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Thermodynamic and magnetic studies on the quantum spin liquid
candidate systems $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ and $\text{Sr}_3\text{CuIr}_2\text{O}_9$

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Thermodynamic and magnetic studies on the quantum spin liquid candidate systems $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ and $\text{Sr}_3\text{CuIr}_2\text{O}_9$:

This thesis presents thermodynamic and magnetic studies on three potential quantum spin-liquid systems: $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ and $\text{Sr}_3\text{CuIr}_2\text{O}_9$. The measurements evidence the presence of quasi-free orphan spins leading to a Schottky anomaly and Brillouin-like behavior at low temperatures. While magnetization and heat capacity data show no evidence of long-range magnetic order down to 1.8 K, the systems exhibit negative Weiss temperatures indicating dominant antiferromagnetic interactions. The obtained Weiss temperature ($\theta_W = -132 \pm 10$ K) in $\text{Sr}_3\text{CuSb}_2\text{O}_9$ implies strong magnetic frustration as expected for a layered triangular spin arrangement. In $\text{Sr}_3\text{ZnIr}_2\text{O}_9$, the expected near $J = 0$ state is confirmed by the observed small effective magnetic moment $\mu_{\text{eff}} = 0.85 \pm 0.09 \mu_B/\text{f.u.}$ and the Weiss temperature amounts to $\theta_W = -39 \pm 8$ K. Surprisingly, AFM interactions in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ ($\theta_W = -17 \pm 5$ K) are weaker than interactions assessed in both other compounds. In all materials under study, the estimated magnetic entropy changes above 1.8 K are much lower than the full magnetic entropy for a $J = 1/2$ system, which in particular for $\text{Sr}_3\text{CuSb}_2\text{O}_9$ and $\text{Sr}_3\text{CuIr}_2\text{O}_9$ hints towards a high ground state degeneracy supporting the hypothesis of a quantum spin liquid ground state.

Thermodynamische und magnetische Untersuchungen an drei potentiellen Quanten-Spin-Flüssigkeiten $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ und $\text{Sr}_3\text{CuIr}_2\text{O}_9$:

In dieser Thesis werden thermodynamische und magnetische Untersuchungen an den drei potentiellen Quanten-Spin-Flüssigkeits-Systemen $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ und $\text{Sr}_3\text{CuIr}_2\text{O}_9$ vorgestellt. Messungen belegen das Vorkommen von quasi-freien Orphan-Spins die zu einer Schottky-Anomalie in der Wärmekapazität und einem Brillouin-ähnlichen Anteil in der Magnetisierung bei niedrigen Temperaturen führen. Auch wenn Wärmekapazität- und Magnetisierungsmessungen keine Anzeichen langreichweitiger magnetischer Ordnung bis hinunter zu 1.8 K zeigen, weisen die Systeme dominante antiferromagnetische Wechselwirkungen anhand von negativen Curie-Weiss Temperaturen auf. Die für $\text{Sr}_3\text{CuSb}_2\text{O}_9$ bestimmte Curie-Weiss Temperatur $\theta_{\text{CW}} = -132 \pm 10$ K deutet auf starke magnetische Frustration hin, wie es für ein Spinsystem in einem geschichteten Dreiecksgitter erwartet wird. In $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ wurde der erwartete Zustand nahe $J = 0$ nachgewiesen, der sich in einem kleinen effektiven magnetischen Moment $\mu_{\text{eff}} = 0.85 \pm 0.09 \mu_B/\text{f.u.}$ äußert und eine Curie-Weiss Temperatur von $\theta_W = -39 \pm 8$ K aufweist. Überraschenderweise sind die antiferromagnetischen Wechselwirkungen in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ ($\theta_W = -17 \pm 5$ K) schwächer als die in den beiden anderen Materialien ermittelten Wechselwirkungen. Für alle drei Verbindungen wurden kleinere magnetische Entropieänderungen über 1.8 K geschätzt als die volle magnetische Entropie eines $J = 1/2$ System. Dies deutet in $\text{Sr}_3\text{CuSb}_2\text{O}_9$ und $\text{Sr}_3\text{CuIr}_2\text{O}_9$ auf eine hohe Grundzustandsentartung hin, wodurch die Hypothese eines Quanten-Spin-Flüssigkeit Grundzustands gestärkt wird.

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Introduction

Frustration is a common phenomenon in science. Besides being present in the daily live of many researchers, in the field of condensed matter physics the concept of frustration was also deployed to their research topic and became a central subject area in the studies of magnetism. Magnetic systems are called frustrated if competing interactions between the magnetic moments of the atoms or ions exist that cannot be simultaneously satisfied [1, 2]. A simple example of frustrated interactions are antiferromagnetically coupled Ising-spins on a triangle. The spins try to align in opposite directions, which is not possible for all three of them, leading to a frustrated system. Frustration has become an intriguing concept in magnetism with many consequent effects like spin glasses [3], spin ice [4, 5], etc. Among the rich variety of phenomena evoked by frustration, quantum spin liquids are especially fascinating. They were proposed in an antiferromagnetic triangular lattice by P.W. Anderson in 1973 as ground state of fluctuating spins without long range magnetic order [6]. Intriguing phenomena as exotic excitations with fractional quantum numbers and high ground state entropy were hypothesized in these systems [1]. Since their prediction based on theoretical ideas about frustration, further investigations about quantum spins liquids in theoretical and experimental work began [7, 8, 9, 10]. An exactly solvable model with a quantum spin liquid ground state was provided by Kitaev in 2006, manifesting the existence of this exotic ground state in theory [11, 12]. On the experimental side, many materials were examined in order to find a quantum spin liquid. Though this ground state was not conclusively confirmed for real materials yet, many quantum spin liquid candidates were found. Prominent examples are κ -(BEDT-TTF)₂Cu₂(CN)₃ [13], Herbertsmithite (ZnCu₃(OH)₆Cl₂) [14] and YbMgGaO₄ [15]. Lately, some triple perovskites were investigated and identified as promising quantum spin liquid candidates [16, 17]. To extend the research on this topic, the compounds Sr₂CuSb₂O₉, Sr₂ZnIr₂O₉ and Sr₂CuIr₂O₉ are studied in this thesis. In these compounds Cu²⁺ and Ir⁵⁺ ions hold magnetic moments with frustrated interactions. Heat capacity and magnetization measurements were deployed to examine the magnetic properties of these materials and gain insight into the magnetic excitations and interactions.

This thesis is divided in the following parts: Chapter 2 presents the theoretical basis of the physical processes observed in the measurements and analysis. Next, in chapter 3, the experimental techniques and the devices on which they were executed are discussed. The following chapters

4 to 6 present the experimental results and their related analysis. In each of these chapters, first the magnetization measurements and then the heat capacity measurements are considered. $\text{Sr}_3\text{CuSb}_2\text{O}_9$ is discussed in chapter 4, followed by $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ in chapter 5 and $\text{Sr}_3\text{CuIr}_2\text{O}_9$ in chapter 6. In closing, chapter 7 summarizes the results of this thesis and puts them in the context of present literature.

Theory

2.1 Magnetism

2.1.1 Units in magnetism

Unlike the SI units used in most areas of physics, magnetism is often described in the Gaussian centimeter-gram-second (cgs) system. A comparison of relevant quantities in SI and cgs units can be found in table 2.1. As cause of the Gaussian unit convention the magnetic flux density B and the magnetic field strength H relate $B \stackrel{\text{cgs}}{=} H$ in free space. In this thesis, all magnetic quantities are expressed in cgs units.

2.1.2 Magnetism in solids

Atoms possess magnetic moments $\vec{\mu}$ because of the spins inherent to their electrons and the orbital momentum of those electrons [19]. In solids, the magnetic moments of its constituents lead to cooperative behavior building a magnetic field called magnetization $\vec{M}$. The magnetization of solids is usually altered by external magnetic fields $\vec{B}$. Therefore, the magnetic susceptibility χ gives a measure of how the magnetization reacts to magnetic fields according to the relation:

$$\chi_{ij} = \frac{\partial M_i}{\partial B_j} \tag{2.1}$$

In general, χ is a matrix. However, in this thesis the magnetic field $\vec{B}$ and the magnetization $\vec{M}$ are measured in the same direction, hence only their magnitudes are considered and χ becomes

Quantity	Symbol	cgs		SI
magnetic flux density	B	1 G	=	10^{-4} T
magnetic field strength	H	1 Oe	=	$10^3/4\pi$ A/m
magnetic moment	μ	1 erg/G	=	10^{-3} J/T
molar magnetic susceptibility	χ	1 erg/G ² mol	=	$4\pi \cdot 10^{-6}$ m ³ /mol
energy	E	1 erg	=	10^{-7} J

Table 2.1: Units in cgs and SI for relevant quantities in magnetism [18].

a scalar. Furthermore, for small magnetic fields, B and M are connected linearly [20]:

$$\chi = \lim_{B \rightarrow 0} \frac{\partial M}{\partial B} \approx \frac{M}{B} \quad (2.2)$$

Thus, when magnetic susceptibility is discussed in this thesis, usually $\chi = M/B$ is considered.

When reacting to external magnetic fields, solids either align M with B causing a positive susceptibility (paramagnetism, $\chi > 0$) or oppose M to B leading to a negative susceptibility (diamagnetism, $\chi < 0$). Paramagnetism and diamagnetism result from different physical effects, which will be discussed in the following paragraphs.

Diamagnetism

Diamagnetism is caused by the effect of the applied magnetic field on the orbits of the electrons in atoms. Though it is a quantum mechanic effect, the classical intuition of electrons orbiting in circles due to the applied magnetic field leading to an opposing magnetization by Lenz's law is often used to describe this effect [21]. In first order approximation, diamagnetism follows the equation:

$$\chi_d = -\frac{ne^2}{6m_e} \sum_{i=1} Z \langle r_i^2 \rangle \quad (2.3)$$

Here, n is the number of atoms or ions per mole, e and m_e are the charge and mass of an electron and Z is the number of electrons per atom/ion. With $\langle r_i^2 \rangle$, the mean squared distance of the i -th electron to the nucleus is denoted. Equation 2.3 is well applicable to isotropic atoms or ions.

Diamagnetism is mainly temperature independent and present in all matter. However, ordinarily the diamagnetic contribution to magnetization is small and often overlaid by other effects. A sketch of the diamagnetic susceptibility compared to other magnetic contributions is shown in figure 2.2 a). Materials in which diamagnetism is dominant are called diamagnetic.

Paramagnetism

The effect of matter developing a magnetization parallel to an external magnetic field, hence causing a positive susceptibility, is called paramagnetism. This effect is present in materials possessing unpaired electrons which hold non-zero magnetic moments [22]. The magnetic moment μ of an atom with unpaired electrons is:

$$\mu = -g\mu_B J \quad (2.4)$$

With μ_B and g being the Bohr magneton and the Landé factor, the magnetic moment relates linear to the total angular momentum $\vec{J} = \vec{L} + \vec{S}$. Assuming the magnetic moments in a solid are independent, the magnetization M in an applied magnetic field B is described by the Brillouin function B_J :

$$M = M_s B_J(y) = ng\mu_B J \left[\frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}y\right) \right] \quad (2.5)$$

$$y = \frac{g\mu_B JB}{k_B T} \quad (2.6)$$

The saturation magnetization $M_s = ng\mu_B J = -n\mu$ depends on the number of atoms n (per mole or per formula unit) and their magnetic moment. In the argument of the Brillouin function $y = g\mu_B JB/k_B T$, T is the temperature and k_B the Boltzmann constant. Increasing the magnetic field or lowering fluctuations by lowering the temperature aligns the magnetic moments of the atoms and saturates the magnetization. The total angular momentum J controls the rate at which saturation is reached. In figure 2.1 some Brillouin functions with varying J are illustrated.

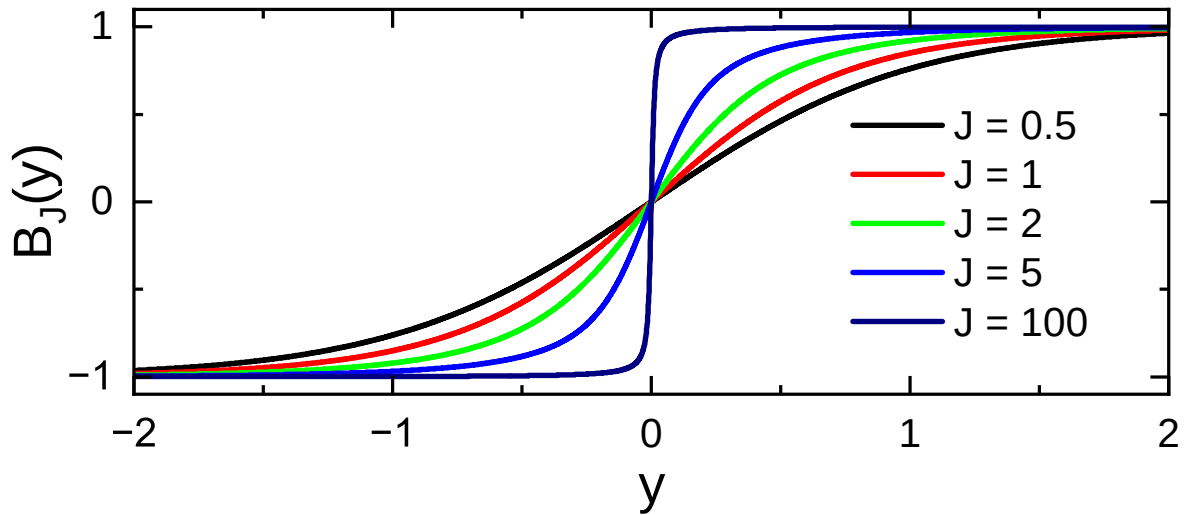


Figure 2.1: Brillouin functions $B_J(y)$ are sketched for various total angular momentum values J . With rising J $B_J(y)$ reaches saturation faster.

At high temperatures the argument $y \ll 1$ and the magnetic susceptibility can be approximated:

$$\chi = \frac{ng^2 J(J+1)\mu_B^2}{3k_B} \cdot \frac{1}{T} = \frac{C}{T} \quad (2.7)$$

This is the Curie law describing the susceptibility of isolated magnetic moments in a solid. $C = ng^2 J(J+1)\mu_B^2/3k_B$ is the Curie constant, which is connected to the effective moment $\mu_{\text{eff}} = g\mu_B \sqrt{J(J+1)}$. A sketch of the temperature dependence of Curie paramagnetism compared to other magnetic contributions is drawn in figure 2.2 a).

So far only the magnetic moment of electrons in their spin-orbital ground state was considered. Atoms with partially filled shells possess excited states holding magnetic moments. When calculating the magnetic susceptibility of a solid in second-order perturbation theory, an additional term to diamagnetism appears [22]. This term is called Van Vleck paramagnetism. Setting $|0\rangle$ and E_0 as the magnetic ground state and the ground state energy of an atom and $|m\rangle$ as excited state with energy E_m , the Van Vleck paramagnetism is:

$$\chi_{VV} = 2n\mu_B^2 \sum_m \frac{|\langle 0 | (\hat{L}_z + g\hat{S}_z) | m \rangle|^2}{E_0 - E_m} \quad (2.8)$$

$\hat{L}_z$ and $\hat{S}_z$ are the angular momentum and spin operator in the direction of the applied magnetic field (z -direction). Van Vleck paramagnetism χ_{VV} is larger than zero and vastly temperature independent. Usually its magnitude is in the same order as diamagnetism. A comparison of Van Vleck paramagnetism, Curie paramagnetism and diamagnetism can be found in sketch 2.2 a).

Magnetic order

As discussed for paramagnetism, atoms with unpaired electrons hold a magnetic moment. In the Curie approximation, which is valid for high temperatures, these magnetic moments are uncorrelated. However, if the magnetic moments interact, the macroscopic magnetization is altered. Interactions between neighboring moments that cause them to align parallel to each other are called ferromagnetic (FM); interactions favoring anti-parallel aligned moments are antiferromagnetic (AFM). When the interactions between magnetic moments in a solid overcome the thermal fluctuations, the moments usually order ferromagnetically or antiferromagnetically. This ordering phenomenon is a magnetic phase transition, which happens at a specific temperature T^* . At temperatures significantly higher than T^* , the magnetization of these materials can be described by the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta_W} \quad (2.9)$$

θ_W is the Weiss temperature. It is a measure of the interaction strength between the magnetic moments in a solid. For FM interactions $\theta_W > 0$, while for AFM interactions $\theta_W < 0$. Considering the inverse magnetic susceptibility χ^{-1} the Curie-Weiss law is linear with temperature and reaches zero at the Weiss temperature. Model Curie-Weiss functions for a paramagnet ($\theta_W = 0$), ferromagnet and antiferromagnet are illustrated in figure 2.2 b).

Usually, the susceptibility described by the Curie-Weiss law is considerably larger than the temperature independent contributions from diamagnetism and Van Vleck paramagnetism. Still, to model the susceptibility caused by all three effects, the Curie-Weiss law can be modified by

adding an offset χ_0 :

$$\chi = \frac{C}{T - \theta_W} + \chi_0 \quad (2.10)$$

The linear behavior of $\chi^{-1}(T)$ defined by the Curie-Weiss law is disturbed by the offset χ_0 . A positive offset leads to right bending in $\chi^{-1}(T)$, negative offsets cause left bending. A sketch of the influence of χ_0 on the inverse magnetization is drawn in figure 2.2 c).

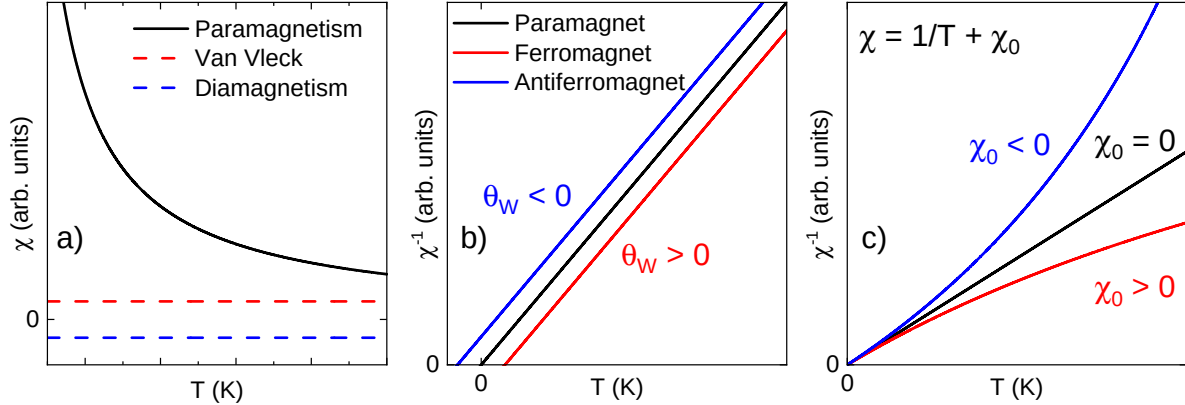


Figure 2.2: Sketches of magnetic phenomena and models in solids. All pictures are drawn in arbitrary units. **a)** Temperature dependence of the magnetic susceptibility caused by paramagnetism, Van Vleck effect and diamagnetism. **b)** Inverse susceptibility $\chi^{-1}(T)$ of Curie-Weiss models for paramagnets, ferromagnets and antiferromagnets. **c)** Influence of a temperature independent offset χ_0 on the inverse magnetic susceptibility $\chi^{-1}(T)$. The black line shows an unperturbed paramagnet ($\chi_0 = 0$), while the blue and red curve show left and right bending due to non-zero χ_0 .

Frustration

Interacting spins can lead to coherent behavior in solids. Nevertheless, special conditions as e.g. the geometric structure of a crystal can lead to competing interactions. If magnetic order is prevented by competing interactions, the material experiences frustration. The frustration index f provides a measure for the frustration present in a solid:

$$f = \frac{|\theta_W|}{T^*} \quad (2.11)$$

The Weiss temperature θ_W is a measure for the interactions in the material and T^* represents the temperature at which the material magnetically orders or freezes. The higher the frustration index, the more magnetic ordering is prevented by competing interactions.

An example for frustration relevant in this thesis is the antiferromagnetic triangular lattice. For spin $S = 1/2$ the triangular geometry of the lattice prevents antiferromagnetic order of

i	b_i	c_i
1	13.1382922	19.1382922
2	38.2639722	129.093725
3	214.74454	597.98788
4	260.983171	1902.06491
5	622.734802	3943.84464
6	186.114208	5164.9974
7	-	3452.67229

Table 2.2: Parameters of the Padé approximation for χ_{TAFM} from equation 2.12 [24].

the spins. These competing interactions influence the magnetization built in this system. The magnetic susceptibility for a spin $1/2$ Heisenberg triangular antiferromagnetic (TAFM) system can be calculated in a high temperature series expansion [23]. Writing the power series in a Padé approximation, the TAFM magnetic susceptibility is [23, 24]:

$$\chi_{\text{TAFM}}(x) = \frac{Ck_B}{J} \frac{4x(1 + b_1x + \dots + b_6x^6)}{1 + c_1x + \dots + c_7x^7} \quad (2.12)$$

$$x = \frac{J}{4k_BT}$$

Here J is the next neighbor interaction strength and $C = n\mu_{\text{eff}}^2/3k_B$ is the Curie constant. The parameters b_i and c_i of the Padé approximation are listed in table 2.2.

Quantum spin liquids

Spin liquids are correlated magnetic materials where the spins interact with each other while fluctuating and avoiding long range magnetic order [1, 2, 8]. If a spin liquid does not freeze or develop long range magnetic order upon cooling down to 0 K, it is called a quantum spin liquid (QSL). Hence, the frustration index f of QSLs is infinite. Driving force of the fluctuations of spins in QSL systems are quantum effects. Consequently, their ground state is not defined by a single configuration of spins but rather a superposition of many possible spin states. Even at 0 K, QSLs hold a finite amount of magnetic entropy in the fluctuating spins.

The concept of QSL was first proposed by Anderson for spin $1/2$ antiferromagnetic triangular lattice systems [6, 25]. Puzzled by the competing interactions in the triangular lattice, Anderson developed the idea of resonating valence bonds (RVB). In RVB systems, each two spins pair up to form a $S = 0$ singlet called valence bond. In this process, the partner of each spin is not restricted to next neighbors but every other spin in the material is possible. Therefore, there are many different configurations of pairing spins into valence bonds. In the ground state of RVBs, all possible valence bond configurations are in superposition. This exotic ground state gives rise to exotic excitations, high ground state degeneracy and new phenomena in QSL materials.

2.2 Heat capacity

The heat capacity of solids is a composition of various effects. Considering an insulating magnetic crystal, typically three contributions are found in the heat capacity [26]. First, lattice vibrations store internal energy in the crystal and are the dominant heat capacity proportion at higher temperatures. Second, magnetic excitations hold a relevant heat capacity contribution at low temperatures. Lastly, Schottky anomalies caused by discrete states with different energies are visible in the specific heat of some solids at low temperatures.

In conclusion, the specific heat C of an insulating crystal is the sum of the lattice specific heat C_{lattice} , the magnetic specific heat C_{mag} and the Schottky specific heat C_{Schottky} :

$$C = C_{\text{lattice}} + C_{\text{mag}} + C_{\text{Schottky}} \quad (2.13)$$

Heat capacity is a useful quantity to estimate the entropy S in a solid, because of the relation:

$$dS = \frac{C}{T} dT \quad (2.14)$$

2.2.1 Lattice specific heat

The crystal lattice vibrations known as phonons store energy in the system and dominate the total heat capacity at high temperatures. With different models, these phonons can be described and their specific heat calculated. Two common models are the Einstein and the Debye model.

Einstein model

In the Einstein model every atom in the lattice is assumed to oscillate harmonically with the same frequency ω_E . From this assumption the specific heat can be calculated to:

$$C_E = 3n_E R \left(\frac{\theta_E}{T} \right)^2 \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left[\exp\left(\frac{\theta_E}{T}\right) - 1 \right]^2} \quad (2.15)$$

R denotes the molar gas constant, n_E is the number of atoms per unit cell and $\theta_E = \hbar\omega_E/k_B$ is the Einstein temperature.

This model describes the lattice specific heat well for high temperatures ($T \gg \theta_E$). However for low temperatures ($T \ll \theta_E$), the Einstein model predicts an exponential relation with temperature which deviates from observations of specific heat.

Debye model

In the Debye approximation, the relation between frequency ω and wave vector k of phonons is assumed linear up to a maximal frequency ω_D called Debye frequency. At higher frequencies than ω_D , no states exist. Consequently, the density of states for phonons in the Debye model is:

$$D(\omega) = \begin{cases} \frac{3n_D\omega^2}{\omega_D^3} & \text{for } \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad (2.16)$$

Here, n_D is the number of atoms per unit cell.

Using the energy relation of a harmonic oscillator, the heat capacity can be calculated in the Debye model:

$$C_D = 9Rn_Dx_D^{-3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad \text{with} \quad x_D = \frac{\theta_D}{T} = \frac{\hbar\omega_D}{k_B T} \quad (2.17)$$

θ_D is called the Debye temperature and n_D is the number of atoms per unit cell which are oscillating according to the Debye model.

The specific heat caused by acoustic and optical phonons can be roughly estimated by Debye and Einstein models respectively. Consequently, the lattice specific heat of a crystal with multiple atoms per unit cell is modeled by a combination of Debye and Einstein functions:

$$C_{\text{lattice}} = \sum C_D + \sum C_E \quad (2.18)$$

2.2.2 Schottky anomaly

Systems with discrete states at different energy levels show a broad peak in the temperature dependence of specific heat. This peak is called Schottky anomaly. Considering two different energy levels of same degeneracy with level splitting $\Delta = E_2 - E_1$, the Schottky specific heat is:

$$C_{\text{Schottky}} = R \left(\frac{\Delta}{k_B T} \right)^2 \frac{\exp\left(\frac{\Delta}{k_B T}\right)}{\left[1 + \exp\left(\frac{\Delta}{k_B T}\right)\right]^2} \quad (2.19)$$

The maximum of the broad Schottky peak is roughly at $T_m = 0.42\Delta/k_B$. Oftentimes, the Zeeman effect is the origin of the Schottky anomaly, as it lifts the angular momentum degeneracy of states in an applied magnetic field. In this case, the energy level splitting Δ relates linear with an applied magnetic field. Consequently, the position of the Schottky anomaly can be shifted by changing the magnetic field.

Experimental setup

3.1 Magnetometry

In this thesis magnetization measurements were conducted on Quantum Designs Magnetic Property Measurement System (MPMS, more precise MPMS3) and Physical Property Measurement System (PPMS) in different modes.

The MPMS measures magnetization using three different modes: vibrating-sample magnetometer (VSM), direct current (DC) and alternating current (AC) magnetization measurement scans [27]. For VSM and DC magnetization measurements, the sample is set in an external magnetic field and subsequently moved through a superconducting pickup coil with a Superconducting Quantum Interference Device (SQUID). The induced current in the pickup coil can be used to calculate the magnetization M of the sample. In VSM mode the sample vibrates in the middle of the coil to induce a current, whereas the DC mode drives the sample through the coil and records the current induced in the coil to calculate the magnetization in a subsequent fit. Both methods provide insight into the static magnetization of the sample. In contrast, AC magnetization measures the dynamic magnetic properties of the sample. Here, an alternating external magnetic field induces an oscillating magnetization in the sample. Two connected detection coils record the magnetization of the sample and can separate the in-phase magnetic susceptibility χ' and the 90° out-of-phase susceptibility χ'' .

