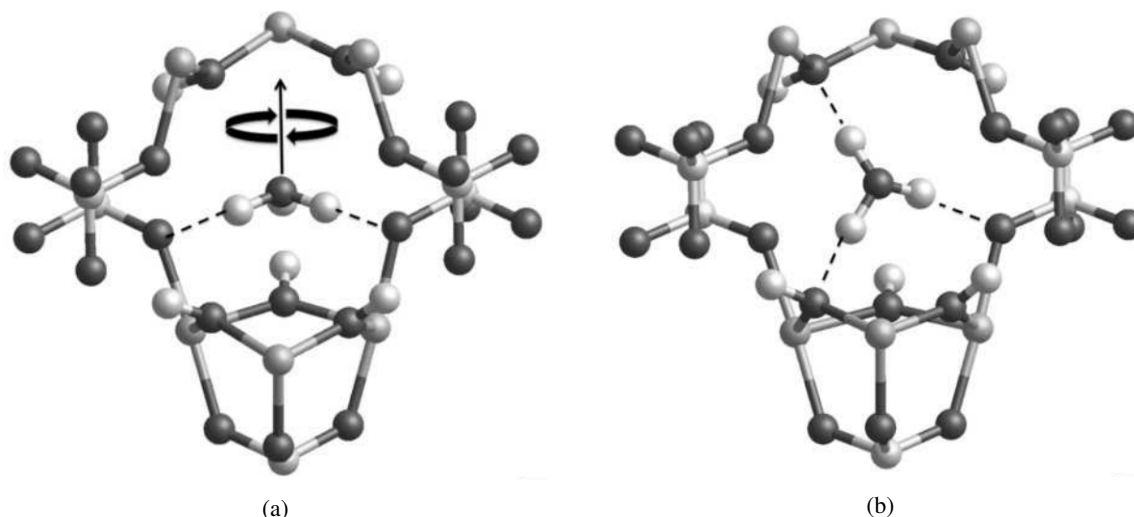


Figure 5.13: **(a)** H_3O^+ -ion with the hydrogen plane parallel to the ab plane **(b)** H_3O^+ -ion rotated to the structure proposed by Gale et al. (see text). Hydrogen bonds are indicated by broken lines. Both figures are from Gale et al. (2010).⁷⁷

therefore seems to be a universal feature of all jarosites. It has however not been possible to definitively determine the structure of the short-ranged correlations in hydronium jarosite, as it cannot be done without a sufficiently large single crystal. Fåk et al. (2008)⁷⁶ postulated that the correlations were of the $\sqrt{3} \times \sqrt{3}$ type.

An issue that is often met in hydronium jarosite studies is the inability to locate the H-atoms in the H_3O^+ -molecule in Rietveld refinement.^{1,45,48} Wills and Harrison (1996)⁴⁵ circumvented the issue by modelling the hydronium ion as a rigid body (112° bond angles and 0.96 Å bond lengths); a "trick" that has been utilised by other researchers as well.^{48,78} Wills and Harrison (1996) proposed that the issue had to do with displacement of the O-atom in H_3O^+ along the c -axis. Majzlan et al. (2004)¹ found no evidence for this claim and instead proposed that the hydronium ion position was disordered. Incorrect choice of space group is a common source of disorder, and Majzlan et al. proposed that instead of crystallising in the $R\bar{3}m$ space group like the other jarosites, hydronium jarosite crystallised in the lower $R3m$ space group; the hydronium ion being to blame for breaking the higher symmetry.

A much later paper by Spratt et al. (2014)⁷⁸ cleared up the issue by performing a very in depth investigation of the location of the hydronium ion atoms. They found that the oxygen in the H_3O^+ ion was best described as occupying the $\bar{3}m$ site in the structure. This was surprising as H_3O^+ has $3m$ symmetry and therefore technically should not be placed on a $\bar{3}m$ site (as it is not a subgroup of $3m$). This indicated that the orientations of the hydrogen atoms in H_3O^+ were in some way disordered around the $\bar{3}m$ site. The H_3O^+ hydrogens were found to be placed on a fractionally occupied m -site (18 expected for the site, but only 9 present in the unit cell). They performed refinements in both the high and low symmetry space groups and found that H_3O^+ -jarosite, despite all, crystallised in the $R\bar{3}m$ space group like the other jarosites. Spratt et al. furthermore determined that the distance from the H_3O^+ hydrogens to the surrounding oxygens was close to the upper limit for hydrogen bonding, hence any hydrogen bonds present would be weak and not sufficient to keep the H_3O^+ -ion still. The authors therefore proposed that the H_3O^+ -ion was undergoing motion within the cavity surrounding the A-site, and that it was this motion, as well as the dynamical disorder of the hydrogens in H_3O^+ , which was the explanation for why researchers had not been able to locate the ion using XRD; The ion simply did not have a defined position. The hydronium ion had been shown to be mobile previously by Nielsen et al.,^{32,36} and we will come back to their results when

Compound	θ_{CW} [K]	T_{max} [K]	T_{max2} [K]	T_D [K]
HFeS	-880	15.7		16
$K_{0.15}FeS$	-860	17.0	44.0	~ 40
$K_{0.32}FeS$	-850	17.2	45.0	~ 40
$K_{0.44}FeS$	-840		46.2	~ 40
$K_{0.73}FeS$	-790		52.0	46
KFeS	-828		65.4	53
KFeS : HFeS		15.7	64.4	53

Table 5.3: Magnetic data for a series of jarosites with varying K^+/H_3O^+ ratio. x in the notation K_xFeS describes how much potassium is present in the compound. $1 - x$ is the H_3O^+ content. HFeS is the compound with full H_3O^+ occupancy and KFeS is the compound with full K occupancy. KFeS : HFeS is a 1 : 1 mixture of the two fully occupied compounds. T_{max} and T_{max2} are the transition temperatures (glass-like transition and 3D long-range order). T_D is the temperature where ZFC and FC susceptibilities diverge. Table is reproduced from Grohol and Nocera (2007)⁵⁶

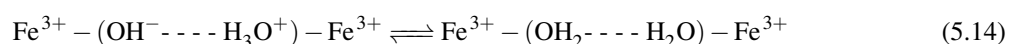
we walk through the theories for why hydronium jarosite does not order in the next section. A DFT (Density Functional Theory) study performed by Gale et al. in 2010 on hydronium alunite⁷⁷ showed that the hydronium ion preferred to rotate such that the plane of the three hydrogen atoms was positioned closer to being parallel to the c -axis rather than parallel to the ab -plane (see Figure 5.13). This allowed the formation of two hydrogen bonds to the OH^- group and only one to the sulfate oxygen; the implication was that the hydrogen bond to the hydroxide group necessarily needed to be stronger than the hydrogen bond to the sulfate. Something similar is likely to be happening in hydronium jarosite. Spratt et al. found no convincing evidence for hydrogen bonds to the sulfate oxygens⁷⁸ and thus supported the claim of dominance of the bridging hydroxide hydrogen bond, despite not having the same orientation of the hydronium ion in their model.

5.4.1 Why the lack of order?

The fact that hydronium jarosite does not order has baffled researchers for decades and no definitive answer has yet been found. This has however not prevented several different theories from appearing, and this short section will attempt to go through the different arguments, so that we may assess the possible explanations from an informed position.

Intrinsic proton transfer

There are two types of A-site cations, the inert cations, such as Na^+ , K^+ and Rb^+ and the cations that can react with the other ions on the lattice. H_3O^+ and NH_4^+ belong to this latter category and the possible reactions are those of hydrogen bonding and proton transfer. The proton transfer is a dynamic process and proceeds according to



where $-$ indicates a covalent bond and $\cdots$ indicates a hydrogen bond. The idea of proton transfer as the cause of disorder was introduced by Grohol et al.⁴⁷ in 2003 and a full paper dedicated to disorder in hydronium jarosite was

put out in 2007 by Grohol and Nocera.⁵⁶ The authors argued that the reaction in Equation 5.14 took place only for H_3O^+ -jarosite and not for NH_4^+ -jarosite, due to the differences in their pK_a -values with respect to the acid-base reaction with OH^- ($K_b \sim 1.8 \cdot 10^{-5}$ for H_3O^+ and $K_a \sim 5.6 \cdot 10^{-10}$ for NH_4^+). It is important to note that this mechanism is separate from the mechanism by which vacancies are charge compensated. The two types of proton transfer are sometimes referred to as the intrinsic (dynamic, ongoing) and extrinsic (static, charge compensation) proton transfers^{46,47} to keep them separate. The authors claim that the intrinsic transfer should create relatively few water molecules in the structure, as compared to the extrinsic, as the reaction is reversible. The fact that the hydronium ion is able to create disorder, irrespective of the process by which the disorder occurs, was shown most starkly in the 2007 study, where a series of jarosites were synthesised with varying ratios of $\text{H}_3\text{O}^+/\text{K}^+$ on the A site, and the ordering temperature was seen to decrease with increasing H_3O^+ -substitution. The results are reproduced in Figure 5.14a and the transition temperatures can be found in Table 5.3.

Intrinsic proton transfer was thought to be able to cause the observed behaviour by way of the nearest-neighbour magnetic exchange, as it happens through the p -orbitals in the $\text{Fe}-\text{OH}-\text{Fe}$ pathway. Proton transfer is expected to disturb the NN exchange (i.e. change J) as the oxygen atom now is the carrier of two hydrogens instead of just one. As was explained in the section on potassium jarosite the 3D order hinges exactly upon this in-plane ordering. The NN interaction was however found to be only moderately affected, which could be inferred from the still very low

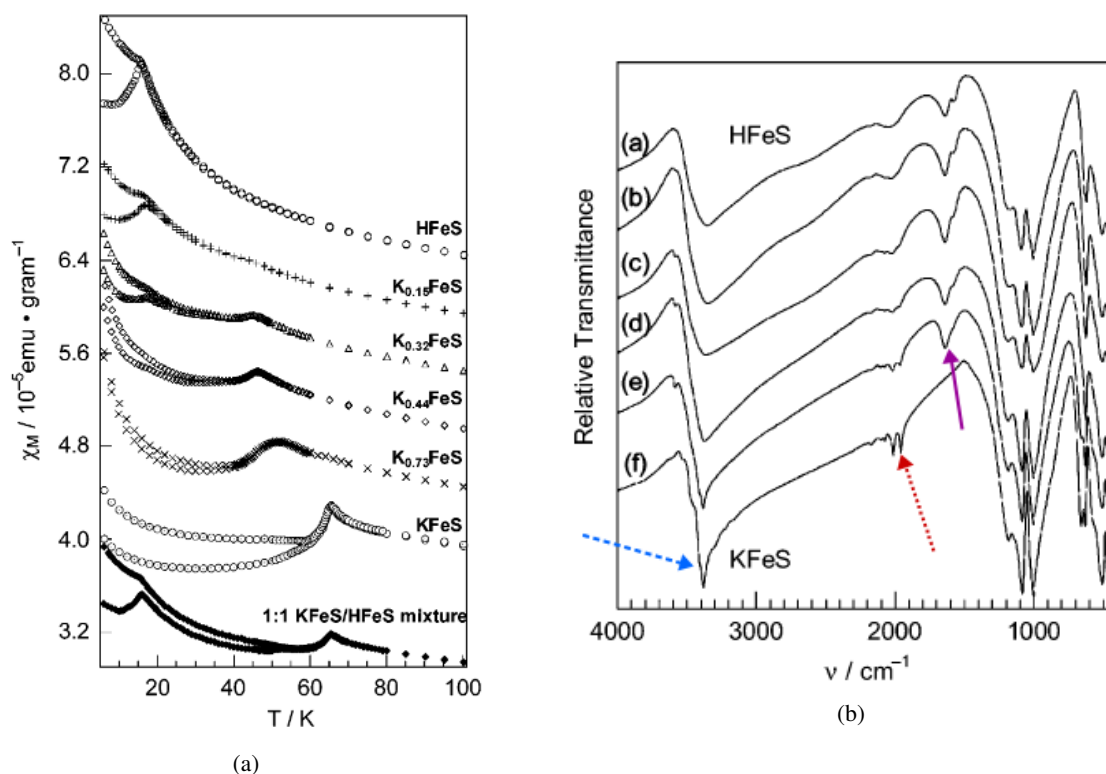


Figure 5.14: **(a)** Magnetic susceptibility for jarosites with varying A-site $\text{H}_3\text{O}^+/\text{K}^+$ occupancy **(b)** IR spectroscopy for the series of jarosites. (a) HFeS (pure hydronium jarosite) (b) $\text{K}_{0.15}\text{FeS}$, (c) $\text{K}_{0.32}\text{FeS}$, (d) $\text{K}_{0.44}\text{FeS}$, (e) $\text{K}_{0.73}\text{FeS}$ and (f) KFeS (pure potassium jarosite). The blue dashed arrow indicates the O-H stretching mode, the red dotted arrow indicates the Fe-O-H bending overtone and the purple solid arrow indicates the H-O-H bending mode. Both figures are from Grohol and Nocera (2007).⁵⁶

Curie-Weiss temperatures that were not concurrent with the decreasing ordering temperatures (Table 5.3). Grohol and Nocera offered the explanation that the dynamic transfer only took place on a few sites at a time, hence not so much affecting the NN interaction, but rather creating a magnetically disordered state in the whole crystal, due to proton transfer being a chemically disordering event, even if it does not take place on the entire lattice. This explanation also ties in with the issues mentioned in defining the H_3O^+ position in refinement, as intrinsic proton transfer would introduce disorder to the crystallographic position.

Evidence speaking for intrinsic proton transfer came through IR-spectroscopy. Grohol and Nocera observed a broadening of the O–H stretching mode (blue dashed arrow on Figure 5.14b) as well as a broadening of the Fe–O–H bending overtone (red dotted arrow on Figure 5.14b), and reasoned that it was caused by a multitude of neighbouring interfering O–H oscillators in the Fe–O–H environment.⁵⁶

Mobility and disorder

The theory regarding intrinsic proton transfer as the reason for spin-glass behaviour was challenged by Nielsen et al. in 2008.³² The NMR study was inspired by an earlier Nielsen et al. study⁵⁸ on hydronium alunite, where it was shown that the $\text{H}_3\text{O}^+/\text{D}_3\text{O}^+$ ion was highly mobile. The high mobility of the ion in alunite was supported by Gale et al.,⁷⁷ who observed no correlations between the hydronium ion orientations as well as both rotations and umbrella inversions of the ion. They saw no signs of neutralisation (the bound H_2O —OH state was never created) and thus agree with Nielsen et al. that the proton transfer reaction is not favoured in alunites and therefore very likely not in jarosites either.

Nielsen et al. (2008)³² tested the proton transfer hypothesis: Did the intrinsic proton transfer happen in hydronium jarosite? Nielsen et al. (2008) hypothesised that a large amount of Fe–OD₂ environments would be present in a stoichiometric sample. The hypothesis was proven not to be in accordance with the relative concentrations of environments observed in the study, and furthermore that the D_3O^+ -ion remained intact in stoichiometric parts of the sample, in contrast to what was expected by Grohol and Nocera (2007). Nielsen et al. (2008) instead proposed that the spin-glass behaviour should be explained in terms of the disorder (multiple positions) of the very mobile D_3O^+ ion. A follow up study (Nielsen et al. (2011)³⁶) supported this idea and added that the disorder was communicated to the rest of the jarosite framework through the (weak) hydrogen bonds from H_3O^+ . Nielsen et al. (2011) furthermore showed that the rotation of the deuterium ion slowed down between 90 K and 73 K, which is right above the ordering temperature of non-hydronium jarosites. They proposed then that freezing of the deuterium ion motion before the Néel ordering temperature could be related to the lack of magnetic order in hydronium/deuterium jarosite as well.

Nielsen et al.³² lastly pointed out that the acid-base reaction proposed by Grohol and Nocera would not, in fact, happen. Based on formal charge calculations the oxygen atoms in the bridging hydroxide group are not actually basic, and they would therefore be expected to be chemically inert when inside the jarosite structure.

Anisotropy and distortion

The theories presented so far all focus on disorder as the deciding factor in differentiating between hydronium jarosite and non-hydronium jarosites. Bisson and Wills,^{79,80} however, develop an explanation based on an ordered energy scale. The theory is based on results from two papers, the first of which was from 2008 and showed that the spin-glass transition temperature seemed to be linearly correlated with the degree of distortion of the Fe-octahedra (see figure 5.15a). The distortion, Δ , was defined as the difference of the ratio of bond lengths (equatorial versus

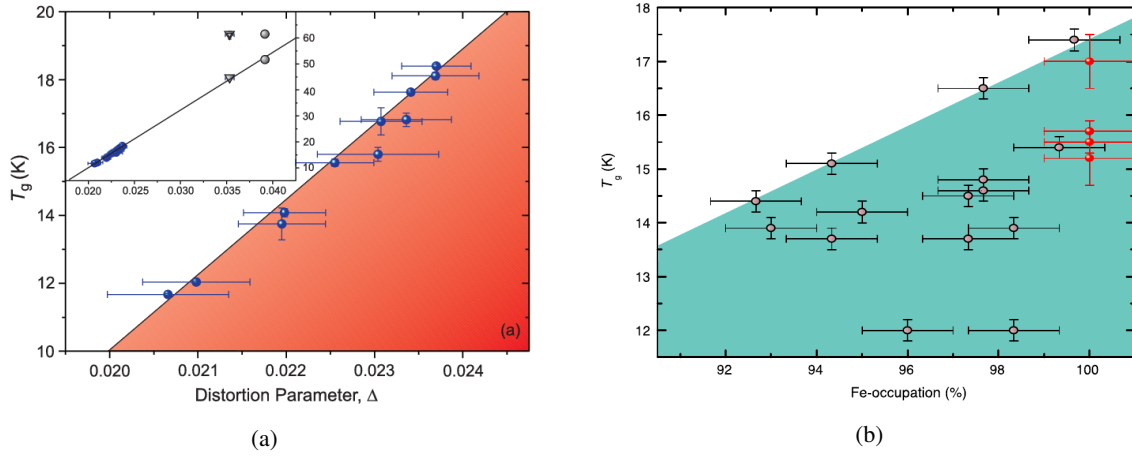


Figure 5.15: **(a)** Relationship between the spin-glass transition temperature (T_g) and the degree of distortion of the Fe-octahedra (Δ). The inset has the linear dependence extrapolated to include ordering temperatures of non-hydronium jarosites $\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$ (grey triangles) and $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$ (grey circles). The figure is from Bisson and Wills (2008)⁷⁹ **(b)** Spin-glass freezing temperature as a function of Fe-occupancy. The red data points indicate samples with near perfect Fe-coverage. The figure is from Wills and Bisson (2011).⁸⁰

apical) from unity

$$\Delta = 1 - \frac{R(\text{Fe} - \text{O})_{eq}}{R(\text{Fe} - \text{O})_{ap}}$$

It is worth noting that the distortion is much smaller in H_3O^+ -jarosite than in the other jarosites, but that the linear dependence was extrapolated to higher temperatures, whereupon it was found to line up with ordering temperatures and distortions for non-hydronium jarosites (the inset in Figure 5.15a). The ensuing study from 2011⁸⁰ dived into the cause of the distortion. A series of hydronium jarosites with varying Fe-occupancies were synthesised and no immediate correlation between the occupancy of the magnetic site and the spin-glass freezing temperature was found. In fact similar values of T_g were seen to be related to very different Fe-site occupancies and jarosites with similar occupancies exhibited very different spin-glass transition temperatures (see Figure 5.15b).

Based on these results Wills and Bisson⁸⁰ speculated that the spin-glass transition was caused by an anisotropy that was proportional to the degree of distortion. The anisotropy had to have a planar component that was able to push the spins into the plane, as a Mössbauer study⁸¹ had shown the spins to be compatible with an in-plane arrangement in the spin-glass phase. The planar anisotropy prevents the "liquid" movements of the spins by making spin orientations out of the plane cost energy, hence inducing the transition. Wills and Bisson precluded the DM-interaction from their pool of possible anisotropies, as they believed it would lead to long-range Néel order like in potassium jarosite. As described above, the temperature at which the transition happens was correlated linearly with the degree of distortion of the Fe-octahedra. This distortion was not caused by the degree of Fe-occupancy, even though the Fe-occupancy did put an upper limit on how high T_g could go, which was explained in term of the number of protons the structure needed to take in to charge compensate the lost Fe^{3+} . Wills and Bisson speculated that the only parameter that could cause the distortion was the locations of the protons. I.e. some mechanism had to be in place to relocate the protons from their positions (i.e. deprotonation of H_3O^+ to make H_2O and protonation of OH^- to create H_2O) and keep them there. The defining factor of the spin-glass transition according to Bisson and Wills is then the crystallographic change brought on by these patterns of proton localisation. We note that they seem much akin to the charge compensation mechanism/extrinsic proton transfer discussed previously, but that

Name	Explanation	Key papers
Intrinsic proton transfer	The reaction is dynamic, it happens reversibly and continuously in a <i>stoichiometric</i> sample, and is therefore not linked to Fe or K vacancies in the structure. It does not happen at all sites at the same time, and is the proposed cause of spin-glass behaviour	Grohol and Nocera (2007) ⁵⁶
Extrinsic proton transfer	The reaction happens to compensate a vacancy. It only happens in <i>unstoichiometric</i> samples near a vacancy. In stoichiometric parts of the sample the D_3O^+/H_3O^+ ion is intact (proven by NMR). The reaction is not the proposed cause of spin-glass behaviour (hydrogen bonding and disorder is)	Nielsen et al. (2008) ³² Nielsen et al. (2011) ³⁶
Patterns of proton localisation	The reaction is the cause of the distortion of the Fe octahedra. It is not dynamic, as it would contradict figure 5.15b. It happens in <i>stoichiometric</i> samples, and it is the proposed cause of spin-glass behaviour	Bisson and Wills (2008) ⁷⁹ Wills and Bisson (2011) ⁸⁰

Table 5.4: Summary of important differences between the proton transfer mechanisms proposed in the literature.

they in this instance are proposed to be present even in a stoichiometric sample.

We have now become acquainted with three different mechanisms based on the same chemical reaction (deprotonation of H_3O^+ to make H_2O and protonation of OH^- to create H_2O). The chemical reactions are similar but subtly different, potentially creating mass confusion, therefore, to sum up this section, their differences are highlighted in Table 5.4.

6 | Synthesis work

In this chapter a brief account of the synthesis work that has been carried out will be given. The chapter can be read independently from the rest of the thesis.

6.1 Synthesis of samples

For this project powder samples potassium jarosite were prepared by Sonja Holm-Dahlin and Mathilde Borup Sørensen in the laboratory of Associate Professor Kirsten Marie Ørnsbjerg Jensen at Copenhagen University (KU). Powder samples of deuterium jarosite were prepared by Nikolaj Niels Neerup Andersen at University of Southern Denmark (SDU) in the laboratory of Professor Ulla Gro Nielsen. The synthesis of potassium jarosite is described in the sections below. Details about the synthesis of deuterium jarosite are found in the report by Nikolaj.⁸²

6.1.1 Powder samples

Powder samples of potassium jarosite were synthesised from August 2020 to mid November 2020. We used steel autoclaves with Teflon liners of volume 36 mL (borrowed from SDU and seen in Figure 5.2a) and 56 mL (fabricated by KU's mechanical workshop). The autoclave design was based on the design from the workshop of SDU and the project was led by Morten Liborius Jensen. The KU autoclaves with their liners are seen in Figure 6.1a and the technical drawings in Figure 6.1b.

Our syntheses			Grohol et al.	
Reactants	Theoretical 36 mL ^a	Theoretical 56 mL ^b	Reactants	Theoretical 900 mL
D ₂ O	14.4 mL	22.4 mL	H ₂ O	375 mL
H ₂ SO ₄	0.6 mL	0.93 mL	H ₂ SO ₄	9.1 mL
K ₂ SO ₄	1.25 g ^c	1.875 g	K ₂ SO ₄	23.53 g
Fe	0.167 g	0.251 g	Fe	4.16 g

^a Syntheses were carried out in autoclaves borrowed from SDU

^b Syntheses were carried out in autoclaves fabricated by the KU workshop

^c We are using an excess amount of K₂SO₄ to combat vacancies. Based on a calculation of 0.5 g product we would only need 0.348 g K₂SO₄

Table 6.1: Overview of amount of reactants used in powder syntheses. The reactants of Grohol et al. that the syntheses are based on are shown for comparison.

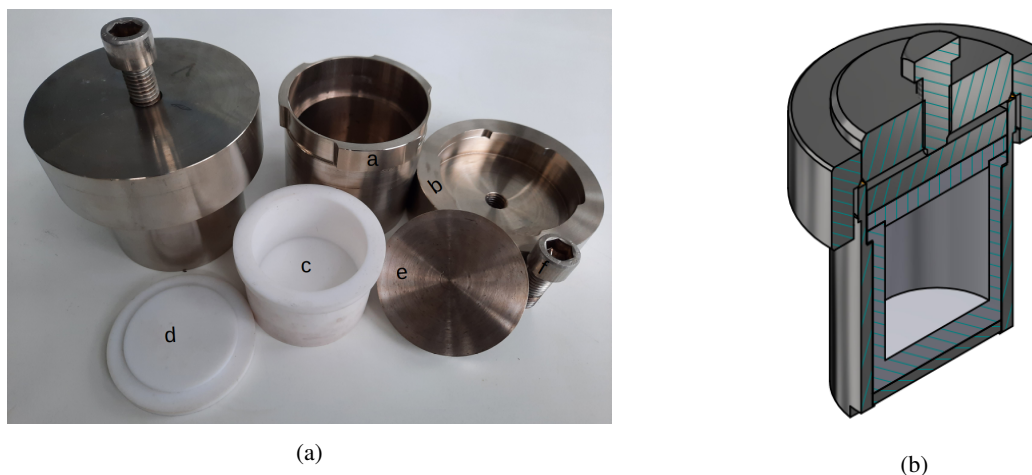


Figure 6.1: 56 mL autoclaves. Symbols on pictures will be referred to in *italics* **(a)** The autoclaves consist of an outer steel container with a loose bottom (*a*) and a lid (*b*) that is turned into place. The bottom can be pushed on to help release the Teflon liner (*c*) and its lid (*d*). When the liner is inserted in the steel container a steel disc (*e*) is put on top of the Teflon lid before the whole autoclave is secured together with a screw (*f*) **(b)** Technical drawing of the 56 mL autoclave.

We followed the synthesis method of Grohol et al.⁵⁷ but changed the acidity of the solution, as synthesis with the original values produced a bright red hematite (Fe_2O_3) powder. We also exchanged H_2O for D_2O as we wanted to perform neutron scattering experiments, and D has a much smaller incoherent scattering cross section than H.⁵ The reactants and reactant amounts are shown in Table 6.1. The reactant mixture was made by first dissolving K_2SO_4 in D_2O on a magnetic stirrer and hotplate set to $\sim 50^\circ$. Next the acid was added and the mixture was poured in the Teflon liners and slid carefully inside the outer steel autoclaves. The mixture filled the liners to $\sim 42\%$ of their full volume. A lump of iron of appropriate weight was placed into each autoclave and the Teflon lid of the liner as well as the steel top were put on. The steel top was secured by one large screw with a hex key. The autoclaves were placed in a universal Memmert UF55 oven at 205° for 16 hours. After the 16 hours the oven was turned off and the autoclaves were left to cool down with the oven door closed to slow the cooling as much as possible (this process took ~ 6 hours). When cooled sufficiently (could be touched by a human hand without the human hand suffering harm) the autoclaves were opened. Visible unreacted iron was removed and the product was washed three times in D_2O before being dried either in air or in the oven at 70° . We synthesised 30 batches of samples using this method (an example is seen in the leftmost panel of Figure 6.4) and performed PXRD on each individual sample. The powder patterns were compared with a pattern from the mineral database RRUFF.⁸³ An example of this comparison can be seen in Figure 6.2. The PXRD comparison was carried out for all samples and Rietveld refinement was performed on 16 samples by PhD student Mikkel Juelsholt. The samples that did not match the calculated pattern and/or the refinement of them failed were discarded; the rest were mixed to make the final sample (christened the "Franken Sample") with a weight of 1.734 g.

6.1.2 Single crystal samples

We attempted to produce single crystal samples of potassium jarosite. Here we will describe two such attempts (from here on denoted CJ1 and CJ2) even though none of them succeeded in creating a large single crystal. Specialised equipment was made and designed based on the equipment described in Grohol et al.⁵⁷ with help from

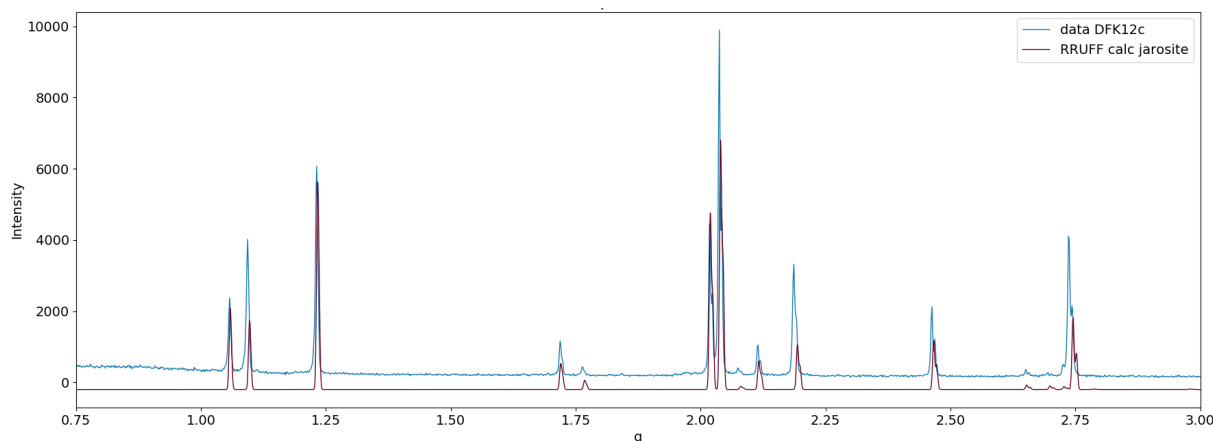


Figure 6.2: Example PXRD pattern of a deuterated potassium jarosite sample. The calculated pattern has been downloaded from RRUFF.⁸³ For q -values larger than $\sim 2 \text{ \AA}^{-1}$ the peaks start deviating from each other. We assume this to be due to a small difference in lattice parameters between our sample and the calculation.

the KU workshop, again led by Morten Liborius Jensen. The equipment is seen in Figure 6.3. Two large (900 mL) autoclaves were produced with a set of Teflon containers to vary the volume inside (like Matryoshka dolls). The volumes of the different parts are seen in Table 6.2. The lids of the autoclaves were made to accommodate a pressure and a temperature sensor. The temperature sensor is inserted directly into the autoclave while the pressure sensor is attached outside the oven and connects to the autoclave via a metal pipe going through the vent at the back of the oven. Both sensors are set up to deliver data through a National Instruments box to a program in LabVIEW (created by Jan Justesen from the electronics department and Claus Birger Sørensen).

The reactant amounts and synthesis conditions for synthesis batches CJ1 (batch consists of one big autoclave) and CJ2 (batch consist of two big autoclaves) are shown in Table 6.3. The reactant mixture was created in the same manner as the mixture for the powder samples described in subsection 6.1.1. We tried to emulate the synthesis conditions of Grohol et al. but were not able to make a setup where the air could be evacuated and filled with pure oxygen before sealing the autoclave. The autoclaves were sealed in normal air using $\sim \frac{1}{3}$ of the threaded holes visible on the big autoclave in Figure 6.3a.

CJ1 was placed in the oven at 205° for 3 days and 18 hours without Teflon lids (as they had yet to be made at the point the synthesis took place). Both sensors were inserted in the autoclave lid. The product cooled down slowly by shutting of the oven and leaving the autoclaves with the oven door closed. CJ1 yielded 0.248 g of jarosite product, which was a dark orange/brown colour, very much like the colour of natural jarosite crystals. The small crystals after the product had been washed and dried are shown in the rightmost panel of Figure 6.4. Microscope pictures of the CJ1 product revealed that the crystals were $\approx 0.5 \text{ mm}$ and had a variety of shapes; small square single crystals and larger octahedral agglomerates dominated. These shapes are very different from the large single crystal produced by Grohol et al. seen in Figure 5.2b.

CJ2 was placed in the oven at 205° for 4 days and 16 hours with Teflon lids. The sensors were removed and both holes in the autoclave lid were filled with steel rods. A more controlled cooling of $\frac{1}{3}^\circ/\text{min}$ was attempted by manually setting the temperature to 5° less every 15 minutes. When the oven temperature reached 100° the oven fan was turned on gradually to help with cooling. This cooling process took ~ 8 hours. Two identical syntheses were made at the same time following this method; in one of them the lid lifted of the reactant solution and stuck

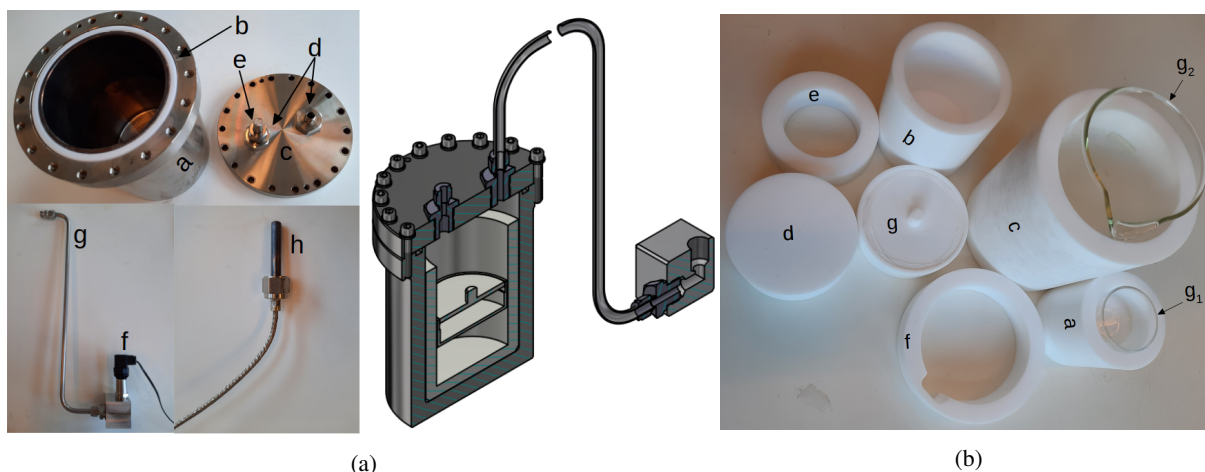


Figure 6.3: Mechanical drawing, autoclave parts and sensors for the big autoclave fabricated by the KU workshop. Symbols on pictures will be referred to in *italics*. **(a)** Outer parts of the big steel autoclave (*a*) and lid (*c*) with threaded holes for screws and a Teflon O-ring (*b*) for tightly securing the two parts together. The lid has two holes (*d*); one for a pressure sensor (*f*) that is connected to the autoclave with a tube (*g*) and one for a temperature sensor (*h*). The holes can also be blocked by steel rods (*e*). The mechanical diagram for the big autoclave fully assembled is seen next to the parts. The break in the pipe indicates the point where the pipe goes through the oven. The diagram was made by Morten Liborius Jensen and the full mechanical diagram with scaling, materials and measurements can be found in Appendix A1. chapter 9. **(b)** Teflon liners and glassware for the big autoclave. They can be assembled in a variety of ways. The smallest container (*a*) has a diameter fitting with a small glass container (*g*₁). It can be inserted into the second largest liner (*b*) and both fit into the biggest container (*c*). When the shaped ring (*f*) is stacked on top of the biggest container (*c*) they have room for a glass container with a lip (*g*₂). The smaller ring (*e*) goes on top of the second largest liner (*b*) and the solid Teflon block (*d*) can be used either as a lid or to raise the containers. The lid (*g*) fits inside the biggest liner (*c*) when the glass is not inserted. It is hollow and therefore able to float on top of the reactant solution.

Volume of liners			Volume of rings		Volume of glassware	
Liner <i>a</i>	Liner <i>b</i>	Liner <i>c</i>	Ring <i>e</i>	Ring <i>f</i>	Glass <i>g</i> ₁	Glass <i>g</i> ₁
27 mL	190	500 mL	45 mL	100 mL	25 mL	400 mL

Table 6.2: Volumes of Teflon liners, Teflon rings and glassware in Figure 6.3b

onto the wall of the Teflon liner (due to the high pressure in the autoclave when the reactant mixture starts boiling). This synthesis produced only hematite and the product was discarded. In the other autoclave the product was 0.67 g of an orange/dirt coloured jarosite powder with some larger crystals mixed in. Pictures of the product are seen in the middle panel of Figure 6.4. The crystals had a broader range of sizes but were overall much smaller than the ones from CJ1. This could be caused by the smaller amount of acid or iron in the reactant mixture. We believe the lid (and perhaps also the slower cooling) had a positive effect on crystal growth, as the same synthesis without the lid completely failed. Our results thus support that slowing down the oxygen uptake is useful in jarosite crystal growth, but it may be that it is not essential based on the good results from the CJ1 synthesis that did not have the lids.

Reactants	Synthesis CJ1	Synthesis CJ2	Parameter	Synthesis CJ1	Synthesis CJ2
H ₂ O	235 mL	250 mL	Temperature	205°	205°
H ₂ SO ₄	10 mL	7 mL	Time	3 days 18 hours	4 days 16 hours
K ₂ SO ₄	20.2 g	15.21 g	Cooling	Free	$\frac{1}{3}^{\circ}/\text{min}$
Fe	3.0 g ^a	2.22 g	Lid	No	Yes

^a two pieces of iron with a collective weight of 3 g

Table 6.3: Overview of amount of reactants used in crystal syntheses CJ1 and CJ2. The amount of acid was increased from the value used by Grohol et al. (the "correctly" scaled acid amount is 6 mL)

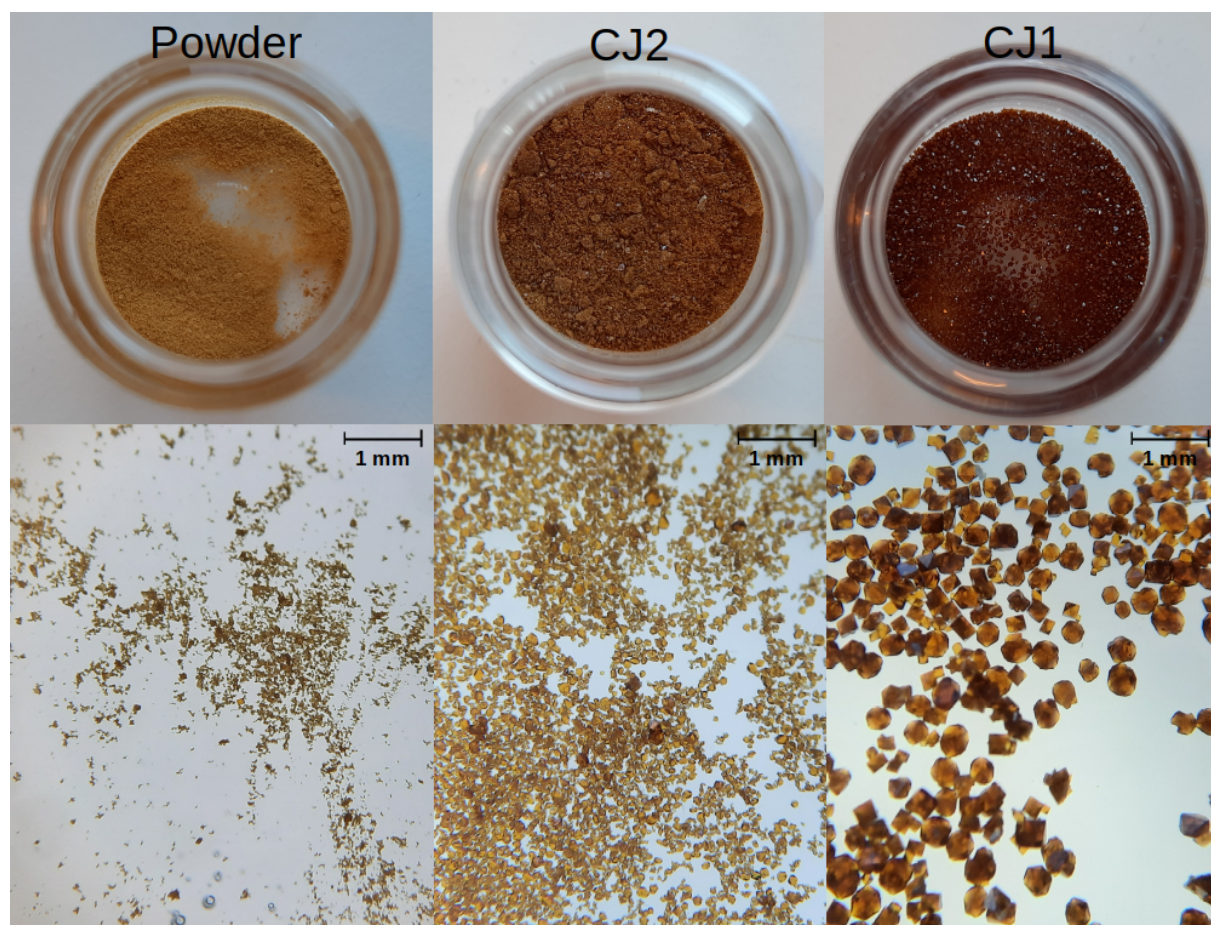


Figure 6.4: Details of powder and crystal syntheses. The top row shows the products of a powder synthesis, CJ2 and CJ1 in their sample holders (going from left to right). The colour of the product changes visibly as the size of the crystallites increase. The bottom row has microscope pictures of the samples in the top row.

7 | Results and discussion

7.1 NMR

In this project ^2H MAS NMR was used on deuterium jarosite. It is an advantage to use deuterium NMR instead of hydrogen NMR; ^2H , like ^1H , has a small electron cloud, but a gyromagnetic ratio $\sim 1/7$ that of regular H. For this reason it has a small chemical shift range and small heteronuclear and homonuclear dipolar coupling, which gives narrow lines that are however broadened by the quadrupolar interaction³³ and the dipolar interaction between nuclei and electrons. This broadening is (almost) removed by MAS. Performing a ^2H NMR study on jarosite specifically is useful for many reasons. The first is that it allows us to quantify the amount of iron vacancies present in the sample. Secondly the shape of the quadrupolar line is very dependent on the movement of deuterons as well as the local hydrogen bonding and lastly the Fermi contact shift holds information on the Fe–D connectivity.³²

^2H MAS NMR was carried out on the deuterium jarosite sample by Nikolaj Niels Neerup Andersen and Ulla Gro Nielsen at University of Southern Denmark. Single pulse and Hahn echo spectra were recorded on an Agilent 600 MHz spectrometer (corresponding to Larmor frequency ≈ 90 MHz for ^2H) using spinning speeds 32, 34 and 38 kHz for the single pulse spectra and spinning speeds 32 and 34 kHz for the Hahn echo spectra. The spectra were referenced relative to the D_2O resonance ($\delta_{\text{iso}}(^2\text{H}) = 4.6$ ppm) and were originally used in the bachelor thesis of Nikolaj Niels Neerup Andersen.⁸⁴ In this project we use the 38 kHz single pulse spectrum (as resonances are simplest to interpret at this spinning speed). The spectrum was processed anew for use in this project by Anders Bruhn Arndal Andersen in the program ssNake⁸⁵ (i.e. it was phased and the baseline was corrected). The resulting spectrum can be seen in Figure 7.1a.

The frequency range of the spectrum is small compared to other jarosites with only a few spinning sidebands (ssb) observed for each set of resonances. Our envelope is only ~ 2400 ppm in width where potassium jarosites (with both Fe, V and Cr as the magnetic ion) are closer to ~ 5000 in width).³⁷ The cause is the mobility of the D_3O^+ ions. It was observed by Nielsen et al. that as the sample is cooled down to around 90 K more ssb turn up, which indicates the slowing down of dynamics expected for a spin-glass.³⁶ Even though the amount of ssb is small the shape of the envelope can still be made out to be asymmetric. This asymmetry is caused by the quadrupolar interaction and the paramagnetic dipole interaction.³⁷

Figure 7.1b shows a zoom of the central region where the different resonances have been attributed to the different deuterium environments causing them. In a stoichiometric sample of potassium jarosite only two sets of ssb are present, that is, we only have a signal for two types of deuterons; namely the deuteron placed in the stoichiometric environment, which we will denote $\text{Fe}_2\text{--OD}$, and the signal from the deuterium deuterons.

In unstoichiometric samples more sets of ssb turn up. The deuteron next to a vacancy will give rise its own pattern

Resonance	δ (ppm)	δ (ppm) Nielsen et al. ³²	Intensity ^a
$\text{Fe}_2\text{--OD}(\text{D}_3\text{O}^+)$	215 ± 70	240 ± 60	61.9%
$\text{Fe}_2\text{--OD}(\text{D}_2\text{O})$	250 ± 80	not observed	
$\text{Fe--OD}_2(\text{D}_3\text{O}^+)$	45 ± 25	not observed	13.5%
$\text{Fe--OD}_2(\text{D}_2\text{O})$	70 ± 25	70 ± 30	
D_nO	0 ± 0.4	0 ± 10	16.7%
U	-19 ± 1.4	not observed	7.9%

^a Percent of the total integrated intensity. It was not possible to separate the two $\text{Fe}_2\text{--OD}$ and Fe--OD_2 environments and therefore the percent stated is for both environments.

Table 7.1: Different local environments in deuterium jarosite and their chemical shifts. $\text{Fe}_2\text{--OD}$ is the stoichiometric environment, Fe--OD_2 is the environment with one Fe vacancy compensated by one deuterium. $\text{D}_3\text{O}^+/\text{D}_2\text{O}$ is parenthesis after the environment denotes the A^+ cation. D_nO is the resonance from $\text{D}_3\text{O}^+/\text{D}_2\text{O}$ in the cavities between kagomé layers and U is a resonance most likely due to D_3O^+ deuterons.

as it resides in an environment with an extra deuterium and a missing magnetic ion (we will denote this environment Fe--OD_2). Resonances from D_2O groups in between the kagomé layers are also possible, but it is in general not possible to distinguish between D_3O^+ and D_2O sitting in the cavity between the kagomé layers in the spectrum and therefore we will say that the resonance results from a D_nO environment (where n will be determined later). The positions of the isotropic resonances have two contributions; the first is the chemical shift, which is small (in the range 3-5 ppm as determined by experiments on diamagnetic jarosites by Grube et al.).³⁷ The second is the Fermi contact (or hyperfine) shift, which is much bigger and therefore the dominant factor for the resonance position in our samples. The interaction happens through the Fe--O--Fe bridging oxygen, and as Fe^{3+} has spin configuration $5d^5$ (high spin) there are interactions with the p_x and p_z orbitals of the O atom and also indirectly

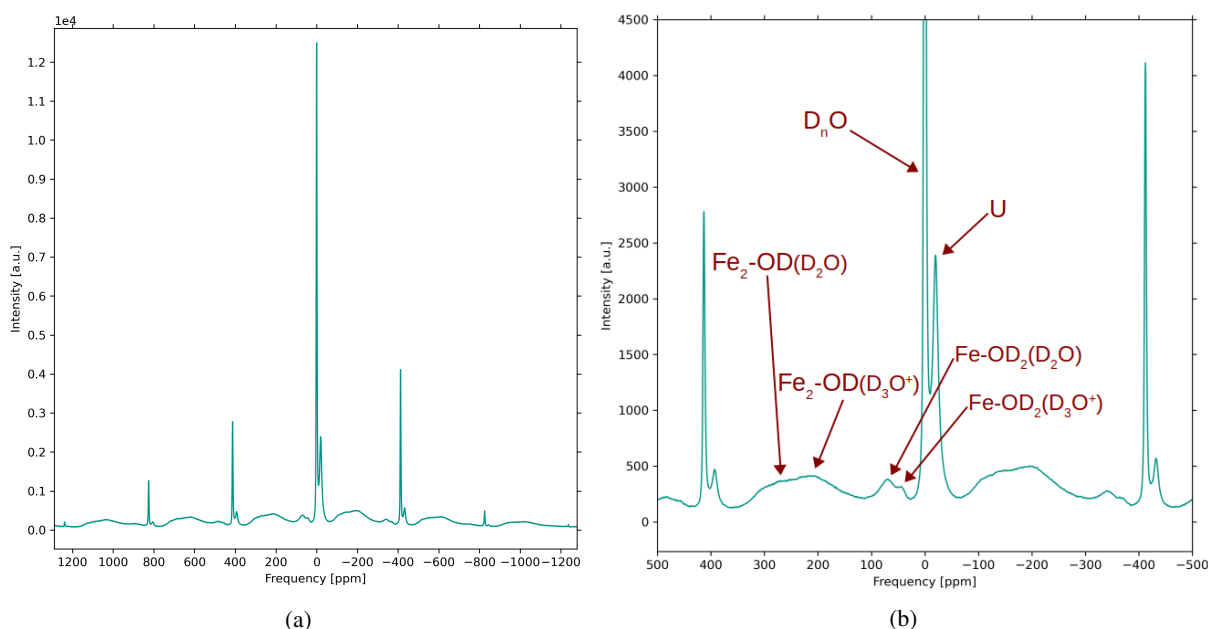


Figure 7.1: NMR single pulse spectrum of deuterium jarosite at spinning speed 38 kHz (a) Full spectrum (b) Zoom on spectrum with resonances identified.