The MPMS possesses a superconducting magnet which is able to produce static magnetic fields up to 7 T [27]. For AC magnetization measurements, additionally to the static magnetic field an alternating magnetic field with maximal amplitude of $10 \cdot 10^{-4}$ T and maximal frequency of $f = 1000$ Hz can be applied [28]. The temperature in the sample chamber can be controlled from 1.8 K to 400 K.

In PPMS, the VSM option is used to measure the magnetization. Similar to the MPMS, temperature can be controlled in the range from 1.8 K to 400 K [29]. The superconducting magnet used in PPMS can produce static magnetic fields up to 14 T, which is twice the size of the maximal field in the MPMS.

For measurements both in MPMS and PPMS, the samples were sandwiched between two quartz cylinders in a brass sample holder together with Apiezon N grease. A picture of a mounted

Parameter	Symbol	Value
gradiometer radius	R	8.5 mm
half gradiometer length	L	8 mm
calibration factor	q	$-5.563 \cdot 10^{-7} \text{ erg/G}^2 \text{ mol V}$

Table 3.1: System specific parameters used in the fit function of the DC scans.

sample in the sample holder is depicted in figure 3.1. The quartz cylinders and the brass holder produce background signals which need to be subtracted from the sample measurement. For VSM and AC measurements, a background measurement of an empty sample holder can be performed and subtracted from the sample measurement [30].

In DC measurements, data acquisition is more complex than in the other modes, leading to a more complex background subtraction. Magnetization measured in DC mode is calculated by fitting following function to the signal $V(z)$ recorded while moving the sample through the pickup coil [30]:

$$V(z) = S + A \left[2 \left(R^2 + (z - C)^2 \right)^{-\frac{3}{2}} - \left(R^2 + (L + z - C)^2 \right)^{-\frac{3}{2}} - \left(R^2 + (-L + z - C)^2 \right)^{-\frac{3}{2}} \right] \quad (3.1)$$

Here $V(z)$ is the measured voltage at the sample position z , C is the center position of the pickup coil and S is an offset voltage. R denotes the radius of the pickup coil and L is half of the length of the gradiometer. The amplitude of the signal is A . From A the magnetic moment of the sample is calculated by multiplying with a system specific calibration factor q . The calibration factor q was determined by fitting the raw signal of DC scans and comparing the obtained amplitude A to the magnetic moment the MPMS provides. As result of this method $q = (-5.563 \pm 0.06) 10^{-7} \text{ erg/G}^2 \text{ mol V}$ was calculated. A summary of the system specific parameters of the MPMS used in this thesis can be found in table 3.1.

For background correction of DC measurements, the voltage $V(z)$ measured for an empty sample holder is subtracted from the $V(z)$ scan of the sample measurement. Consequently, the corrected voltage signal is fitted with equation 3.1 and from the amplitude A the magnetic moment of the sample is obtained. Background correction and post processing of DC measurements were performed in this thesis using the open-source program SquidLab [31].

3.2 Heat capacity

Heat capacity $C = (dQ/dT)_p$ can be measured with Quantum Designs PPMS at constant pressure via a thermal relaxation method [32]. In this method, the sample temperature curve of a heated and relaxing sample is used to calculate the heat capacity. In PPMS, the sample is mounted

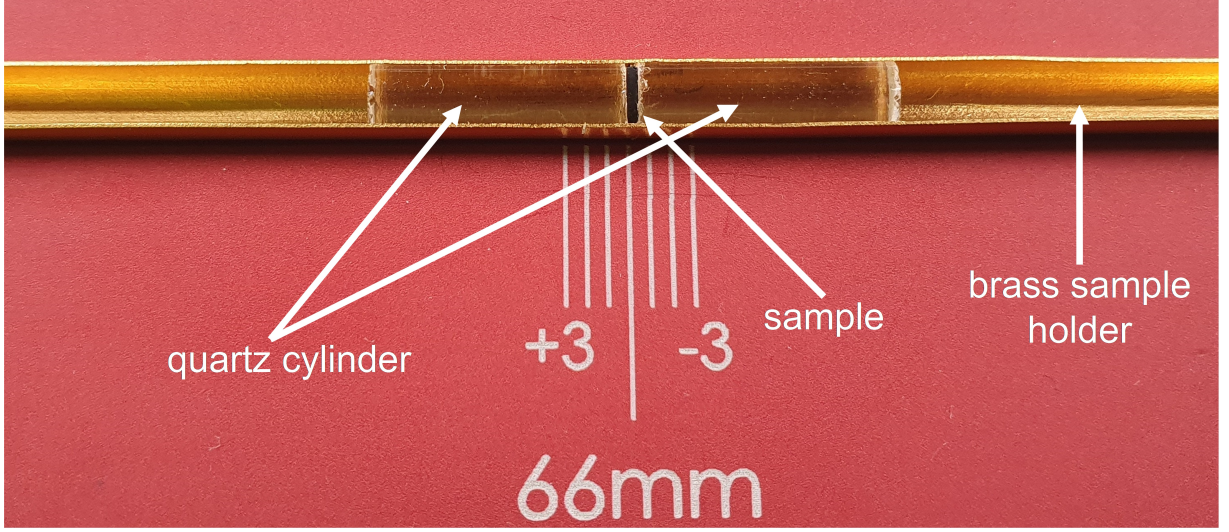


Figure 3.1: Picture of a brass sample holder used in magnetization measurements in MPMS. Between the quartz cylinders a $\text{Sr}_3\text{CuIr}_2\text{O}_9$ sample is mounted with Apiezon N grease. The sample holder lies on a mounting station used for MPMS to place the sample in the right position for the pickup coils.

with Apiezon N grease on a $2.5 \times 2.5 \text{ mm}^2$ platform with a thermometer and a heater, which is connected by small wires to a heat bath (puck). When measuring heat capacity C , the sample and platform are heated by the heater with a small heat pulse and their temperature relaxes back to bath temperature T_b after turning off the heater. If platform and sample are assumed to be in perfect thermal contact, a simple model can be assumed:

$$C_{\text{total}} \frac{dT}{dt} = -K_w(T - T_b) + P(t) \quad (3.2)$$

Here, C_{total} is the total heat capacity of the sample, the platform and grease. T denotes the temperature of the three components. The wires connect the sample and platform to the thermal bath with temperature T_b by the thermal conductivity K_w . While heating, the heater power $P(t)$ equals a constant value P_0 , meanwhile during cooling $P(t)$ is 0. In this equation, t denotes the time.

The solution of the differential equation 3.2 is an exponential function with time constant $\tau = C_{\text{total}}/K_w$:

$$T(t) = A \exp\left(-\frac{t}{\tau}\right) + T_b + \frac{P(t)}{K_w} \quad (3.3)$$

A is a constant determined by the initial condition of the initial value problem. By fitting the measured data to the model, C_{total} can be obtained. To calculate the sample heat capacity, an additional addenda measurement of only the platform and grease needs to be conducted.

Substracting the addenda heat capacity C_{addenda} leads to the sample heat capacity:

$$C_s = C_{\text{total}} - C_{\text{addenda}} \quad (3.4)$$

A more sophisticated model can be put forward if the sample and platform are considered in good but not perfect thermal contact. Then, sample and platform have different temperatures and heat capacities named T_s and C_s for the sample and T_p and C_p for the platform. The following coupled differential equations can be derived for this model:

$$C_p \frac{dT_p}{dt} = P(t) - K_w (T_p(t) - T_b) + K_g (T_s(t) - T_p(t)) \quad (3.5)$$

$$C_s \frac{dT_s}{dt} = -K_g (T_s(t) - T_p(t)) \quad (3.6)$$

K_g is the thermal conductance of the grease between sample and platform. Again, the solution of both equations are exponential functions. The platform heat capacity C_p is fixed to the beforehand measured addenda heat capacity. Sample heat capacity C_s and thermal conductance K_g are retrieved by fitting the model to measured data.

The standard heat capacity mode of PPMS is able to measure and fit with these models in temperature ranges from $T = 1.8$ K to 400 K and magnetic fields from $B = 0$ T to 14 T. A picture of a puck used in the heat capacity option of PPMS can be found in figure 3.2. There, a sample glued with Apiezon N grease on the platform of the puck is visible.

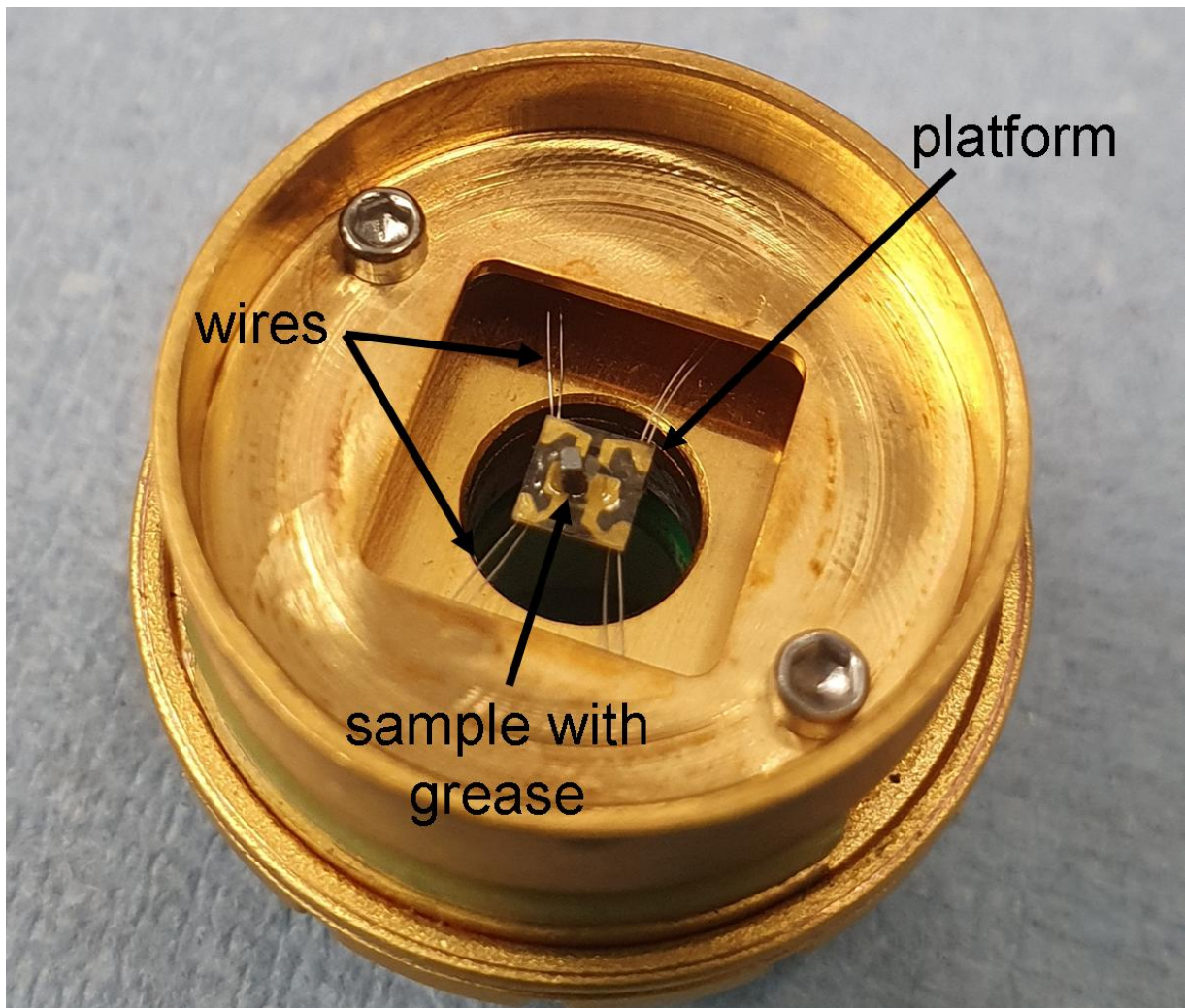


Figure 3.2: Picture of a puck used in PPMS to measure heat capacity. The mounted sample is a GdRu_2Si_2 crystal, which was measured for Lukas Gries.

Sr₃CuSb₂O₉

Since the prediction of a new ground state for triangular lattice antiferromagnets by Anderson [6] and Anderson and Fazekas [25] in 1973 to 1974, the experimental search for this exotic state called quantum spin liquid (QSL) started. With more theoretical investigation, the presence of QSLs was hypothesized in different structures and model systems [12, 33]. Thus on experimental side, along with many other systems, copper and iridium based triple perovskites became target in the search for QSL materials. For compounds such as Ba₃CuSb₂O₉ [16, 34] and Ba₃ZnIr₂O₉ [17], quantum spin liquid ground states have been declared. To extend the investigations in this class of materials, the larger Barium ions were exchanged to smaller Strontium ions.

Sr₃CuSb₂O₉ belongs to the triple perovskites of the form A₃B₃X₉ [35]. Like for perovskites of form ABX₃, the B-sites form a cubic lattice with A-sites in the center. Additionally, every B-site is surrounded by an octahedron of X ions, with X-sites occupying the edges of the cubic lattice. By combining three perovskite unit cells in line a triple perovskite unit cell can be created. In Sr₃CuSb₂O₉, Sr²⁺ ions sit on the A-sites and O²⁻ ions on the X-sites. The B-sites of this structure are occupied by Cu²⁺ and Sb⁵⁺ ions. It is argued that copper and antimony order 1:2 on these sites, so following the edges of the cubic perovskite lattice, every third B site is occupied by copper [35]. Considering these Cu²⁺ ions, it can be seen that they form layers of triangular lattices in the (111) plane. The developing triangular lattice is drawn in figure 4.1. The crystal structure was determined to the body-centered tetragonal space group *I*₄/*mcm* (140) by Rietveld refined analysis of x-ray diffraction measurements [35].

Electronically, the formal formula is Sr₃²⁺Cu²⁺Sb₂⁵⁺O₉²⁻ [35]. Hence, Sr, Sb and O all possess fully filled shells leaving Cu²⁺ ions with unoccupied 4s shells and 3d⁹ shells. The presence of oxygen octahedra around the Cu²⁺ ions breaks the degeneracy of the d-orbitals, generating threefold degenerate t_{2g} and twofold degenerate e_g orbitals. As t_{2g} is lying energetically lower it is fully filled, while e_g possesses an unoccupied orbital. Consequently, Sr₃CuSb₂O₉ has a spin of $S = 1/2$ while the angular momentum L is quenched, i.e. $L \approx 0$. Following theory, this leads to the Landé factor $g_{\text{theory}} = 2$ and $\mu_{\text{eff}} = \sqrt{4S(S+1)}\mu_B \approx 1.73 \mu_B$.

Temperature dependence of magnetization measured on a polycrystalline sample showed no phase transition down to 1.8 K [35]. Anyhow, applying a Curie-Weiss fit to their measurement yielded a Weiss temperature $\theta_W = -143$ K. By using a triangular lattice spin 1/2 model, the

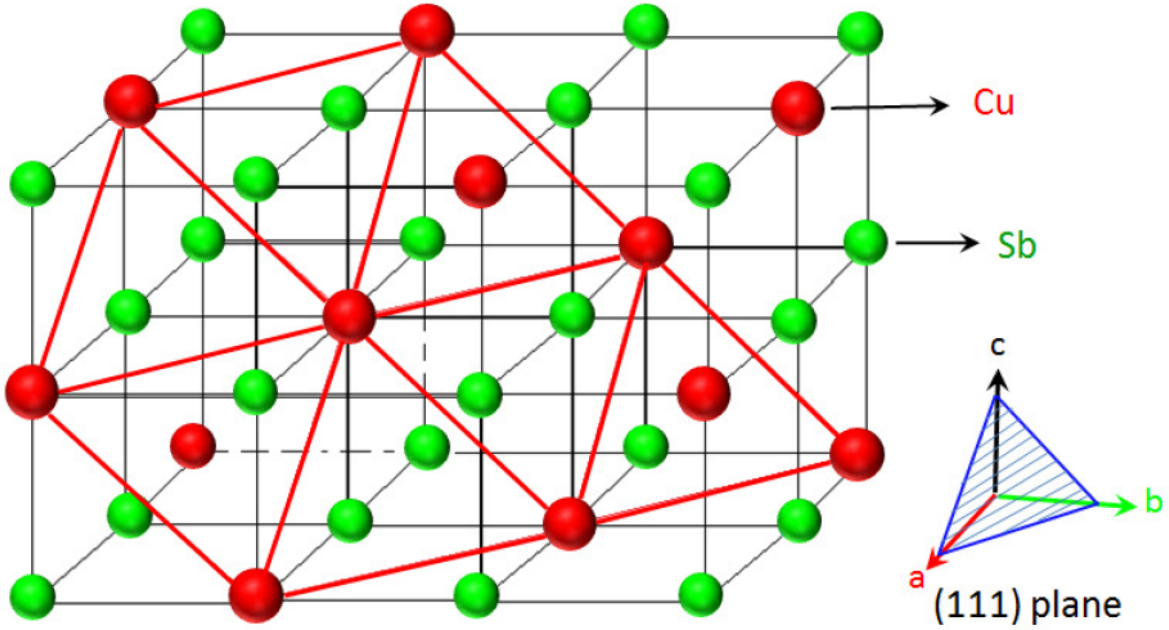


Figure 4.1: Cu^{2+} (red) and Sb^{5+} (green) ions in the crystal structure of $\text{Sr}_3\text{CuSb}_2\text{O}_9$. Red lines show the connection between Cu^{2+} next neighbors forming a triangular lattice in the (111) plane. This figure is taken from the supplement of [35].

interaction strength between the Cu^{2+} ions was determined to $J = 70$ K. The absence of long range magnetic order down to temperatures way smaller than the Weiss temperature shows the great amount of frustration inherent in the material.

FC and ZFC measurements showed no bifurcation. Furthermore, no anomaly was found in ac susceptibility measurements. From these observations spin glassy behavior was ruled out.

Measurements of heat capacity were performed in the temperature range from 0.35 K to 200 K and in magnetic field range from 0 to 9 T [35]. All measurements showed no sign of a magnetic phase transition. At temperatures below 10 K, a small Schottky anomaly was visible. By assuming a two level Schottky contribution by free $S = 1/2$ spins, the fraction of those so called orphan spins was determined to $f = 2.5$ %. Furthermore, in the low temperature heat capacity well below 6 K, dominant scaling with T^2 was detected. This is a hint on linearly dispersing excitations in this temperature regime, suggesting gapless excitations until zero temperature.

Electron spin resonance (ESR) measurements were used to determine the Landé g-factor of the Cu^{2+} spins [35]. Averaged over direction towards the applied field, the g-factor is $g = 2.24$. However, for temperatures smaller than $T \approx 10$ K considerable temperature dependence appeared in g . This observation was assigned to the onset of spin fluctuations and internal

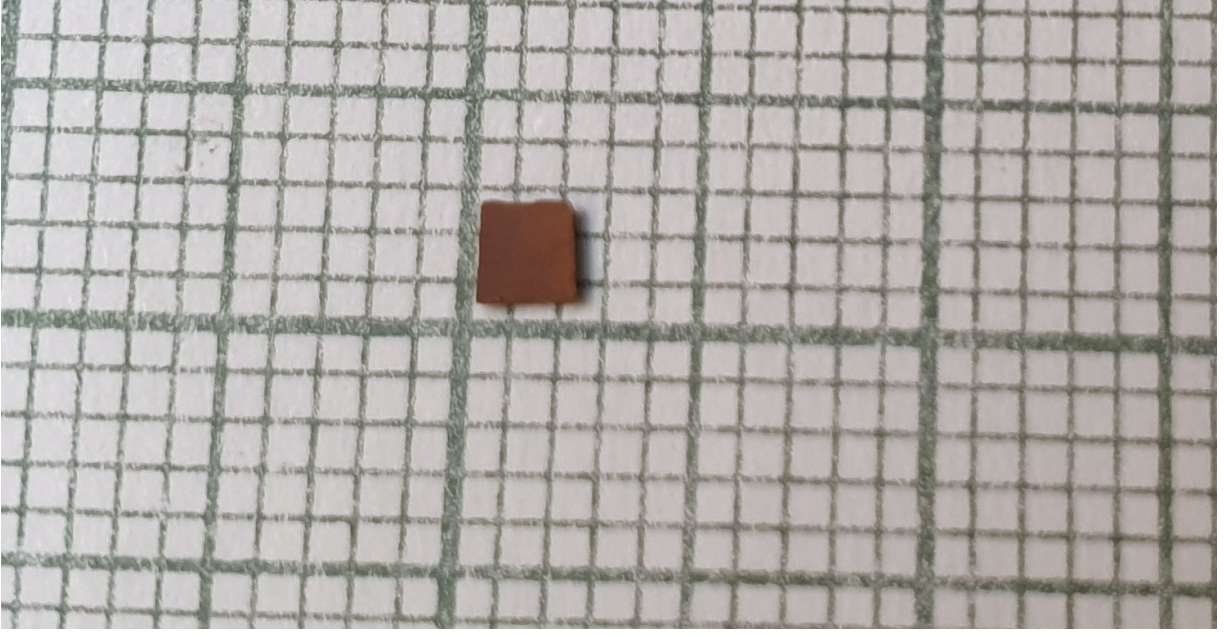


Figure 4.2: Example of a $\text{Sr}_3\text{CuSb}_2\text{O}_9$ sample studied in this thesis.

magnetic fields.

In conclusion, strong frustration in combination with spin fluctuations until lowest measured temperatures were observed in $\text{Sr}_3\text{CuSb}_2\text{O}_9$ [35]. Based upon these findings $\text{Sr}_3\text{CuSb}_2\text{O}_9$ was claimed to be a gapless QSL.

4.1 Experimental details

This thesis presents magnetization and heat capacity measurements conducted on polycrystalline samples, which were provided by Dr. Charu Garg and Prof. Dr. Sunil Nair (both from Indian Institute of Science Education and Research Pune). The samples are pressed pellets cut to appropriate size for the measurement setup. For different measurements different samples from the same batch were used. To avoid absorption of water and oxygen in room air, the samples were stored in an argon atmosphere. An example of the $\text{Sr}_3\text{CuSb}_2\text{O}_9$ samples is shown in figure 4.2.

Magnetic measurements were performed using a Magnetic Properties Measurement System (MPMS3) and a Physical Properties Measurement System (PPMS) both by Quantum Design. Field dependence of the magnetization was measured in PPMS using a vibrating-sample magnetometer (VSM) setup. The sample had a mass of $m_1 = 15.23 \pm 0.05$ mg. Before the measurement, the sample was cooled in zero field followed by measuring while sweeping the field up to $B = 14$ T and consequently down to $B = -0.1$ T. Background was measured by the same setup without

sample and the measurements are corrected with respect to it. This protocol was followed for the temperatures $T = 1.8$ K, 50 K, 100 K, 150 K, 200 K and 300 K.

Temperature dependence of the magnetization was measured both in PPMS and MPMS for samples of mass $m_1 = 15.23 \pm 0.05$ mg and $m_2 = 11.64 \pm 0.05$ mg. Measured temperatures span from $T = 1.8$ K to 300 K in both devices. By use of PPMS, the magnetization was measured using the VSM setup at a magnetic field $B = 1$ T. Hereby, a zero field cooled warming (ZFCW) measurement protocol was performed, followed by a field cooled cooling (FCC) sequence.

With MPMS, the magnetization was measured in DC mode using a SQUID magnetometer. The whole temperature range from 1.8 K to 300 K was measured in fields $B = 1$ T, 3 T and 7 T following a field cooled sequence (FCW, also called FC). The measurements are corrected with respect to the background.

For heat capacity measurements, PPMS was used. A polished sample was fixed with Apiezon N grease on the PPMS heat capacity setup. The mass of the sample was $m = 6.26 \pm 0.05$ mg. Heat Capacity was measured in zero field from $T = 1.8$ K up to 200 K. Afterwards, it was measured in a magnetic field of $B = 14$ T until good overlap with the zero field measurement was reached. This happened at roughly 115 K. Additional measurements in fields of 5 T and 10 T were conducted up to 64 K.

4.2 Magnetization

4.2.1 Field dependence of magnetization

In figure 4.3, the magnetization as function of magnetic field at different temperatures is shown. For all temperatures, the magnetization shows paramagnetic behavior. The $T = 1.8$ K curve shows below 5 T applied magnetic field a steep rise in combination with right bending. The right bending lessens with field until it becomes almost linear from $B = 8$ T on up to $B = 14$ T. At highest magnetic field, the magnetization amounts to $\sim 0.16 \mu_B/\text{f.u.}$, which is far off from the theoretical saturation value of $M_{\text{sat}} = gJ\mu_B = 1.12 \mu_B/\text{f.u.}$ for spin $1/2$ systems with $g = 2.24$. Right bending at lower fields can be attributed to a Brillouin like behavior originating from orphan spins in the sample [36]. These orphan spins are spins which decouple from the correlated part of the material and behave like free spins. Usually, orphan spins make up a small fraction of the spins in the material and might originate from edge spins of correlated regions or defects. Above 8 T, the magnetization of orphan spins saturates and a linear part which is attributed to the correlated spin magnetization can be seen.

For $T \geq 50$ K $M(T)$ is mostly linear. Except for the $T = 50$ K measurement, the magnetization shows no hysteresis for fields larger than ~ 0.2 T. Below 0.2 T a small hysteresis is visible, which

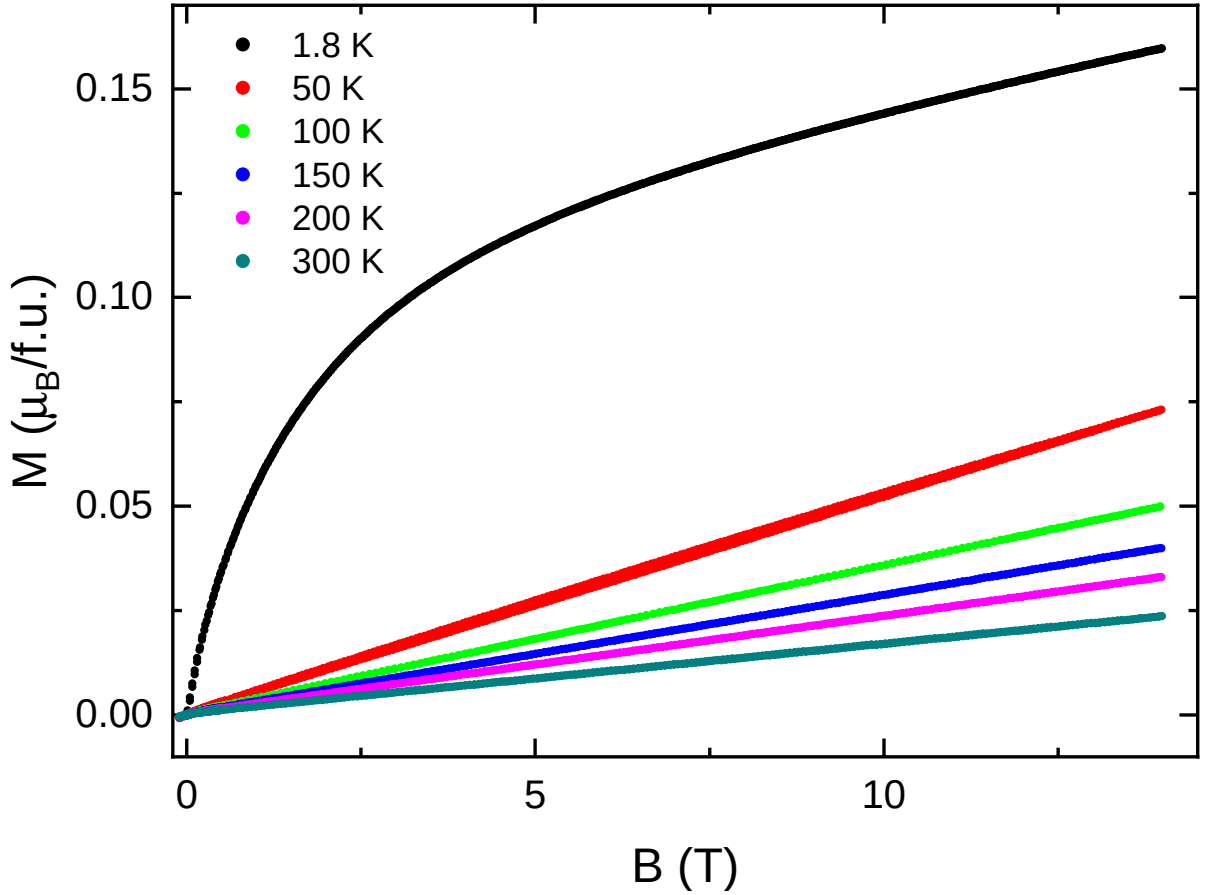


Figure 4.3: Magnetization M vs. applied magnetic field B at different temperatures.

might originate from remanent field effects in the measurement device. At 50 K, magnetization in decreasing magnetic field is higher than in rising field with the highest difference at roughly 7 T (see figure 4.4).