with the half-filled d -orbitals of Fe. The interaction with the d_{xy} orbital is expected to be the strongest and the Fermi contact shift of one Fe–O–D bond is expected to be ≈ 115 ppm.³²

Where it was possible, the isotropic chemical shifts of the resonances were determined by fitting Lorentzian/Gaussian line shapes in ssNake and taking the centre of the peak as the chemical shift value. For resonances where this procedure failed the approximate centre of the peak was determined by adjusting the peak by eye until it seemed to fit the resonance. The error was taken to be the FWHM of the peak. To determine which resonances correspond to which environments we compare our spectra with similar spectra from deuterium jarosite recorded by Nielsen et al.³² (see Table 7.1). In our case we have six resonances to identify, as all three main environments (D_nO , Fe_2-OD and $Fe-OD_2$) in our sample seem to have split into two. We suggest that the splitting is due to the presence of two stoichiometric and two unstoichiometric resonances; one with D_3O^+ as the A^+ ion and one with D_2O as the A^+ ion. For the stoichiometric regions of the sample we will refer to the two environments as $Fe_2-OD(D_3O^+)$ and $Fe_2-OD(D_2O)$ and for the unstoichiometric region they will be referred to as $Fe-OD_2(D_3O^+)$ and $Fe-OD_2(D_2O)$. The suggestion is based on the fact that a similar situation has been observed for K^+ and D_3O^+ in chromium jarosites.⁴⁹

The deuterons in D_nO molecules in the cavity resonate at $\delta = 0 \pm 0.4$ ppm. The D_nO resonance is by far the sharpest of all the resonances in the spectrum; the ssb disappear very quickly, which indicates movement of the molecules. An extra resonance at $\delta = -19 \pm 1.4$ ppm (resonance U on Figure 7.1b) has not been observed in jarosite samples before. It is possible that it is due to an impurity in the sample, but we believe that it is more likely that it is a part of the larger D_nO peak that has been shifted outside the expected region. Nielsen et al.³⁶ has observed that deuterons in D_3O^+ can resonate at negative frequency shifts ($\delta \approx -8.5$ ppm at 300 K and falling linearly with increasing temperature).³⁶ It is likely that we had a temperature that was larger than 300 K in our experiment (the experiment was carried out at room temperature and spinning further heats the sample), and hence we attribute the resonance at -19 ± 1.4 ppm to deuterons in D_3O^+ . It is however not certain whether it is the deuterons in D_3O^+ in the $Fe_2-OD(D_3O^+)$ or the $Fe-OD_2(D_3O^+)$ environment, or both, that gives rise to the resonance. The possibility exists that one of the environment could resonate at -19 ppm and the other at 0 ppm, and as such it is still not possible to separate the D_nO resonance exactly. Lastly we mention that the reason this resonance has not been observed before can be that a lower magnetic field and lower spinning speeds were used in previous studies.³²

The two stoichiometric Fe_2-OD resonances are placed at 250 ± 80 ppm and 215 ± 70 ppm, but it is very hard to separate them. Nielsen et al. found that the stoichiometric resonance, which has a similar shape to what is observed here, was placed at 240 ± 60 ppm. Based on the Fermi-contact shift alone (two Fe–O–D bonds) the resonance should be at ≈ 230 ppm, which is very close to the observed. In a stoichiometric environment we would expect to see mostly intact D_3O^+ ions and hence this resonance should be the largest of the two. Based on these considerations we attribute the resonance with the largest shift to $Fe_2-OD(D_2O)$ ($\delta = 250 \pm 80$ ppm) and the smaller shift (but the most intense resonance) to $Fe_2-OD(D_3O^+)$ ($\delta = 215 \pm 70$ ppm). The two unstoichiometric $Fe-OD_2$ resonances are placed at 70 ± 25 ppm and 45 ± 25 ppm. In this case we would expect the most intense resonance to be the one where $A^+ = D_2O$, as more deuterons will have been used to charge compensate vacancies. Nielsen et al. determined that the $Fe-OD_2$ resonance was placed at $\delta = 70 \pm 30$ ppm, which is in excellent agreement with what we observe. We therefore attribute the largest shift (and most intense resonance) to $Fe-OD_2(D_2O)$ ($\delta = 70 \pm 25$ ppm) and the smaller shift (and less intense resonance) to $Fe-OD_2(D_3O^+)$ ($\delta = 45 \pm 25$ ppm). We note here that 70 ppm is much less than the ≈ 115 ppm shift expected for a single Fe–O–D bond, Nielsen et al.³² ascribe this difference to a change in bond angles and bond lengths of the Fe–O–D bonds in stoichiometric and

unstoichiometric environments. Lastly we can conclude that removing a deuteron seems to shift the signal towards higher frequencies, which would also align with the fact that some D_3O^+ deuterons resonate at negative frequency shifts, while the D_2O deuterons resonate closer to 0 ppm. The difference in position is too large (25-35 ppm) to be caused by the chemical shift alone, and we must therefore assume that it is the Fermi contact interaction that is responsible for the splitting of the signals. Nielsen et al.³⁶ found that, if a Fe^{3+} ion is removed from the lattice, residual antiferromagnetic couplings are present, even at 300 K. The removal of a magnetic ion lifts the frustration locally and allows the spins to couple; in this case the paramagnetic shift of one spin is subtracted from the paramagnetic shift of the other spin. This will result in the resonance being moved to a lower frequency, which is exactly what we observe.

The D_3O^+ and D_nO resonances are very sharp due to the mobility of the molecules, and their ssb therefore disappear quickly (we only have ~ 4 ssb for each resonance in Figure 7.1a). The Fe_2-OD and $Fe-OD_2$ resonances, however, have very broad lines and low intensity, which makes it very difficult to simulate them in ssNake. Due to these difficulties we have not been able to determine the quadrupolar and dipolar coupling strength. It is similarly difficult to reliably determine the integrated intensities (total areas) of the resonances, as we cannot be sure that the different resonances relax with the same rate. If one relaxes much faster than the others it could end up lower in intensity than it actually is.⁸⁶ The integrated intensities have been obtained by Anders in MNova despite this, and a larger error on the integrated values has been included to attempt to convey the issues mentioned. Due to the defect mechanism in jarosites being known we can quantitatively determine, based on the integrated intensities, the amount of iron vacancies present in the sample. The general formula for a defect deuteronium jarosite is given by $ce[(D_3O)_{1-x}(D_2O)_y]_A Fe_{3-x}(SO_4)_2(OD)_{6-4x}(OD_2)_{4x}$ i.e. by removing x from the "pure" Fe-occupancy of 3 we will make the following happen: Four terminal OD groups are created from the six in each octahedron ($(OD)_{6-4x}$). All four will be protonated ($(OD_2)_{4x}$) by deuterons from D_3O^+ ($(D_3O)_{1-x}$) leaving an amount ($(D_2O)_y$) of water on the A-site.

Based on the relative integrated intensities of each ssb envelope the amount of vacancies can then be determined as

$$4x = 6 \frac{\frac{1}{2}I(Fe - OD_2)}{I(Fe_2 - OD) + \frac{1}{2}I(Fe - OD_2)} \quad (7.1)$$

Where I is the integrated intensity of that environment, and where it was assumed that the vacancies are isolated from each other. For the calculation we did not differentiate between the (D_3O^+) and (D_2O) environments. The calculation yields $x = 0.15 \pm 0.04$, which corresponds to an occupancy of the Fe site of $95.1 \pm 1.3\%$. The average amount of deuterons present on the A-site ($[D_nO]_A$) can similarly be determined by

$$n = 6 \frac{\frac{1}{2}I(D_nO)}{I(Fe_2 - OD) + \frac{1}{2}I(Fe - OD_2)} \quad (7.2)$$

Which yields $n = 2.2 \pm 0.7$. In this calculation $I(D_nO)$ was taken to include both the D_nO resonance and the U resonance. If the U resonance is excluded the calculation yields $n = 1.5 \pm 0.7$. This is sensible within error limits, but still very far from what we would expect, which adds validity to the suggestion that the resonance at -19 ppm is due to D_3O^+ deuterons. If we assume the A^+ site is fully occupied $n = 2.2$ indicates that the majority of the A^+ sites (four out of five) in the sample are occupied by D_2O molecules. Due to the large error on n it is, however, also likely that more than half of the sites are occupied by D_3O^+ ($n = 2.6$) or less than fully occupied ($n = 1.7$). If we do not assume full A^+ -site occupancy, $n = 2.2$ could indicate that the A^+ -site is occupied by D_3O^+ , but that

many sites are empty (as D_2O on the A^+ site is not necessary for charge compensation).

7.2 Susceptibility

The susceptibility measurements were performed by PhD student Anders Bruhn Arndal Andersen and bachelor student Nikolaj Niels Neerup Andersen in collaboration with Associate Professor Kasper Steen Pedersen on the DTU Quantum Design DynaCool Physical Properties Measurement System (PPMS) equipped with a 9 T DC magnet in Vibrating Sample Magnetometer (VSM) mode. The measurements were performed in an applied field of 10000 Oe (1 Tesla) while the temperature was decreased from 300 K to 2 K. The results can be found in Figure 7.2a. A clear difference between the hydrogenated and the deuterated jarosite is observed. The behaviour of the susceptibility is the same until approximately 150 K where the deuterated and hydrogenated response begins deviating from each other; the susceptibility of the deuterated sample reaches a higher maximum value ($\sim 0.038 \text{ cm}^3\text{mol}^{-1}$ compared to $\sim 0.028 \text{ cm}^3\text{mol}^{-1}$). In both curves we observe a kink at low temperature, which we attribute to a spin-glass transition. The spin-glass transition for deuterium jarosite occurs at a lower temperature (14 K) compared to hydronium jarosite (16.5 K). In other words: The deuterated sample need to be cooled down to a lower temperature before the spin dynamics freeze out completely, but the magnetism reaches higher values already from ~ 160 K.

From section 3.1 we know that a plot of χ^{-1} versus temperature yields a straight line for a paramagnet. Since jarosites are only paramagnetic far from the ordering (or spin-glass transition) temperature, we expect a deviation from linearity upon lowering of the temperature. This is indeed what is observed. In the case of hydronium and deuterium jarosite the linearity persists to around 160 K; close to the temperature where the behaviour of the two samples starts deviating. By performing a linear fit to the data above 160 K the Curie-Weiss temperatures were extracted as the intercepts with the x-axis. The fits can be seen in Figure 7.2b. The difference in the transition temperatures carries into the Curie-Weiss temperatures and deuterium jarosite has a higher θ_{CW} ($\theta_{CW} = -860 \pm 23$ K) than hydronium jarosite ($\theta_{CW} = -880 \pm 88$ K), although the difference is within the error bars. Table 7.2 compares our results with other studies. θ_{CW} varies from -700 ± 5 K to -1200 ± 200 K; our values fall nicely within this range and are close to the values determined by Grohol and Nocera⁵⁶ and Majzlan et al.¹ for the

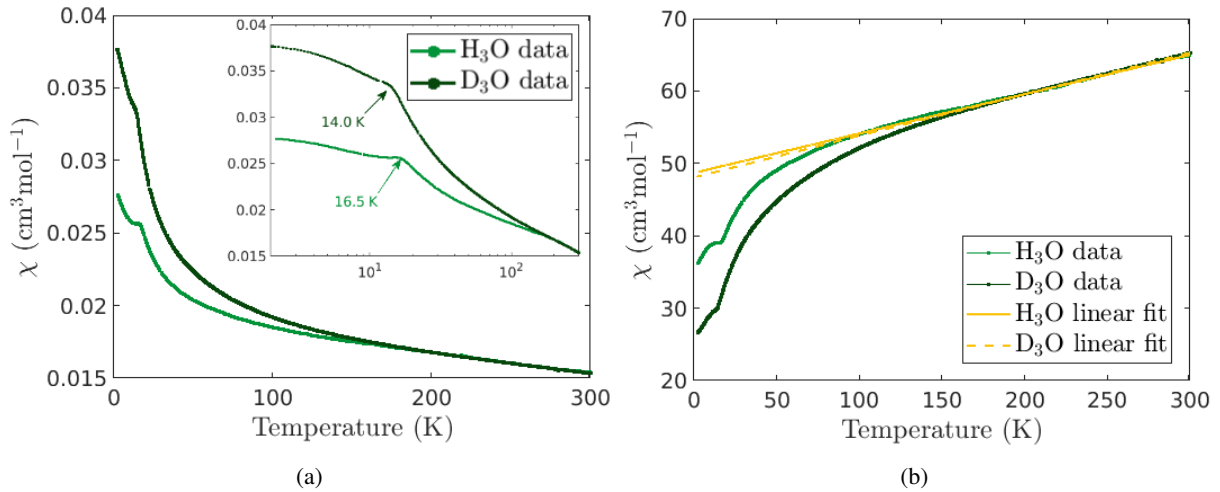


Figure 7.2: **(a)** Susceptibility versus temperature for deuterium (dark green) and hydronium (bright green) jarosite. The inset shows the same data on a logarithmic temperature scale. The arrows indicate the temperatures at which the spin-glass transition occurs **(b)** Linear θ_{CW} fits to inverse susceptibility.

Compound	T_g [K]	θ_{CW} [K]	Reference
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	15.2 ± 0.5 to 17.0 ± 0.5		Wills and Bisson ⁸⁰
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	15.7	−880	Grohol and Nocera ⁵⁶
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	17.2	-1200 ± 200^a	Wills and Harrison ⁴⁵
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	17.8		Bonville et al. ⁸¹
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	17.8	-1200 ± 200	Wills et al. ⁸⁷
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	18	−833	Majzlan et al. ¹
$\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	16.5	-880 ± 88	This work
$\text{D}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	13.8	-700 ± 5	Wills et al. ⁶⁹
$\text{D}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	15		Wills et al. ⁴⁸
$\text{D}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$	14.0	-860 ± 23	This work

^a broad inflection in the high temperature part of the inverse susceptibility is present and makes determination of θ_{CW} more difficult than in other studies.

Table 7.2: Overview of glass transition temperatures (T_g) and Curie-Weiss temperatures (θ_{CW}) in literature compared with values obtained in this work for $\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$ and $\text{D}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$.

hydrogenated sample. Our value of T_g also falls within what is expected for both compounds and the lower T_g for deuterium jarosite seems to be supported by the literature; deuterium jarosite generally has a lower T_g than hydronium jarosite (with the caveat that there are, to the best of our knowledge, only two deuterium studies). Our results thus indicate that an isotope effect is present in the susceptibility; exchanging H for D has an effect on when spin freezing occurs and in general on the low temperature behaviour of the magnetism. We note, however, that Wills and Bisson⁸⁰ showed that the glass transition temperature can vary ± 2 K for chemically similar compounds with the same level of Fe occupancy (first row in Table 7.2). The possibility that the isotopic effect is due to this fluctuation in T_g can therefore not be ruled out. A third possibility is that the change in transition temperature is due to the Fe vacancies and A^+ -site substitutions found by NMR. We cannot conclude anything about this possibility as we do not have NMR spectra for hydronium jarosite.

If the isotope effect is truly present it could serve as evidence for the fact that the spin-glass transition is linked directly to the nature of the $\text{D}_3\text{O}^+/\text{H}_3\text{O}^+$ molecule in the cavity. This would align well with the explanation put forth by Nielsen et. al that it is the mobility of the D_3O^+ molecule that causes spin-glass behaviour. On the other hand the difference in transition temperature could also be caused by disorder regarding $\text{D}_2\text{O}/\text{D}_3\text{O}^+$ present on the A^+ -site. More NMR studies on samples with different (and better characterised) A^+ -site compositions are needed to clear up this question.

There are no signs of an isotope effect in potassium jarosite. Inami et al.⁶ prepared a deuterated and a hydrogenated sample of potassium jarosite (both by the conventional synthesis), but the deuteration did not change the transition temperature, which was 65 K in both cases. Other jarosite compounds do however show signs of some type of isotopic effect; Matan et al.⁶⁴ performed magnetisation measurements on deuterated and hydrogenated silver jarosite and found that the deuterated version of the compound had a larger canted moment than the hydrogenated. Matan et al. speculated that the change of isotope in some way affects the in-plane component of the DM interaction D_y (as we know D_y is responsible for the canting). This is in line with the larger magnetic moment we observe for deuterium jarosite; although deuterium jarosite does not order and therefore does not (should not) have the canted structure.

7.3 Neutron scattering

Neutron scattering measurements were performed on two separate occasions; one remotely (due to Covid restrictions) in December 2020 and one in person in June 2021. Notice that we in this part of the thesis as well as in the figures will refer to the scattering vector as Q and the energy transfer as E , where we previously denoted them q and $\hbar\omega$. We will first go through the December data, but the focus of this thesis will mainly be on the June data.

7.3.1 Results from the December neutron data

Initial inelastic neutron scattering measurements were performed (remotely by Henrik Jacobsen and Jan Peter Embs) on the Time-of-Flight spectrometer FOCUS at PSI. The samples were powder samples of deuterated potassium jarosite (1.841 g) and deuterium jarosite (1.770 g). They were loaded in cylindrical aluminium sample holders and placed in an Orange cryostat in the beam for approximately 8 hours for each temperature. Data was taken at three different temperatures for each sample. For deuterium jarosite the temperatures were 2 K, 25 K and 250 K (below spin-freezing, right above spin-freezing and the high temperature regime) and for potassium jarosite they were 2 K, 75 K and 250 K (in the ordered regime, right above ordering and the high temperature regime). The incoming energy was $E_i = 20$ meV in both cases, which gave a Q -range of $Q = 0.50 \text{ \AA}^{-1}$ to $Q = 6.65 \text{ \AA}^{-1}$ and an energy range of $E = -17.27$ meV to $E = 17.27$ meV. Initial data reduction was performed by Henrik Jacobsen using the software package DAVE.⁸⁸ Data analysis was carried out in MATLAB using the packages spec1d (by D. McMorrow and H. M. Rønnow) and mslice.

Background subtraction

Empty can (EC) measurements at 75 K were used to perform a background subtraction under the assumption that the background was temperature independent. An unexplained broad, instrumental effect for $Q \sim 0.5 \text{ \AA}^{-1}$ to $Q \sim 2 \text{ \AA}^{-1}$ along zero energy transfer (see figure 7.3a), not present in any of the other data sets, complicated this

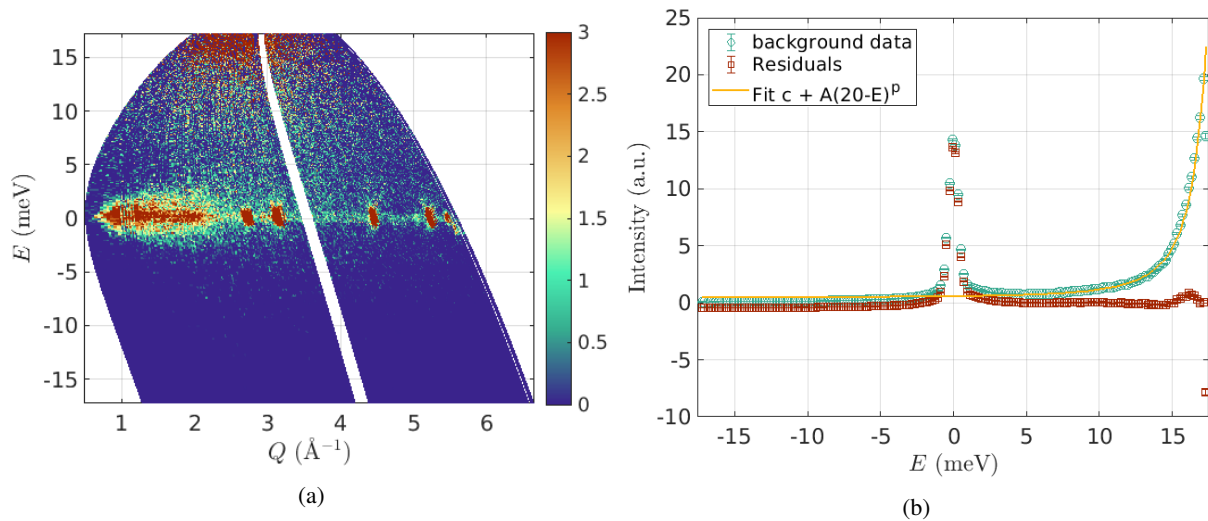


Figure 7.3: Empty can measurement for aluminium sample holder at 75 K. **(a)** Intensity plot showing the entire Q and E range. **(b)** Fit to sum of entire Q range above $E = 4$ meV with fitting function $I_B = c + A(20 - E)^p$.

process. The white lines in the figure are removed faulty detectors (detectors 180, 181, 182 and 367 specifically). Furthermore the edges (high Q and low Q) of the data have been excluded from the analysis as the elastic line is not fully resolved here. To avoid the unexplained feature a fit was performed to the EC measurement above $E = 4$ meV where the effect was absent, and then extrapolated to lower energy transfers. This means that the structural peaks for aluminium due to the sample container will not be subtracted, and we will need to keep this in mind in the analysis.

It was found that the following formula fitted the shape of the time-of-flight background well

$$I_B = c + A(E_i - E)^p \quad (7.3)$$

Where $E_i = 20$ meV is the incoming energy of the neutrons. A fit to an average of the background shape (sum over the entire Q -range) was used to approximate the parameters

$$c = 0.52 \pm 0.02$$

$$A = 317.02 \pm 0.75$$

$$p = -2.66 \pm 0.04$$

The fit can be seen in Figure 7.3b. The background shape was then assumed to be independent of Q , and the background was subtracted from each detector. A Q -dependent fit was attempted but failed, as the errors in the high energy transfer region were so large that their impact on the χ^2 was minimal. The Q -dependent fitting routine therefore fit the ToF specific part of the background very poorly, and the attempt was abandoned. The full data with the background subtracted for both potassium and deuterium jarosite are found in Figure 7.4. The background subtraction is incomplete and a large intense feature can be seen at low Q and high energy transfers in all data sets. The fit only being performed on higher energy transfers furthermore resulted in the background for the low energy transfers being slightly overestimated. The error on the result is propagated using the standard formula for error propagation.⁸⁹ In our case

$$\sigma_{I_B}^2 = \left(\frac{\partial I_B}{\partial c}\right)^2 \sigma_c^2 + \left(\frac{\partial I_B}{\partial A}\right)^2 \sigma_A^2 + \left(\frac{\partial I_B}{\partial p}\right)^2 \sigma_p^2 + \left(\frac{\partial I_B}{\partial E}\right)^2 \sigma_E^2 \quad (7.4)$$

Performing the differentials gives us the error on each background measurement as (the square root of)

$$\sigma_{I_B}^2 = \sigma_c^2 + (20 - E)^{2p} \left[\sigma_A^2 + \left(\frac{Ap\sigma_E}{20 - E}\right)^2 + (A \ln[E_i - E] \sigma_p)^2 \right] \quad (7.5)$$

The error on the corrected intensity is obtained by adding the errors in quadrature

$$\sigma_{I_{subt}}^2 = \sigma_I^2 + \sigma_{I_B}^2 \quad (7.6)$$

where σ_I are the original errors on the measurements. The errors on c , A and p come from the fitting of the binned, average data and are very small. Due to the smallness of these errors $\sigma_{I_B} \ll \sigma_I$ and we can approximate the errors after background subtraction as just the original errors on the measurements: $\sigma_{I_{subt}} = \sigma_I$. We need to keep in mind that the background subtraction has introduced a systematic error (underestimation of the low-energy transfer background and the incomplete subtraction at high energy transfer at low Q) and that it dominates the statistical one, adding validity to the above approximation. The features we are looking at in potassium jarosite

and deuterium jarosite are far removed from the areas the systematic error affects. It is therefore not an issue and will not be dealt with further.

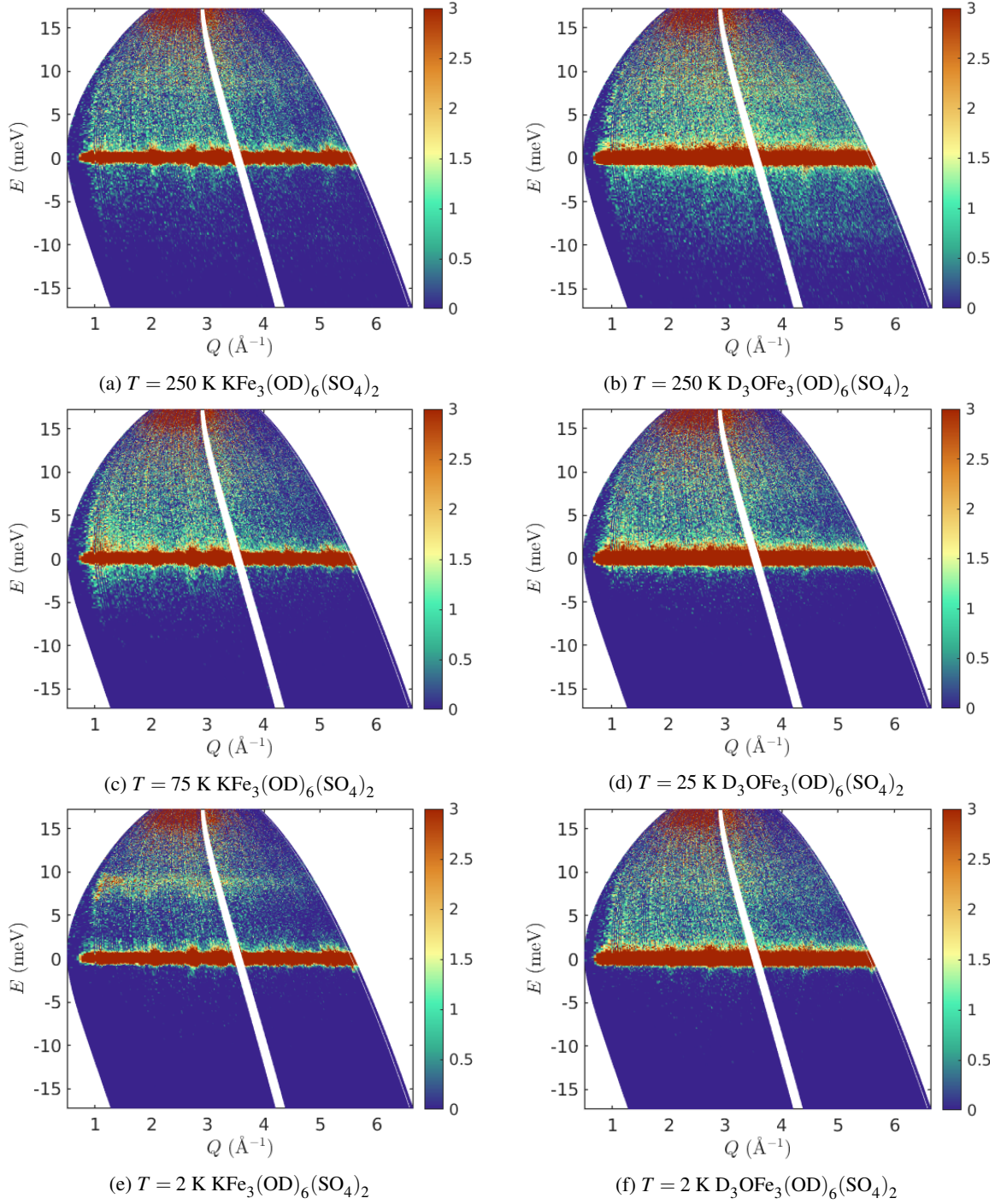


Figure 7.4: Neutron scattering data taken with $E_i = 20 \text{ meV}$ at FOCUS for $\text{KFe}_3(\text{SO}_4)_2(\text{OD})_6$ and $\text{D}_3\text{OFe}_3(\text{SO}_4)_2(\text{OD})_6$ at the indicated temperatures. The expected clean background at 2 K for potassium jarosite shows that the background subtraction works reasonably in the region of the inelastic signal. The red intense feature present in all plots at high energy transfers is an artefact from the background subtraction that does not work perfectly at high energies.

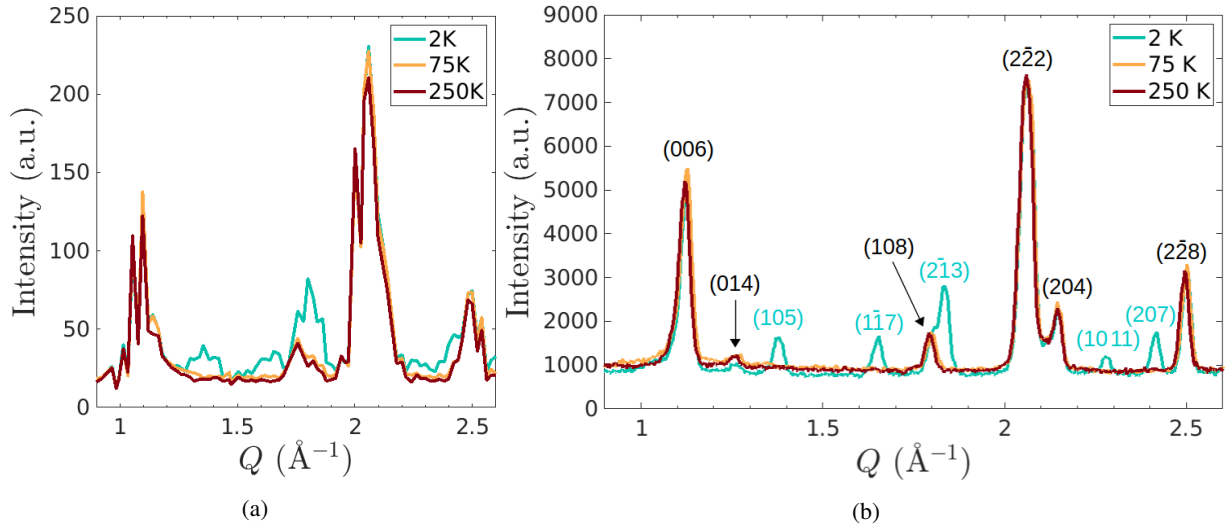


Figure 7.5: **(a)** Cut along the elastic line between $E \pm 0.31$ meV in the FOCUS data for potassium jarosite. The low temperature data show extra peaks indicating magnetic ordering. **(b)** HRPT diffraction data for potassium jarosite at the indicated temperatures with $\lambda = 1.49$ $\text{\AA}$. The peaks are indexed in double unit cell (magnetic unit cell) units. Nuclear Bragg peaks are written with black and have even l indexes. Magnetic peaks are written with blue and have odd l indexes. The peak indexing was carried out in collaboration with Dr. Machteld Elizabeth Kamminga with use of the Jana software.⁹⁰

Potassium Jarosite

The magnetic behaviour, both elastic and inelastic, of potassium jarosite has already been studied in great detail in the literature and is well understood (see chapter 5). In this section we therefore merely confirm that our results do not deviate from those in the literature. The data for potassium jarosite are shown in Figure 7.4a (250 K), Figure 7.4c (75 K) and Figure 7.4e (2 K) after background subtraction has been performed.

Elastic scattering

In this experiment we did not have time to take Vanadium measurements and we therefore determine the resolution function for the instrument by performing cuts across the elastic line along Q where the Bragg peaks were absent. The cuts were fitted with a Gaussian (see Figure 7.8b). The width of the elastic line, σ , was the same for potassium jarosite and deuterium jarosite (0.31 meV). This is the width we sum over when assessing the features of the elastic line that can be seen in figure 7.5a. The elastic lines for $T = 250$ K and $T = 75$ K are almost identical, but at $T = 2$ K new magnetic Bragg peaks appear (most prominently a $Q \sim 1.35$ $\text{\AA}^{-1}$ and $Q \sim 1.60$ $\text{\AA}^{-1}$, while the peak at $Q \sim 1.8$ $\text{\AA}^{-1}$ increases in intensity) indicating that the transition to a magnetic LRO state has taken place. FOCUS is not an ideal instrument for measuring purely elastic scattering. For this reason we also include later measurements from HRPT (High-Resolution Powder Diffractometer for Thermal Neutrons situated at PSI) where the peaks are much easier to index (see Figure 7.5b for the indexing). In the range from $Q = 0.9$ to $Q = 2.6$ $\text{\AA}^{-1}$ five new distinctly magnetic Bragg peaks appear: (105), (117), (213), (1011) and (207). The magnetic Bragg peaks all have odd values of crystallographic parameter l . This is caused by the magnetically ordered unit cell doubling in size as described in chapter 5.

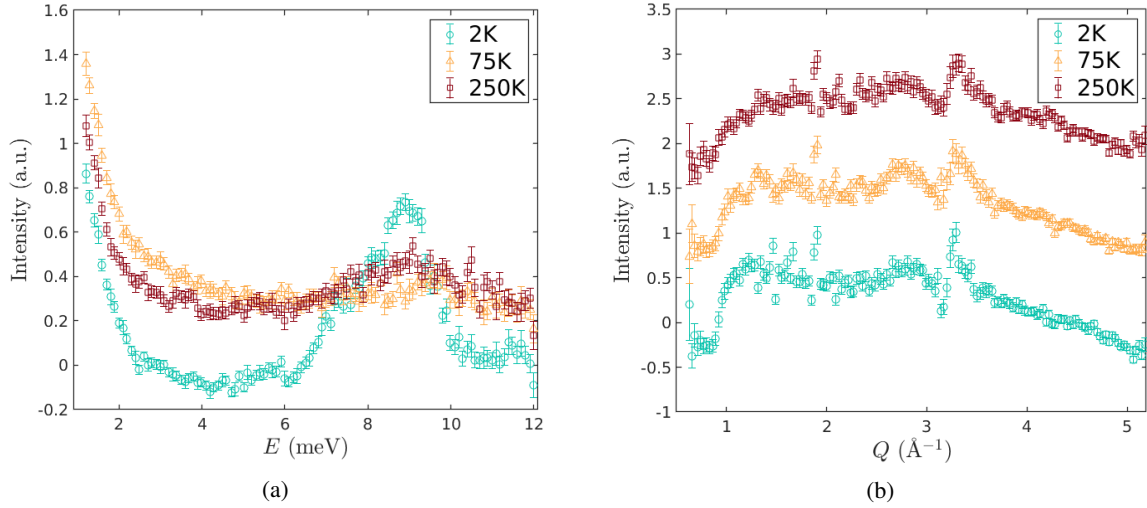


Figure 7.6: Scattering from potassium jarosite at the indicated temperatures **(a)** E -dependence. The bin width is 0.1 meV and the cut is performed over the entire Q range with E between 1.2 meV and 12 meV (contributions from high energy transfers and the elastic line are therefore left out). **(b)** Q -dependence. The bin width is $0.03 \text{ \AA}^{-1}$ and the cut is performed around the lifted zero mode ($E = 5 \text{ meV}$ to $E = 10 \text{ meV}$) with Q from 0.5 to $5.2 \text{ \AA}^{-1}$. The three data sets are offset with 1 in the positive direction for clarity. The intensity going below zero in some areas is a systematic error introduced by the background subtraction.

Inelastic scattering - spin-waves

A weakly dispersive "zero" mode is observed in Figure 7.4e beginning at $\sim 7 \text{ meV}$ in accordance with the lifted zero-energy mode observed by Matan et al.⁶¹ and Coomer et al.⁶⁸ (see chapter 5). The mode disappears when the temperature is raised above the ordering temperature (Figure 7.4c and Figure 7.4a). Due to the relatively lower incident energy used in this experiment we are not able to see the spin-wave branches of Coomer et al.⁶⁸ The intensity is modulated in E and weakly in Q . The dependence of the mode on Q and E is highlighted in Figure 7.6a and Figure 7.6b, respectively. The mode is seen most clearly in the 2 K data in figure 7.6a, with the intensity centred between 7 and 9 meV, as also observed in the literature. The feature is completely absent from the 75 K and 250 K data, although a small bump is observed at this position in the 250 K data. The scattering is in general increased in the higher temperature data sets, as expected for the paramagnetic regime. The 2 K data dips below zero, which is an unphysical effect introduced by background subtraction. The dependence on Q is less clear. In the literature two maxima have been observed: One at $Q = 1.1 \text{ \AA}^{-1}$ and one at $Q = 2.8 \text{ \AA}^{-1}$. The first maximum has been attributed to a Brillouin zone centred at $|Q| = 4\pi/\sqrt{3}a = 1.00 \text{ \AA}^{-1}$ and the second has been speculated to reflect the zone-boundary energy of either a one-magnon or two-magnon excitation spectrum.⁶⁸ The data in Figure 7.6b reflect this behaviour but the maxima are less well defined. The features in the $Q = 1 \text{ \AA}^{-1}$ to $Q = 3 \text{ \AA}^{-1}$ regions are smeared out gradually as the temperature is raised, but seem mostly independent of temperature. This is in line with the diffuse scattering results for deuterium jarosite⁷⁶ and demonstrate the universality of this feature across different jarosites. A sharp peak is observed around $Q = 3.1 \text{ \AA}^{-1}$. This could be the fault of the faulty detectors removed in this area - in that case it is just the tail end of the $Q = 2.8 \text{ \AA}^{-1}$ broad feature. It could also stem from the background subtraction yet again. The odd high points at $Q \approx 2 \text{ \AA}^{-1}$ also seem to stem from some systematic error in the data treatment.

Despite the issues with data treatment the overall results from potassium jarosite are well within the what we

expected from the literature.

Deuteronium jarosite

The results from deuteronium jarosite are shown in Figure 7.4b (250 K), 7.4d (25 K) and 7.4f (2 K). No immediate magnetic features are visible in the colour plots as expected for a spin-glass. A cut along the elastic line was performed (Figure 7.7a) and showed no magnetic Bragg peaks appearing at any temperature. Diffraction data from HRPT similarly showed no magnetic Bragg peaks (Figure 7.7b). The 2 K (below spin freezing) and 25 K (above spin freezing) cuts in the FOCUS data are practically identical. The shape of the 250 K cut is similar to the other two, but the intensity is less overall, signalling that some scattering intensity has been lost. Summing up the intensity of the elastic line for 2 K and 250 K and comparing we get that 22% intensity has been lost between the two temperatures. To make sure that this intensity is not missing due to a fault in the data acquisition the intensity was summed over the entire Q and E range yielding only a $\approx 6\%$ loss in intensity from 2 K to 250 K. The loss in intensity was examined further by performing the sum several times, each time including 0.31 meV more on each side. The results are plotted in Figure 7.8a. As more of the energy range is included the scattering intensity is slowly regained; elastic scattering has become inelastic scattering, which is exactly what the Debye-Waller factor mentioned in subsection 3.2.2 describes. The shift in scattering intensity could be caused specifically by the deuteronium ion becoming more mobile at high temperatures and it can be seen as an indication of the very gradual freezing of spins, which is characteristic for a spin-glass.⁹¹ Another possibility is the presence of quasi-elastic scattering in deuteronium jarosite. To examine this possibility a cut was performed across the elastic line for both potassium and deuteronium jarosite at all temperatures, avoiding Bragg peaks (the same cut that was used to determine the width of the elastic line; Figure 7.8b). The cut was put on a logarithmic scale to highlight the possible presence of (Lorentzian) tails not captured by the Gaussians. Regarding quasi-elastics in deuteronium jarosite the range from 1 to 2 meV on Figure 7.8b is the most interesting; a small bump is seen next to the Gaussian peak going well above the intensity described by the fitted Gaussian. The behaviour is most pronounced for the 2 K and 25 K data sets, and is comparatively absent from the potassium data. It could be caused by a Lorentzian component in the data, but without better resolution of the elastic line and knowledge about the resolution function for the instrument it is hard to say anything more concrete about the possibility for quasi-elastic scattering in $\text{D}_3\text{OFe}(\text{OD})_6(\text{SO}_4)_2$. The potential for quasi-elastic scattering was therefore examined in much greater detail using the neutron data from the June experiment; an experiment that was designed exactly for this purpose.

7.3.2 Results from the June neutron data

Further neutron scattering measurements on D_3O -jarosite were obtained from July 2nd to July 5th 2021 using the ToF spectrometer FOCUS at PSI with the help of instrument responsible Jan Peter Embs. An extra round of temperatures was measured by Jan Peter Embs from July 27nd to July 28th 2021. The incident energy of neutrons in both rounds was $E_i = 3.55$ meV. The drop in incident energy compared to the December measurements was done in order to improve the resolution of the elastic line, which is necessary when we want to study the (potentially) quasi-elastic behaviour of D_3O -jarosite. An overview of the obtained data sets can be found in Table 7.3. The original round of data is labelled KJM and the second round is labelled J. The counting time for each data set was 3 hours. The 2 K data was recorded once each round to make sure the measurements could be compared. In the following analysis only the original 2 K data will be analysed. EC measurements were performed for 2 hours each at temperatures 2 K, 75 K, 150 K, 200 K and 250 K. Vanadium measurements were performed on a

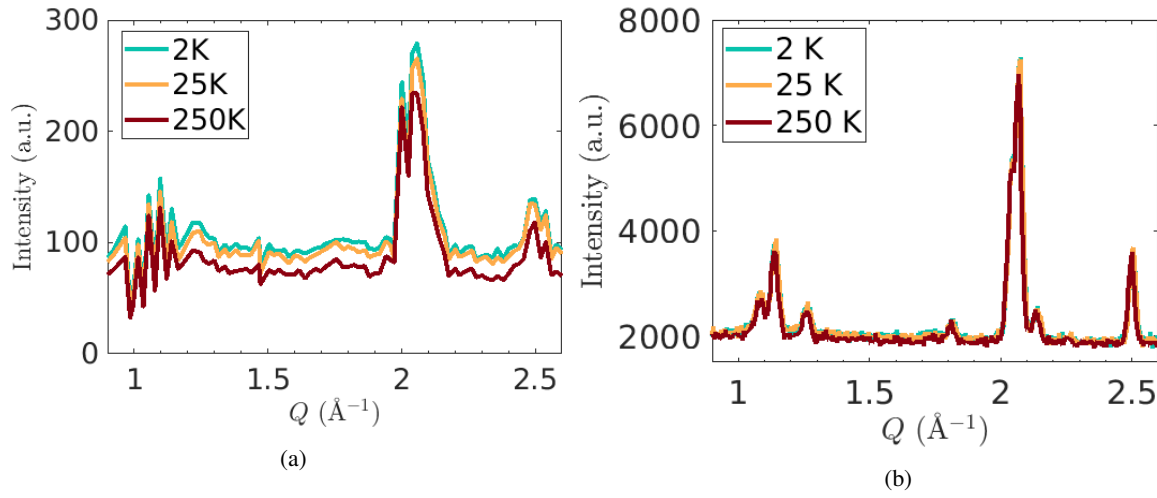


Figure 7.7: **(a)** Sum over elastic line from $Q_{min} = 0.5 \text{ \AA}^{-1}$ to $Q_{max} = 6.65 \text{ \AA}^{-1}$ for energy transfers $\pm 0.31 \text{ meV}$ (FOCUS data) **(b)** HRPT diffraction data for deuterium jarosite. No magnetic Bragg peaks are seen at any temperatures. The difference in intensity from low temperature to high temperature is not seen in diffraction measurements as only elastic scattering is measured.

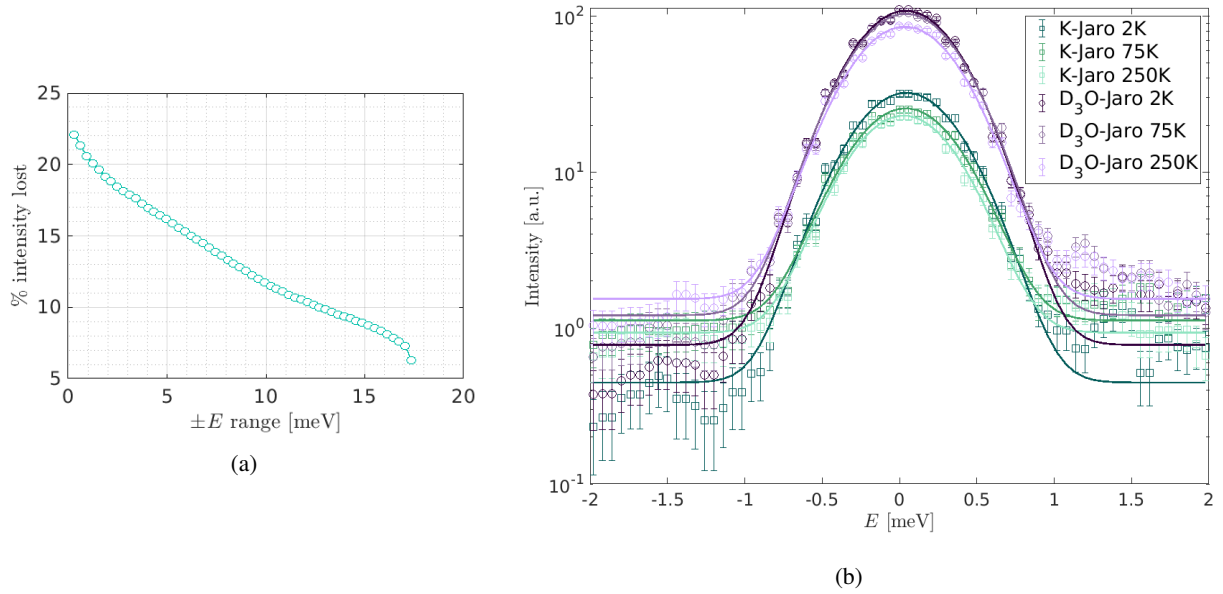


Figure 7.8: **(a)** Percent of scattering intensity lost when comparing 250 K and 2 K data. The shape of the points is described by the Debye-Waller factor **(b)** Cut across the elastic line in Q -range 2.2 to $2.3 \text{ \AA}^{-1}$ and E -range $\pm 2 \text{ meV}$. The cut is performed away from any Bragg peaks. All cuts were fitted with a Gaussian line shape. All Gaussians have fitted standard deviations of $\sigma = 0.31 \text{ meV}$.

facility-provided Vanadium sample of dimensions roughly that of the sample for approximately one hour at 2 K. The sample holder used in both experiments as well as the EC measurements was an aluminium cylinder. Since the sample was not able to fully fill the sample holder a hollow-cylinder was imitated by wrapping the sample in aluminium foil before insertion along the wall of the sample holder. After data acquisition the raw (hdf) data files were reduced in the program DAVE⁸⁸ by Jan Peter Embs and Henrik Jacobsen. Further data analysis was carried out in MATLAB using the packages `spec1d` and `Mslice`.

An example of the raw data (after reduction, before background subtraction) can be seen for two different temperatures in Figure 7.9. The intensity along high energy transfers is the ToF-specific background described in depth for the December data. It will be removed by subtracting the background. Note that the energy transfer has changed drastically from the previous section due to the lower E_i .

Several features are immediately visible. Firstly we see that we need to remove the same faulty detectors as in the December data. The entire data set is made up of 374 detectors, each recording 639 pixels. The removed areas are detectors 180-182 (dubbed the 'Machteld line') and detectors 364-374 (a small spurion for small negative energy transfers). The elastic line at the smallest Q 's is not well resolved either and will therefore also be left out of the fits. Secondly, and most strikingly, broad scattering, indicative of short-ranged order, is seen to emerge from a point around $Q = 1.2 \text{ \AA}^{-1}$ as the temperature is increased from 2 K to 35 K (greenish-yellow on the colour plots). In the data treatment we are interested in determining exactly how the characteristics of this (potentially quasi-elastic) scattering change with temperature and Q . Before we can do this, we, however, need to perform the background subtraction and model the resolution function of the experiment. This will be the objective of the next two sections.

Background subtraction

The EC measurements had none of the inexplicable features present in the December data. In the case of the KJM data sets (Table 7.3) the data sets were the exact size of the EC measurements (374×891 pixels) and the signal intensity of the EC could therefore be subtracted directly (pixel by pixel) from the signal intensity of the sample data. The J data sets could not be reduced to the exact size of the EC measurements (they ended up being 374×890 pixels). For this reason a linear interpolation (using a predefined MATLAB function) was carried out to "squish"

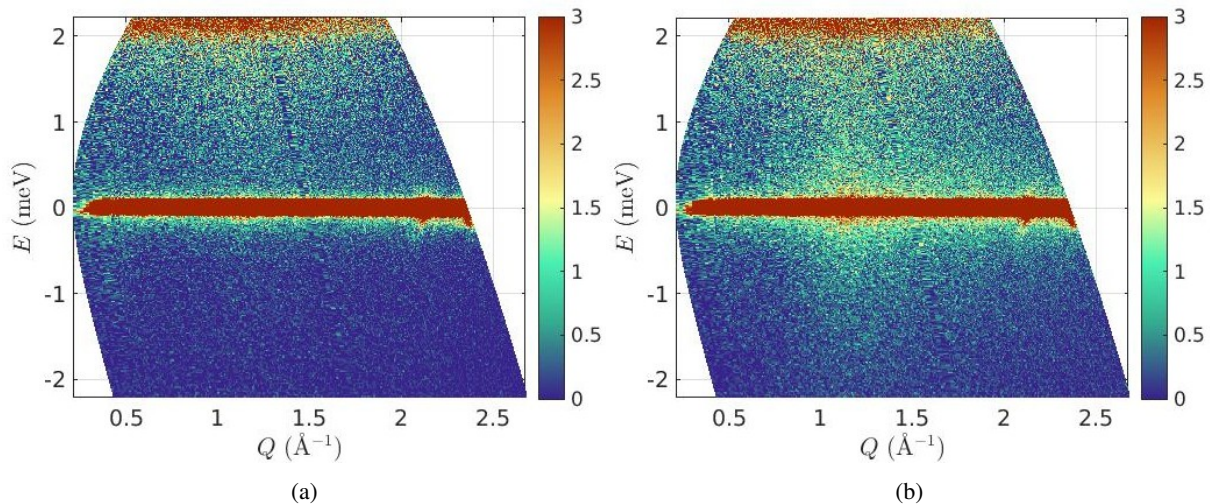


Figure 7.9: Scattering from deuterium jarosite at (a) 2 K and (b) 35 K before background subtraction and clean up of data.

the EC data to the size of the sample data before subtraction. In the following we will denote the subtracted intensities $I(E)$ and calculate them as,

$$I(E) = S(E) - \gamma \cdot EC(E) \quad (7.7)$$

where $S(E)$ is the signal from the sample and $EC(E)$ is one of the 5 EC data sets or a linear combination hereof (see Table 7.3 for the details on which EC measurements were subtracted from which data sets). γ is a correction factor due to self absorption by the sample. By self absorption is meant that more scattering from the sample holder reaches the detector when it is empty compared to when it is full. The way to intuitively understand this is that the sample absorbs and scatters some of the neutrons that would otherwise reach the detector. γ was assumed for simplicity to be independent of Q and temperature, and hence the same value of gamma was used for all data sets. The value of γ was approximated by picking an area in the 2 K data where the signal should be zero or close to zero after background subtraction, i.e. before the ToF background really sets in and out of the way of the elastic line. For the chosen area (visualised in Figure 7.10a) the signal was summed and an average was computed for a range of possible values of γ (0.1 to 1). These averages are shown in Figure 7.10b. The average signal in this area never reaches zero with a minimum value of 0.11 intensity units at $\gamma = 1$. We cannot raise the value of γ to above 1, and for this reason $\gamma = 1$ was chosen as the best value for the subtraction. We expect the subtraction in the high- E region to be less than perfect and will ignore this region in what follows.