To show this unusual behavior, the difference $\Delta M = M_{50\text{ K, decreasing } B} - M_{50\text{ K, rising } B}$ is shown in the inset of figure 4.4. From zero applied field the difference starts roughly at zero, forms a broad peak over the whole measurement range and reaches zero again at 14 T. The origin of this hysteresis is unknown and might as well arise from the sample or by measurement issues.

The measurements at temperatures of 100 K and higher are used to determine possible ferromagnetic contributions in the sample. Therefore, a linear function is fitted to the magnetization in the linear regime from $B = 1$ T to 14 T. The intersection of the linear fits with the y-axis show the ferromagnetic contribution to the magnetization. This can be seen in figure 4.5. On average, the y-intersect for measurements at these temperatures is $M_{\text{FM offset}} = (4.2 \pm 0.3)10^{-4} \mu_B/\text{f.u.}$. Thus, this ferromagnetic contribution is at least one magnitude smaller than the paramagnetic magnetization in further analysis, hence it is neglected.

The measurement at 1.8 K resembles a combination of a Brillouin-like part and a linear term.

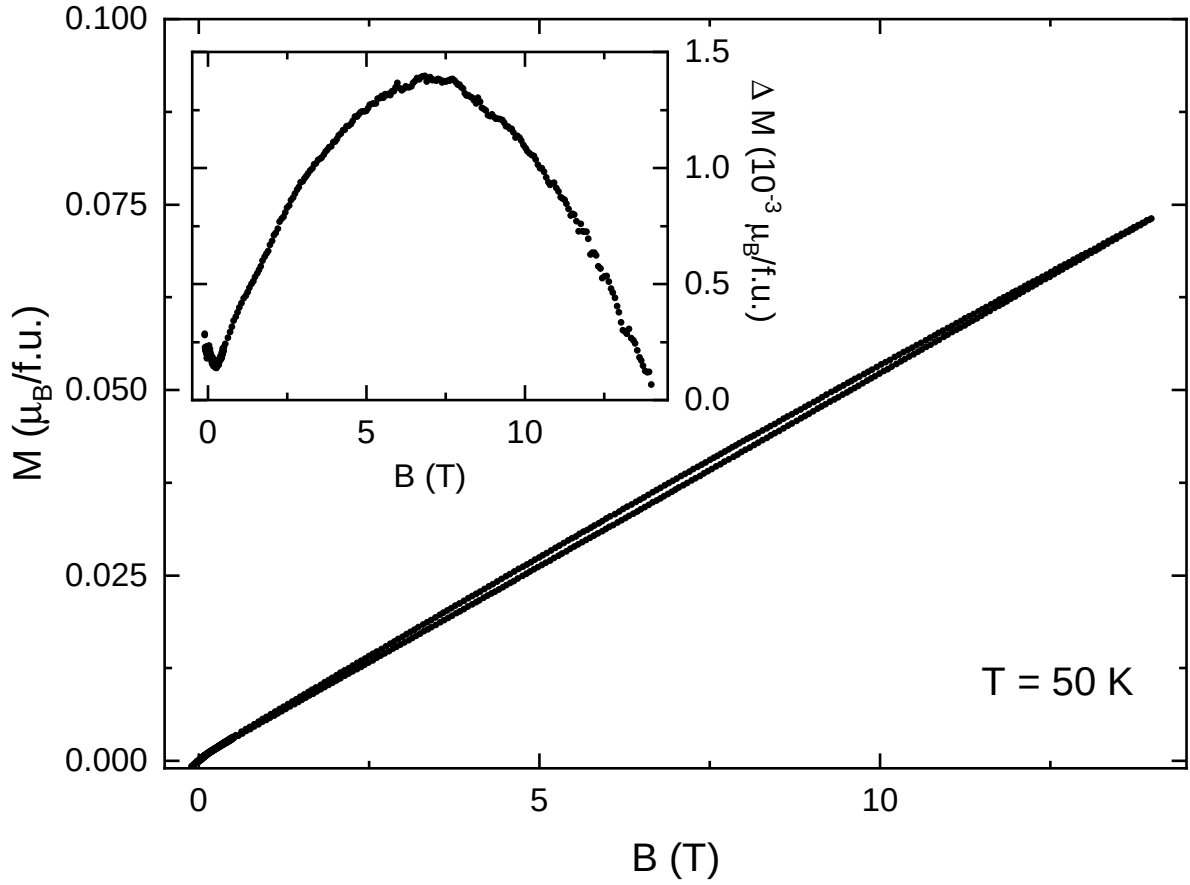


Figure 4.4: Magnetization M vs. applied magnetic field B at 50 K. **Inset:** The difference in magnetization between rising and decreasing the magnetic field is plotted against the applied magnetic field.

Therefore, the data are fitted by following function:

$$M = fg\mu_BJB_J \left(\frac{g\mu_BJB}{k_B T} \right) + a_0 B \quad (4.1)$$

In equation 4.1, the temperature T was set to the measurement temperature 1.8 K. Furthermore, the Landé factor g was set to $g = 2.24$ as estimated by [35]. By use of a fit with free parameters f , J and a_0 , the fraction of orphan spins per formula unit was determined to $f = 4.03 \pm 0.07$ %. The orphan spins show a total angular momentum $J = 1.04 \pm 0.02$. A linear function with slope $a_0 = (4.92 \pm 0.03)10^{-3} \mu_B/\text{f.u. T}$ describes the correlated spins.

The fitted curve does not represent the measured data well, so interpretations with these parameters need to be regarded carefully. Still, interpreting the results naively, $\sim 4\%$ of unit cells contain free spin $S = 1$. It is surprising that the best parameter for J is close to 1. Given that the Brillouin part is a result of Cu^{2+} ions, total angular momentum of $J = 1/2$ was expected.

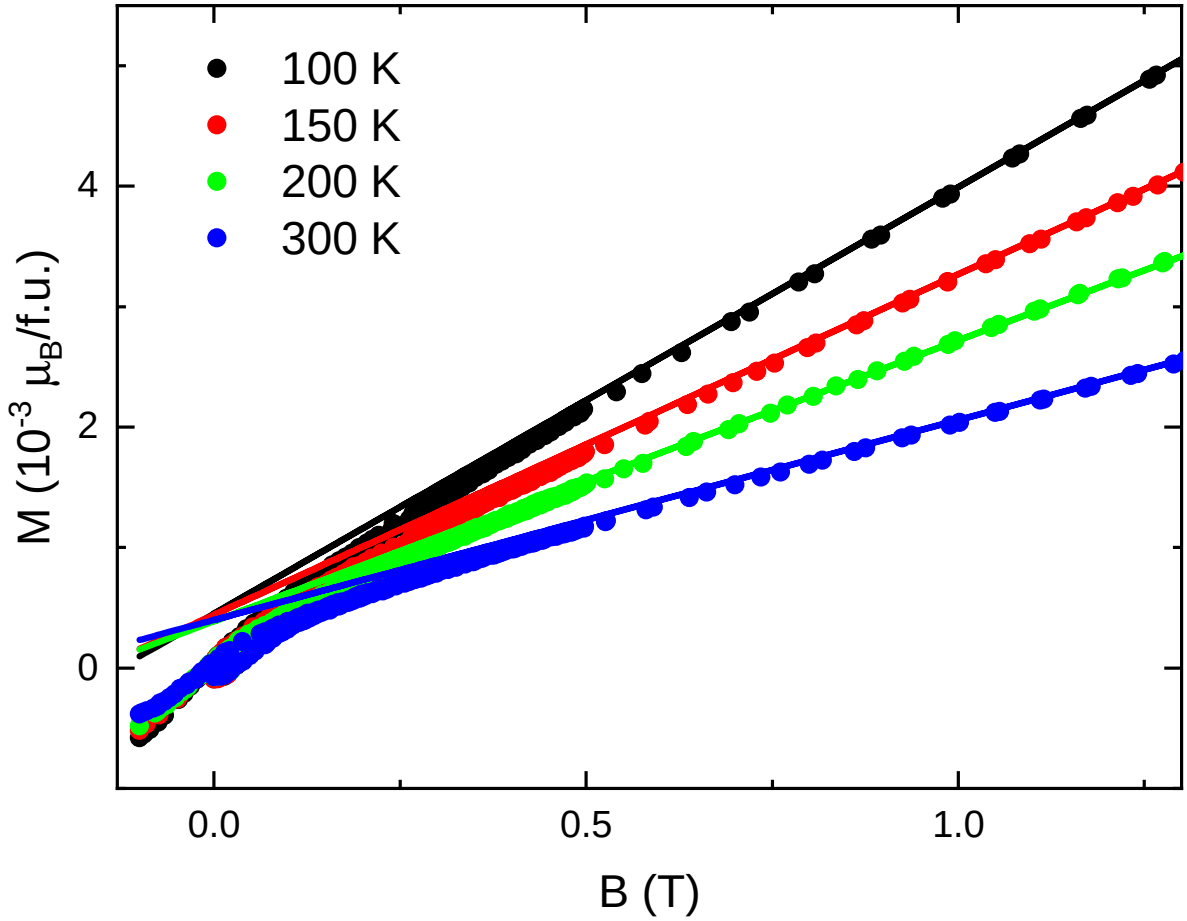


Figure 4.5: Magnetization M plotted vs. applied magnetic field B near zero magnetic field. The solid lines show linear fits to the data above 1 T.

As a model of only free orphan spins and correlated spins seems insufficient to describe the magnetization of $\text{Sr}_3\text{CuSb}_2\text{O}_9$, a different approach is invoked. The new model function reads:

$$M = f_1 g_1 \mu_B J_1 B_{J_1} \left(\frac{g_1 \mu_B J_1 B}{k_B (T - \theta)} \right) + f_2 g_2 \mu_B J_2 B_{J_2} \left(\frac{g_2 \mu_B J_2 B}{k_B T} \right) + a_0 B \quad (4.2)$$

Here, orphan spins are described by the first Brillouin function with parameters indexed by 1. These orphan spins are from Cu^{2+} ions, hence their spin $S = J_1 = 1/2$ and $g_1 = 2.24$ are fixed [35]. Furthermore, in this model small interactions between the orphan spins itself and the surrounding environment are incorporated by an effective temperature $T - \theta$. Besides the orphan spins, some other magnetic contributions with unknown origin are assumed by the second Brillouin function with parameters indexed by 2. As g_2 and J_2 are strongly correlated, g_2 was fixed to 2.24 to simplify the numerical problem. The bulk magnetization of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ is expected to be roughly linear at $T = 1.8$ K and $B \leq 14$ T. Consequently, a linear term is added to describe the correlated spins.

The resulting fit is shown in figure 4.6. This fit represents the measured data better than a single Brillouin function. It shows how spin $S = 1/2$ and $g = 2.24$ electrons of the Cu^{2+} ions can describe the high field data from ~ 4 T on. By means of this model, the fraction $f_1 = 5.21 \pm 0.03$ % of unit cells contains Cu^{2+} orphan spins. Only small correlations described by $\theta = -0.774 \pm 0.015$ K alter the Brillouin like behavior of the orphan spins. The correlated spins are described by a linear term with slope $a_0 = (4.05 \pm 0.01)10^{-3} \mu_B/\text{f.u. T}$. They dominate the behavior of $M(B)$ for $B \geq 8$ T.

However, in the low field regime up to 2 T, the second Brillouin function with unknown origin dominates. Only a small fraction of $f_2 = 0.576 \pm 0.011$ % of unit cells yield these unknown magnetic contribution. With total angular momentum $J_2 = 3.50 \pm 0.04$ and $g_2 = 2.24$ it is unclear which compound or ion provides these characteristics. Hence, this model has two problems: First, the model includes an unknown magnetic contribution which is not expected in the material. Further constituents besides the ones in the structure formula should not be present in the sample with an abundance in the mid per mille magnitude. Second, the characteristics $J_2 = 3.5$ and $g_2 = 2.24$ of this unknown constituent are surprising and could not be attributed to a sensible possible impurity phase compound for $\text{Sr}_3\text{CuSb}_2\text{O}_9$. With this knowledge, both models with one and two Brillouin functions need to be regarded with care.

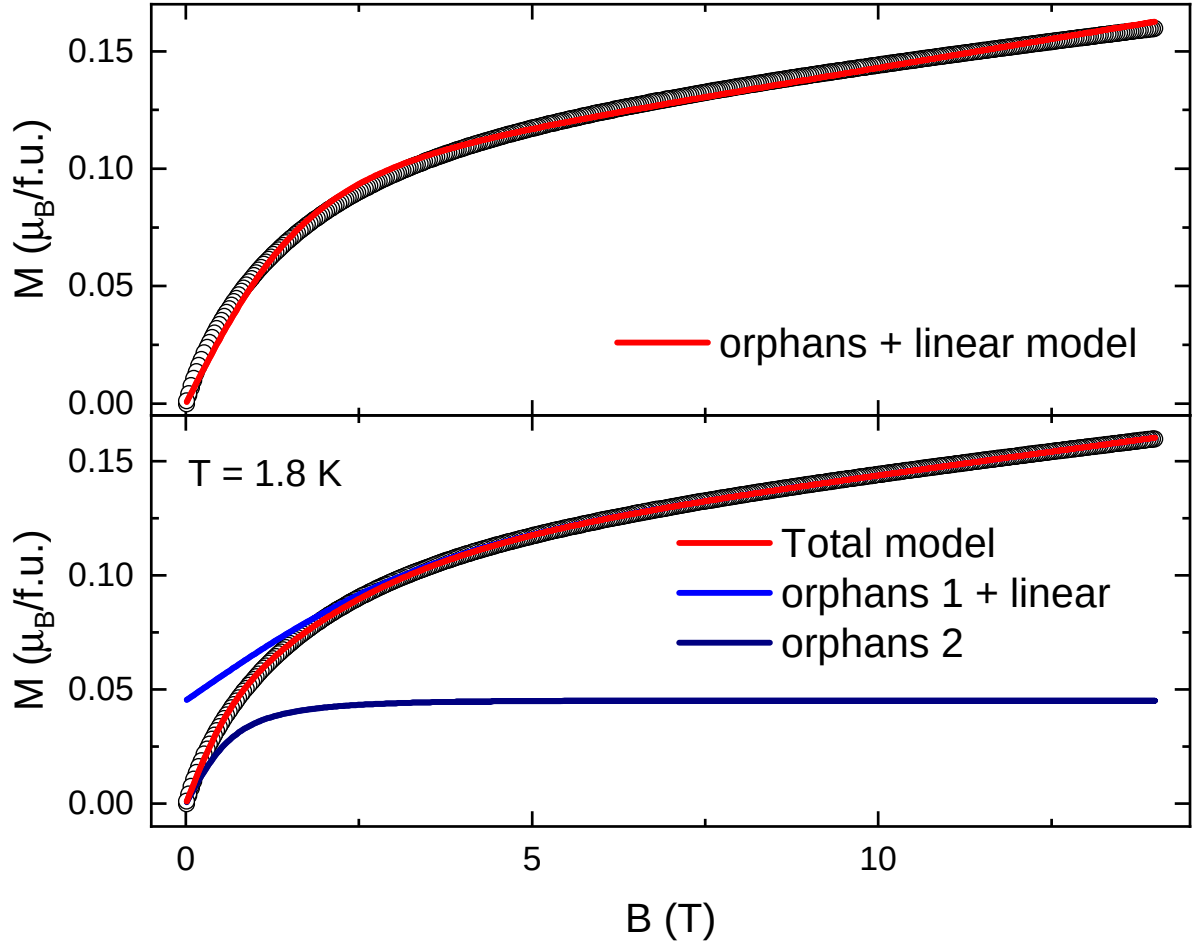


Figure 4.6: Magnetization is plotted against magnetic field at $T = 1.8$ K. **top:** The red line shows a combination of a Brillouin function for orphan spins and a linear function to describe the bulk magnetization. **bottom:** In red, a model combining two Brillouin functions representing orphan spins and a linear function representing the correlated spins are drawn (see equation 4.2). The blue curve shows how the high magnetic field regime is described by one Brillouin component associated with Cu^{2+} orphans and a linear component of the total fit. In dark blue the remaining Brillouin function from the total fit is depicted.

4.2.2 Temperature dependence of magnetization

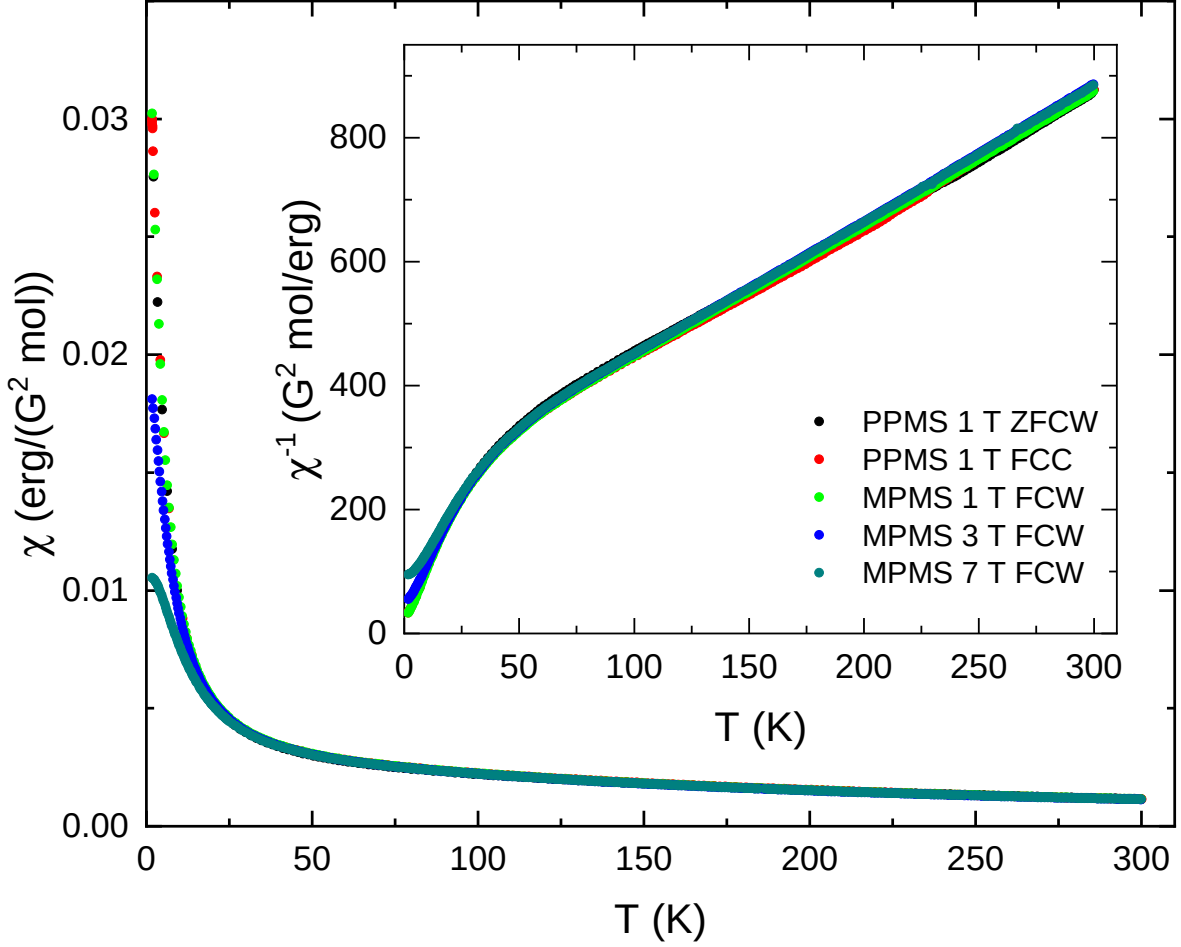


Figure 4.7: Magnetic susceptibility $\chi = M/B$ is shown against temperature in various field and measurement protocols. **Inset:** Inverse magnetic susceptibility χ^{-1} is depicted vs. temperature.

Magnetic susceptibility $\chi(T) = M(T)/B$ and inverse susceptibility $\chi^{-1}(T)$ is shown in figure 4.7. At $T > 50$ K, the measurements align well with each other. For $T \leq 50$ K, the magnetic susceptibility of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ gets suppressed with rising field. In inverse susceptibility $\chi^{-1}(T)$ an almost linear regime is visible for high temperatures (see inset figure 4.7). Small bending in this regime is likely caused by small temperature independent magnetic contributions (e.g. Van-Vleck, Diamagnetism) or slight misvaluations of background [37].

The measurements conducted in PPMS are used to test for hysteresis effects. In figure 4.8 both measurements are shown.

The inset of figure 4.8 depicts the difference between both measurement protocols $\Delta\chi = \chi_{\text{ZFCW}} - \chi_{\text{FCW}}$. It is visible that for higher temperatures only a small difference between the measurements exists. Around ~ 50 K, a small hump can be assigned to oxygen which is absorbed by the

porous sample [38]. For temperatures below 18 K a strong increase in $\Delta\chi$ is observed. In this low temperature domain interactions between the orphan spins grow, leading to complex spin dynamics [35]. Hence, there might be a small hysteresis originating from the orphan spins. The ferromagnetic offset $\chi_{\text{FM offset}} = M_{\text{FM offset}}/B = (2.3 \pm 0.2)10^{-4} \text{ erg/G}^2 \text{ mol}$ matches the jump in $\chi_{\text{ZFCW}} - \chi_{\text{FCC}}$ from 1.8 K to 18 K, which hints to a connection of these observations.

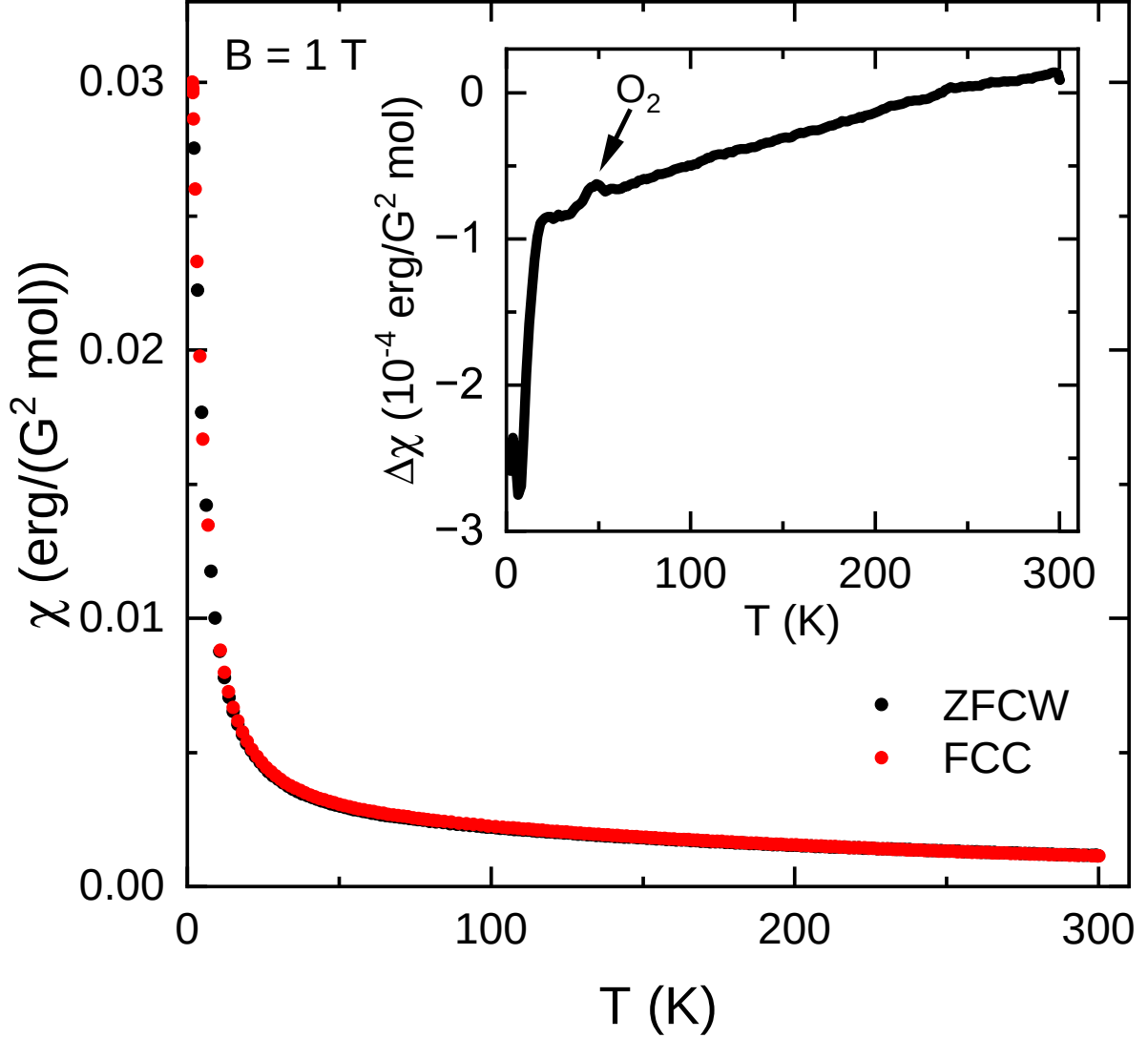


Figure 4.8: Magnetic susceptibility χ in ZFCW (black) and FCC (red) measurement protocols are depicted. **Inset:** Difference between ZFCW and FCC measurements $\Delta\chi = \chi_{\text{ZFCW}} - \chi_{\text{FCC}}$ is drawn.