In the cases where only one EC data set was subtracted from one sample data set the errors were added in quadrature as previously described. For the subtractions where a linear combination was used the error was propagated twice; once for adding the EC data sets and one for the subtraction. In the cases where an interpolation was carried out the error was interpolated in the same manner as the signal. The interpolation introduces a systematic lowering of the signal intensity, which is most pronounced in the peaks. This cannot be avoided, as the data points in the peaks are far from each other and a weighted average of them will necessarily not end up exactly at the topmost data point. As this uncertainty was hard to quantify no attempt was made to include it, and it was therefore assumed that the interpolation did not alter the original error. The intensity maps for all temperatures after background subtraction are found in Figure 7.18 and will be commented on in subsection 7.3.2.

Vanadium measurements and modelling of the resolution

The vanadium data provides us with the energy resolution of the instrument at the chosen setting. The energy resolution is Q -dependent and highly important in reliably separating elastic and quasi-elastic scattering.

The data run from $Q_{min} = 0.21 \text{ \AA}^{-1}$ to $Q_{max} = 2.68 \text{ \AA}^{-1}$. The Q -range is cut into slices of width $\Delta Q = 0.099 \text{ \AA}^{-1}$ yielding 25 slices. Only slices 2 to 21 were fit, as there was not enough data along the edges to make a meaningful fit. Data points in the cuts with value ≤ 0 (exactly) were removed. The cuts yielded a peak centred around zero with both a Gaussian (G_R) and a Lorentzian (L_R) contribution; this is the resolution we are looking for. We denote the function $R(E)$ and write it as

$$R(E) = G_R(A_{GR}, \sigma_R, E_{0R}) + L_R(A_{LR}, \Gamma_R, E_{0R}) \quad (7.8)$$

All parameters relating to the resolution function have subscript R . In the above A is the area of each distribution, E_{0R} is the common centre of the distributions (≈ 0), and σ_R (Γ_R) is the width (HWHM) of the Gaussian (Lorentzian). An example fit is seen in Figure 7.11a. For our particular measurements additional small Gaussian-like contributions were found next to the central Gaussian peak as two small shoulders. We believe them to be

Data set temperature [K]	Set	EC subtracted
2	KJM	EC(2K)
10	KJM	EC(2K)
15	KJM	EC(2K)
20	KJM	EC(2K)
25	KJM	$\frac{1}{3}[\text{EC}(75\text{K})] + \frac{2}{3}[\text{EC}(2\text{K})]$
30	J	$\frac{2}{5}[\text{EC}(75\text{K})] + \frac{3}{5}[\text{EC}(2\text{K})]$
35	KJM	$\frac{7}{15}[\text{EC}(75\text{K})] + \frac{8}{5}[\text{EC}(2\text{K})]$
45	J	$\frac{3}{5}[\text{EC}(75\text{K})] + \frac{2}{5}[\text{EC}(2\text{K})]$
55	J	$\frac{55}{75}[\text{EC}(75\text{K})] + \frac{20}{75}[\text{EC}(2\text{K})]$
65	J	$\frac{65}{75}[\text{EC}(75\text{K})] + \frac{10}{75}[\text{EC}(2\text{K})]$
75	KJM	EC(75K)
100	J	$\frac{2}{3}[\text{EC}(75\text{K})] + \frac{1}{3}[\text{EC}(150\text{K})]$
125	J	$\frac{1}{3}[\text{EC}(75\text{K})] + \frac{2}{3}[\text{EC}(150\text{K})]$
150	KJM	EC(150K)
200	KJM	EC(200K)
250	KJM	EC(250K)

Table 7.3: Overview of D_3O -jarosite data and background subtraction. KJM means that the data was acquired by Kim Lefmann, Jan Embs and Mathilde Borup Sørensen at the original June beam time (from July 2nd to July 5th 2021). Data sets labelled J were acquired later by Jan Embs (from July 27nd to July 28th 2021). For the low temperature data sets (up to 20 K) the 2 K EC data was used. For all other temperatures that do not correspond exactly with an EC measurement a linear combination of EC measurements were used.

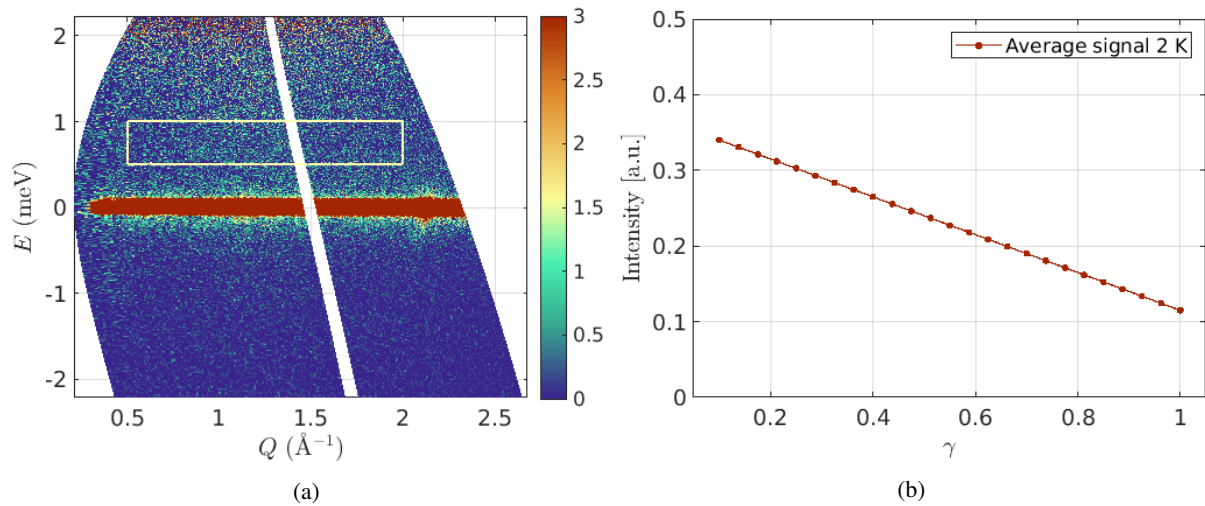


Figure 7.10: Determination of the self absorption factor γ used for background subtraction. The white line is the removed faulty detectors (see text) (a) Region in the 2 K data set used for performing the average ($Q = 0.5 \text{ \AA}^{-1}$ to $Q = 2 \text{ \AA}^{-1}$ and $E = 0.5 \text{ meV}$ to $E = 1 \text{ meV}$). (b) Average signal for a range of possible γ 's.

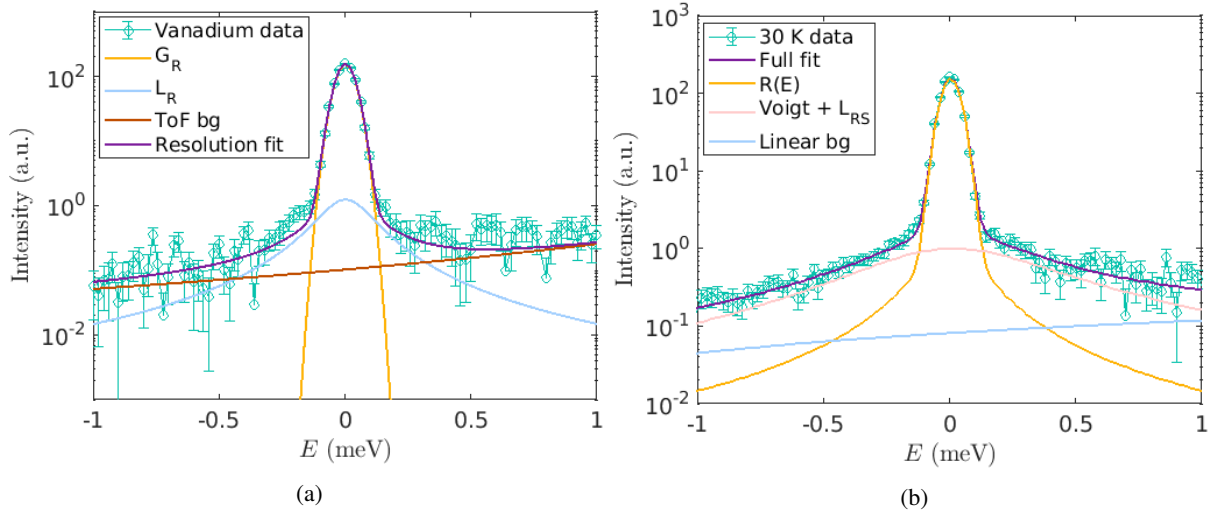


Figure 7.11: **(a)** Example fit to vanadium data taken at 2 K at $Q = 1.4 \text{ \AA}^{-1}$. The Gaussian (yellow), Lorentzian (light blue), Time-of-Flight background (brown) and full fit (purple) are shown **(b)** Example fit to 30 K deuteronium jarosite data at $Q = 1.4 \text{ \AA}^{-1}$. The resolution function (yellow), dynamical scattering (light pink), linear background (light blue) and full fit (purple) are shown.

due to scattering from the vacuum chamber in the cryostat, which is made of aluminium. The "extra" peaks were not consistently positioned (sometimes only the one was there, sometimes both, sometimes none). In Figure 7.11a such an extra peak is seen at $\sim -0.1 \text{ meV}$. Ignoring their presence did not hinder the fitting procedure or worsen the quality of the fit, and for this reason they have been ignored in both the Vanadium fitting and the later sample fitting. It was furthermore necessary to add a curved background. For this purpose we used the ToF background in Equation 7.3 with the constant set to zero, $E_i = 3.55$ and the power held constant at -2.77 (based on an average of an initial fitting where this parameter was not held constant). The fit was carried out in the energy range $\pm 1.0 \text{ meV}$ (full range is ± 2.21) and the Q -dependence of the fits was assessed. Most of the parameters show a trend in their behaviour and to smooth out inconsistencies the parameters that are to be set constant in the fitting of the data are themselves fitted with polynomials of an appropriate degree. The fits and the polynomials used to fit the parameters are detailed in Figure 7.12. The area, width and centre of the Gaussian component have a clear dependence on Q . The area and the position of the centre decreases with increasing Q while the width increases with increasing Q . From the plot of the area it is clear that the first two slices (cut 2 and cut 3) do not yield correct parameters and hence they have been excluded for the rest of this analysis (i.e. we are only fitting cuts 4 to 21). The Q -dependence of the Lorentzian contributions is less clear as the errors on the found parameters were large in case of both the area and HWHM. Following the polynomial fitting it was checked whether the smoothing of the trends hindered a good fit to the resolution function. As this was not the case the smoothed parameters were used in subsequent analysis.

Sample data modelling and model fitting

The data with the background subtracted gives us the sample signal convoluted with the resolution function. We will denote this

$$I(E) = R(E) \otimes S(E) \quad (7.9)$$

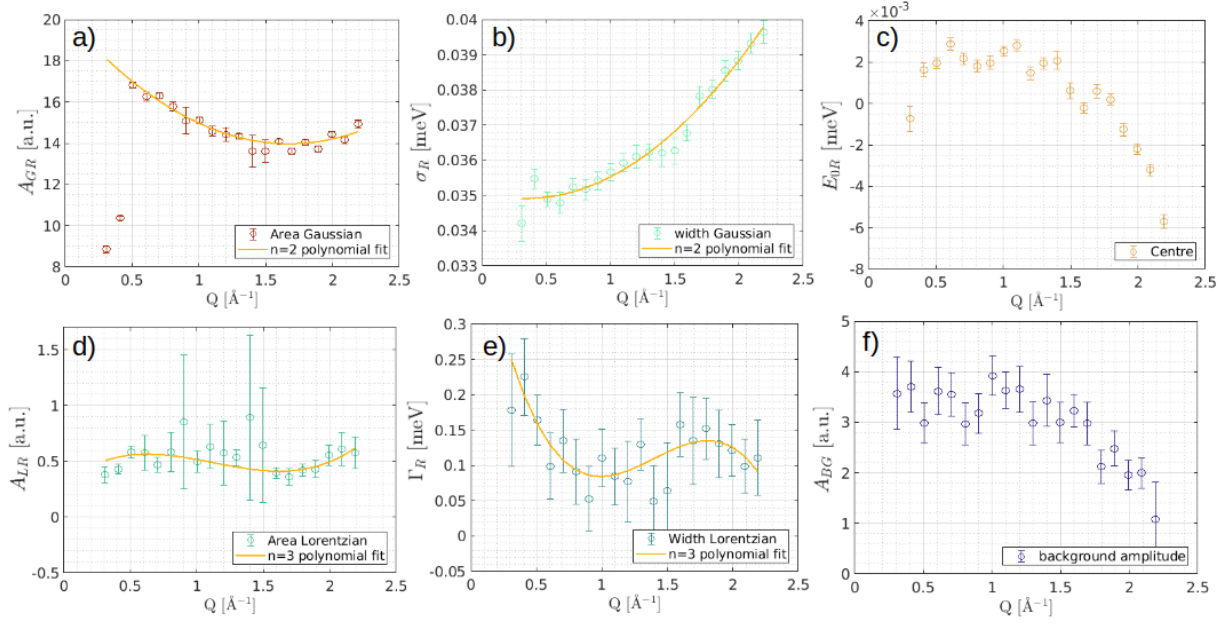


Figure 7.12: Q -dependence of the parameters in the Vanadium fit. The first two points in each plot have been left out of the polynomial fitting **(a)** Area of the Gaussian component, fit with a $n = 2$ degree polynomial. The polynomial fit yielded parameter vector $p_1 = [2.20, -7.37, 20.14]$ with $\chi^2 = 1.93$ **(b)** Width of the Gaussian component, fit with a $n = 2$ degree polynomial. The polynomial fit yielded parameter vector $p_2 = [0.0014, -0.001, 0.035]$ with $\chi^2 = 0.65$ **(c)** Centre of the Gaussian component. The centre is allowed to vary in the sample data fitting and hence it is not fitted with a polynomial **(d)** Area of the Lorentzian component, fit with a $n = 3$ degree polynomial. The polynomial fit yielded parameter vector $p_3 = [0.31, -1.06, 0.96, 0.30]$ with $\chi^2 = 0.49$ **(e)** HWHM of the Lorentzian component, fit with a $n = 3$ degree polynomial. The polynomial fit yielded parameter vector $p_4 = [-0.18, 0.78, -1.00, 0.49]$ with $\chi^2 = 3.92$ **(f)** ToF background amplitude. The amplitude is not used in the sample fitting, as the background has been subtracted, hence it is not fitted with a polynomial.

In an ideal world the resolution function would be a delta function, such that $I(E) = S(E)$, but as we have already seen above, the resolution function has a Lorentzian and a Gaussian contribution. To determine the final fitting function we therefore need to carry out the convolution of the signal with the resolution. For this calculation we will need the following known expressions

$$L_1(A_1, \Gamma_1, \mu_1) \otimes L_2(A_2, \Gamma_2, 0) = L_{12}(A_1 \cdot A_2, \Gamma_1 + \Gamma_2, \mu_1) \quad (7.10)$$

$$G_1(A_1, \sigma_1, \mu_1) \otimes L_1(1, \Gamma_1, 0) = \text{Voigt}(A_1, \sigma_1, \Gamma_1, \mu_1) \quad (7.11)$$

That is, the convolution of two Lorentzians gives a new Lorentzian and the convolution of a Gaussian and a Lorentzian gives the Voigt function, which does not have an analytical expression. The signal we will deem appropriately described by a delta function (elastic part) with an amplitude parameter (I_δ) and a Lorentzian (quasi-elastic) part.

$$S(E) = L_S(A_{LS}, \Gamma_S, 0) + \delta \cdot I_\delta \quad (7.12)$$

The subscript S differentiates the parameters of the signal from those of the resolution function. With these expressions in hand we can calculate the final fitting function

$$I(E) = R(E) \otimes S(E) \quad (7.13)$$

$$= [G_R(A_{GR}, \sigma_R, E_{0R}) + L_R(A_{LR}, \Gamma_R, E_{0R})] \otimes [L_S(A_{LS}, \Gamma_S, 0) + \delta \cdot I_\delta] \quad (7.14)$$

$$= G_R(A_{GR}, \sigma_R, E_{0R}) \otimes L_S(A_{LS}, \Gamma_S, 0) + L_R(A_{LR}, \Gamma_R, E_{0R}) \otimes L_S(A_{LS}, \Gamma_S, 0) \quad (7.15)$$

$$\begin{aligned} &+ [G_R(A_{GR}, \sigma_R, E_{0R}) + L_R(A_{LR}, \Gamma_R, E_{0R})] \otimes \delta \cdot I_\delta \\ &= \text{Voigt}(A_{GR}A_{LS}, \sigma_R, \Gamma_S, E_{0R}) + L_{RS}(A_{LR}A_{LS}, \Gamma_R + \Gamma_S, E_{01R}) \\ &+ I_\delta [G_R(A_{GR}, \sigma_R, E_{0R}) + L_R(A_{LR}, \Gamma_R, E_{0R})] \end{aligned} \quad (7.16)$$

The most important parameters to keep track of in this lengthy expression is the HWHM of the signal Lorentzian (Γ_S) and the area of the signal Lorentzian (A_{LS}) as this is where the information on quasi-elastic behaviour is stored. To this analytically calculated fitting function was added a temperature parameter, which we need for implementing detailed balance (see paragraph 3.2.3 and the paragraph below) and a linear background (see paragraph below). The fit was carried out in energy range $E = \pm 1$ meV and from $Q = 0.5 \text{ \AA}^{-1}$ to $Q = 2 \text{ \AA}^{-1}$. A_{GR} , A_{LR} , σ_R and Γ_R from the resolution function were set equal to the value determined in the vanadium fit and not allowed to vary. For the centre of the resolution function (E_{0R}) the parameter in the vanadium fit was used as a starting guess, but the parameter was allowed to change during the fitting routine. This leaves A_{LS} , Γ_S and I_δ to be determined solely based on the sample measurements. Eventually I_δ was set constant as well (see paragraph below). An example of a full fit to deuterium data at 30 K is seen in Figure 7.11b.

Detailed Balance

Detailed balance is described in detail in paragraph 3.2.3. For the dynamic (inelastic) parts of the signal, i.e. the Lorentzian and the Voigt in the fitting function we need to multiply with a detailed balance factor²²

$$DB = (E - E_{0R}) \left(1 + \frac{1}{e^{(E - E_{0R})/(k_B T)} - 1} \right) \frac{1}{T} \quad (7.17)$$

where $1/T$ is a normalisation factor, without which the amplitude of the signal would increase with temperature. Having the normalisation allows us to compare the areas from different temperatures. It is important to note that the multiplication also changes the normalisation of the areas of the different components of the fitting function - hence they are no longer strictly areas.

Linear background

It was necessary to implement a temperature-dependent linear background with a small positive slope. The blue line in Figure 7.11b is such a linear background at 30 K. Here we are going to describe how we arrived at the slope and intercept point for the linear backgrounds at all the different temperatures. The background we are trying to describe is what is left after the ToF background has been subtracted, i.e. incoherent scattering originating from the sample. As this scattering is dependent on temperature each data set should have at least slightly different values of the slope and intercept point. It was not possible to fit the parameters of the background along with the Voigt and Lorentzian of the fitting function, as one could compensate for the other. This is worth noting, as it means the signal is small enough to be effectively obscured by the background. We therefore need to be extra careful when determining the parameters of the background and especially when we interpret the results of the fitting later on.

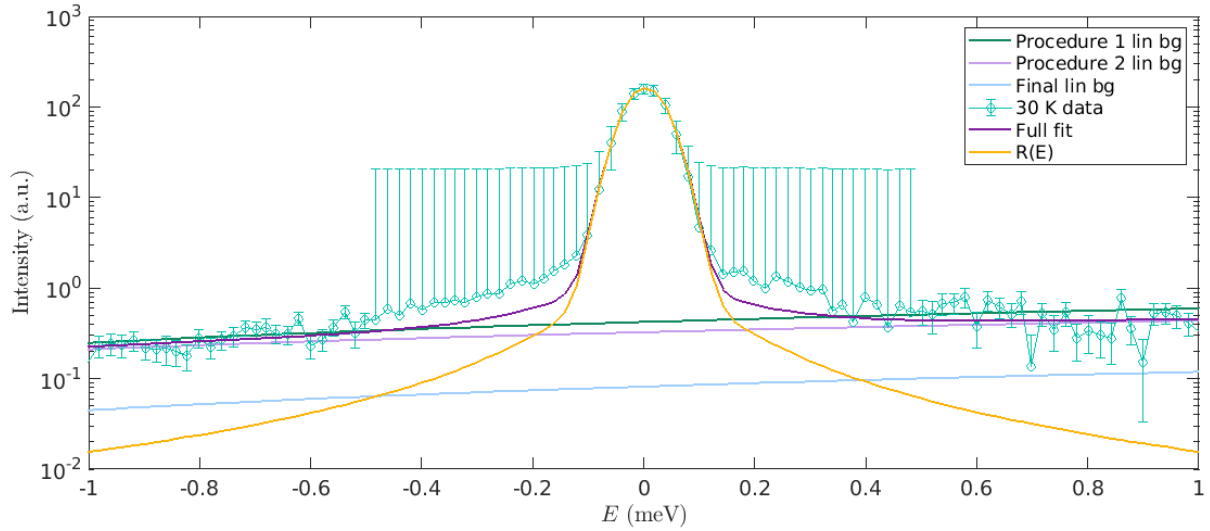


Figure 7.13: Example of linear background fits at $Q = 1.4 \text{ \AA}^{-1}$ used for determining the final background. The final background is shown for comparison (blue). When the dynamical part of the scattering is not fitted the linear background is able to compensate much of the signal, which is why the two contributions cannot be fitted at the same time. Here we fit only the linear background and the resolution function to identify where in Q the compensation happens. Procedure 1 (green) fits the entire shown E -range in this manner. Procedure 2 (lilac) performs the same fit but has increased error bars between $\pm 0.5 \text{ meV}$ (as shown).

To determine the value of the slope and intercept without it compensating for the dynamical signal we first identified where the (assumed) signal was placed in Q and temperature. The data at each temperature were fitted in the usual Q -slices, but with only the resolution function and the linear background. At places where there is an inelastic signal (as around $Q \approx 1.2 \text{ \AA}^{-1}$) the background will compensate for the signal by increasing the slope and intercept. Plotting the Q - and temperature dependence of the two parameters then provides an overview of where the (assumed) signal is placed. As the background compensates for the signal there exists the possibility that the parameters of the background will become too large. Therefore the procedure was carried out twice; the first time the E -range was $\pm 1 \text{ meV}$ as in all the other fits carried out thus far (henceforth denoted procedure 1). The second time the data points in the E -range believed to hold most of the elastic and inelastic scattering (between -0.5 meV and 0.5 meV) had their errors increased from ~ 0.02 intensity units to 20 intensity units (henceforth denoted procedure 2). This makes fitting well to the signal points almost inconsequential with respect to the χ^2 and the fitting routine will not need to go out of its way to incorporate them. An example of the two procedures is seen for the 30 K data set in Figure 7.13. The dependencies on Q and temperature for the two procedures are shown in Figure 7.14. Intense features are seen clearly in the intensity maps for both procedures around $Q \approx 1.1\text{-}1.5 \text{ \AA}^{-1}$ for temperatures 10-55 K in case of the slope, and $Q \approx 0.9\text{-}1.6 \text{ \AA}^{-1}$ for temperatures 10-75 K (with long tails along both axes) in case of the intercept. Especially the slope is markedly less intense in procedure 2, but the areas away from the assumed signal are very similar for both parameters.