To analyze the measured data, at first a similar approach as in [35] is chosen. A Curie-Weiss law according to 2.10 and a TAFM function (see 2.12) is fitted to the 1 T data in the temperature range from 150 K to 300 K. The susceptibility $\chi(T)$ as well as the inverse susceptibility $\chi^{-1}(T)$ are shown in figure 4.9 in combination with their theoretical models. From the Curie-Weiss fit,

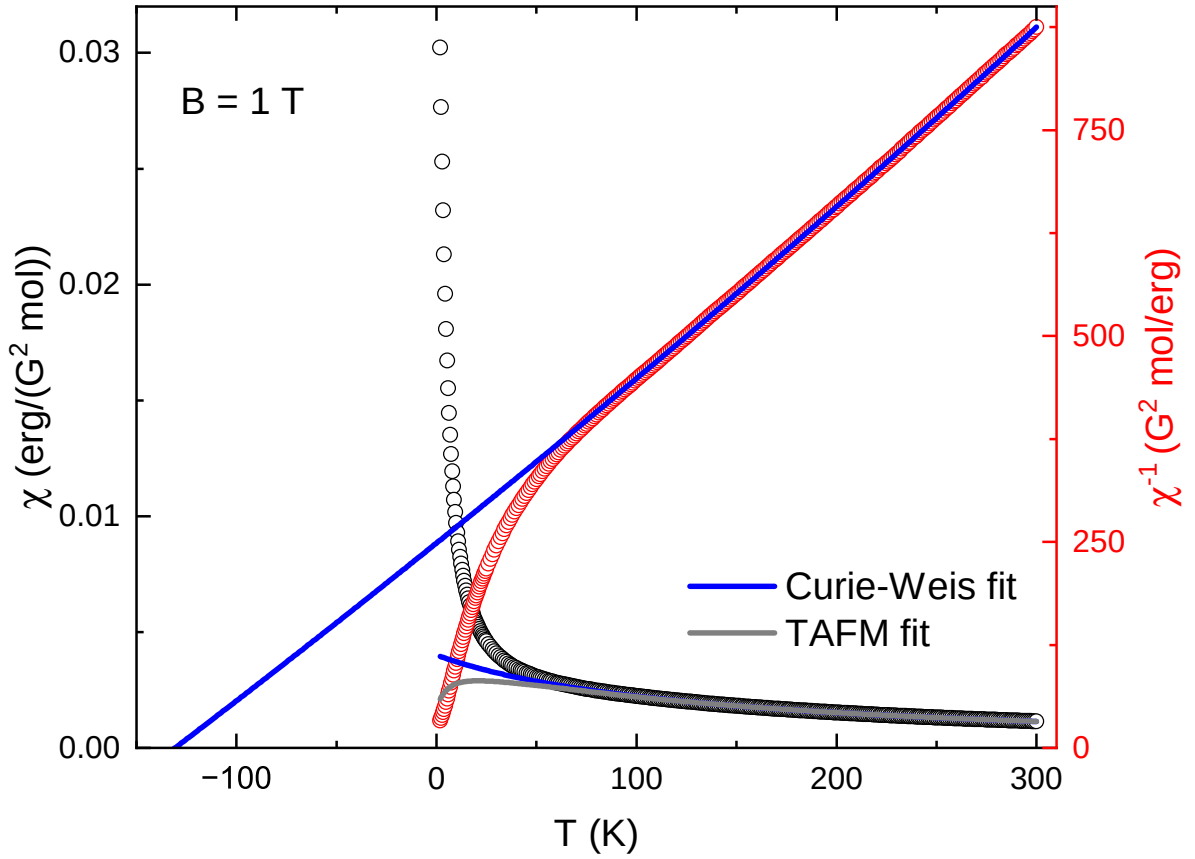


Figure 4.9: Magnetic susceptibility $\chi(T)$ is depicted in black with the corresponding y-axis on the left. A modified Curie-Weiss law according to 2.10, which is fitted to the data from 150 K to 300 K, is shown in blue. The gray curve shows a TAFM function, which was also fitted to $\chi(T)$ in the temperature regime from 150 K to 300 K. In red, the inverse susceptibility $\chi^{-1}(T)$ is drawn with its y-axis on the right. A modified Curie-Weiss model is fitted to $\chi^{-1}(T)$ from 150 K to 300 K and drawn in blue.

the Weiss temperature is estimated to $\theta_W = -132 \pm 10$ K. The Curie constant $C = 0.54 \pm 0.04$ erg K/G² mol and the temperature independent susceptibility contribution $\chi_0 = (-1.2 \pm 0.3)10^{-4}$ erg/G² mol are the remaining parameters of the Curie-Weiss model.

In the TAFM fit, the Curie constant is determined to $C_{\text{TAFM}} = 0.45 \pm 0.02$ erg K/G² mol. Antiferromagnetic interactions in the triangular lattice are calculated to $J/k_B = 55 \pm 5$ K. An almost neglectable temperature independent susceptibility $\chi_0 = (-1 \pm 2)10^{-5}$ erg/G² mol was computed by the TAFM fit.

Both the Curie-Weiss model and the TAFM model reveal strong antiferromagnetic interactions in $\text{Sr}_3\text{CuSb}_2\text{O}_9$. In combination with the fact that no long range magnetic order can be seen down to $T = 1.8$ K, this demonstrates strong frustration in $\text{Sr}_3\text{CuSb}_2\text{O}_9$.

The Curie constant is a measure of how many spins per unit cell are in the material. A single

spin $1/2$ per unit cell is expected for $\text{Sr}_3\text{CuSb}_2\text{O}_9$. This would lead to a Curie constant of $C_{\text{spin } 1/2} = \frac{N_A g^2 \mu_B^2}{4k_B} \approx 0.471 \text{ erg K/G}^2 \text{ mol}$ (with $g = 2.24$). The Curie-Weiss model seems to overestimate the amount of paramagnetic spins in the material, whereas the TAFM model yields a Curie constant close to expectations. Further fits of the Curie-Weiss and TAFM model in different temperature regions are presented in the appendix.

As the Curie-Weiss model and the TAFM model both are high temperature approximations, the orphan spins, which become dominant at low temperatures, cannot be studied. To quantify the orphan spins and get a deeper understanding of the whole temperature range of the magnetization measurements, some different approaches are tested in the whole temperature domain.

First, an approach similar to [36] is tested. Here, correlated spin magnetization and orphan spin magnetization are described by two separate Curie-Weiss functions. However in this thesis, for the correlated spin magnetization in $\text{Sr}_3\text{CuSb}_2\text{O}_9$ a TAFM function is used rather than a Curie-Weiss function. For the orphan spins, a Brillouin function with effective temperature $(T - \theta)$ is used to avoid high temperature approximations. The resulting model can be found in equation 4.3:

$$\chi^{-1} = \left(\text{TAFM}(T, C_{\text{TAFM}}, J) + \frac{fg\mu_B N_A J_1}{B} B_{J_1} \left(\frac{g\mu_B J_1 B}{k_B(T - \theta)} \right) + \chi_0 \right)^{-1} \quad (4.3)$$

In this model, some parameters are fixed in order to assign the TAFM function to the correlated domain and the Brillouin function to the orphan spins. C_{TAFM} is set to the theoretical value $0.471 \text{ erg K/G}^2 \text{ mol}$, while for the orphan spins $J_1 = 1/2$ and $g = 2.24$. The remaining parameters are determined by fitting the model to the 1 T measurement. The fit is performed for inverse susceptibility $\chi^{-1}(T)$ to stress high temperature data for better results in this regime [36, 37]. However, for better visibility of the orphan spin tail, the resulting curves are presented as $\chi(T)$ in figure 4.10.

The fitted model describes the high temperature regime above 100 K very well with the interaction strength between neighboring spins in the bulk of the material $J = 90 \pm 5 \text{ K}$ and the temperature independent contribution $\chi_0 = (-1.2 \pm 0.4)10^{-4} \text{ erg/G}^2 \text{ mol}$. Intermediate temperatures down until $\sim 20 \text{ K}$, where the orphan spin magnetization begins to dominate are also described well. The fraction of orphan spins is $f = 15 \pm 2 \%$ with an interaction $\theta = 0.9 \pm 0.2 \text{ K}$, determined by the fit. Down until roughly 20 K, these orphan spins act mostly like free spins. However, for lower temperatures, the orphan spin magnetization predicted by the model is far higher than the measurement. A possible explanation for this observation are beginning interactions between the orphan spins itself and the environment with lower temperature.

A different approach to describe the low temperature behavior of the $\text{Sr}_3\text{CuSb}_2\text{O}_9$ is using the results from the $M(B)$ analysis. The magnetization at 1.8 K was well described by a model with

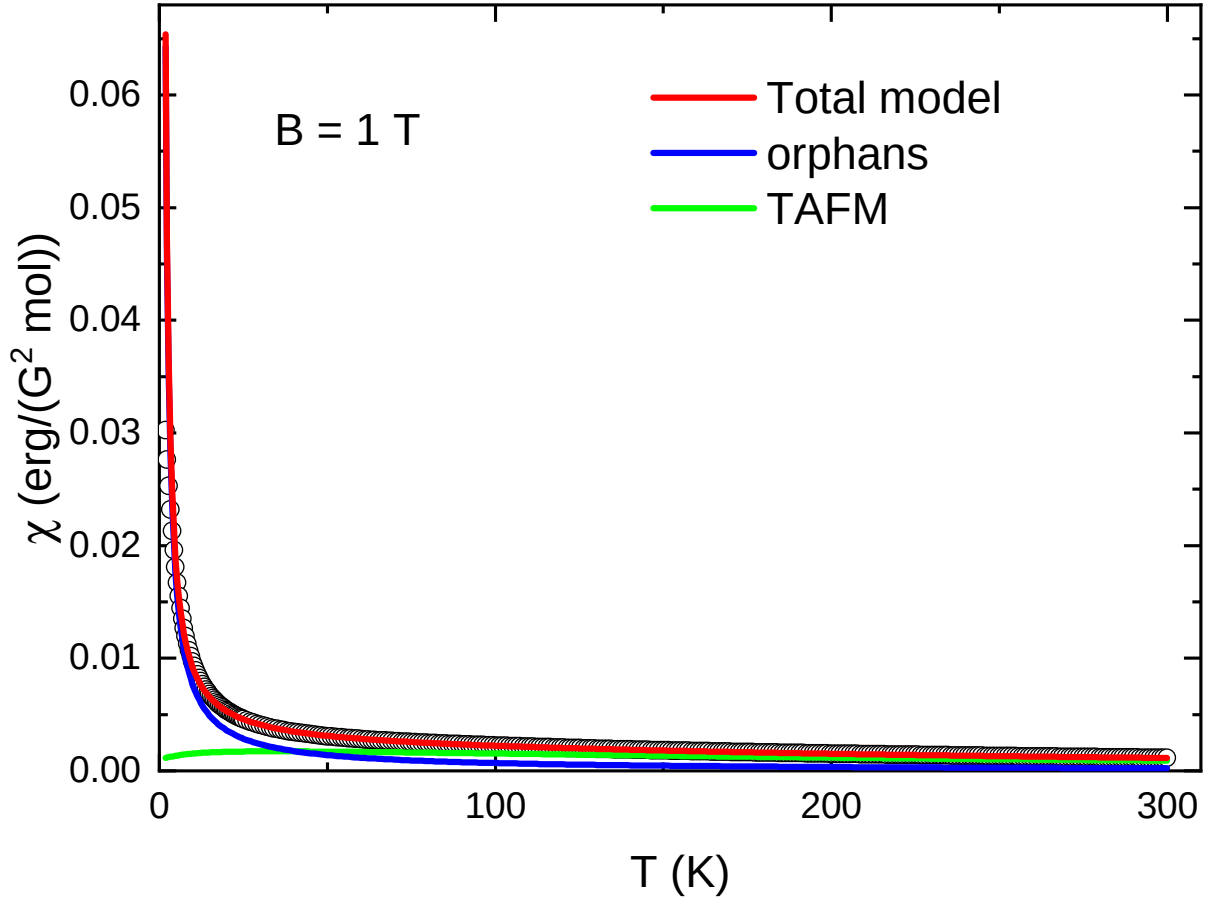


Figure 4.10: Magnetic susceptibility χ is depicted against temperature at $B = 1$ T. The model from equation 4.3 is drawn in red. In green, the curve of the bulk magnetization is shown in form of a TAFM function. The Brillouin function representing the orphan spins is drawn in blue.

two Brillouin functions in equation 4.2. The model can be reused for the $M(T)$ measurement by replacing the linear term of equation 4.2 with a TAFM function and changing prefactors to adjust the units, leading to the following model:

$$\chi = \frac{f_1 g_1 \mu_B J_1 N_A}{B} B_{J_1} \left(\frac{g_1 \mu_B J_1 B}{k_B (T - \theta)} \right) + \frac{f_2 g_2 \mu_B J_2 N_A}{B} B_{J_2} \left(\frac{g_2 \mu_B J_2 B}{k_B T} \right) + \text{TAFM}(T, C_{\text{TAFM}}, J) \quad (4.4)$$

As for the $M(B)$ model, the total angular momentum of the orphan spin Brillouin function J_1 is fixed to $1/2$ and the Landé factor $g_1 = 2.24$. The second Landé factor was also set to $g_2 = 2.24$ and the remaining parameters of the Brillouin functions were fixed to the values found in the $M(B)$ analysis. Consequently, only the parameters of the TAFM function are determined in a fit to the 1 T FCW measurement.

Next neighbor antiferromagnetic interactions are calculated to $J/k_B = 90 \pm 5$ K with the according

Curie constant $C_{\text{TAFM}} = 0.40 \pm 0.02 \text{ erg K/G}^2 \text{ mol}$.

In figure 4.11, the complete model as well as all three single contributions are drawn with the 1 T measurement.

The Curie constant C_{TAFM} is remarkably lower than the theoretical value. A reason for that could be that the existence of orphan spins reduces the amount of spins per unit cell. By building the fraction $\frac{C_{\text{TAFM}}}{C_{\text{spin } 1/2}} = \frac{0.40}{0.471} \approx 0.85$, the measured C_{TAFM} implies that only ~85 % of Cu^{2+} spins are in the correlated phase, while ~15 % of Cu^{2+} spins are orphan spins. This result matches the finding of model 4.3. As well, the interaction strength J fits together well for both models. By using two Brillouin functions, the magnetization of the whole temperature domain can be described well. However, only one Brillouin function can be physically explained by orphan spins. The second Brillouin function is of unknown origin and casts doubts on the physical justification of this model. In conclusion, the two Brillouin function models should be regarded as phenomenological models with parameters which might not describe reality.

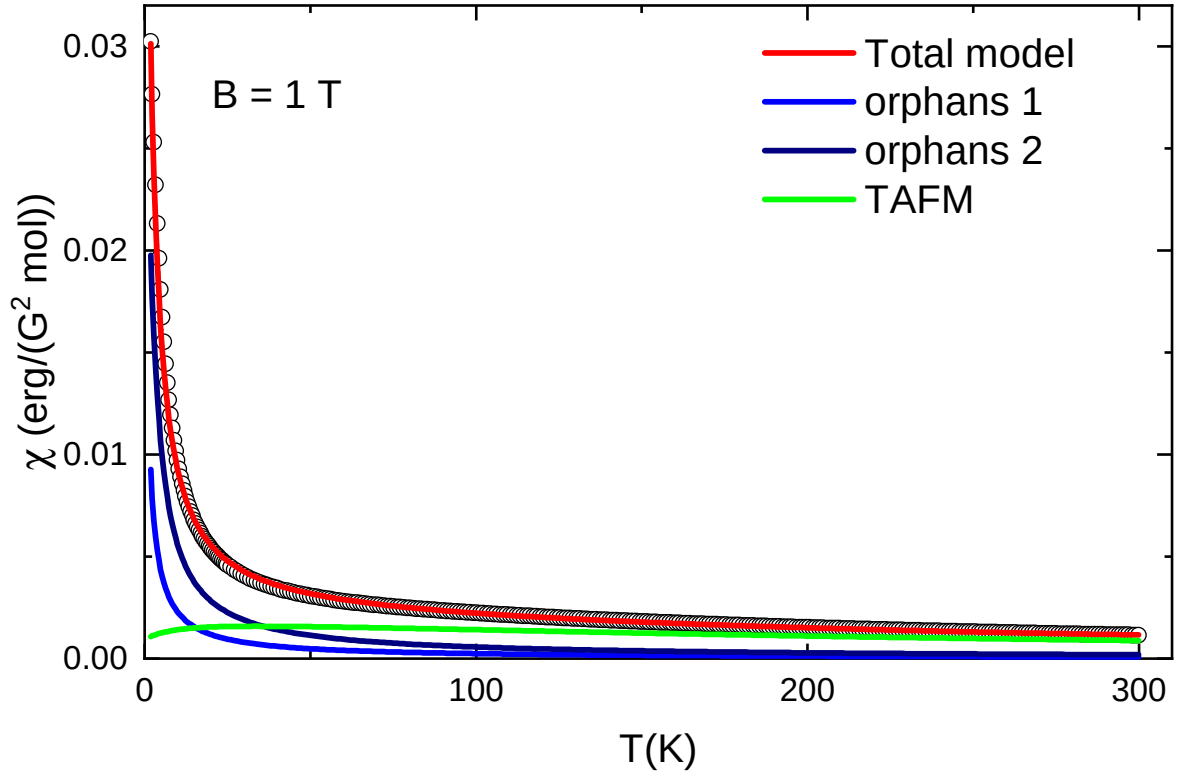


Figure 4.11: Magnetic susceptibility χ is depicted vs. temperature at $B = 1$ T. The model from equation 4.4 is drawn in red. Two orphan components are plotted as blue and dark blue line. They show the magnetization of the two Brillouin functions index by 1 and 2 from equation 4.4. In green, the curve of the correlated spin magnetization is shown in form of a TAFM function.

4.3 Heat capacity

Heat capacity was measured in different fields up to 200 K. The corresponding specific heat data is depicted in figure 4.12. For temperatures above 35 K, all measurements align well and follow a phonon like behavior. No phase transition is visible in the temperature regime studied in this thesis.

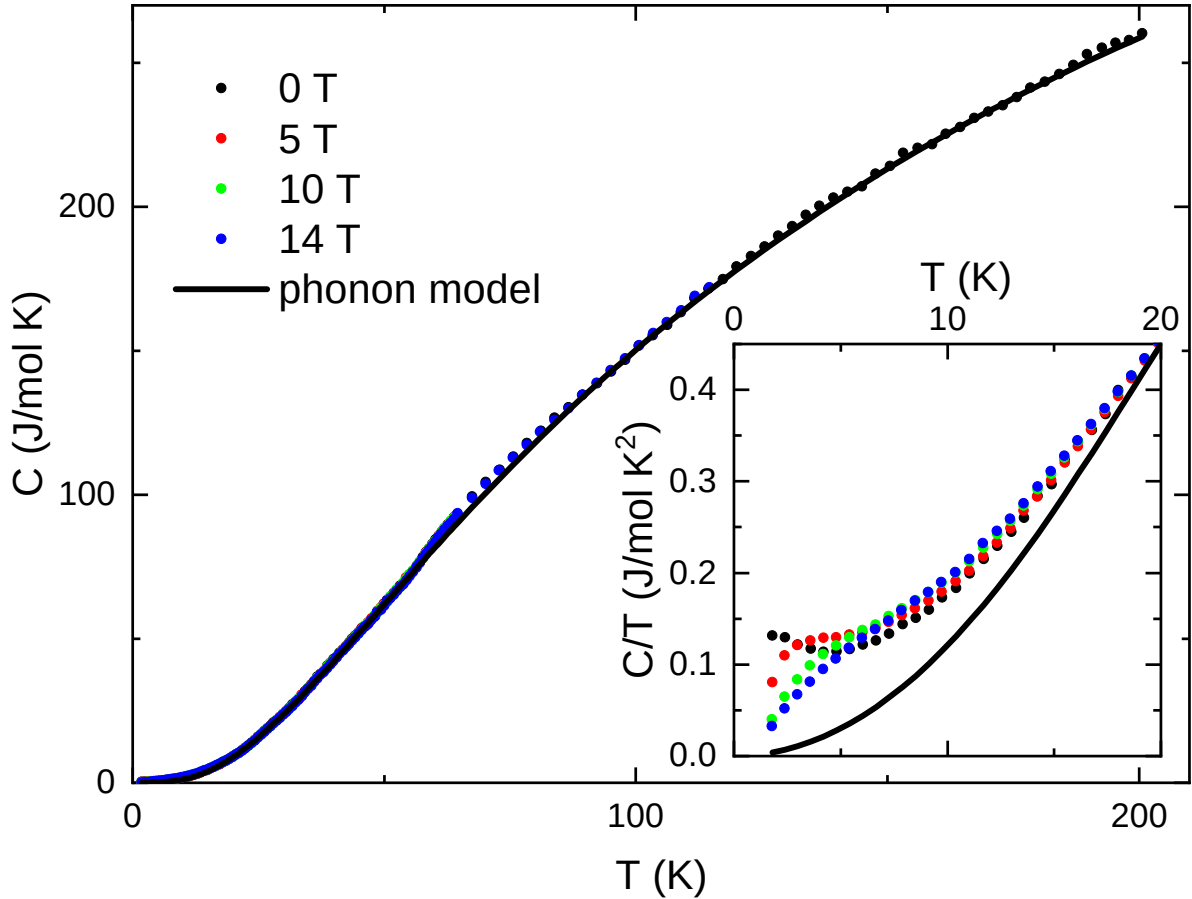


Figure 4.12: Specific heat is plotted against temperature for $B = 0$ T, 5 T, 10 T and 14 T applied magnetic field. The black line shows the lattice specific heat approximated by a phonon model combining Debye and Einstein functions. **Inset:** C/T is drawn in the low temperature regime up to 20 K.

The inset of figure 4.12 shows C/T in the low temperature region. For lowest temperatures, the beginning of a broad peak is visible on the left flank of the zero field data. With rising field, this peak shifts towards higher temperatures and spreads more. This shows the existence of a small Schottky contribution, which will be analyzed later.

The zero field measurement is used to determine the lattice contribution of the specific heat. Testing different models, best results for aligning the lattice specific heat with as large domains

of the measurement as possible, while not producing negative non-lattice specific heat, led to a model with one Debye function and three Einstein functions:

$$C_{\text{lattice}} = C_{\text{D}} + \sum_{i=1}^3 C_{\text{E}, i} \quad (4.5)$$

Some temperature regions in the measured data needed to be excluded in order to obtain positive non-lattice specific heat. The excluded temperature regions are:

1.8 K $\rightarrow$ 21 K
 23 K $\rightarrow$ 30 K
 33 K $\rightarrow$ 47 K
 55 K $\rightarrow$ 92 K
 109 K $\rightarrow$ 161 K
 181 K $\rightarrow$ 200 K

By fitting the phonon model in the remaining temperature region to the zero field measurement, the lattice specific heat is estimated. The resulting parameters of this fit are in table 4.1.

	Debye	Einstein		
n	2.9	3.8	4.6	4.6
$\theta_{\text{D/E}}$ (K)	167	248	446	892

Table 4.1: Parameters of the Debye and Einstein functions representing the lattice specific heat of $\text{Sr}_3\text{CuSb}_2\text{O}_9$. $\theta_{\text{D/E}}$ denotes the Debye or Einstein temperature of the according model, n is the weighting of the function.

All prefactors n_{Debye} of the Debye and Einstein functions add up to $n \approx 15.9$, which is close to the total amount of ions in one unit cell. This model is used as lattice contribution in all measurements of this compound. The non-lattice contribution can be calculated by subtracting the lattice function from the data. Figure 4.13 on the left shows the non-lattice specific heat $C_{\text{non-lattice}}$.

$C_{\text{non-lattice}}$ shows additional specific heat contributions up to ~ 90 K. However, the magnetic specific heat is expected to be present at lower temperatures and without local minima [17, 34, 39, 40]. Therefore, the analysis presented below focuses on the low temperature region up to the first minimum at roughly 23 K.

On the right side of figure 4.13, the non-lattice specific heat in the low temperature regime up to 35 K is plotted. In this low temperature domain all measurements show a similar broad peak. Nevertheless, with rising field, the height of the peak increases and the low temperature

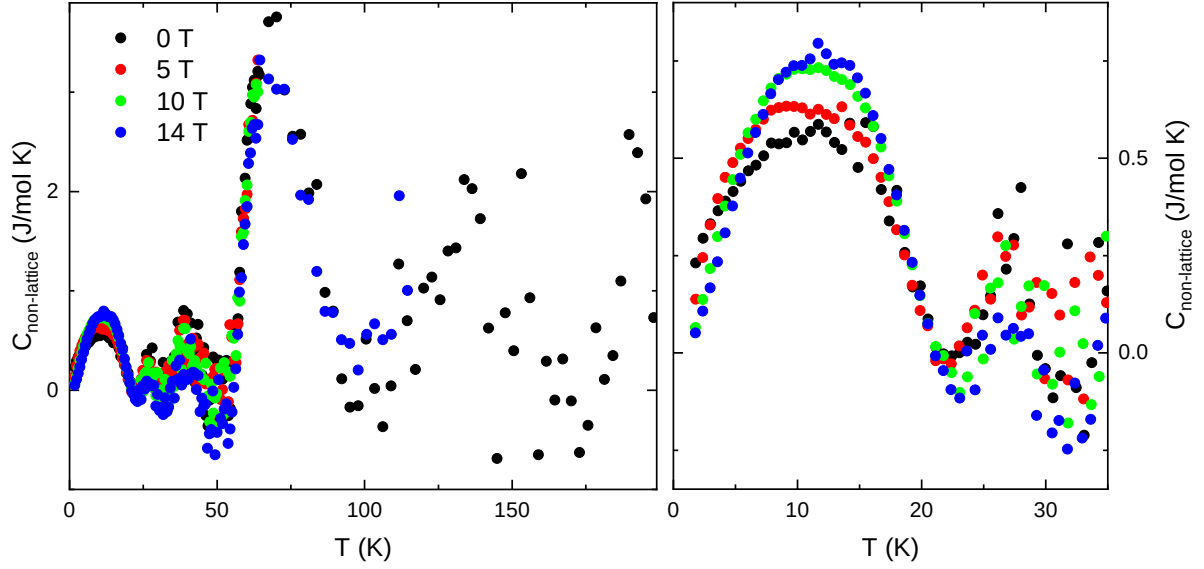


Figure 4.13: **left:** Non-lattice specific heat of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ for all measured temperatures. **right:** Non-lattice specific heat in the low temperature regime where magnetic specific heat is expected.

flank moves to higher temperatures. Like the findings in C/T , these observations hint towards a Schottky contribution in the data. To quantify the Schottky term, following ansatz is used [34, 39, 41]:

$$\frac{\Delta C_{\text{non-lattice}}}{T^2} = \frac{C_{\text{non-lattice}}(B) - C_{\text{non-lattice}}(B = 0)}{T^2} \quad (4.6)$$

The difference between field data and zero field data is calculated and weighted by $1/T^2$. Because of the weighting, low temperature data is stressed more than high temperature data. The measured data is then approximated by the following model:

$$\frac{\Delta C_{\text{non-lattice}}}{T^2} = \frac{f}{T^2} [C_{\text{Schottky}}(\Delta(B \neq 0)) - C_{\text{Schottky}}(\Delta(B = 0))] + C_0 \quad (4.7)$$

Here, $C_{\text{Schottky}}(\Delta)$ is the standard two-level Schottky term from equation 2.19 with the energy gap Δ between the two levels. Not all spins but only a fraction f are expected to contribute to the Schottky term. C_0 accounts for a small offset. This Schottky model was fitted to the weighted non-lattice specific heat.

The measured data and the model functions are displayed in figure 4.14. The results of the fit can be seen in table 4.2.

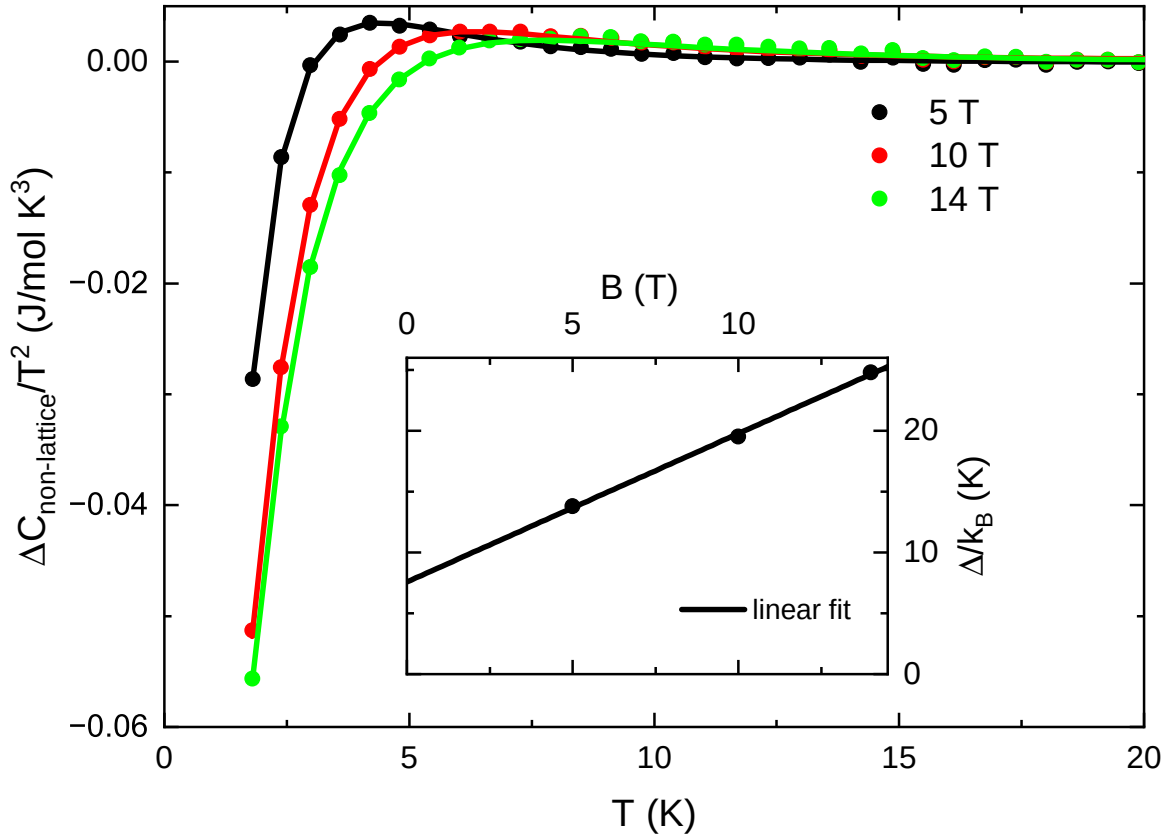


Figure 4.14: Difference of in-field and zero field non-lattice specific heat divided by T^2 vs. temperature. Lines in the respective colors show the Schottky model to the corresponding data.

Inset: In-field energy gaps Δ calculated from the Schottky contributions against magnetic field. As the points roughly depend linearly on field, a linear fit is depicted as black line.

Equation 4.7 describes a Schottky model for free spins with two non-degenerate energy levels. As seen in the magnetization measurements, at low temperatures orphan spins exist which seemingly represent free spins. Hence, the Schottky contribution to specific heat can be assigned to orphan spins. The fraction f claims around 3 % to 5 % of Cu^{2+} spins are orphan spins. In $M(B)$ measurements at $T = 1.8$ K, the fraction of orphan spins was calculated to be roughly 5 %, which matches with the Schottky model result. $M(B)$ and the Schottky model give rise to low temperature conclusions as $M(B)$ was performed at 1.8 K and the Schottky model is most dominant below 8 K.

In contrast, the $\chi(T)$ measurement determined the fraction $f \approx 15$ %. However, $\chi(T)$ models were most accurate at higher temperatures and could only describe the measurement down to roughly ~ 20 K. In light of these results, it seems that the amount of free-like orphan spins rises with temperature.

	$B = 5 \text{ T}$	$B = 10 \text{ T}$	$B = 14 \text{ T}$
$\Delta(B)/k_B \text{ (K)}$	13.8 ± 0.4	19.5 ± 0.3	24.8 ± 0.5
$\Delta(B=0)/k_B \text{ (K)}$	3.22 ± 0.15	4.83 ± 0.06	5.30 ± 0.05
$f \text{ (\%)}$	3.06 ± 0.07	4.67 ± 0.02	5.24 ± 0.03
$C_0 \text{ (} 10^{-5} \text{ J/mol K)}$	-8.8 ± 5.3	8.2 ± 4.3	-10.2 ± 4.7

Table 4.2: Parameters of the Schottky model 4.7 determined by fitting the function to the measurements at different fields.

Following the assumption of orphan spins causing the Schottky specific heat, the energy level splitting Δ is caused by the Zeeman effect [34, 39]. With $S = 1/2$, Δ should obey the law:

$$\Delta = \Delta_0 + g\mu_B B \quad (4.8)$$

Here, Δ_0 is the energy gap between the levels in zero magnetic field and g is the Landé factor. The energy gaps $\Delta(B)$ and the linear model 4.8 are depicted in the inset of figure 4.14. From this model, the Landé factor $g = 1.82 \pm 0.08$ and the zero field energy splitting $\Delta_0/k_B = 7.6 \pm 0.5 \text{ K}$ are calculated.

Surprisingly, the zero field energy level splitting Δ_0 is not zero. This contradicts the concept of free-like orphan spins where the zero field states should be degenerate. However, this phenomenon has been observed also in the similar compound $\text{Ba}_3\text{CuSb}_2\text{O}_9$ [34] with a smaller deviation from zero. There, the zero field splitting is assigned to site disordered Cu^{2+} orphan spins which couple weakly to the correlated spin liquid phase.

The Landé factor originating from the Zeeman model $g = 1.82 \pm 0.08$ is notably smaller than $g_{\text{ESR}} = 2.24$ measured in ESR by [35]. Also, the zero field splitting Δ_0 calculated by the Schottky models for every field measurement yield smaller values than the Zeeman linear model (see table 4.2). Further field dependencies besides the Zeeman effect may be altering the orphan spins. Hence the Zeeman results should be regarded with caution.

The non-lattice specific heat can be corrected with respect to the Schottky term by subtracting a Schottky contribution with the parameters from table 4.2. For the zero field measurement, the parameters calculated in the $B = 14 \text{ T}$ Schottky model are used to calculate the Schottky contribution.

The remainder after subtraction is the magnetic contribution to the specific heat C_{mag} , which is plotted in figure 4.15.

The observed magnetic specific heat is approximately field-independent, as all field dependence was eliminated in the Schottky analysis. The shape of the magnetic specific heat is a broad peak with center at roughly 12 K, extending to ~23 K.

To get insight into the magnetic ground state of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ the magnetic entropy S_{mag} can be

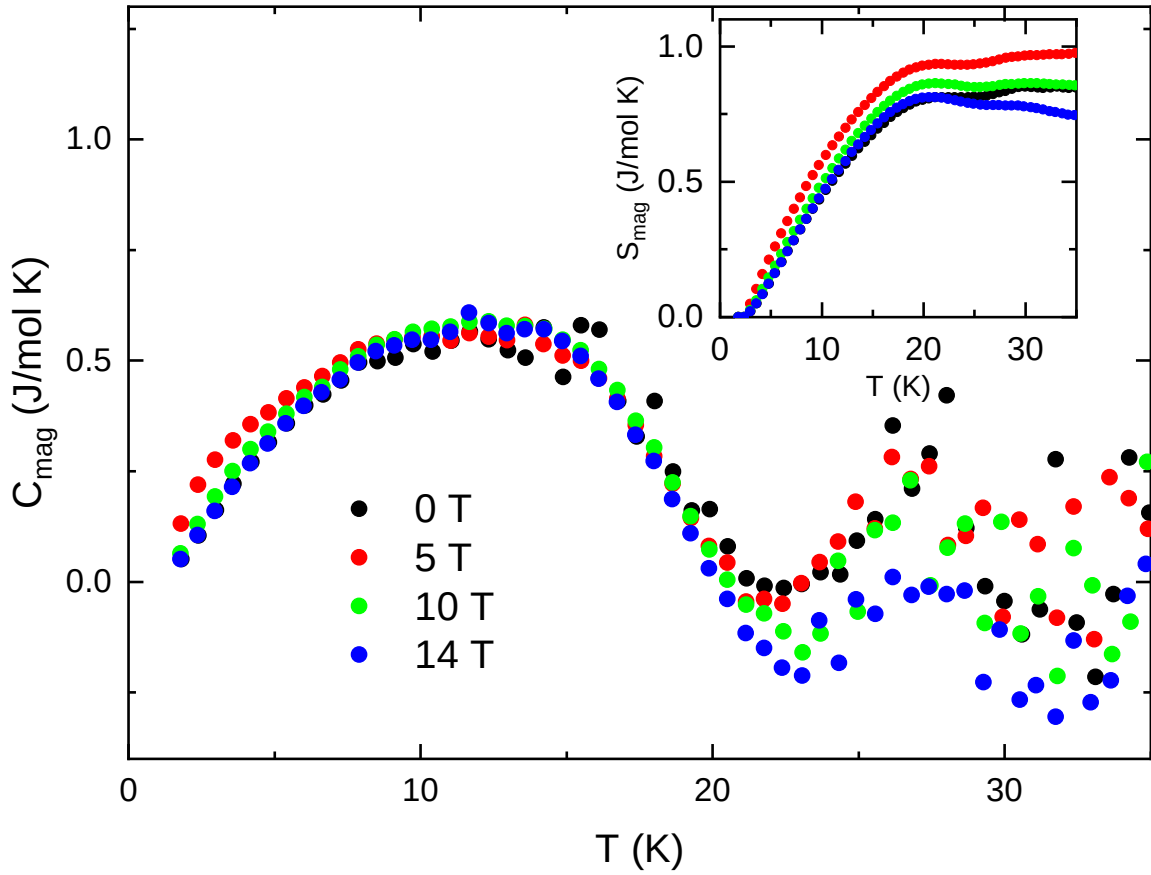


Figure 4.15: Magnetic specific heat of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ vs. temperature.
Inset: Magnetic entropy S_{mag} vs. temperature.

calculated with following equation:

$$S_{\text{mag}} = \int \frac{C_{\text{mag}}}{T} dT \quad (4.9)$$

In the inset of figure 4.15, the magnetic entropy is shown. For all measurements, the magnetic entropy rises similarly. It saturates from ~ 23 K on at roughly $S_{\text{sat}} \approx 0.9$ J/mol K. To estimate the full magnetic entropy in the compound, also the specific heat at lower temperatures than 1.8 K needs to be regarded. From 1.8 K to 0 K, the magnetic specific heat can be extrapolated linearly to zero.

The mean of the measurements at 1.8 K for all measured fields is ~ 0.08 J/mol K. With this the magnetic entropy can be extrapolated:

$$S_{\text{ext}} = \int_0^{1.8} \frac{0.08}{1.8} \frac{T}{T} \text{ J/mol K}^2 dT = 0.08 \text{ J/mol K} \quad (4.10)$$

Thus, a vague estimate of the full measured magnetic entropy is the sum $S_{\text{max}} = S_{\text{sat}} + S_{\text{ext}} \approx$

1.0 J/mol K.

The theoretical value of the maximum magnetic entropy is $S_{\text{theory}} \approx 5.76$ J/mol K.

The large difference between measured S_{max} and S_{theory} might indicate that there is entropy in the ground state left. A highly degenerate ground state supports the assumption of a quantum spin liquid state in $\text{Sr}_3\text{CuSb}_2\text{O}_9$. However, the calculated magnetic entropy highly depends on how the lattice specific heat and the Schottky specific heat were determined. Furthermore, restricting the magnetic specific heat to temperatures lower than 23 K might be a wrong assumption. If the magnetic specific heat is extended to higher temperatures, the magnetic entropy adds up more. However, even for considering magnetic specific heat up to 200 K, the theoretical value is not reached.

Sr₃ZnIr₂O₉

In the search for quantum spin liquids, Iridium based compounds have been intensely studied. Often materials hosting Ir⁴⁺ ions are investigated as they seem to be good candidates for Kitaev quantum spin liquids [11, 42, 43]. In the family of triple perovskites, Ba₃CoIr₂O₉ [44, 45], Ba₃MgIr₂O₉, Ba₃SrIr₂O₉, Ba₃CaIr₂O₉ [46] and Ba₃ZnIr₂O₉ [17, 47] were studied among others. In these compounds, iridium was attested to form Ir⁵⁺ ions, which would lead to a $J = 0$ ground state in the case of free ions [17, 44, 46]. Intriguingly, these materials were still found to be magnetic and hold interesting magnetic phenomena.

Ba₃ZnIr₂O₉ serves as prefiguration for Sr₃ZnIr₂O₉, as it is the closest relative to Sr₃ZnIr₂O₉ published in literature. The space group of Ba₃ZnIr₂O₉ was determined to P6₃/mmc (194) [17]. In this structure, iridium is surrounded by a O₆ octahedron. Along the c -axis, two IrO₆ octahedra share a face, leading to an Ir₂O₉ dimer. Within the a - b plane, the iridium dimers form a triangular lattice. The structure of Ba₃ZnIr₂O₉ is depicted in figure 5.1. The space group P6₃/mmc (194) was also measured in Sr₃ZnIr₂O₉ by Dr. Charu Garg.

Electronically, with the structure formula Ba₃²⁺Zn²⁺Ir₂⁵⁺O₉²⁻ all ions possess fully filled shells except for the 5 d^4 orbitals in the Ir⁵⁺ ions [17]. Because of the crystal field by the surrounding O₆ octahedra, the 5 d orbitals split in threefold degenerate t_{2g} and twofold degenerate e_g orbitals. Hereby, t_{2g} lies lower in energy than e_g . As a result of spin orbit coupling (SOC) t_{2g} splits into twofold degenerate Γ_7 and fourfold degenerate Γ_8 orbitals. In the ground state, Γ_8 is occupied by the four valence electrons of Ir⁵⁺. Nominally, the full Γ_8 gives rise to a $J = 0$ state. However, Ir⁵⁺ compounds are found to be magnetic, which has been attributed to intra dimer superexchange interactions and reduced SOC by solid state effects [46]. Therefore, Ba₃ZnIr₂O₉ is called to be in a near $J = 0$ state.

Measurements of magnetization, heat capacity and muon spin spectroscopy show no sign of spin freezing or phase transitions down to 100 mK [17]. From magnetization measurements an effective magnetic moment $\mu_{\text{eff}} \approx 0.2 \mu_B/\text{Ir}$ and a Weiss temperature $\theta_W \approx -30$ K were determined [17]. This evidences strong frustration in Ba₃ZnIr₂O₉. Magnetic specific heat was detected up to 30 K, which gives rise to magnetic entropy of roughly $S_{\text{mag}} = 1.3$ J/mol K [17]. The strong frustration and low magnetic entropy might indicate a QSL state in Ba₃ZnIr₂O₉.

Sr₃ZnIr₂O₉ studied in this thesis is expected to behave similarly to Ba₃ZnIr₂O₉ because of the

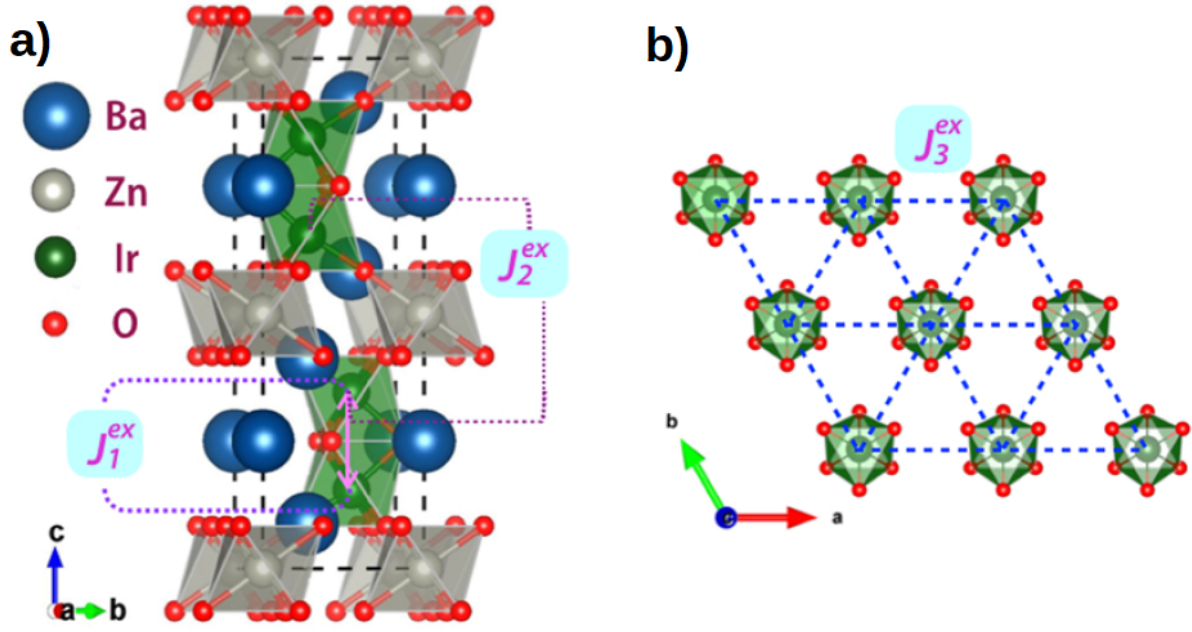


Figure 5.1: Crystal structure of $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ (space group $P6_3/mmc$ (194))[17]. **a)** shows the b - c plane, where Ir_2O_9 dimers form along the c -axis. **b)** illustrates the triangular lattice of Ir_2O_9 dimers in the a - b plane.

similar constituents in both compounds.

5.1 Experimental details

$\text{Sr}_3\text{ZnIr}_2\text{O}_9$ polycrystals studied in this thesis were grown by Charu Garg and Sunil Nair (both from Indian Institute of Science Education and Research Pune). The samples are pressed pellets which were cut to appropriate size for measurements. Different measurements were conducted on different samples from the same batch. The $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ pellets are very fragile, which made sample preparation challenging as the sample easily breaks or small parts flake off. To avoid absorption of water or oxygen, the samples were stored in an argon atmosphere between measurements. An example of the $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ samples is shown in figure 5.2.

Measurements of magnetization were conducted employing a MPMS both in DC and in VSM mode. For the field dependence of the magnetization, a sample of mass $m = 11.51 \pm 0.08$ mg was used. The magnetization was measured in DC mode by cooling the sample to 1.8 K, then driving the field up to $B = 7$ T and consequently down to $B = -0.5$ T. Temperature dependence of the magnetization was measured on the same sample using a FC sequence. In this process, the field was fixed to $B = 1$ T, 3 T and 7 T and temperature was driven up from 1.8 K to 300 K. For the 7 T measurements, data was not recorded from 15 K to 25 K because of unknown technical issues.



Figure 5.2: Example of an $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ sample studied in this thesis.

Further temperature dependence measurements of magnetization were performed using the VSM mode of MPMS. The same sample measured in $B = 1$ T from $T = 1.8$ K to 300 K in a ZFCW and FCC sequence. For all magnetization measurements according background measurements were recorded and the data was corrected.

Heat capacity was measured using a thermal relaxation method provided by an option of a physical properties measurement system (PPMS). A sample of mass $m = 3.1 \pm 0.1$ mg was fixed on the measurement setup with Apiezon N grease and inserted in the device. In fields of $B = 0$ T and 14 T, heat capacity was measured from 1.8 K up to 200 K. Supplementary measurements with $B = 5$ T and 10 T were performed in the temperature range from 1.8 K to 64 K.

5.2 Magnetization

5.2.1 Field dependence of magnetization

Measurements of the field dependence of magnetization were conducted at $T = 1.8$ K in fields up to 7 T. The resulting curve is plotted in figure 5.3.

For $B \leq 2$ T the magnetization shows right bending which decreases with rising field. At fields larger than ~ 4 T, the magnetization is almost linear. The curve does not show any sign of saturation. At highest measured magnetic field ($B = 7$ T), the magnetization reaches $M \approx 0.08 \mu_B/\text{f.u.}$. Further, no hysteresis can be detected in the measurement.

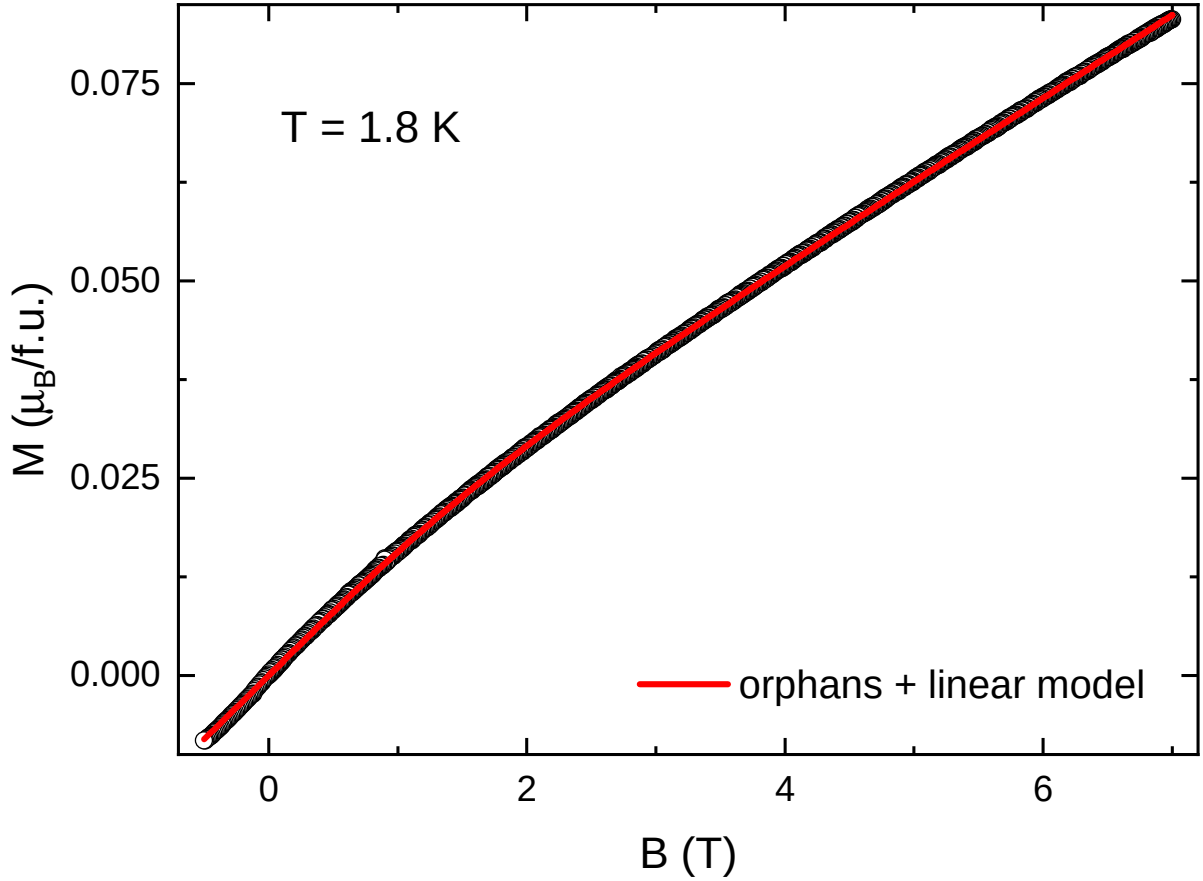


Figure 5.3: Magnetization M vs. applied magnetic field B at 1.8 K. The black circles show the measured data. The red line represents a fit to the data using a model combining an orphan contribution described by a Brillouin function and a linear function for the bulk of the material.

Magnetization in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ is influenced by different inherent structural characteristics. First, next neighbor iridium ions form dimers with unclear effective total angular momentum J . Secondly, these dimers are arranged in a triangular lattice. For antiferromagnetic inter dimer coupling, this leads to frustrated interactions. Lastly, dimers can decouple from the correlated dimer region giving rise to "orphan dimers" similar to orphan spins in $\text{Sr}_3\text{CuSb}_2\text{O}_9$ and many other compounds [36]. To quantify the influence of these effects on the shape of $M(B)$, different models are applied to the measured data. Isolated dimers can be modeled in units of $\mu_B/\text{f.u.}$ by equation 5.1 [48]:

$$M_{\text{Dimer}} = 2fg \frac{\sinh\left(\frac{g\mu_B B}{k_B T}\right)}{2 \cosh\left(\frac{g\mu_B B}{k_B T}\right) + \exp\left(\frac{J_{\text{Dimer}}}{k_B T}\right) + 1} \quad (5.1)$$

In this model, f describes the amount of dimers per formula unit and J_{Dimer} denotes the exchange interaction strength within the dimer. Here, $J_{\text{Dimer}} > 0$ corresponds to antiferromagnetic

coupling.

This model of isolated dimers was fitted to the data. Furthermore, a combination of a linear function and the dimer model was deployed to describe the measurement. In this case, few isolated dimers are considered by the Dimer function, whereas the linear term describes the magnetization of a large correlated domain.

Ignoring the dimer formation of the Ir ions, also the combination of a Brillouin function and a linear term served as model for $M(B)$. Here, Ir_2O_9 dimers are assumed to couple strongly so they form one single magnetic moment which behaves like an ordinary spin. Most of these dimers form a correlated region which is described by the linear term, while some "orphan dimers" or orphan spins decouple from the rest and give rise to a Brillouin like magnetization.

The model of isolated dimers, the sum of a linear function and isolated dimers and the sum of a linear function and a Brillouin function were fitted to the data. For the Brillouin function, the Landé factor g was fixed to 2 to reduce correlations with J . The results of the fits can be found in table 5.1.

Dimer	Dimer + linear function	Brillouin + linear function
$f = 0.19 \pm 0.05$	$f = (3.3 \pm 0.2)10^{-3}$	$f = (4.28 \pm 0.06)10^{-3}$
$g = 0.628 \pm 0.12$	$g = 3.00 \pm 0.12$	$g = 2$ (fixed)
$J_{\text{Dimer}}/k_B = 5.8 \cdot 10^{-15} \pm 1.0$ K	$J_{\text{Dimer}}/k_B = 1.3 \cdot 10^{-12} \pm 0.3$ K	$J = 1.223 \pm 0.012$
	$a_0 = (1.054 \pm 0.002)$ $\cdot 10^{-2} \mu_B/\text{f.u. T}$	$a_0 = (1.046 \pm 0.001)$ $\cdot 10^{-2} \mu_B/\text{f.u. T}$

Table 5.1: Parameters of different models fitted to $M(B)$ at $T = 1.8$ K. The fraction f describes the amount of dimers/orphans per unit cell and g is the Landé factor which was fixed to $g = 2$ in the Brillouin function. For the dimer models J_{Dimer} is the intra dimer exchange interaction. In the Brillouin model J is the total angular momentum. For the models containing a linear part a_0 is the slope of the linear function.