To determine the final values of the two parameters we performed a weighted average at each temperature over the Q -slices with values that did not correspond to the intense signal feature. Based on the slope in Figure 7.14a we chose the Q -ranges $0.5\text{-}0.8 \text{ \AA}^{-1}$ and $1.6\text{-}2.0 \text{ \AA}^{-1}$. The large Q edge was excluded due to bad fit quality. The averages at different temperatures are plotted in Figure 7.15a. The two procedures give slightly different results; the highpoint of the peak moves a tiny bit towards higher temperatures and flattens out for both parameters when we are using procedure 2. The values of the parameters in the intermediate range from 65 K to 125 K increase and

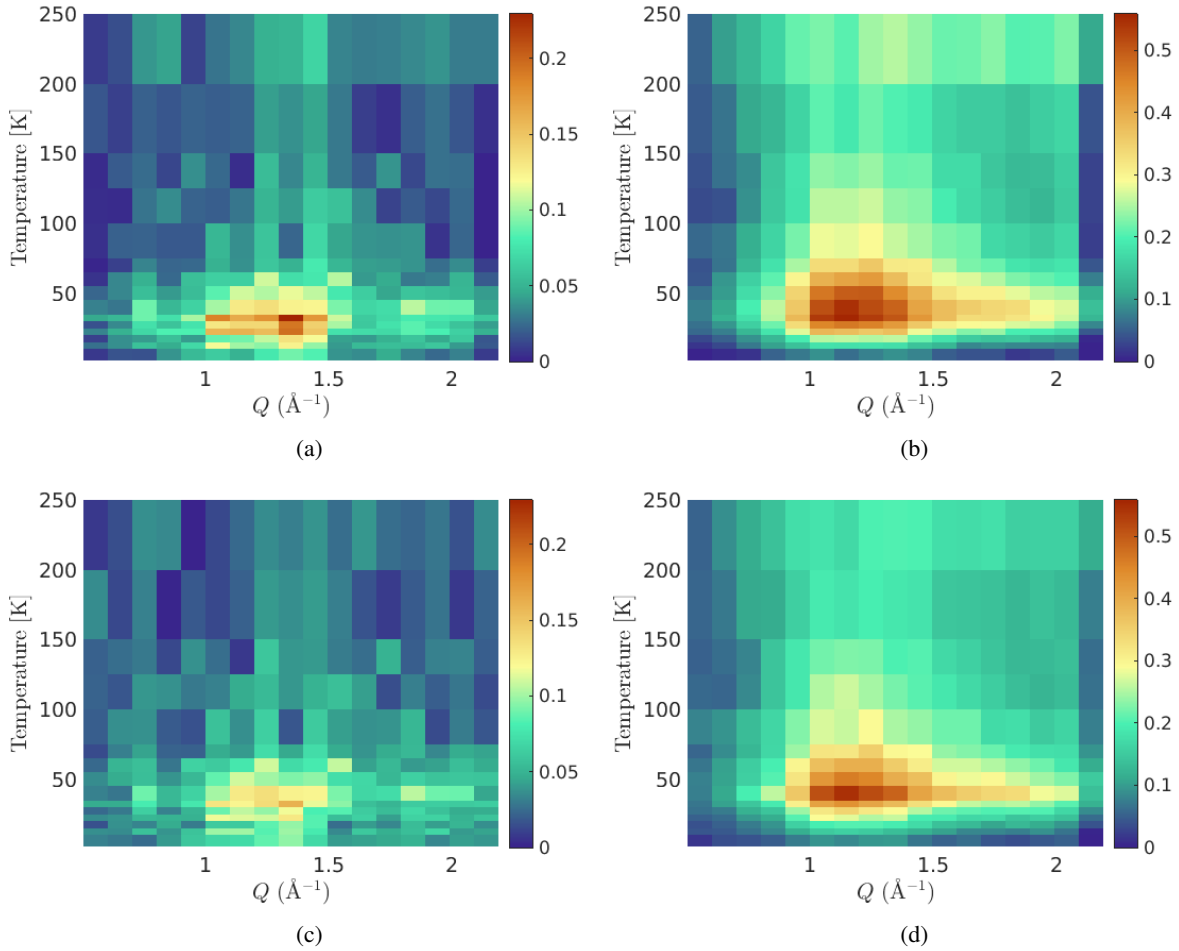


Figure 7.14: Intensity map for parameters of linear background. The intense features are assumed to be caused by the dynamic (inelastic) scattering in the sample being compensated by the background fit. Notice that the maximum value of the intensity bar changes between plots on the left and the right side **(a)** Slope for procedure 1 **(b)** Intercept for procedure 1 **(c)** Slope for procedure 2 **(d)** Intercept for procedure 2. For a description of the procedures see the text.

the high temperature value decrease. The peaked behaviour is however still present for both procedures. This is not ideal: The background should not peak where the signal peaks, as the two should not be dependent on each other. For this reason the average slopes and average intercepts were fitted with polynomials (see Figure 7.15b) of second and third degree, respectively. The fit of the average slopes included the temperatures 2 K and 65-250 K. In case of the intercept temperatures 2 K and 100-250 K were used, as the peak is spread over more temperatures in this case. We will use the parameters from these two fits to lock the linear background in place in the final fit.

Before moving on we note that performing these procedures is introducing human bias into the results. We are assuming the presence of an inelastic signal, as it seems "obvious" from the intensity plots that such a signal should be present.

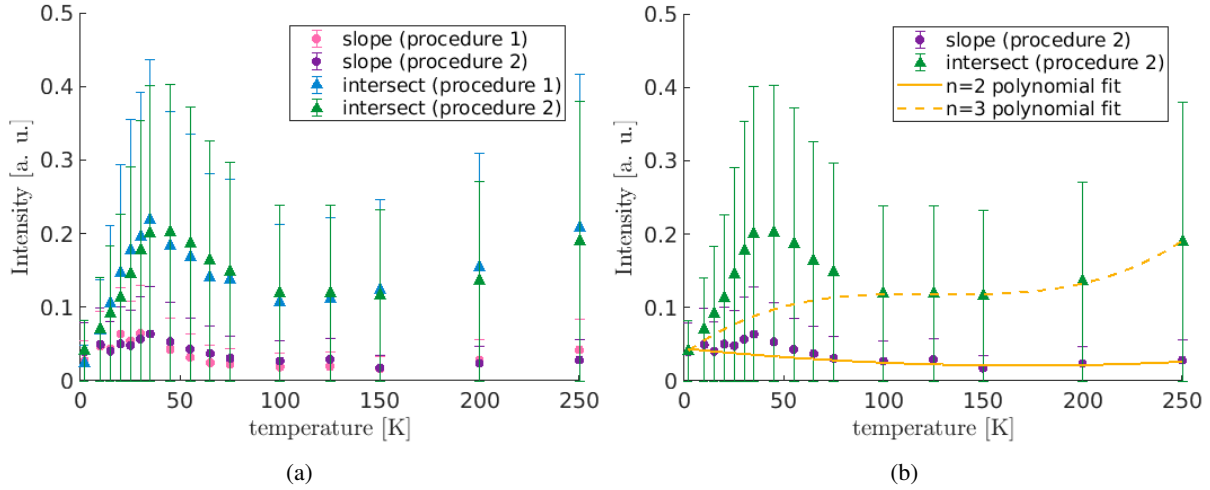


Figure 7.15: **(a)** Average slope and intercept for the linear background. The averages were taken over the Q -range $0.5\text{--}0.8 \text{ \AA}^{-1}$ and $1.6\text{--}2.0 \text{ \AA}^{-1}$ (described in the text) in figure 7.14 **(b)** Polynomial fits to slope and intercept of the averages from procedure 2. For the slope temperatures 2 K and 65–250 K were included in a second degree polynomial fit (solid yellow line) which returned parameters $p_2 = (0, -0.0003, 0.045)$. For the intercept the temperatures 2 K and 100–250 K were included in a third degree polynomial fit (dashed yellow line) which returned parameters $p_3 = (0, 0, 0.0019, 0.0373)$.

Setting I_δ constant

All the parameters of the $I(E)$ fitting function (Equation 7.13) apart from I_δ , Γ_S and A_{LS} have been determined by the previous processes. A full fit of the sample data from $Q = 0.5 - 2.0 \text{ \AA}^{-1}$ is now carried out. The fit revealed that I_δ has a strong Q -dependence while the temperature dependence for each Q -value is almost linear with a slight negative slope. The value of I_δ as a function of Q and T can be seen in Figure 7.16a. Along $Q = 1.1 \text{ \AA}^{-1}$ I_δ has a very intense feature for all temperatures. This is due to the presence of a Bragg peak, which is highlighted with orange in Figure 7.16c. The Bragg peak is nuclear as it is present with approximately unchanged intensity at all temperatures. We would like to keep I_δ constant in the fit, such that the only parameters we are fitting are those from the signal Lorentzian that contain the information about quasi-elastic scattering. To smooth the behaviour of I_δ we need to describe it with a suitable fitting function. As a function of temperature I_δ is highest at low temperature and decreases with increasing temperature. Since I_δ describes the intensity of the elastic line this decrease can be explained by movement of atoms; as the sample heats up the atoms start vibrating and the amount of strictly elastic scattering decreases. From subsection 3.2.2 we know that the factor that describes the nuclear vibrations in a sample is the Debye-Waller factor (repeated here for convenience)

$$e^{-2W} = e^{-\langle (iQ \cdot \mathbf{u}_0(0))^2 \rangle} \quad (7.18)$$

where $\mathbf{u}_0(0)$ is the displacement of the atoms from their equilibrium positions. $\mathbf{u}_0(0)$ is temperature dependent (increases with temperature). We will write the temperature dependence explicitly and perform a Taylor expansion around small values of the displacement, giving us a fitting function for $I_\delta(T)$ of the form

$$e^{-2W} \approx A_1(1 - A_2T) \quad (7.19)$$

where A_1 and A_2 are inserted as amplitudes for the fitting routine. An example of a fit is seen in Figure 7.16d and

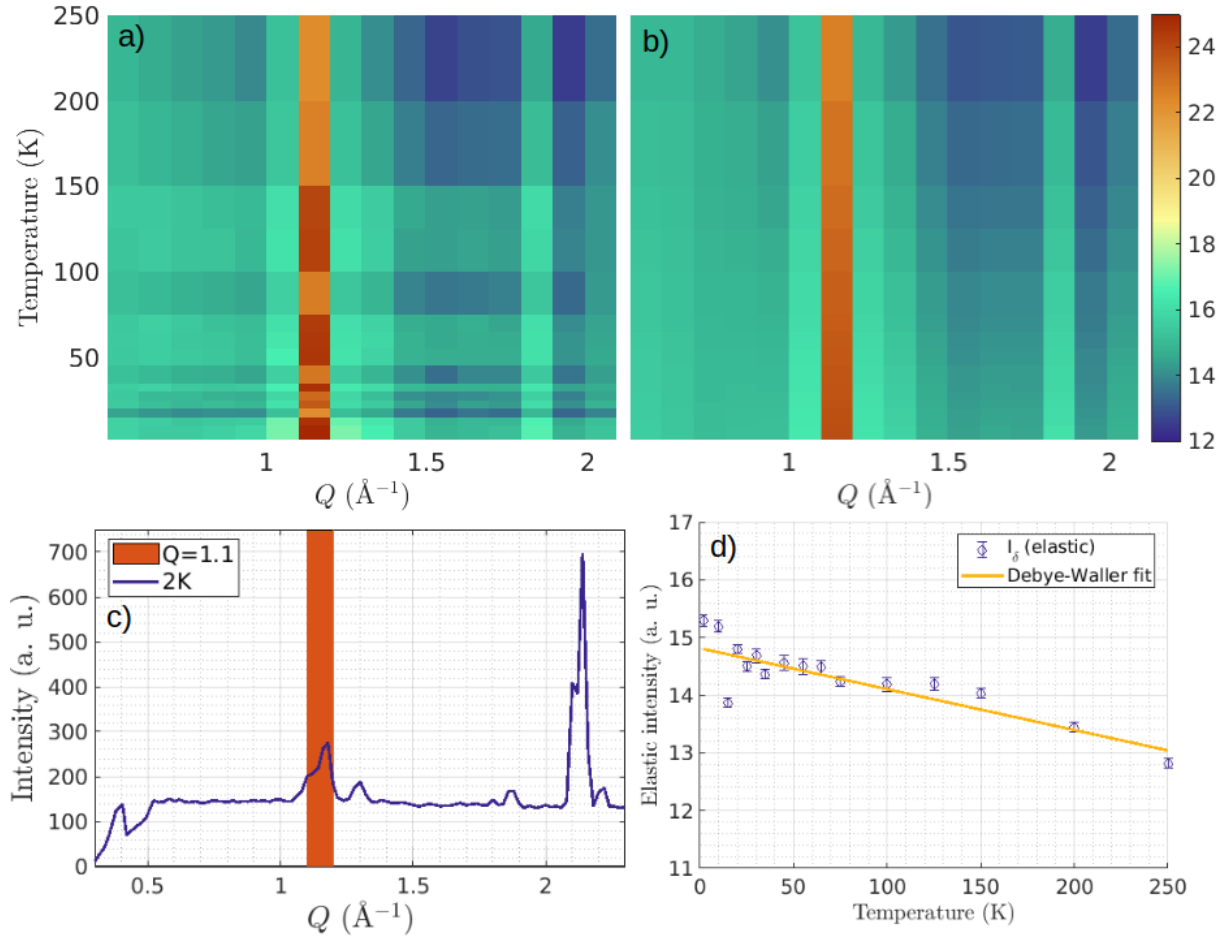


Figure 7.16: **(a)** Colourmap of the value of the I_δ -parameter before the parameter was fitted with the Taylor expanded Debye-Waller factor **(b)** Colourmap of the value of the I_δ -parameter after the parameter was fitted with the Taylor expanded Debye-Waller factor **(c)** Cut around the elastic line at 2 K. The cut was performed over the entire Q -range and from $E \pm 0.036$ ($\sim$ width of the elastic line determined from Vanadium measurements). The cut looks the same for all temperatures. **(d)** Debye-Waller fit to temperature dependence of I_δ for $Q = 2 \text{ \AA}^{-1}$.

the smoothed behaviour of I_δ is seen in Figure 7.16b.

Interpretation

Figure 7.18 shows all the intensity maps with the background subtracted. Around $Q \approx 1.2 \text{ \AA}^{-1}$ a broad effect emerges as the temperature is raised from 2 K. The intensity of the feature peaks around 30 K, whereupon the intensity of it decreases until ~ 75 K where it is almost completely absent. As the temperature is raised to 200 and 250 K scattering growing out from the elastic line is observed anew; the scattering does not seem to extend from a specific Q -value, rather it is smeared out evenly over the entire Q -range. Both of these scattering processes are believed to be quasi-elastic in nature, but their origins are different. The first scattering phenomenon is typical of short-range ordered magnetic correlations, such as would be seen within the kagomé layers in jarosite. The second is most likely linked to high-temperature movement of molecules and atoms within the compound. The movements of the atoms at high temperature are uncorrelated and each therefore scatter independently giving an

approximately uniform distribution of scattering along the entire Q -range, although there does seem to be slightly more scattering for $Q > 1.5 \text{ \AA}^{-1}$ than for $Q < 1.5 \text{ \AA}^{-1}$.

There is no indication of magnetic Bragg scattering at any temperature (see Figure 7.17a), and hence no indication of long range magnetic order in line with spin-glass behaviour observed previously for deuterium and hydronium jarosite. Total elastic scattering intensity at high temperature is, like in Figure 7.7, lower than the low temperature elastic intensities.

The total amount of scattering should be approximately constant across all temperatures, but this is not entirely the case (see Figure 7.17b). The overall intensity falls off when the temperature is raised and the J datasets are slightly higher in overall intensity than the KJM datasets. The same behaviour is seen for the data before and after background subtraction and errors in the background subtraction process can therefore be excluded as a cause. To fix the issue all results appertaining to intensities from J datasets are multiplied by 0.965 as this multiplier was found to align all of them with KJM datasets (see grey arrows in Figure 7.17b). The 15 K data set dips inexplicably below all the other KJM datasets. We suspect the cause to be either instrumental or incorrect normalisation to monitor in the data reduction process. As this is an isolated anomaly with no clear explanation it has been left as is, but it will be kept in mind in the following data analysis.

Q and T dependence of Lorentzian signal parameters

The dependence of A_{LS} and Γ_S on T and Q are seen in Figure 7.19. In both intensity maps large areas of red indicate that the fit failed and the parameter went to infinity. This is due to the fact that no scattering of Lorentzian character is present and the resolution function alone is adequate to describe the data. For the fitting routine making a very

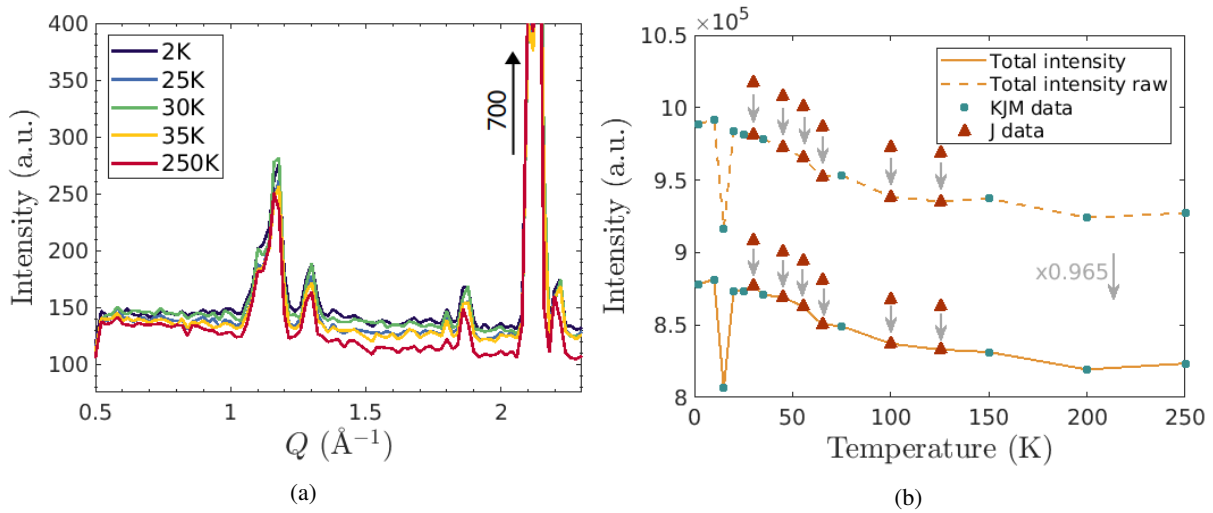


Figure 7.17: (a) Elastic scattering from deuterium jarosite at the indicated temperatures. The sum was carried out over the entire Q -range and the elastic line width was taken to be 0.036 meV based on the widths determined in subsection 7.3.2. No indications of magnetic Bragg peaks were found. The 30 K intensity was multiplied by 0.965 (see text and (b)). (b) Total scattering intensity summed up over the entire Q -range (but excluding the 20 first and last detectors) in E -range going from -2.3 to 2.2 meV before (dashed yellow line) and after background subtraction (solid yellow line). There is a difference in the total intensity between KJM data sets (teal) and J datasets (red). It was found that a multiplier of 0.965 aligned KJM and J datasets (grey arrows). Henceforth all results from J datasets will be multiplied by 0.965.

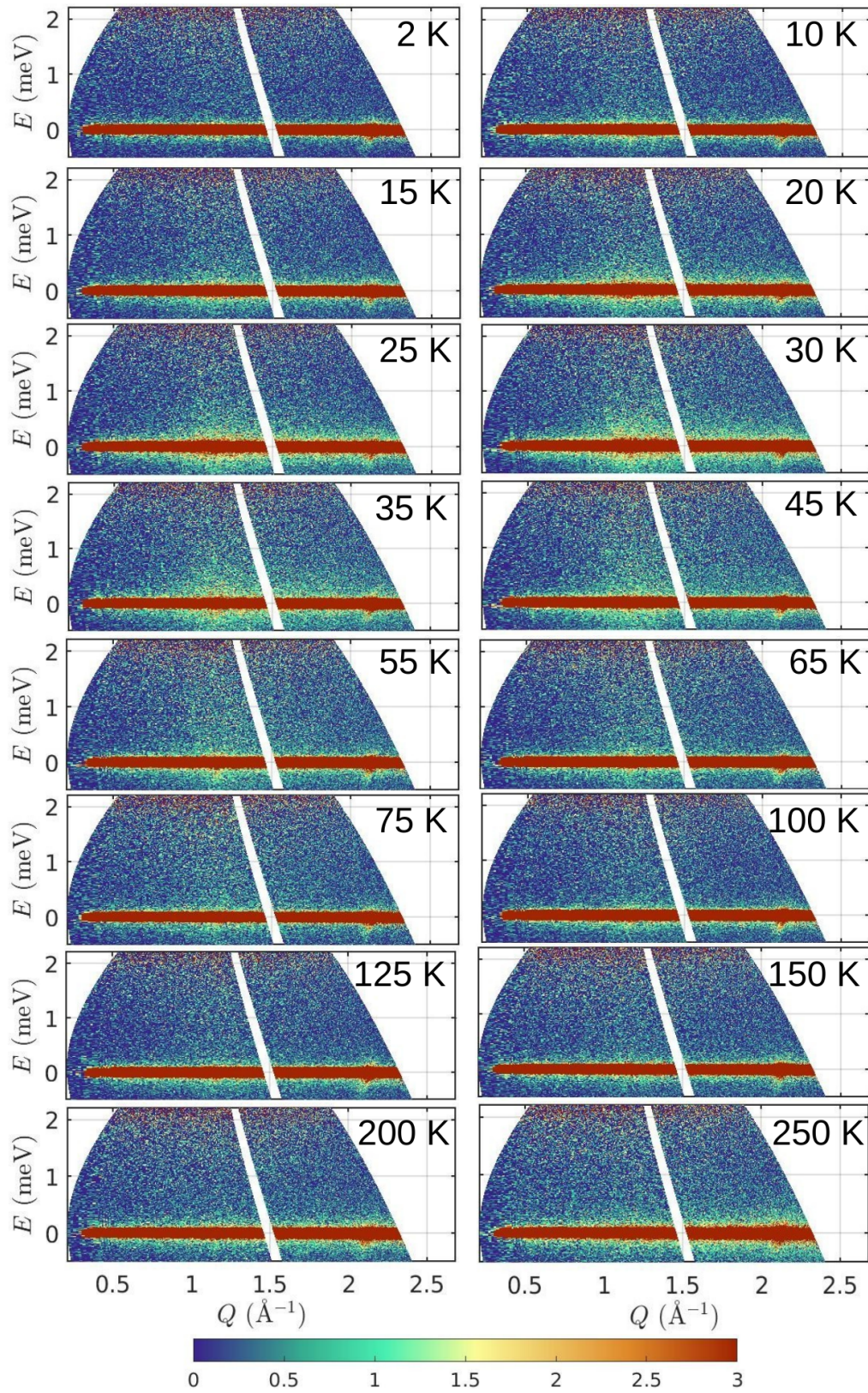


Figure 7.18: All datasets after background subtraction has been performed. The temperature of each data set is indicated on the corresponding image.