The model of only isolated Dimers fails to describe the measured data well. Furthermore, the resulting g factor and the exchange interaction J_{Dimer} are unusually low, which rejects the assumption of isolated dimers in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$. The combination of the dimer model with a linear function matches well with the measured magnetization data. However, the parameters resulting from this model contain a too high g value and too low J_{Dimer} . The model containing a Brillouin function and a linear function describes the data best and yields reasonable results. It is depicted in figure 5.3 as red line. Consequently, the right bending near zero field in $M(B)$ can be assigned to roughly 0.4 % "effective" orphan spins per formula unit with total angular momentum $J \approx 1.2$. Whether these orphan spins origin from dimers which decouple from the correlated domain of the sample or from other defects is unclear.

5.2.2 Temperature dependence of magnetization

Temperature dependence of magnetization was measured from $T = 1.8$ K up to $T = 300$ K at constant fields $B = 1$ T, 3 T and 7 T. The resulting magnetic susceptibility $\chi(T)$ and the inverse susceptibility $\chi^{-1}(T)$ can be found in figure 5.4.

In all measurements a small hump around ~ 50 K appears. This hump is a signal produced by oxygen trapped on the porous sample [38]. The peak provides no information about the magnetic properties of the sample itself. In the following discussion, the oxygen peak is ignored and fits are executed without the oxygen peak region from 40 K to 58 K.

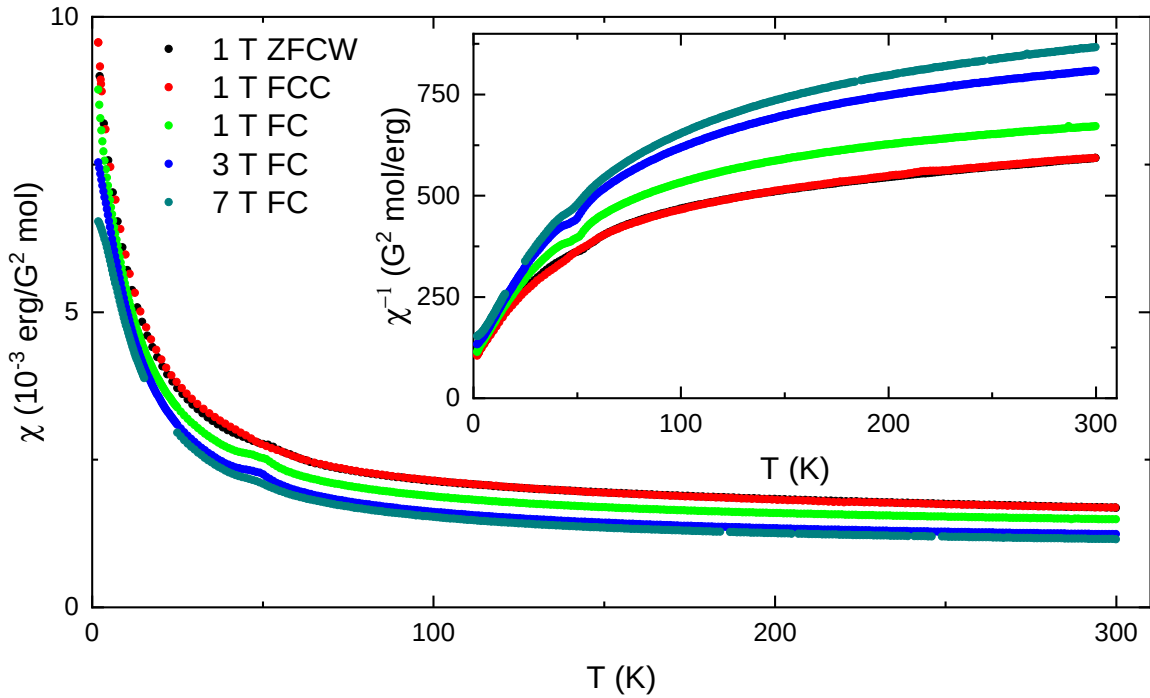


Figure 5.4: Magnetic susceptibility χ vs. temperature for different measurement protocols as described in the text. **Inset:** Inverse susceptibility χ^{-1} vs. temperature.

Besides the oxygen peak, no sign of magnetic phase transition can be found in the $\chi(T)$ measurements. The inverse susceptibility $\chi^{-1}(T)$ shows right bending which lessens with rising temperature (see inset in figure 5.4). Up until 300 K, there is still a little right bending left but the curves slowly saturate to a constant value. This hints towards a large temperature independent contribution to the magnetic susceptibility.

At a field of 1 T, measurements while heating and cooling the sample were performed to check for hysteresis in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$. The susceptibility of this ZFCW and FCC measurements are depicted in figure 5.5.

There is only little difference visible between both measurements. For better visualization, the

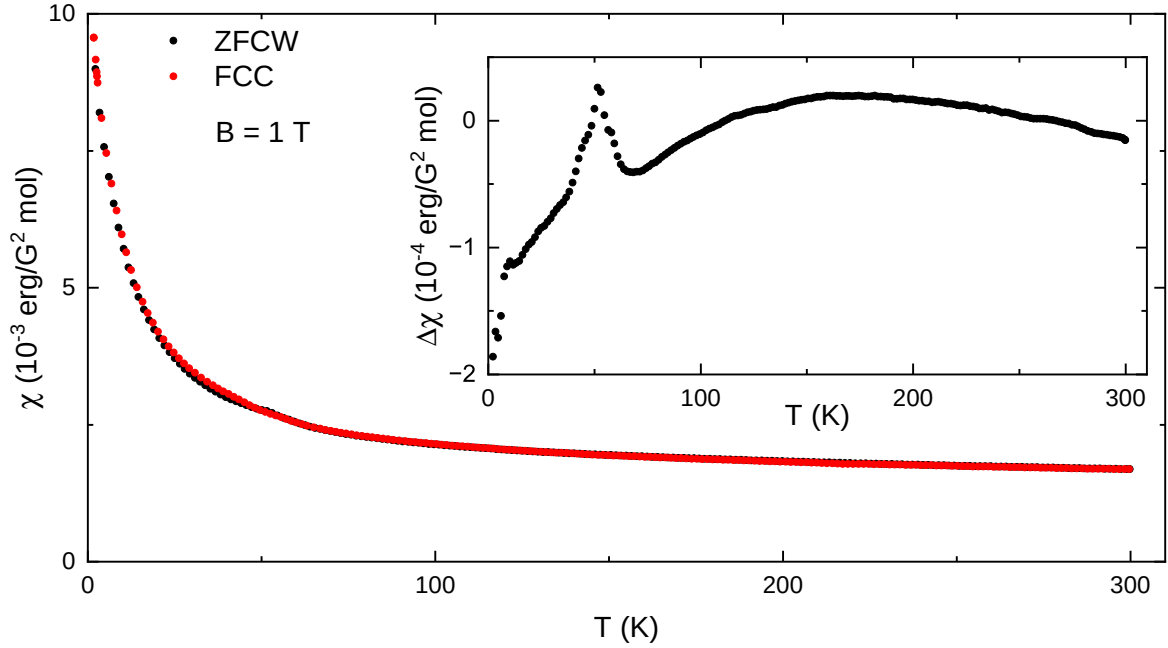


Figure 5.5: Magnetic susceptibility χ vs. temperature measured at $B = 1$ T with a ZFCW and FCC protocol. **Inset:** Difference $\Delta\chi = \chi_{\text{ZFCW}} - \chi_{\text{FCC}}$ vs. temperature.

difference between both measurements $\Delta\chi = \chi_{\text{ZFCW}} - \chi_{\text{FCC}}$ is plotted in the inset of figure 5.5. At temperatures above 100 K, $\Delta\chi$ is small. Below 100 K the difference generally becomes larger with decreasing temperature. Around 50 K, the oxygen peak is clearly visible. Overall, the difference between the measurements is at least one magnitude smaller than the susceptibility data. In conclusion, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ shows very little and negligible hysteresis.

To quantify the interactions in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ a modified Curie-Weiss fit (see equation 2.10) in the range of 150 K to 300 K was performed on the $B = 1$ T data. The susceptibility $\chi(T)$ and inverse susceptibility $\chi^{-1}(T)$ with the according model functions are shown in figure 5.6.

The resulting fits align well with the measured data in the high temperature region down until ~ 130 K. As strong right bending of $\chi^{-1}(T)$ implies, a large temperature independent susceptibility $\chi_0 = (1.23 \pm 0.05)10^{-3}$ erg/G² mol is found by the fit. The Curie constant $C = (9 \pm 2)10^{-2}$ erg K/G² mol reflects the near $J = 0$ state. This Curie constant corresponds to an effective magnetic moment of $\mu_{\text{eff}} = 0.85 \pm 0.09 \mu_B/\text{f.u.}$. Furthermore, the fit yields a Weiss temperature of $\theta_W = -39 \pm 8$ K, which implies intermediate AFM interactions. These results give rough estimates of the characteristics of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$, but their precise value should be considered with care. As seen for $\text{Ba}_3\text{ZnIr}_2\text{O}_9$, the values of especially θ_W and C strongly vary with different temperature fit ranges [49]. A comparison of Curie-Weiss fits in different temperature regions is presented in the appendix.

To improve on the high temperature Curie-Weiss fit, a model using the results from the $M(B)$

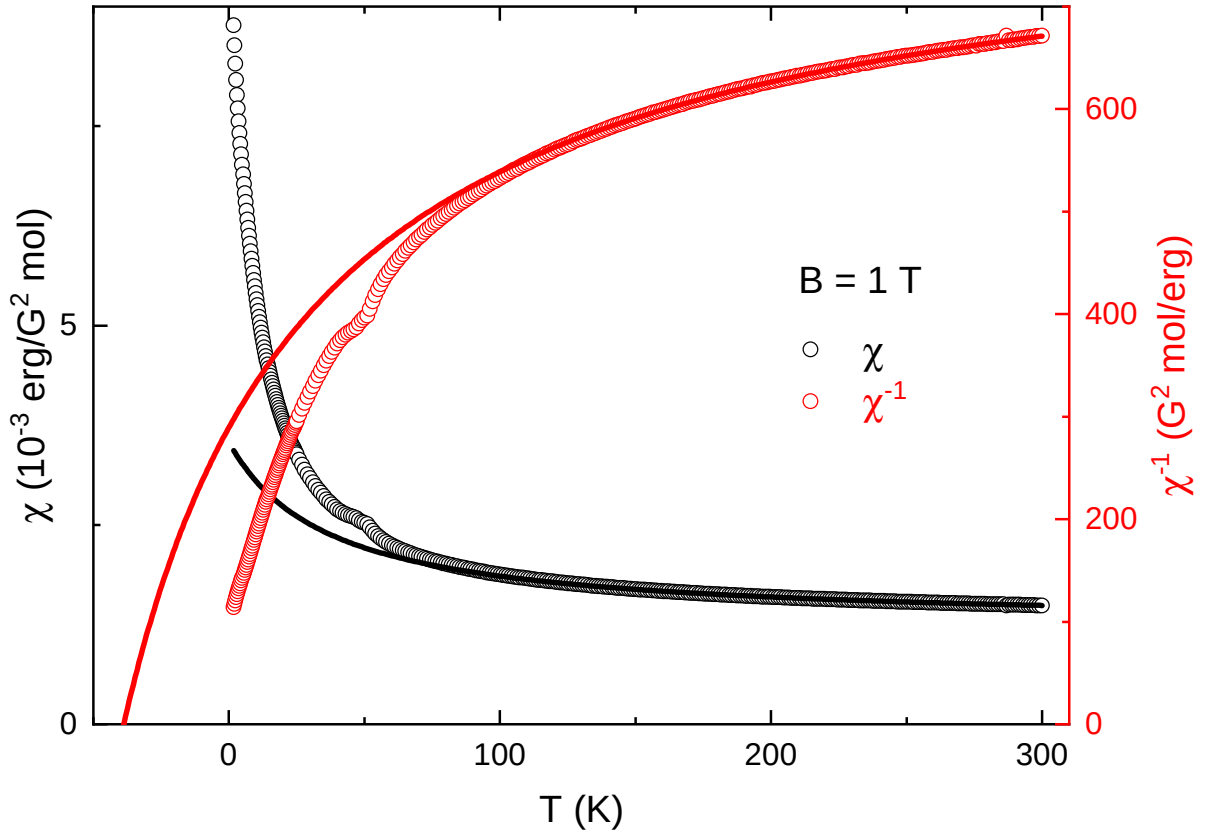


Figure 5.6: Magnetic susceptibility χ on the left in black and inverse susceptibility χ^{-1} on the right axis in red vs. temperature measured at $B = 1$ T. The lines show a modified Curie-Weiss fit (see equation 2.10) to the data in the temperature range from 150 K to 300 K.

measurements is applied. In $M(B)$ orphan spins giving rise to a Brillouin like magnetization were found. Including this Brillouin function and allowing a temperature independent offset leads to the following model:

$$\chi = \frac{fg\mu_B N_A J}{B} B_J \left(\frac{g\mu_B J B}{k_B T} \right) + \frac{C}{T - \theta_W} + \chi_0 \quad (5.2)$$

The parameters f , g and J of the Brillouin function are taken from table 5.1. This model is fitted to χ^{-1} data only excluding the oxygen peak in the temperature region from $T = 40$ K to 58 K. The resulting functions are plotted in figure 5.7. With this model, the Curie constant amounts to $C = (6 \pm 1)10^{-2}$ erg K/G² mol which corresponds to an effective magnetic moment $\mu_{\text{eff}} = 0.69 \pm 0.06$ $\mu_B/\text{f.u.}$. The Weiss temperature is obtained as $\theta_W = -7 \pm 2$ K and the temperature independent magnetization $\chi_0 = (1.28 \pm 0.05)10^{-3}$ erg/G² mol. Weiss temperature and Curie constant differ strongly from the high temperature Curie model applied for temperatures above 150 K. Still, the function described by 5.2 matches well with the measurement.

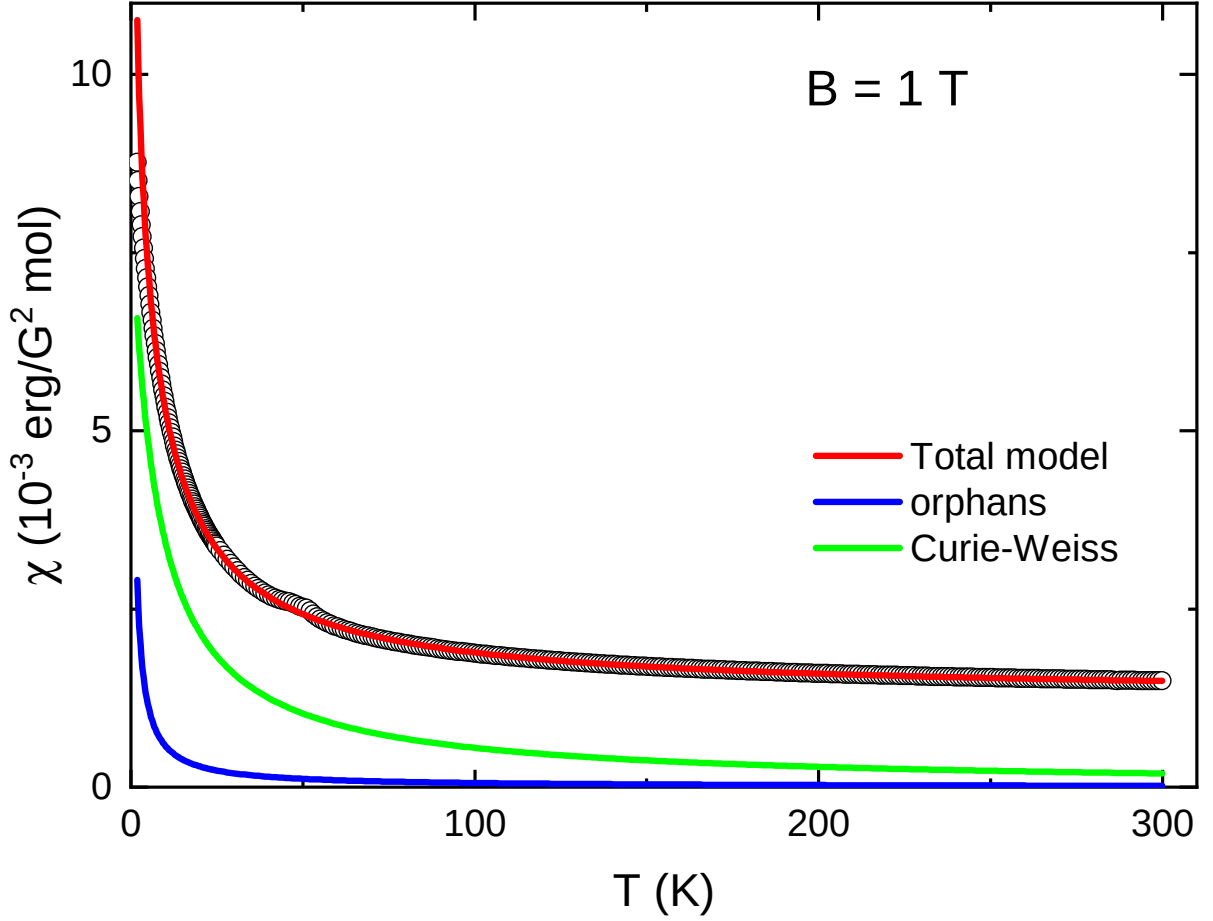


Figure 5.7: Magnetic susceptibility χ at $B = 1 \text{ T}$ vs. temperature. In red the model from equation 5.2 is drawn. Blue shows the Brillouin curve representing the orphan magnetization determined in the $M(B)$ analysis, green shows the Curie-Weiss function of the correlated region according to the model 5.2.

5.3 Heat capacity

Heat capacity of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ was measured in fields up to $B = 14$ T from 1.8 K on to 200 K. The measured curves are presented in figure 5.8.

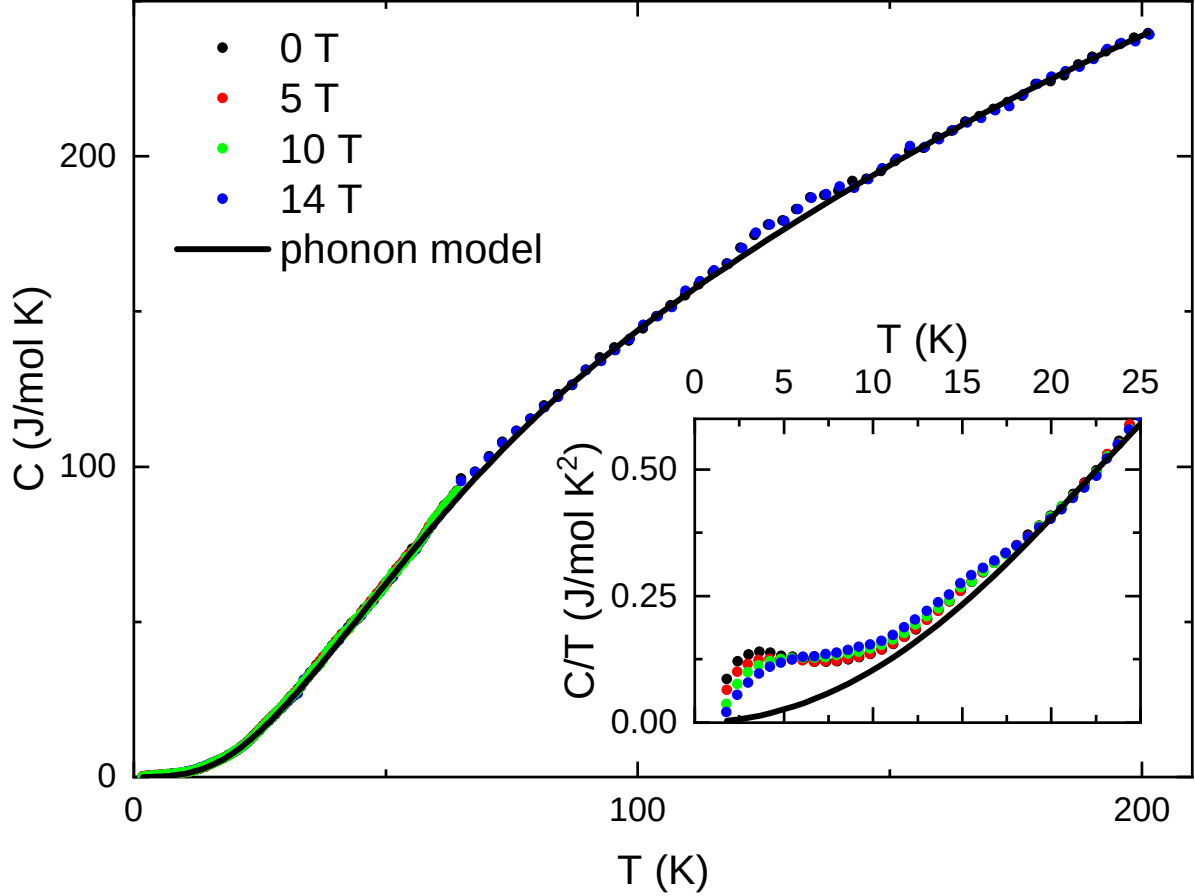


Figure 5.8: Specific heat C of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ is plotted against temperature at different applied magnetic fields. The black line shows a phonon model consisting of one Debye and two Einstein functions, which was fitted to the zero field measurement. **Inset:** Specific heat over temperature (C/T) is drawn in the low temperature regime up to 25 K.

Specific heat of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ shows mostly a phonon-like behavior. For $T \geq 50$ K, the curves measured in different fields lie on top of each other. No features indicating a magnetic phase transition can be found in the specific heat. In the temperature range above 30 K, lattice specific heat caused by phonons is dominating. This lattice specific heat can be modeled by a combination of one Debye and two Einstein functions:

$$C_{\text{lattice}} = C_{\text{D}} + \sum_{i=1}^2 C_{\text{E}, i} \quad (5.3)$$

Compared to the phonon model, some regions of the measured specific heat deviate from the

phonon behavior. These temperature regions were excluded in the phonon fit in order to obtain positive non-lattice specific heat. The excluded temperature regions are:

1.8 K $\rightarrow$ 20 K
 23 K $\rightarrow$ 47 K
 55 K $\rightarrow$ 87 K
 109 K $\rightarrow$ 150 K

The fit of the phonon model to the zero field measurement is shown in figure 5.8 as black line. In table 5.2, the results of the phonon fit are listed.

	Debye	Einstein	
n	4.1	4.5	6.4
$\theta_{D/E}$ (K)	198	304	811

Table 5.2: Parameters of the phonon model fitted to the zero field specific heat. The Debye or Einstein temperature of the respective function is denoted by $\theta_{D/E}$, n is the weight factor of the function.

The weight factors of the Debye and Einstein functions n add up to 15 which is the number of ions per unit cell in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$.

The inset of figure 5.8 shows specific heat over temperature up to 25 K. Below 5 K, small humps can be seen in C/T , that move to higher temperatures with rising field. These features can be assigned to Schottky contributions from orphan spins [34, 39, 41]. Below 20 K, C/T is significantly higher than the lattice specific heat calculated by the phonon model. This shows the presence of magnetic specific heat in this temperature range.

To investigate the non-lattice specific heat of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$, the lattice contribution represented by the phonon model is subtracted from the measurement data. In non-lattice specific heat, there is a magnetic specific heat contribution and a Schottky contribution as seen in C/T in the inset of figure 5.8. To estimate the Schottky contribution the model 4.7 already applied to $\text{Sr}_3\text{CuSb}_2\text{O}_9$ was used. In figure 5.9 the difference between field and zero field measurement $\Delta C_{\text{non-lattice}}/T^2 = 1/T^2 (C_{\text{non-lattice}}(B) - C_{\text{non-lattice}}(B = 0))$ are shown with the respective Schottky fits.

Below 5 K, the data is described well by the model. However, in the domain from 5 K to roughly 16 K, $\Delta C_{\text{non-lattice}}/T^2$ overshoots the model clearly, especially for higher fields. Reason for that might be other unknown field dependences of the specific heat in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$.

Table 5.3 lists the parameters determined by the Schottky model.

For the energy level splitting $\Delta(B)$ no clear and in particular no linear field dependence is visible

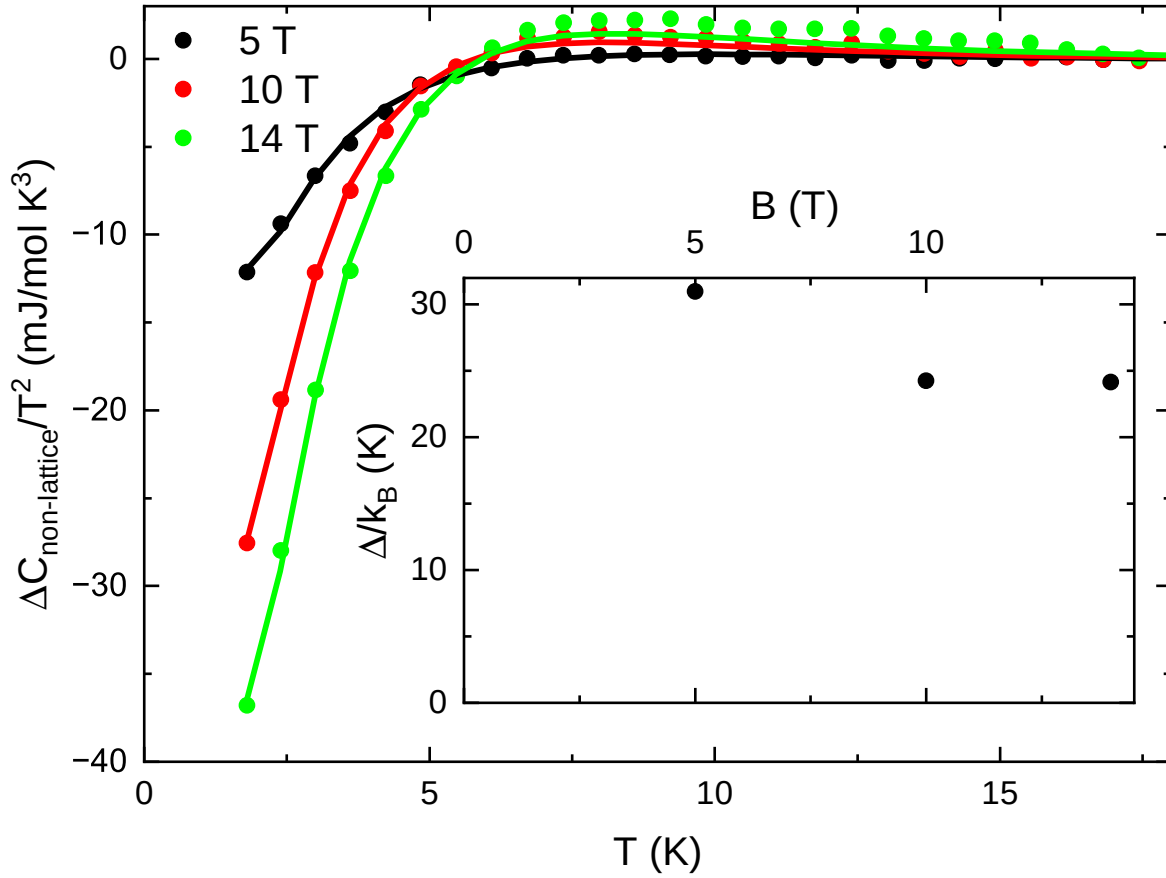


Figure 5.9: The difference $\Delta C_{\text{non-lattice}}/T^2 = (C_{\text{non-lattice}}(B) - C_{\text{non-lattice}}(B = 0))/T^2$ is plotted in the low temperature regime. Solid lines show corresponding Schottky fits. **Inset:** Energy level splitting $\Delta(B)$ determined by Schottky models are drawn vs. magnetic field.

(see inset of figure 5.9). Surprisingly, $\Delta(B = 5 \text{ T})$ is larger than $\Delta(B)$ at 10 T and 14 T. This contradicts the expectation of energy level splitting caused by Zeeman effect. Furthermore, the fraction of ions f contributing to the Schottky specific heat is estimated around $\sim 3 \%$. This is one magnitude larger than the fraction of orphan spins calculated from $M(B)$ measurements. Potentially, the Schottky specific heat might arise from excitations with complex field dependence which are more abundant than the orphan spins. Alternatively, the Schottky model might estimate the field dependence wrong, as there might be further field dependent effects in specific heat.

Anyhow, the Schottky model is used as best guess to describe the effect of orphan spins. Hence, to calculate magnetic specific heat, the Schottky contribution is subtracted from the non-lattice specific heat. For zero field, the parameters calculated in the 14 T fit are used to estimate the Schottky contribution. In figure 5.10 a) the magnetic heat capacity is drawn.

	$B = 5 \text{ T}$	$B = 10 \text{ T}$	$B = 14 \text{ T}$
$\Delta(B)/k_B \text{ (K)}$	31.0 ± 1.5	24.2 ± 0.7	24.1 ± 0.9
$\Delta(B=0)/k_B \text{ (K)}$	7.21 ± 0.10	6.51 ± 0.08	7.11 ± 0.11
$f \text{ (\%)}$	1.64 ± 0.03	3.20 ± 0.05	4.92 ± 0.11
$C_0 \text{ (} 10^{-4} \text{ J/mol K}^3 \text{)}$	-1.2 ± 0.2	-1.5 ± 0.3	-1.1 ± 0.6

Table 5.3: Parameters of the Schottky contribution to specific heat.

For all measured fields, the magnetic heat capacity forms a broad hump with two maxima before reaching down to zero at roughly 22 K. There are slight differences between measurements with different applied magnetic fields, still all curves follow the same shape. Around 22 K, the specific heat measured in field, especially the 14 T measurement, has a negative sign. Due to imprecise assessment of the lattice specific heat a too large phonon contribution was subtracted from the measurement data leading to slightly negative C_{mag} . The similar compound $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ shows a broad hump of magnetic specific heat that reaches down to zero at 30 K [17]. In comparison to this result, only the data up until 22 K, where the specific heat of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ reaches zero for the first time, is considered as magnetic specific heat.

The magnetic entropy S can be calculated by integrating the magnetic specific heat divided by temperature:

$$S = \int \frac{C_{\text{mag}}}{T} dT \quad (5.4)$$

Figure 5.10 b) shows the evolution of S with temperature. Around $\sim 22 \text{ K}$, the magnetic entropy reaches a plateau for all fields. The mean height of the plateau for all fields is $S_{\text{sat}} \approx 0.7 \text{ J/mol K}$. To calculate the full magnetic entropy of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ specific heat below 1.8 K has to be considered. To estimate the magnetic entropy below 1.8 K, the specific heat is extrapolated to zero temperature by going from the measurement at 1.8 K to zero linearly. With $C_{\text{mag}}(T = 1.8 \text{ K}) \approx 0.08 \text{ J/mol K}$, the magnetic entropy below 1.8 K is:

$$S_{\text{ext}} = \int_0^{1.8} \frac{0.08 T}{1.8 T} \text{ J/mol K}^2 dT = 0.08 \text{ J/mol K} \quad (5.5)$$

Combining the extrapolated magnetic entropy and the measured saturation value leads to the total magnetic entropy $S_{\text{max}} = S_{\text{sat}} + S_{\text{ext}} \approx 0.8 \text{ J/mol K}$. $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ is in a near $J = 0$ state. For $J = 0$, the magnetic entropy can be calculated to $S_{\text{theory}} = R \ln(2J + 1) = 0$. Assuming $0 < J \ll 1/2$, a magnetic entropy much smaller than the spin $1/2$ magnetic entropy $S_{1/2} = 5.76 \text{ J/mol K}$ is expected. The estimated entropy S_{max} of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ is in agreement with this assumption, hence it might confirm the near $J = 0$ state. This result reflects roughly the observations made for the magnetic entropy estimated for $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [17].

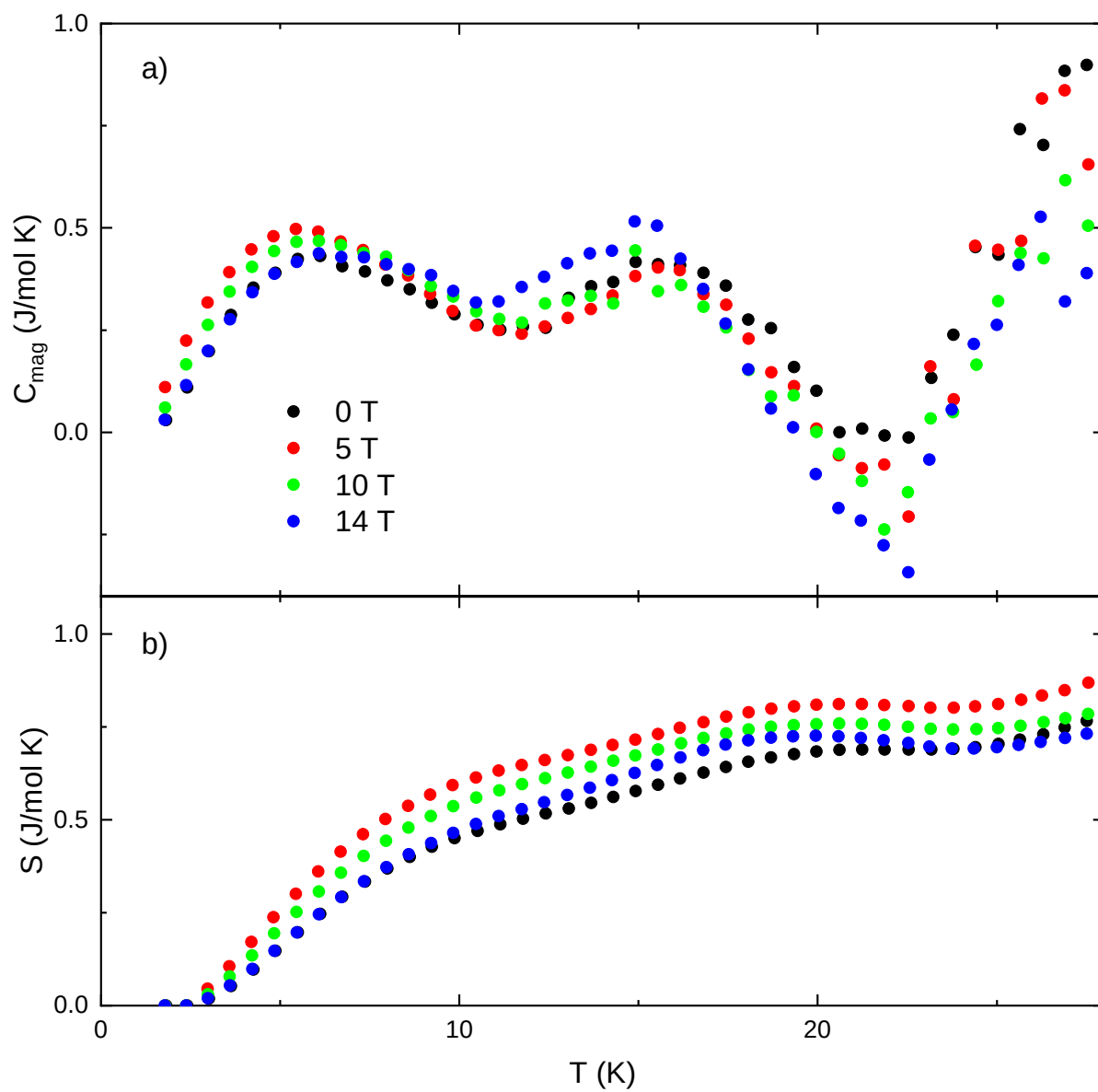


Figure 5.10: a) Magnetic specific heat is plotted against temperature up to 35 K. b) Magnetic entropy S vs. temperature for all measured fields.

Sr₃CuIr₂O₉

Both previously shown materials contain only one magnetic center per unit cell. In Sr₃CuSb₂O₉ Cu²⁺ ions on a triangular lattice lead to complex magnetic phenomena caused by frustrated interactions. For Sr₃ZnIr₂O₉, the Ir⁵⁺ ions are in a near $J = 0$ state leading to surprising magnetic effects. Combining both magnetic sources in Sr₃CuIr₂O₉ allows to investigate the interplay of both magnetic ions.

Sr₃CuIr₂O₉ is proposed to crystalize in the hexagonal space group $P-62c$ (No. 190) based on Rietveld refined x-ray diffraction measurements [50]. In this structure Ir ions have two different crystallographic sites (Ir1 and Ir2). At Ir1 sites, Ir ions are surrounded by an oxygen octahedron. As two Ir1 ions are located closely together along the c -axis, their oxygen octahedra share a face leading to an Ir₂O₉ dimer. On Ir1 sites, these dimers are separated from other Ir₂O₉ dimers. In contrast, the Ir2 sites form a linear chain along the c -axis. However, the distance between the Ir ions alternates between a short and a long interval. Similar to the Ir1 sites, Ir on Ir2 sites are surrounded by oxygen octahedra. The octahedra of near together Ir2 sites share a face forming again Ir₂O₉ dimers. In conclusion, on Ir2 sites Ir₂O₉ dimers form a linear chain along the c -axis, whereas on Ir1 sites Ir₂O₉ dimers are separated in the unit cell. Considering the a - b -plane, both sites of Ir ions form triangular lattices.

As discussed for the Ir ions, Sr has two distinct crystallographic sites (Sr1 and Sr2) in Sr₃CuIr₂O₉ [50]. Sr1 forms two equilateral triangles in the a - b -plane separated from each other along the c -axis. Along the a - b -plane, Sr1 triangles do not share sites or edges with another. Sr2 sites are arranged in three layers parallel to the a - b -plane. Here, Sr2 sites order in edge sharing equilateral triangles forming a triangular lattice. The triangles from Sr1 and Sr2 are of similar size.

Cu ions are supposed to settle on Sr1 and Sr2 sites [50]. However, due to similar electronic charge and ionic radii, it is unclear which Sr sites are occupied by Cu ions. Rietveld results are similar for Cu ions on Sr1 positions, Cu ions on Sr2 positions or Cu ions equally divided on Sr1 and Sr2. Possibly, Cu is randomly distributed on both Sr sites leading to a diluted triangular lattice. The structure of Sr₃CuIr₂O₉ is depicted in figure 6.1. Besides the unit cell, there is also the triangular lattice emerging from Sr2 sites and from Ir sites visible.

By use of x-ray photoemission spectroscopy the ionic charges in Sr₃²⁺Cu²⁺Ir₂⁵⁺O₂²⁻ were confirmed [50]. This leads to magnetic states $J = S = 1/2$ for Cu²⁺ ions and near $J = 0$ states in Ir⁵⁺.

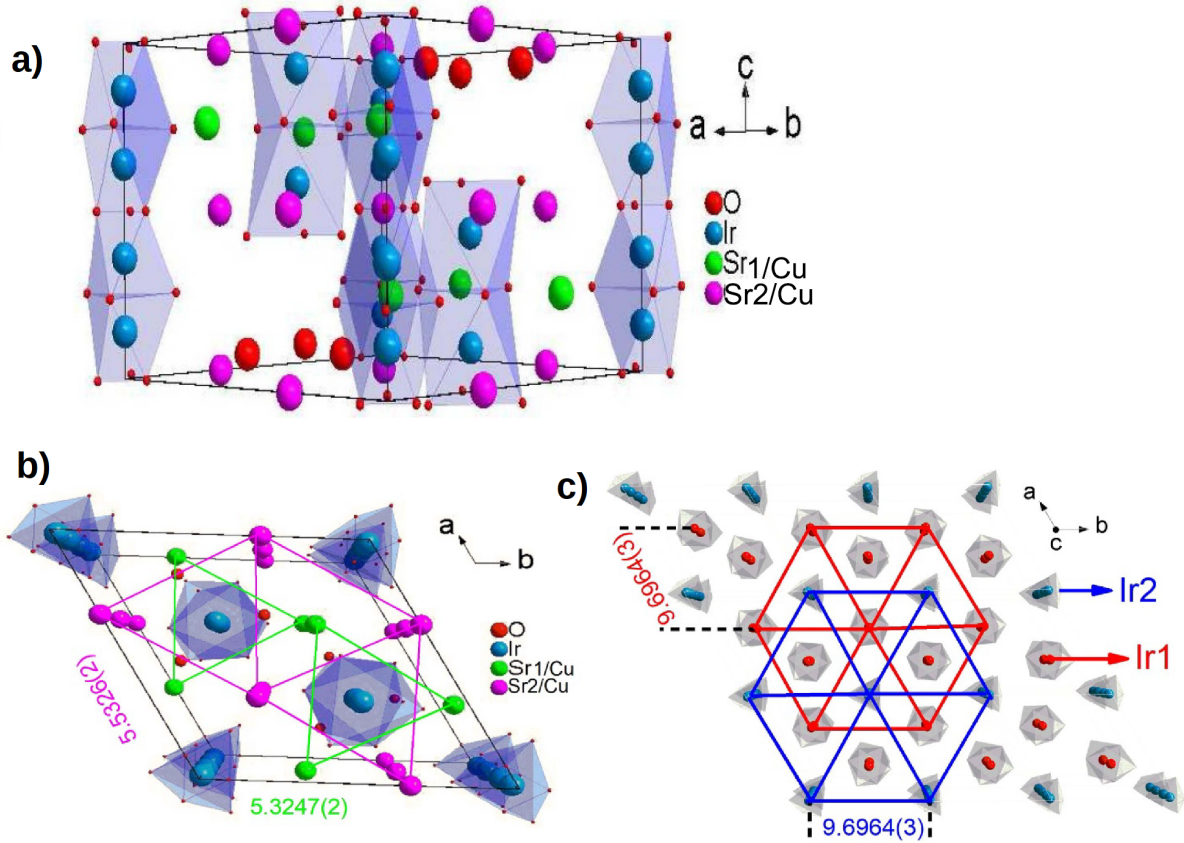


Figure 6.1: Crystal structure of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ ($P-62c$ (No. 190)) [50]. Ir ions are drawn in pink. They are surrounded by oxygen depicted in red. The resulting octahedra are outlined by colored planes. Sr1 and Sr2 sites are drawn in yellow and blue respectively. Cu ions occupy these Sr sites at random. **a)** Unit cell of $\text{Sr}_3\text{CuIr}_2\text{O}_9$. **b)** a - b -plane of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ unit cell. The Sr1 triangle and the Sr2 triangular lattice are marked with lines in the respective color. **c)** Simplified structure of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ showing the Ir_2O_9 dimers in the a - b -plane. Ir1 sites are drawn in red, Ir2 sites in blue. The formation of triangular lattices is illustrated in lines of corresponding color.

In magnetization measurements, no long range magnetic order was observed down to $T = 2$ K [50]. In the temperature range from 300 K down to 100 K, the magnetization behaves according to the Curie-Weiss law. However, for temperatures lower than 20 K a hump was detected in $\chi(T)$. This hump was visible for an applied magnetic field $B = 0.1$ T, but the feature was suppressed in higher fields. In measurements of the ac susceptibility, the existence of the hump was confirmed. Below 10 K, a slight bifurcation between ZFC and FC measurements of $\chi(T)$ was recorded. Analogously, in measurements of $M(B)$ at $T \leq 10$ K a small loop opening was detected. These observations were interpreted as onset of weak ferromagnetic short range spin correlations.

Magnetic correlations in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ were estimated by a Curie-Weiss model revealing the Weiss temperature $\theta_W = -30 \pm 6$ K and the effective moment $\mu_{\text{eff}} = 2.26 \pm 0.05 \mu_B/\text{f.u.}$ ($C = 0.64 \pm 0.03 \text{ erg K/G}^2 \text{ mol}$) [50].

Similar to magnetization measurements, heat capacity measurements show no sign of long range magnetic order down to $T = 1.8$ K [50]. Magnetic heat capacity was observed as broad hump around ~ 6 K, extending up to roughly 15 K. Slight field dependence was detected in the magnetic specific heat. Calculating the magnetic entropy changes from the measured heat capacity revealed a saturation at the value of $S_{\text{mag}} = 2.29 \text{ J/mol K}$ from ~ 15 K on. This amounts to only half of the expected entropy in a spin $1/2$ system ($S_{1/2} = R \ln(2) = 5.76 \text{ J/mol K}$). From the lack of magnetic entropy and the absence of long range magnetic order a QSL ground state was hypothesized in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ [50].

In conclusion, $\text{Sr}_3\text{CuIr}_2\text{O}_9$ is expected to exhibit a QSL ground state, which coexists with weak ferromagnetic spin correlations [50].

6.1 Experimental details

$\text{Sr}_3\text{CuIr}_2\text{O}_9$ samples studied in this thesis are pressed pellets of polycrystals grown by Charu Garg and Sunil Nair (both from Indian Institute of Science Education and Research Pune). Measurements were performed on different samples from the same batch. Between the measurements, the samples were stored in an argon atmosphere to avoid water and oxygen absorption. $\text{Sr}_3\text{CuIr}_2\text{O}_9$ is fragile, but if handled with care the samples can be prepared for measurements without breaking or spalling. A picture of one of the used $\text{Sr}_3\text{CuIr}_2\text{O}_9$ samples is shown in figure 6.2.

Magnetization measurements were performed in MPMS in VSM, DC and AC mode, respectively. For all magnetization measurements background was measured with an empty sample holder and data was corrected with respect to background.

A sample of mass $m_1 = 19.10 \pm 0.08$ mg was mounted in a brass holder for MPMS and ac

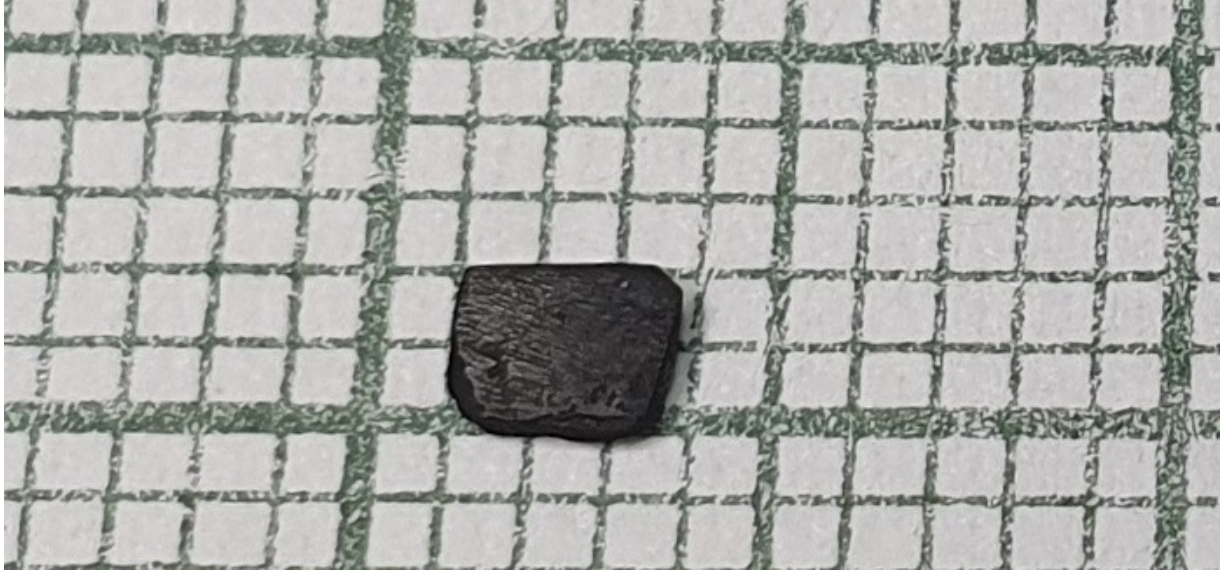


Figure 6.2: Example of an $\text{Sr}_3\text{CuIr}_2\text{O}_9$ sample.

magnetic susceptibility was measured in the temperature range from $T = 1.8$ K to 50 K. The applied ac magnetic field had an amplitude of $B_{\text{ac}} = 9 \cdot 10^{-4}$ T and six different frequencies $f = 15$ Hz, 45 Hz, 85 Hz, 135 Hz, 235 Hz and 435 Hz. No permanent field was added, so $B_{\text{dc}} = 0$ T for all measurements.

In DC mode, two samples of mass $m_1 = 19.10 \pm 0.08$ mg and $m_2 = 17.34 \pm 0.08$ mg were measured. On sample 1, field dependence of magnetization $M(B)$ was measured after cooling in zero field to $T = 1.8$ K. Consequently, data was recorded while sweeping the field up to 7 T and back down to 0 T. Furthermore, temperature dependence of magnetization $M(T)$ was measured on sample 1 in the temperature range from $T = 1.8$ K to 300 K. In an applied field $B = 0.1$ T, first a ZFC and consequently a FC measurement protocol was performed. Sample 2 was measured in fields $B = 1$ T, 3 T and 7 T in the temperature range $T = 1.8$ K to 300 K with a FC sequence. Furthermore, $M(B)$ was measured on sample 2 in VSM mode. Here, the sample was cooled in zero field to $T = 1.8$ K. Afterwards, $M(B)$ was measured by increasing the field to 7 T and consequently to -0.5 T.

Heat capacity measurements were conducted in a PPMS. The sample of mass $m_2 = 17.34 \pm 0.08$ mg was fixed on the measurement table with Apiezon N grease. In the temperature range $T = 1.8$ K to 200 K heat capacity was measured in the fields $B = 0$ T and 14 T.

6.2 Magnetization

6.2.1 Field dependence of magnetization

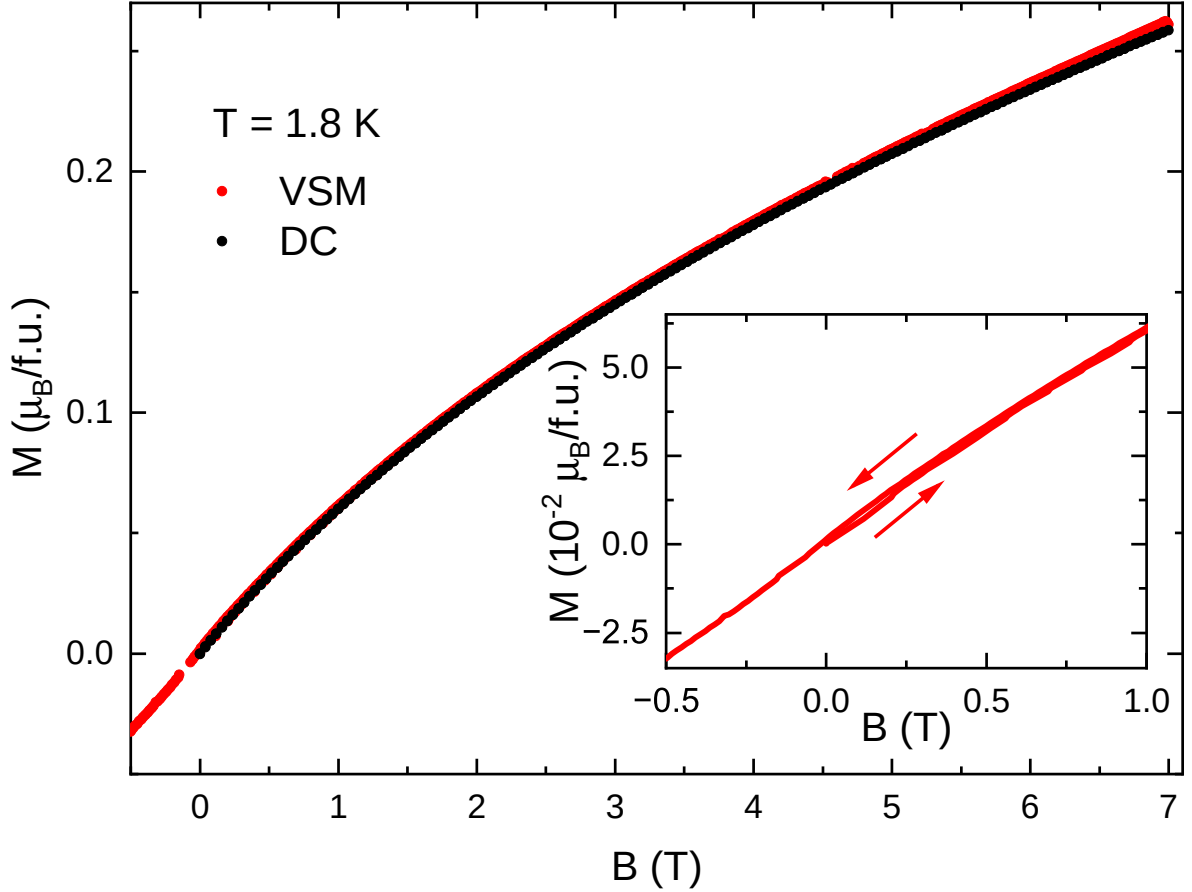


Figure 6.3: Magnetization M is plotted against magnetic field B . The data were recorded at $T = 1.8$ K. Red shows the measurement in VSM mode, whereas DC data are black. **Inset:** VSM measurement of $M(B)$ in the low field domain. The data was acquired by driving the field up to 7 T and consequently down to -0.5 T.

The field dependence of the magnetization is plotted in figure 6.3. There, measurements in VSM mode and DC mode at $T = 1.8$ K are depicted. $M(B)$ exhibits right bending which lessens with rising field. At the highest measured field ($B = 7$ T), the magnetization is still rising and does not show any signs of saturation. It reaches up to $M(B = 7 \text{ T}) \approx 0.26 \mu_B/\text{f.u.}$, which is roughly $1/4$ of the expected saturation magnetization of a system with single spin $S = 1/2$ and $g = 2$ per unit cell. By these observations, the magnetization in the measured field range is expected to be the combination of a linear term and Brillouin like term. The linear term is associated with the correlated moments of the compound, which should make up the bulk of the sample. In contrast, the Brillouin like term can be attributed to orphan spins, which are spins that decouple from

the correlated region as cause of e.g. site disorder or edge spins [36].