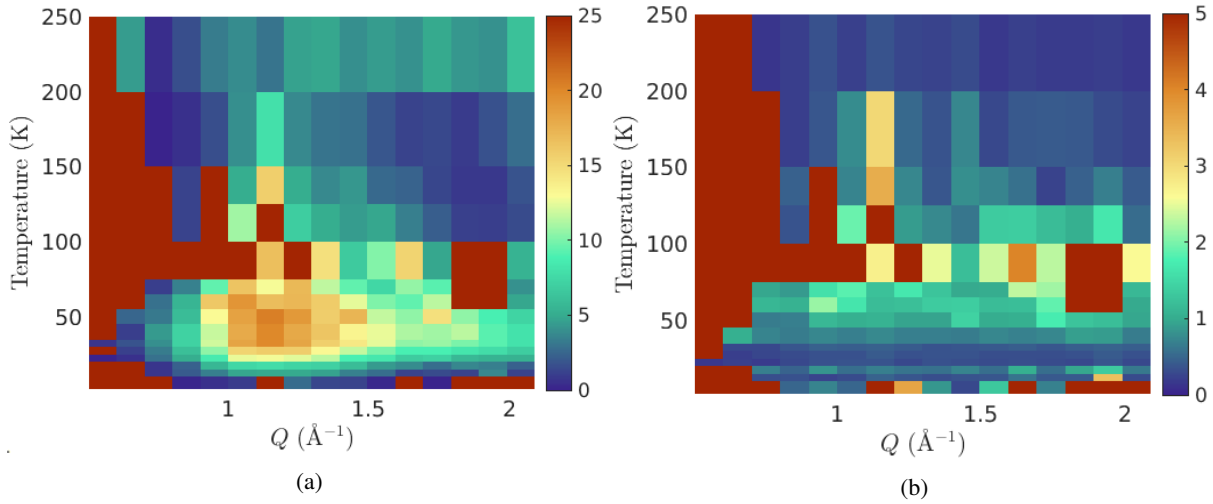


Figure 7.19: Final fitted parameters for the signal Lorentzian. The intensely red areas are failed fits where the value of the parameter went to infinity (a) A_{LS} (area of signal Lorentzian). For J datasets, the areas have been multiplied by 0.965 (b) Γ_S (HWHM of signal Lorentzian).

broad Lorentzian is "better" than a very slim one with respect to minimising the χ^2 . This behaviour is generally dominant for the fits of the 2 K data and the cuts along $Q = 0.5-0.7 \text{ \AA}^{-1}$. In the following we will remove the near infinite parameters from the 1D plots.

A_{LS} (Figure 7.19a) has a very clear dependence on both Q and T . A broad feature stretching from $Q \sim 0.8-1.6 \text{ \AA}^{-1}$ for temperatures 10-65 K is seen. The placement of the feature in Q is very reminiscent of the scattering feature in Figure 7.18 with the centre of the peak placed at $Q = 1.2 \text{ \AA}^{-1}$ (it almost looks like a kids drawing of the "real" intensity maps). From this we can conclude that a quasi-elastic magnetic signal *is* present in the sample. A_{LS} also increases at 250 K for all Q in accordance with the observed high temperature scattering in Figure 7.18. The dependence of Γ_S on Q and T is less clear. There seems to be a valley where Γ_S decreases between 10-35 K (approximately the temperature range where A_{LS} is maximum) and again at 250 K, where A_{LS} also increases. The value of Γ_S from 75 K to 150 K does not seem to follow any discernable pattern. The two parameters are obviously very correlated and Γ_S seems to be at its minimum in almost the same region as A_{LS} is at its maximum. We suspect this to be due to the fitting routine favouring broad Lorentzians for situations where there is no signal; when there is a signal and the fitted Lorentzian is actually physically sensible it comes out looking very narrow in comparison. 1D plots of A_{LS} as a function of Q for different temperatures are seen in Figure 7.20. The signal is seen to emerge already at 10 K and it keeps increasing until 30 K. The shape of the peak top is almost identical for 30, 35 and 45 K, where the highest point in the peak has a value of ~ 20 intensity units. The highpoint/centre of the peak is placed between $Q = 1.0$ and $Q = 1.2 \text{ \AA}^{-1}$. At $Q = 1.1 \text{ \AA}^{-1}$ the signal overlaps with a Bragg peak (Figure 7.16c) and hence the maximum of the signal is probably lower; around 18-19 intensity units based on the value at $Q = 1.2 \text{ \AA}^{-1}$. The peak is very broad at 10 K and 15 K, but it sharpens to an asymmetric peak between 20 K and 30 K. The tail of the peak is quite high and extends to the end of the measured Q -range. At 30-35 K a small bump is seen at $Q \approx 1.6 \text{ \AA}^{-1}$, which is probably due to other magnetic signals mixing in. At 45 K the fit quality deteriorates, although the shape of the peak is mostly intact. Between 55-75 K the fit struggles and the shape is completely lost at 75 K; this indicates that the signal is lost somewhere within this temperature interval, which corresponds well with what is seen in Figure 7.18. The fits from 45-125 K are not shown in Figure 7.20, but they can be found in

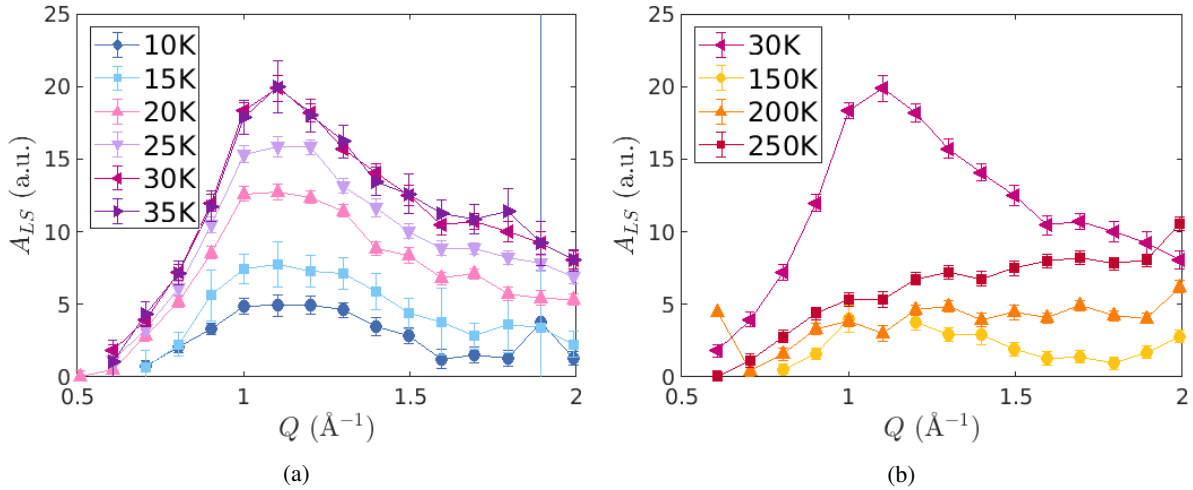


Figure 7.20: Q -dependence of the area of the signal Lorentzian (a) A_{LS} for temperatures 10-35 K (b) A_{LS} for temperatures 150-250 K with 30 K used for comparison with the low temperatures. Points with infinite values have been removed along with points with infinite errors. The solid lines are guides to they eye.

the appendix (specifically in Figure A.4).

At $T > 100$ K the second type of scattering phenomenon slowly emerges and increases all the way up to the highest measured temperature (250 K). At 150 K there is still something reminiscent of the peaked shape of the lower temperatures present. The value of A_{LS} , however, diverges for this temperature at $Q = 1.1 \text{ \AA}^{-1}$ so the (potential) "top" of the signal is missing. A slight upward trend is seen when we reach higher Q -values. At 200 K the Q -dependence is almost flat, with the same upward trend. At 250 K the upward trend dominates with a factor 10 more scattering present at the highest Q -value compared with the lowest. The increase in scattering intensity at high temperature and high Q is typical for the presence of lattice vibrations. A_{LS} is overall much lower for this second scattering phenomenon than for the phenomenon assumed to be due to short-ranged correlations. The temperature dependence of A_{LS} is highlighted for a variety of Q -values in Figure 7.21a; the shape of A_{LS} as a function of temperature is fairly similar for all Q apart from the change in amplitude already discussed. Figure A.6 holds the full range of temperature-dependence plots.

1D plots of Γ_S as a function of Q for different temperatures are seen in Figure 7.22. Temperature ranges 2-15 K and 45-125 K have been excluded from the figure due to poor fit quality. All temperatures can be found in the appendix (Figure A.5). Γ_S is almost independent of Q for all temperatures. This flat Q -dependence indicates that it is the same physics that is responsible for the quasi-elastic scattering at all Q -values (we could sum up all Q -values and describe them with the same Lorentzian). At temperatures 20-30 K the Lorentzian is quite narrow (between 0.2 and 0.4 meV). It increases to ~ 0.5 meV at 30 K and to ~ 0.7 at 35 K. A small bump is seen in the Q -range where A_{LS} peaks at 20-30 K. The same trend as for A_{LS} is also seen with respect to the fit quality; between 45 and 75 K any trend in the values disappears and the errors increase (due to a lack of quasi-elastic signal). The fit quality is regained somewhat at the higher temperatures, where the Lorentzian narrows gradually to approximately 0.15 meV at 250 K. Figure 7.21b highlights the shape of the HWHM as a function of temperature for different Q -values. The shape is similar across all values of Q (see Figure A.7 for the full range) and seems to peak in the area 65-125 K where not much scattering is present in accordance with what was discussed for Figure 7.19b.

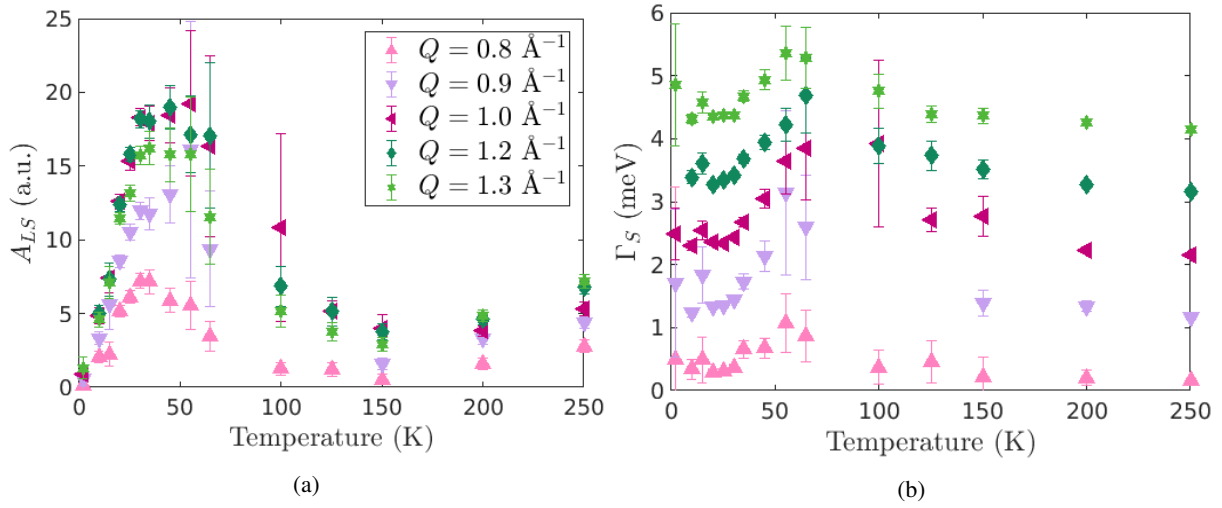


Figure 7.21: (a) A_{LS} at $Q = 0.8$ - $1.3 \text{ \AA}^{-1}$ (with $Q = 1.1 \text{ \AA}^{-1}$ excluded due to the presence of a Bragg peak) versus temperature. Values for J data sets have been multiplied by 0.965 (b) Γ_S at the same Q -values as (a). Each set of points have been displaced with +1 from the last to increase visibility. Values at 75 K have been removed due to very large errors on the fitted parameter.

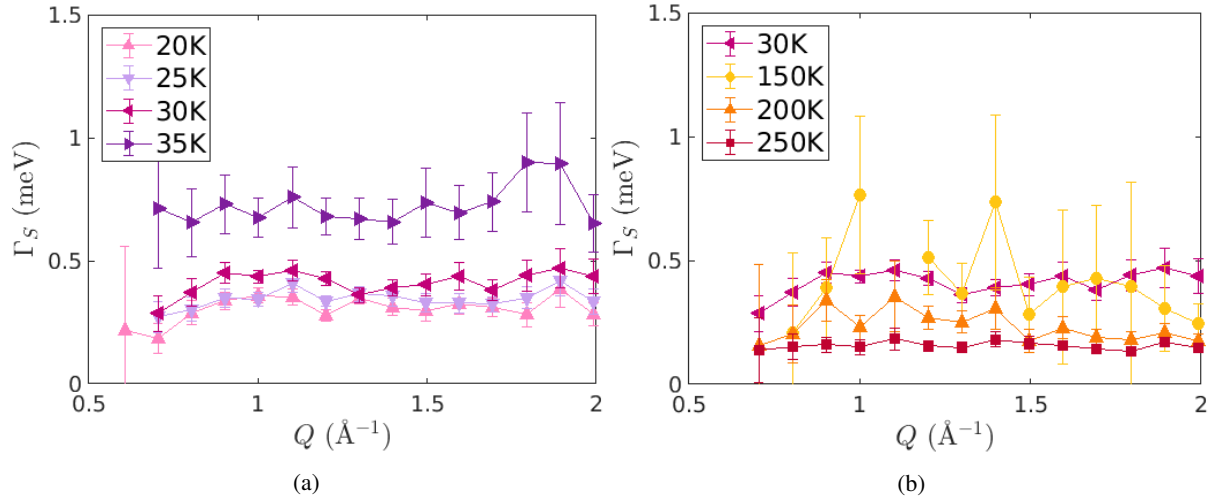


Figure 7.22: (a) Γ_S for temperatures 20-35 K (b) Γ_S for temperatures 150-250 K with 30 K used for comparison with the low temperatures. Points with infinite values have been removed along with points with infinite errors. The solid lines are guides to they eye.

Magnetic correlation lengths

The shape of A_{LS} in Figure 7.20 is very reminiscent of magnetic scattering of deuterium and hydronium jarosite observed by other studies (see for example page 52). We assume the scattering causing the shape of A_{LS} to be purely magnetic, although, due to the difficulties with the fitting routine, this may not entirely be the case. The asymmetrically shaped peak is typical of scattering from a powder averaged two-dimensional magnetically ordered feature.⁹² This type of scattering can be modelled by a Warren function (Equation 5.12). The Warren function is calculated for a specific magnetic 2D reflection. The first magnetic peak in our case is the (101) peak (i.e. the $(hk) = (10)$ peak in 2D). We can calculate the Q position of this peak by utilising that $Q = 2\pi/d$, where d for a

Temperature (K)	ξ Warren ($\text{\AA}$)	ξ 2D rod ($\text{\AA}$)
15	18.5 ± 8.9	5.0 ± 1.0
20	17.9 ± 9.0	4.8 ± 1.2
25	18.9 ± 14.3	5.5 ± 1.6
30	19.1 ± 12.0	5.5 ± 1.3
35	21.1 ± 16.0	6.7 ± 1.8
45	19.8 ± 6.7	6.6 ± 1.4

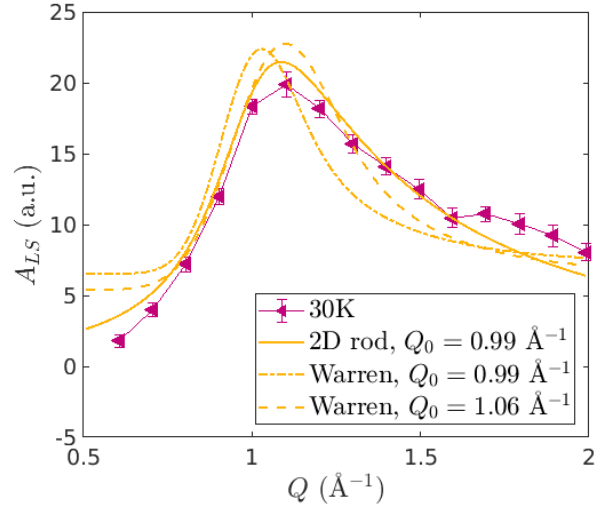


Table 7.4: **Left:** Correlation lengths of 2D scattering in deuterium jarosite based on a fit to a Warren function (unphysical with centre in $Q = 1.06 \text{ \AA}^{-1}$, see text) and a function based on the powder average of a generic 2D scattering feature (with centre in $Q = 0.99 \text{ \AA}^{-1}$). **Right:** Fit of Warren function and 2D scattering rod function to A_{LS} at 30 K. The solid line is the 2D rod fit, the dot-dashed line is the Warren function with centre in $Q = 0.99 \text{ \AA}^{-1}$ and the dashed line is the Warren function with centre in $Q = 1.06 \text{ \AA}^{-1}$

hexagonal structure is given by

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (7.20)$$

Inserting the lattice parameters for hydronium jarosite ($a = 7.32 \text{ \AA}$ and $c = 16.92 \text{ \AA}$)⁴⁵ the formula yields $Q = 1.06 \text{ \AA}^{-1}$ for the 3D peak and $Q = 0.99 \text{ \AA}^{-1}$ for the 2D peak. The Warren peak was fitted to A_{LS} for the temperatures where the signal is well defined (from 15 K to 45 K). An example of such a fit is seen in Table 7.4(right). The fit is poor as the data is not actually centred around $Q = 0.99 \text{ \AA}^{-1}$. If we move the peak centre to the 3D value the fit is much better, although still not good; the tail is too low at the higher Q -values and the peak is much too intense in the centre. The correlation lengths obtained from these fits are in the range 18.4 to 21.1 $\text{\AA}$ and have very large errors (see Table 7.4(left)). The values correspond well with the $\xi \sim 19 \pm 2 \text{ \AA}$ obtained in a study by Wills et al..⁶⁹ Moving the peak is, however, not physically sensible and the results of the Warren fitting can therefore not be used further.

Similarly shaped scattering has been observed for the inelastic signal from chromium jarosite by Lolk⁹³ and Holm-Janás⁹⁴ above the long-range magnetic order. Holm-Janás also found that a Warren function was a poor fit to the data but that a line shape based on a 3D powder average of a 2D short-range ordered magnetic feature was a better fit. The derivation is due to Kim Lefmann and can be found in its entirety in Holm-Janás.⁹⁴ The resulting line shape is

$$C_L(Q) = |f_m(Q)|^2 \int_{-\infty}^{\infty} dx \frac{1}{Q(Q^2 - Q_0^2)^{1/2}} \frac{\Gamma^2}{\Gamma^2 + (Q - x)^2} \quad (7.21)$$

Here $|f_m(Q)|^2$ is the magnetic form factor, Q_0 is the placement of the (hk) feature and Γ is the width of a Lorentzian. The idea is to calculate directly the overlap between a rod of scattering (hk) and a 3D (hkl) sphere. When Q just

touches the edge of the rod the scattering is at its lowest, it increases rapidly as $Q \rightarrow Q_0$ and then decreases slowly as we move away from Q_0 , giving rise to the asymmetric peak shape. $C_L(Q)$ has been convoluted with a Lorentzian as the function otherwise diverges at Q_0 , which is entirely unphysical. The convolution introduces a smearing that represents the short-ranged correlations with correlation length $\xi = 1/\Gamma$. The convolution also causes the centre of the peak to shift slightly towards higher Q -values.

We have fitted this model to the results in Table 7.4(right). The fit is much better than the Warren fit; the centre is where it should be and the function even fits the higher Q -values reasonably well (not accounting for the extra scattering around $Q = 1.6 \text{ \AA}^{-1}$). The amplitude of the fitted peak still overshoots the real maximum value, but less severely than the Warren fit. The correlation lengths obtained are very different ranging from $4.8 - 6.7 \text{ \AA}$. The distance between two iron ions in jarosite is $\sim 4 \text{ \AA}$ (two times the distance from the iron ion to the hydroxide oxygen, which is $1.99 \text{ \AA}$.⁹⁵) The correlations are then very short ranged; only reaching between two to three spins. There is an indication of the correlation length increasing with A_{LS} , i.e. as the quasi-elastic signal grows stronger the spins are correlated over a longer distance. The correlation length should decrease when we enter the paramagnetic regime, but since it is not possible to fit the high temperature values of A_{LS} we cannot ascertain whether this is the case. We also cannot see the spin-glass transition, as T_g for this sample is at 14 K , but the magnetisation signal we observe is indicative of spin-glass behaviour; the spins are correlated locally in 2D in small clusters that never freeze into a 3D ordered structure. It is remarkable that deuterium jarosite, despite being a spin-glass and hence showing no magnetic elastic scattering, has quantifiable dynamic magnetic scattering emanating around the Q -value where a magnetic Bragg peak would be expected in other jarosites.

8 | Summary and conclusion

In this thesis the goal was to investigate the spin-glass deuterium jarosite and the 3D magnetically ordered potassium jarosite in order to collect clues regarding the unexplained spin-glass behaviour in deuterium jarosite. A deuterium jarosite sample with $95.1 \pm 1.3\%$ occupancy of the magnetic sites and less than ideal occupation of the A⁺-site by D₃O⁺ was analysed by susceptibility measurements and neutron scattering. The susceptibility measurements showed the presence of a spin-glass transition at 14 K. Susceptibility measurements were also carried out on a hydronium jarosite sample where the spin-glass transition moved to 16.5 K. We were not able to fully identify why the transition moved but speculate that it is either an isotope effect or an effect of the sample not being fully stoichiometric. To answer this question we would need to record NMR spectra of hydronium jarosite as well.

Inelastic neutron scattering measurements were performed at FOCUS at temperatures ranging from 2 K to 250 K. Additionally, neutron diffraction was performed on HRPT. The HRPT measurements of potassium jarosite showed the emergence of several magnetic Bragg peaks below the reported ordering temperature of 65 K. The inelastic measurements at 2 K showed clearly the lifted zero-energy mode that had been reported in the literature. Neutron diffraction measurements of deuterium jarosite on HRPT showed no indication of magnetic Bragg peaks appearing at any temperature. In the inelastic neutron scattering measurements a broad signal, which was attributed to quasi-elastic magnetic scattering, was seen to emerge from $Q \approx 1.0 - 1.1 \text{ \AA}^{-1}$. This is a Q -value where 3D magnetic scattering is found to emanate in other jarosites and it also overlaps with the first 2D magnetically ordered peak in jarosites. The quasi-elastic magnetic scattering was described well by a Lorentzian with width Γ_S and area A_{LS} . Γ_S was found to be almost independent of Q for all temperatures, which led us to conclude that it was the same underlying physics that was responsible for the magnetic scattering at all Q . The shape of A_{LS} was found to be typical of scattering from short-ranged magnetically ordered structures in 2D. A model of a powder averaged 2D scattering feature was fitted to A_{LS} as a function of Q . The model fit the scattering very well and allowed us to estimate that the spins were correlated over distances of $4.8 - 6.7 \text{ \AA}$ (corresponding to the distance between two to three Fe³⁺-ions in the kagomé lattice), which is much less than the $\approx 20 \text{ \AA}$ that had been found by earlier studies. Our results therefore support that deuterium jarosite is a spin-glass with dynamical short-ranged 2D correlations between the spins in the kagomé plane.

9 | Appendix

A.1 Mechanical diagrams of autoclaves

The mechanical diagrams, made by Morten Liborius Jensen, for the small 56 mL autoclave and the big 900 mL autoclave fabricated by the KU workshop are seen in Figure A.1 and Figure A.2, respectively.

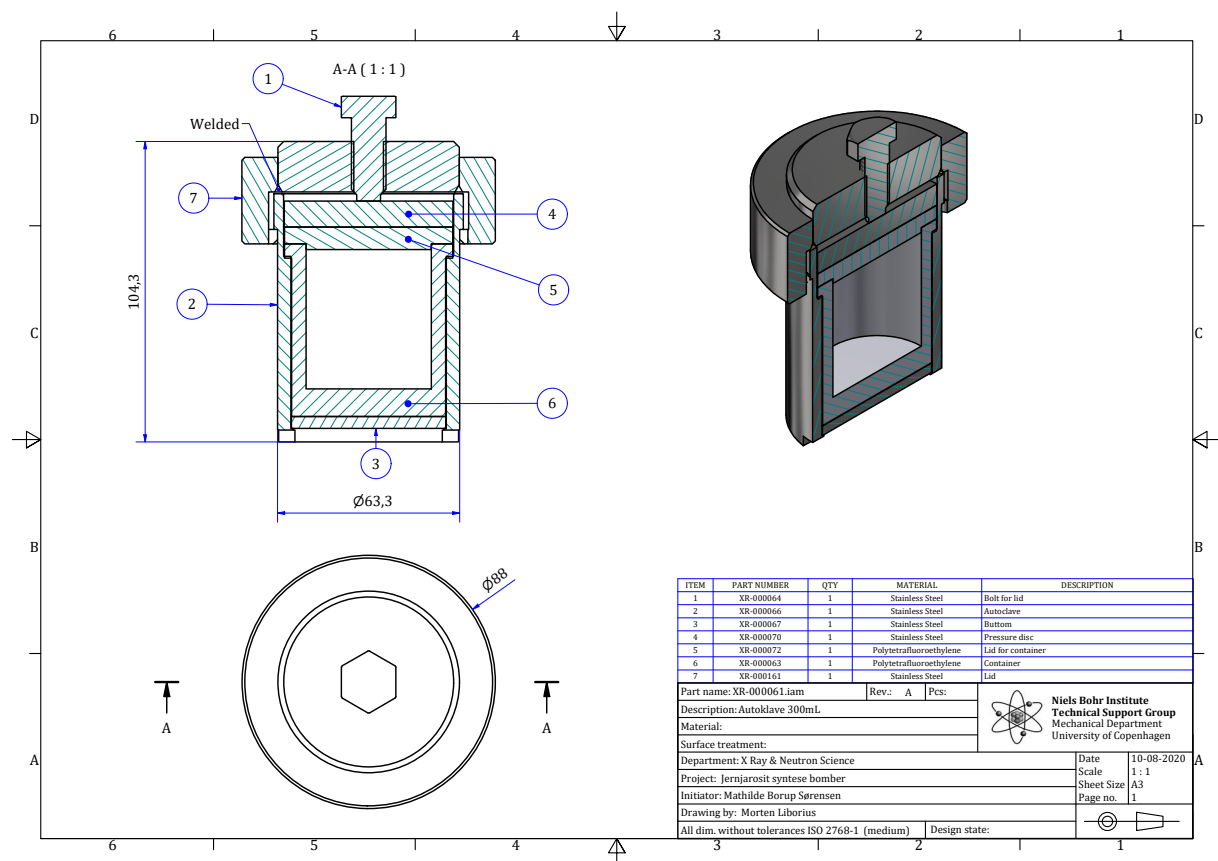


Figure A.1: Mechanical diagram of the 56 mL autoclave used for powder synthesis. The diagram was made by Morten Liborius Jensen. On the diagram all measurements are in mm and $\varnothing$ is a diameter. A-A (1:1) indicates that the size of the diagram frame is 1:1 scale if printed out in A3 format. A horizontal line with an arrow indicates a welding.

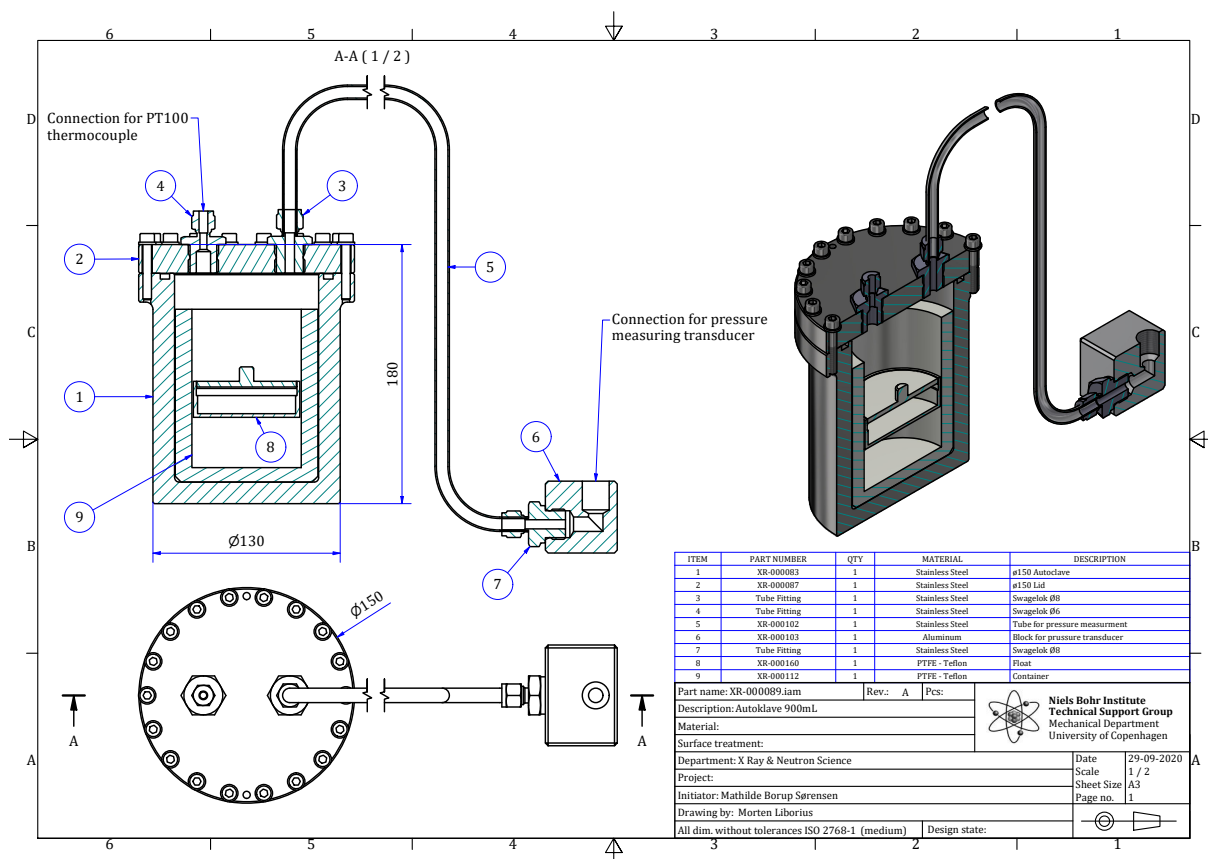


Figure A.2: Mechanical diagram of the 900 mL autoclave used for crystal synthesis. The diagram was made by Morten Liborius Jensen. On the diagram all measurements are in mm and $\varnothing$ is a diameter. A-A (1/2) indicates that the size of the diagram frame is 1/2 scale if printed out in A3 format. A horizontal line with an arrow indicates a welding.

A.2 Determination of the Curie-Weiss temperature

The Curie-Weiss temperature and its appertaining error was estimated by fitting a linear function to the high temperature part of the inverse susceptibility. Since the data was obtained without errors on the individual data points these first had to be approximated. The data is obtained in steps and small jumps of similar height ($\sim 0.05 \text{ cm}^3 \text{ mol}^{-1}$ in the y -direction) are seen to happen between each point (see Figure A.3a); we will use the height of such a jump as the error on each individual measurement. These "step" errors are originally numerical errors, but here we treat them as statistical errors. θ_{CW} is very dependent on how much of the high temperature data is included. For this reason we performed the fit for a variety of temperature cutoffs. The results are visualised in Figure A.3b. The most "correct" value of θ_{CW} was taken to be at the point where the curves seem most stable in their values. For deuterium (hydronium) jarosite this value is -860 K (-880 K). Hydronium jarosite has a much less stable value of θ_{CW} than deuterium jarosite; the error on θ_{CW} needs to reflect this. We cannot use the errors from the fitting routine as they are artificially small ($\approx 3.5 \text{ K}$). We will approximate the error to be the distance from the "correct" θ_{CW} to value of θ_{CW} that is the furthest removed. This means that the final results are for deuterium (hydronium) jarosite: $-860 \pm 23 \text{ K}$ ($-880 \pm 88 \text{ K}$). The error determined in this manner is a systematic error that comes from the choice of fitting region, rather than a statistical one.

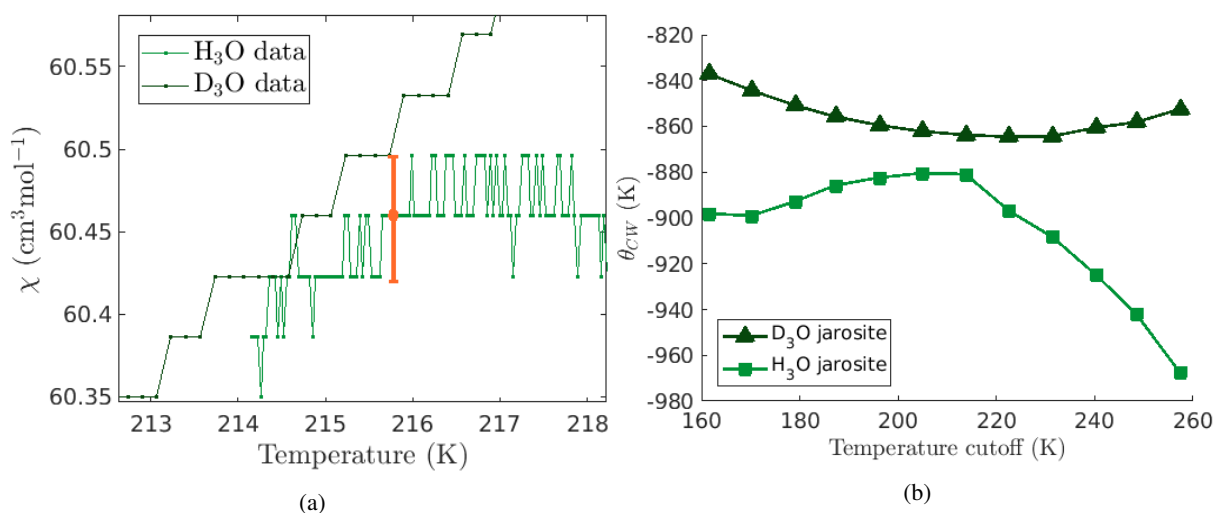


Figure A.3: **(a)** Estimation of error on the susceptibility. The error is estimated to be the size of a vertical step as indicated by the orange point with error bars. A step is $\sim 0.05 \text{ cm}^3 \text{ mol}^{-1}$. **(b)** θ_{CW} as a function of cutoff temperature for deuterium jarosite (triangles) and hydronium jarosite (squares).

A.3 Neutron analysis parameter overviews

The Q -dependence of A_{LS} and Γ_S for all temperatures are seen in Figure A.4 and Figure A.5, respectively. The temperature dependence of A_{LS} and Γ_S for all Q -values are seen in Figure A.6 and Figure A.7, respectively.

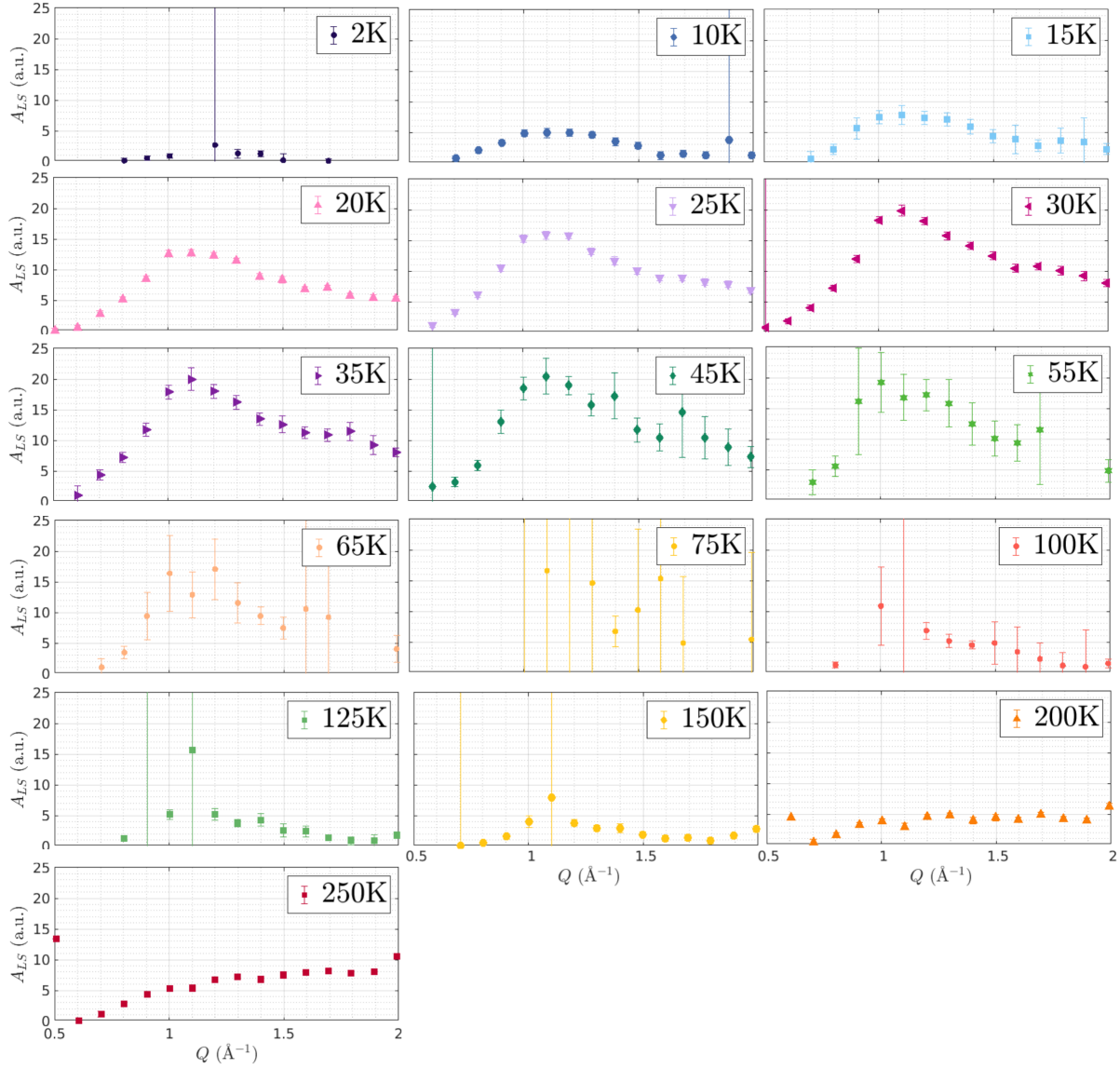


Figure A.4: Q -dependence of the area of the Lorentzian (fitting parameter A_{LS} in the quasi-elastic part of the signal) at the indicated temperatures.

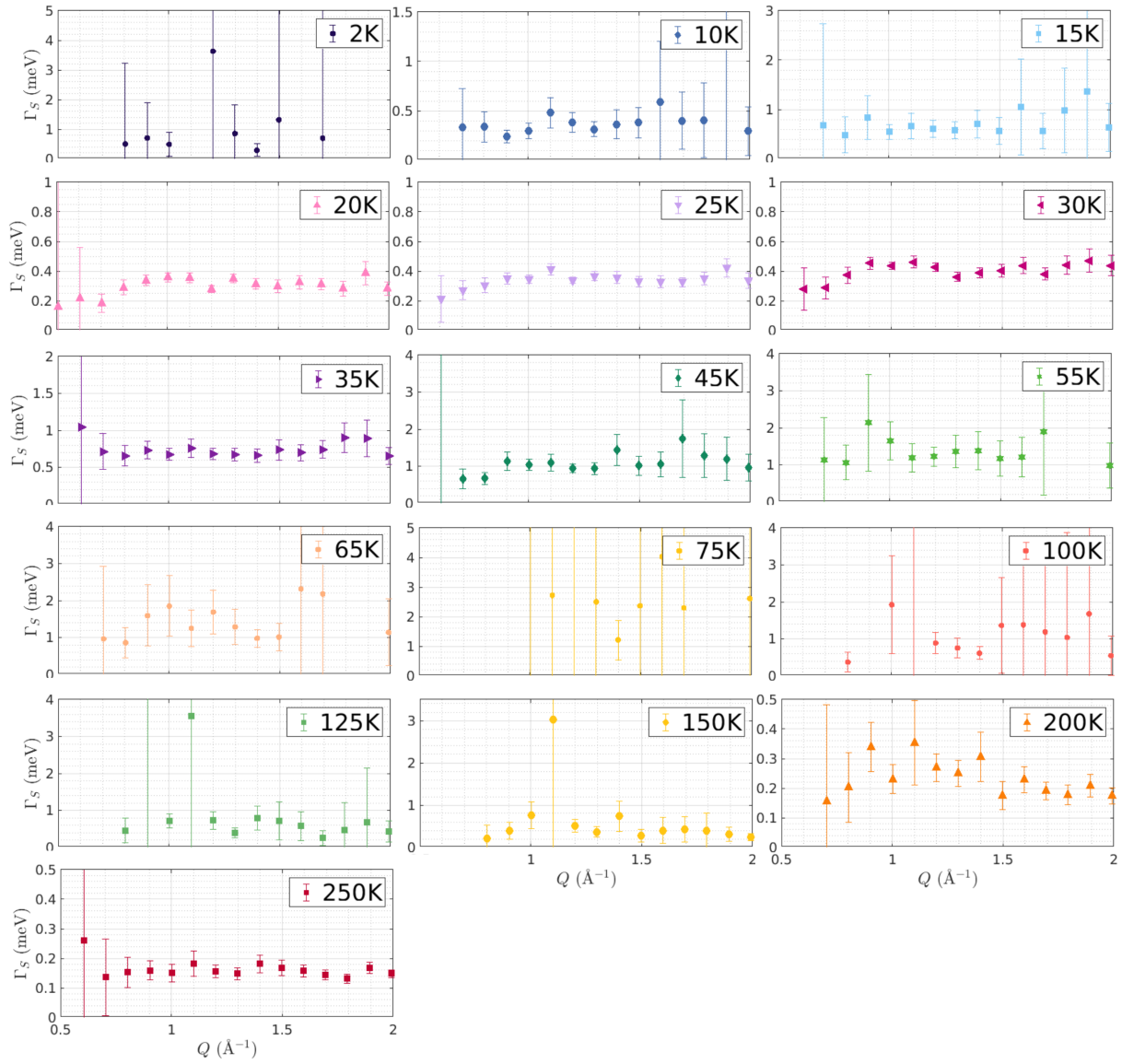


Figure A.5: Q-dependence of the HWHM of the Lorentzian (fitting parameter Γ_S in the quasi-elastic part of the signal) at the indicated temperatures. Note that the y-axis changes between temperatures.

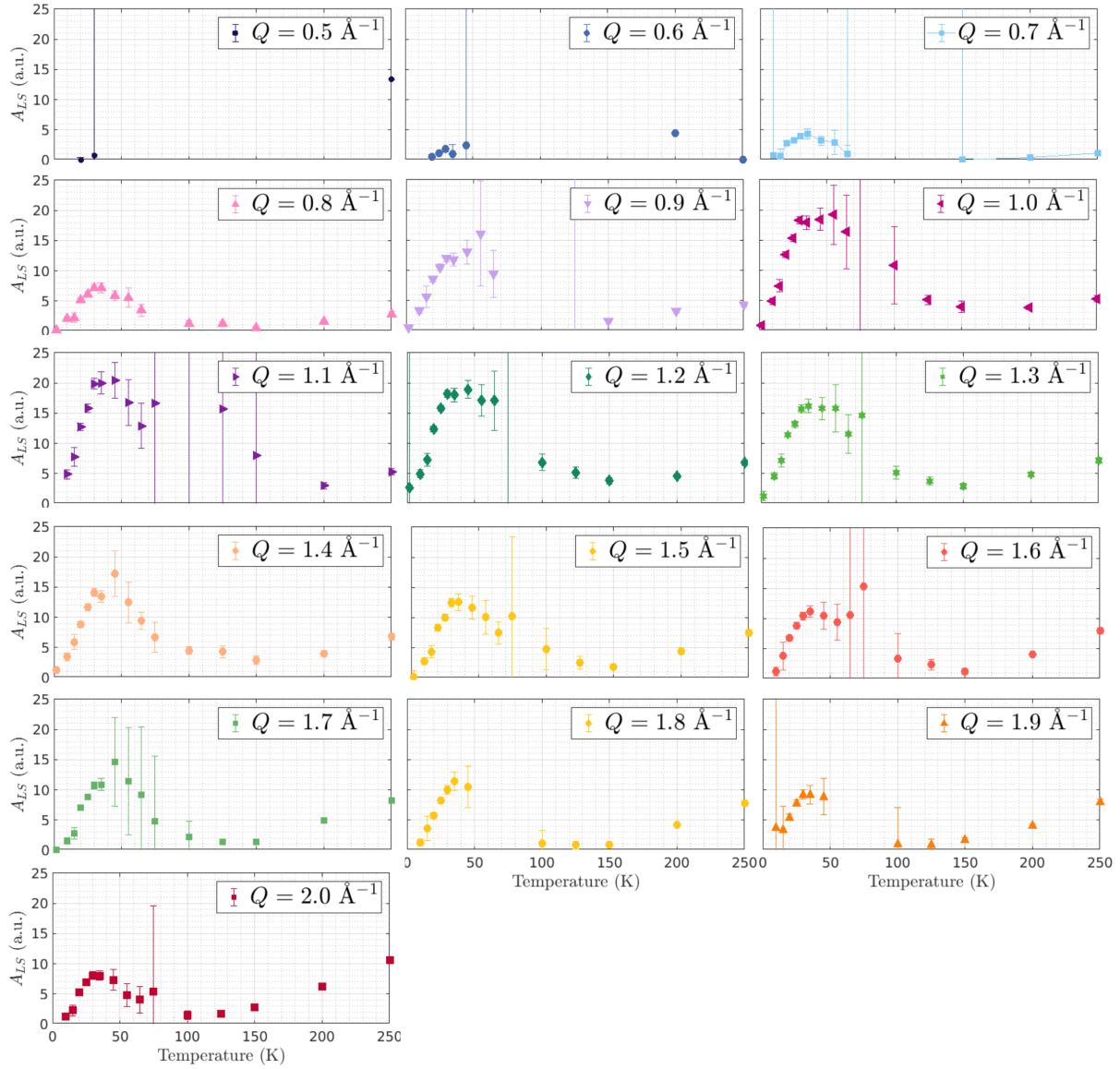


Figure A.6: T-dependence of the area of the Lorentzian (fitting parameter A_{LS} in the quasi-elastic part of the signal) at the indicated Q -values.

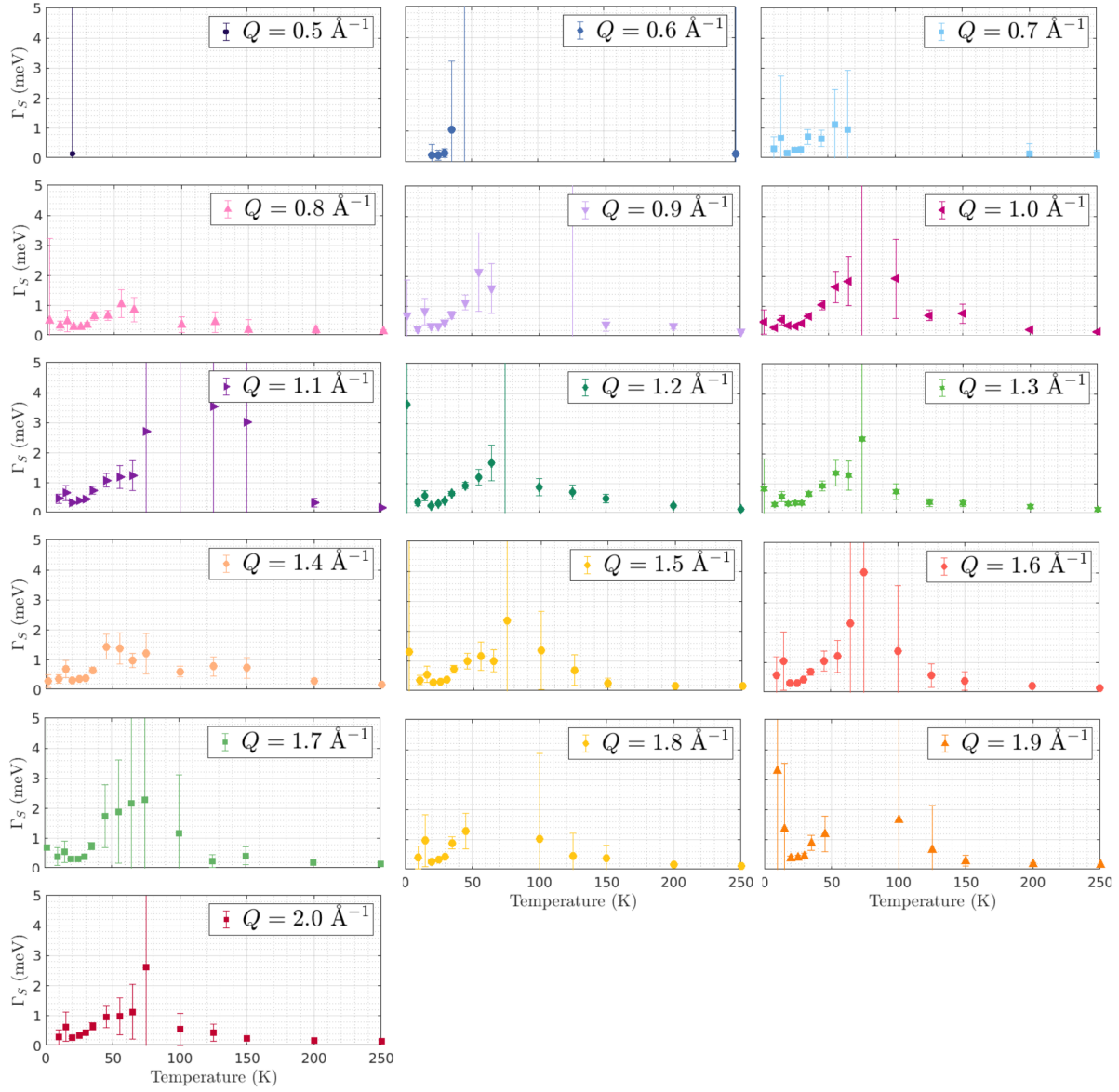


Figure A.7: T-dependence of the HWHM of the Lorentzian (fitting parameter Γ_S in the quasi-elastic part of the signal) at the indicated Q -values.

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