The inset of figure 6.3 shows the VSM measurement of $M(B)$ in the low field domain from $B = -0.5$ T to 1 T. A marginal loop opening can be seen. The coercive field was estimated to ~ -0.016 T. This value can be attributed to measurement errors and the remanent field of the coil in the measurement device. In conclusion, no substantial hysteresis was observed in $\text{Sr}_3\text{CuIr}_2\text{O}_9$. To quantify the number of orphan spins, a model already known from equation 4.1 was fitted to the data measured in DC mode:

$$M = fg\mu_BJB_J \left(\frac{g\mu_BJB}{k_B T} \right) + a_0 B \quad (6.1)$$

In the fit g was fixed to 2 in order to reduce correlations with other parameters. As stated for equation 4.1, f describes the fraction of orphan spins per formula unit with total angular momentum J . The correlated region of spins is described by the linear term with slope a_0 . In figure 6.4 a), the model and the measured data are depicted. $M(B)$ is represented well by the model with orphan spins possessing a total angular momentum of $J = 0.809 \pm 0.013$. The fraction of orphan spins is $f = 4.81 \pm 0.11$ % per formula unit. The correlated domain is described by a linear function with slope $a_0 = (2.616 \pm 0.009)10^{-2} \mu_B/\text{f.u. T}$.

In $\text{Sr}_3\text{CuIr}_2\text{O}_9$ orphan spins are expected to originate from decoupled Cu^{2+} spins and Ir_2O_9 moments. Cu^{2+} yield $J_{\text{Cu}^{2+}} = 1/2$. Ir_2O_9 dimers are in a near $J = 0$ state, however they are supposed to possess $J_{\text{Ir}_2\text{O}_9} = 1$ excitations [17]. Hence, $J \approx 0.8$ estimated by the model 6.1 can be interpreted as both Cu^{2+} and Ir_2O_9 moments decouple from the correlated region and form orphan spins. Naively, the fractions of Cu^{2+} orphans and Ir_2O_9 orphans can be determined with following ansatz:

$$p_{\text{Cu}^{2+}}J_{\text{Cu}^{2+}} + p_{\text{Ir}_2\text{O}_9}J_{\text{Ir}_2\text{O}_9} = 0.809 \quad (6.2)$$

$$p_{\text{Cu}^{2+}} + p_{\text{Ir}_2\text{O}_9} = 1 \quad (6.3)$$

Here, J is the total angular momentum and p the fraction of Cu^{2+} and Ir_2O_9 orphan moments respectively. With $J_{\text{Cu}^{2+}} = 1/2$ and $J_{\text{Ir}_2\text{O}_9} = 1$ follows $p_{\text{Cu}^{2+}} \approx 40$ % and $p_{\text{Ir}_2\text{O}_9} \approx 60$ %. Hence, 40 % of orphan moments are Cu^{2+} spins and 60 % of orphans are Ir_2O_9 dimers.

A more sophisticated way to determine the orphan spins and their origin was attempted by modeling the $M(B)$ data with two separate Brillouin functions and a linear term. One Brillouin function is attributed to the Cu^{2+} orphans while the other Brillouin function describes Ir_2O_9 orphans. The linear term still refers to the correlated part. The model can be found in the

following equation:

$$M = f_{\text{Cu}^{2+}} g_{\text{Cu}^{2+}} \mu_B J_{\text{Cu}^{2+}} B J_{\text{Cu}^{2+}} \left(\frac{g_{\text{Cu}^{2+}} \mu_B J_{\text{Cu}^{2+}} B}{k_B T} \right) + f_{\text{Ir}_2\text{O}_9} g_{\text{Ir}_2\text{O}_9} \mu_B J_{\text{Ir}_2\text{O}_9} B J_{\text{Ir}_2\text{O}_9} \left(\frac{g_{\text{Ir}_2\text{O}_9} \mu_B J_{\text{Ir}_2\text{O}_9} B}{k_B T} \right) + a_0 B \quad (6.4)$$

To apply this model to the measured data, some parameters were fixed to literature values and results from previous chapters. For Cu^{2+} , $g_{\text{Cu}^{2+}} = 2.24$ [35] and $J_{\text{Cu}^{2+}} = 1/2$. For Ir_2O_9 , $g_{\text{Ir}_2\text{O}_9} = 2$ and $J_{\text{Ir}_2\text{O}_9} = 1.2$ (see chapter 5).

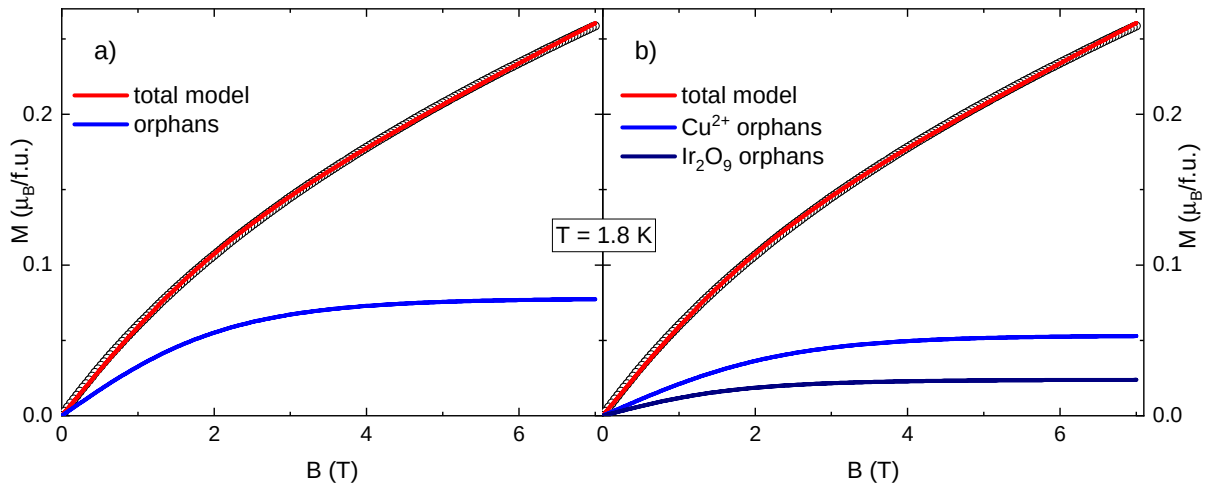


Figure 6.4: Magnetization $M(B)$ at $T = 1.8$ K is depicted as black circles together with different models. **a)** The model 6.1 is shown as red line. The orphan part represented by a Brillouin function is drawn blue. **b)** Model 6.4 is illustrated in red. Cu^{2+} orphan magnetization is depicted in blue, Ir_2O_9 orphans in dark blue.

This model applied to the $M(B)$ measurement is illustrated in figure 6.4 b). It represents the data similarly well as the model 6.1. The fractions of orphan moments are determined to $f_{\text{Cu}^{2+}} = 4.7 \pm 0.2$ % and $f_{\text{Ir}_2\text{O}_9} = 1.00 \pm 0.07$ %. For the linear term a slope $a_0 = (2.627 \pm 0.007)10^{-2} \mu_B/\text{f.u. T}$ was found.

Both models yield a similar linear term describing the magnetization of the correlated regime of $\text{Sr}_3\text{CuIr}_2\text{O}_9$. Considering orphans, the sum of both Brillouin functions of model 6.4 is roughly equal to the Brillouin part of model 6.1 (M_s is roughly equal for the orphans of both models). However, the composition of orphan spins is different in both models. Fitting both Cu^{2+} orphans and Ir_2O_9 orphans separately to $M(B)$ reveals that roughly 83 % of orphan moments are Cu^{2+} spins and only 17 % are Ir_2O_9 dimers. Furthermore, model 6.4 claims that there are roughly 1% more orphan moments in the sample than model 6.1.

6.2.2 Temperature dependence of magnetization

Measurements of the temperature dependence of magnetization in fields $B = 0.1$ T, 1 T, 3 T and 7 T are illustrated in figure 6.5. In $\chi(T)$ no sign of a magnetic phase transition is observed. All data sets follow roughly a Curie-Weiss like behavior without any other features. For $T \leq 20$ K, $\chi(T)$ is slightly suppressed with magnetic field. The inset of figure 6.5 shows $\chi^{-1}(T)$. Curie-Weiss like behavior is present in all measurements in combination with right bending of $\chi^{-1}(T)$ at high temperatures, associated with a temperature independent susceptibility offset χ_0 . A discrepancy between the data measured at $B = 0.1$ T and higher field data is visible. This difference likely arose from imprecise background correction on the 0.1 T measurements, where the signal to data ratio is way worse than for the higher field measurements. However, for $T \geq 20$ K, all measurements with $B \leq 1$ T align well with each other.

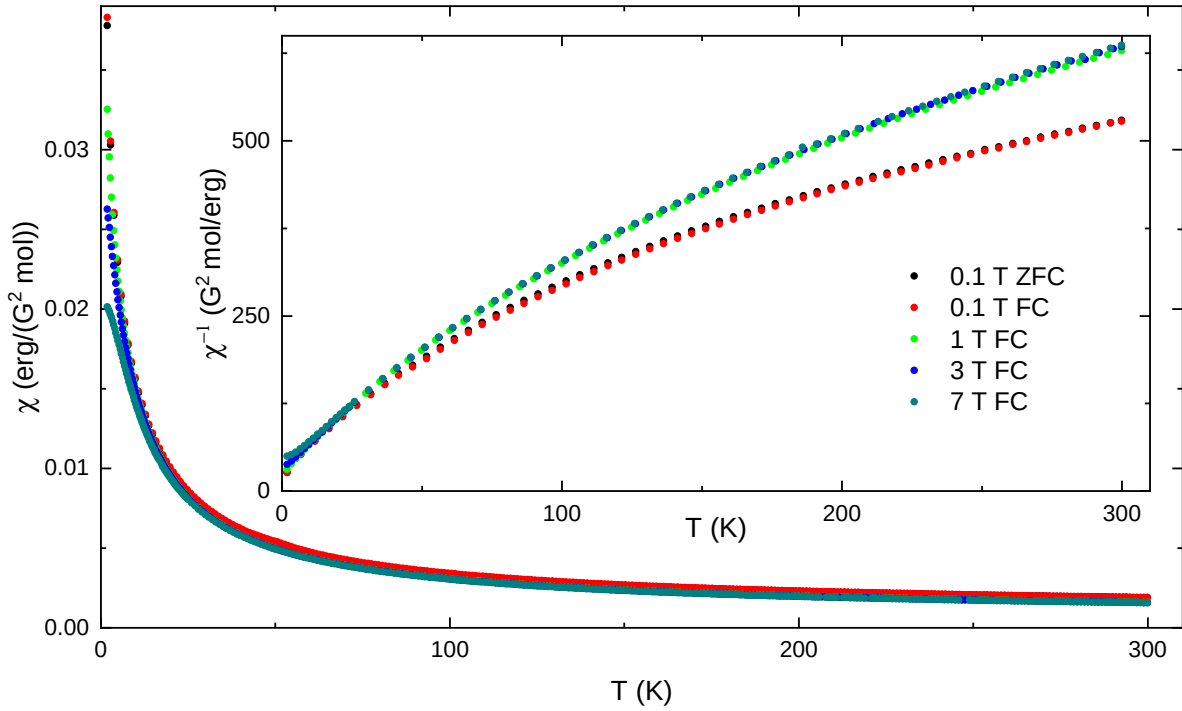


Figure 6.5: Magnetic susceptibility $\chi(T)$ at different applied magnetic fields. **Inset:** Inverse magnetic susceptibility $\chi^{-1}(T)$.

To check for hysteresis effects, $\chi(T)$ at field $B = 0.1$ T is analyzed. Figure 6.6 shows the ZFC and FC measurements. Unlike in measurements conducted in reference [50], no feature at $T = 20$ K is visible neither in ZFC and FC data. In $\chi(T)$ no bifurcation is apparent between the ZFC and FC data. To have a closer look on hysteresis effects, the difference $\Delta\chi = \chi_{\text{ZFC}} - \chi_{\text{FC}}$ is shown in the inset of figure 6.6. $\Delta\chi$ is roughly zero in the high temperature region but decreases with decreasing temperature for $T \leq 150$ K. At ~ 50 K, a small peak appears in Δ . This peak can be

attributed to O_2 absorbed in the porous sample [38]. During the time of the measurement O_2 gases out of the sample altering the signal at the paraantiferromagnetic transition of O_2 in the ZFC and FC measurement.

A smaller broad peak arises around $T \approx 25.9$ K. Measurements performed in reference [50] detected a hump in $\chi(T)$ in this temperature region and the onset of ferromagnetic correlations were concluded. As no such hump is detected in the measurements of $\chi(T)$ conducted within this thesis, the peak around 25.9 K in $\Delta\chi$ is the only feature which arises in the same temperature region as the hump detected in reference [50]. However, the signal of the peak in $\Delta\chi$ is very low and does not represent the observations made by Gondh et al. [50], hence conclusions made in reference [50] are not supported by measurements performed in this thesis.

Below 10 K, $\Delta\chi$ falls sharply with decreasing temperature. This hints towards a small bifurcation between ZFC and FC measurements in the order of 1 % of $\chi(T)$. The bifurcation observed here between ZFC and FC data is marginal and way smaller than the bifurcation observed in [50].

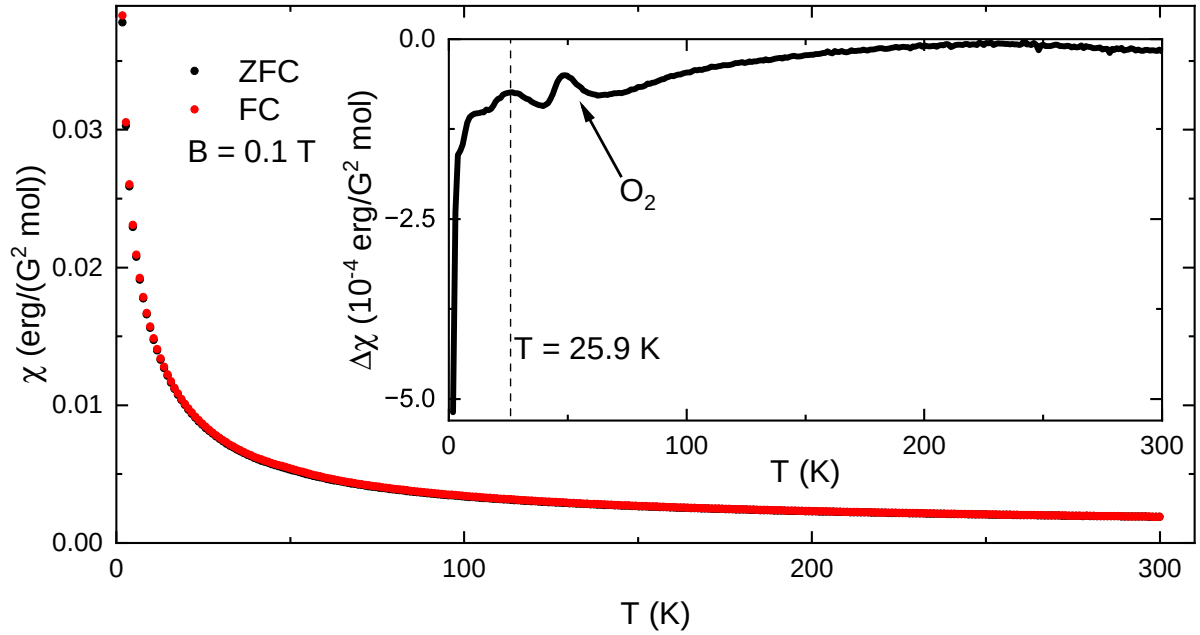


Figure 6.6: Magnetic susceptibility $\chi(T)$ at $B = 0.1$ T. Red points show ZFC data and blue FC data. **Inset:** The difference $\Delta\chi = \chi_{ZFC} - \chi_{FC}$ is plotted against temperature. At ~ 50 K a small peak caused by trapped O_2 in the sample is visible.

To study spin dynamics and check for spin freezing ac magnetic susceptibility was measured. The in-phase part χ' and the out-of-phase part χ'' at constant field $B_{dc} = 0$ T are shown in figure 6.7 a) and b). χ' shows Curie-Weiss like behavior comparable to the dc measurements. No particular features are visible. Furthermore, the data show no frequency dependence. In χ'' only noise with neither temperature nor frequency dependence is visible. Consequently, the spin dynamics in $Sr_3CuIr_2O_9$ are faster than the applied ac fields, so no dispersion was detected.

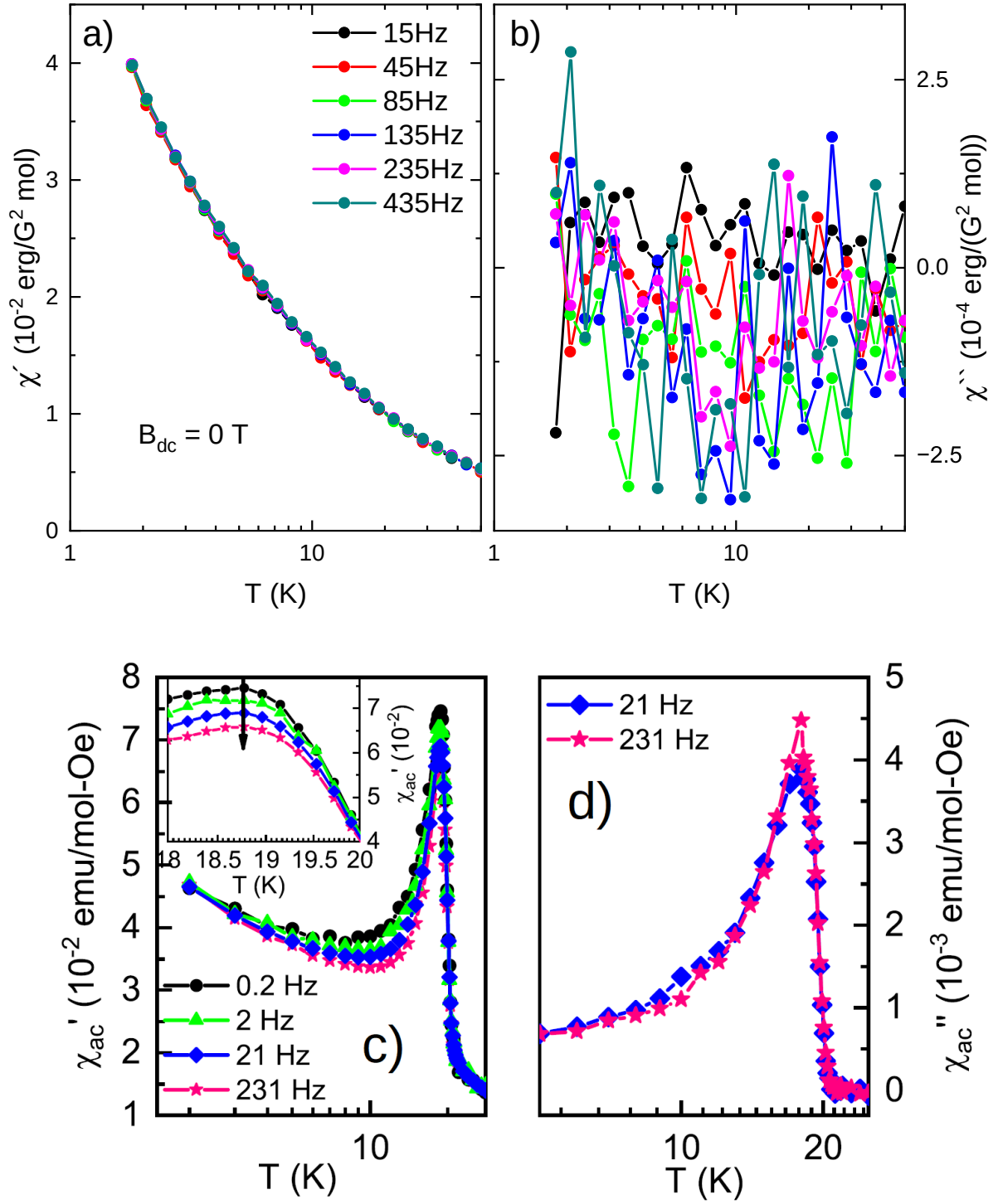


Figure 6.7: Ac magnetic susceptibility χ' and χ'' against temperature. The data plotted in a) and b) were recorded in this thesis, c) and d) were taken from [50].

The ac susceptibility measured in this thesis is in contrast with measurements published in reference [50]. In figure 6.7 c) and d) χ' and χ'' measured in an oscillating field $B_{ac} = 3 \cdot 10^{-4}$ T by [50] are illustrated. For both χ' and χ'' a large peak at $T \approx 19$ K was detected at all measured frequencies. The onset of short range ferromagnetic spin correlations for $T \leq 20$ K were concluded by Gondh et al. [50].

These observations have not been confirmed in this thesis. Furthermore, a hump in $\chi(T)$ at roughly 20 K detected by Gondh et al. [50] is not seen in the measurements presented in this work. Reason for this mismatch could be an impurity phase present in the sample of reference [50] but not in the sample used in this thesis.

Using the FC measurement of $\chi(T)$ at $B = 1$ T, magnetic interactions in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ are estimated. To do this, a modified Curie-Weiss law according to 2.10 was fitted to the data in the temperature range from $150 \text{ K} \leq T \leq 300 \text{ K}$. In figure 6.8, the susceptibility $\chi(T)$ and inverse susceptibility $\chi^{-1}(T)$ are depicted together with the Curie-Weiss model. The fit describes the measured data well down to ~ 100 K.

The Weiss temperature amounts to $\theta_W = -17 \pm 5$ K and the Curie constant is $C = 0.27 \pm 0.01 \text{ erg K/G}^2 \text{ mol}$. This leads to an effective moment of $\mu_{\text{eff}} = 1.47 \pm 0.03 \mu_B/\text{f.u.}$. The temperature independent susceptibility was determined to $\chi_0 = (7.4 \pm 0.3)10^{-4} \text{ erg/G}^2 \text{ mol}$.

As $\theta_W < 0$, dominant antiferromagnetic interactions are present in $\text{Sr}_3\text{CuIr}_2\text{O}_9$. However, $|\theta_W|$ is much smaller as compared to the literature [50]. Furthermore, the effective magnetic moment is smaller than in the literature [50]. Considering only a spin $1/2$ system with $g = 2$ (model for Cu^{2+} systems), theory predicts an effective moment of $\mu_{\text{eff}} = 1.7 \mu_B/\text{f.u.}$

The effective moment of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ is lower than the moment expected for only Cu^{2+} ions. Strangely, adding near $J = 0$ Ir_2O_9 dimers to a spin $1/2$ Cu^{2+} system in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ seems to lower the effective magnetic moment. However, this observation is the result of a Curie-Weiss fit that is susceptible to errors. Changing the temperature range to which the fit is applied can alter the result significantly [49]. Furthermore, the data governing the fit parameters in the Curie-Weiss model are the high temperatures ones where the measured signal is lowest. This makes the Curie-Weiss fits vulnerable to inaccuracies in measurement and background subtraction. The influence of different fit ranges on the parameters of the Curie-Weiss fit is discussed in the appendix.

Using the results of the $M(B)$ measurements of this thesis, the Curie-Weiss analysis can be improved. First, the results of model 6.1 were used to estimate the orphan contribution to the magnetization. With this approach, $\chi(T)$ can be modeled by the following equation:

$$\chi = \frac{fg\mu_B N_A J}{B} B_J \left(\frac{g\mu_B J B}{k_B T} \right) + \frac{C}{T - \theta_W} + \chi_0 \quad (6.5)$$

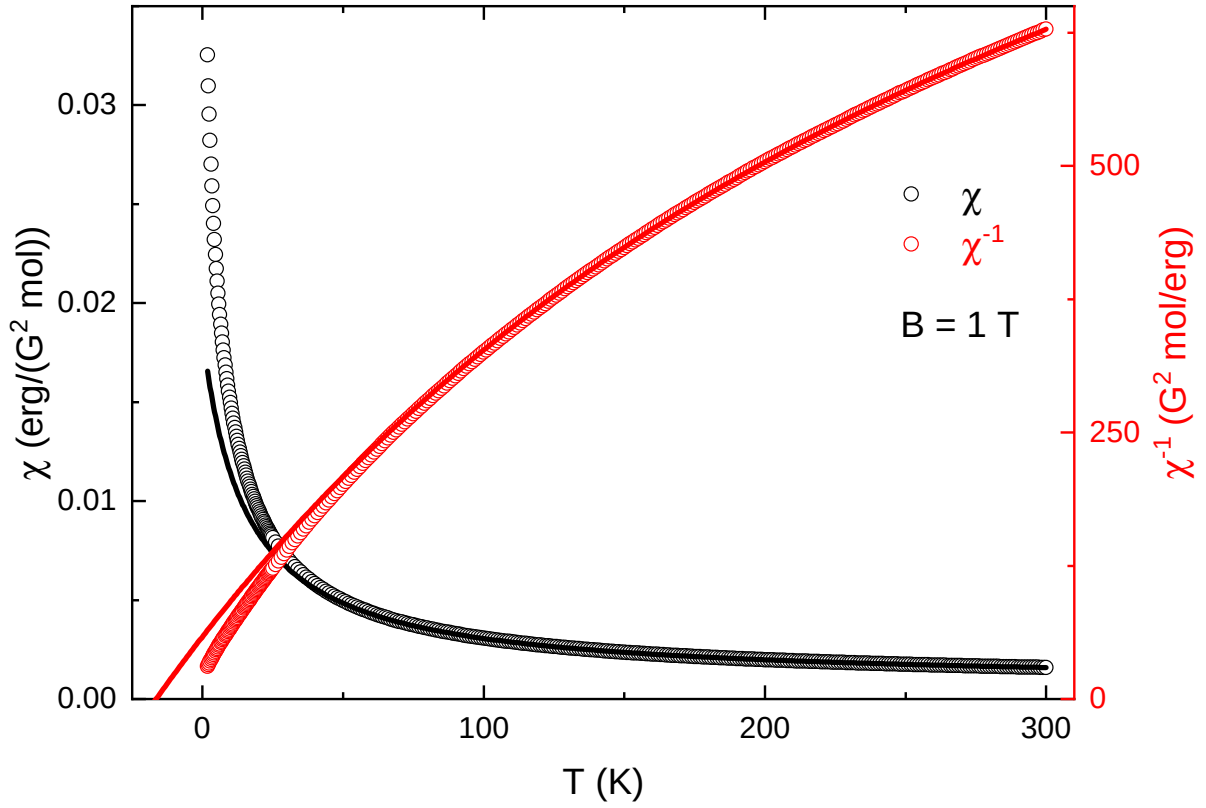


Figure 6.8: Magnetic susceptibility $\chi(T)$ (black) and inverse susceptibility $\chi^{-1}(T)$ (red) at $B = 1$ T are illustrated. The lines show a modified Curie-Weiss model fitted to the data from 150 K to 300 K.

According to the $M(B)$ results, the parameters $f = 4.81$ %, $J = 0.809$ and $g = 2$ were fixed. Using this model, the measured susceptibility at $B = 1$ T can be described well. The measured data, the model function and the orphan and Curie-Weiss contribution are plotted in figure 6.9 a).

In this model, the correlated part of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ has a Weiss temperature $\theta_W = -11 \pm 3$ K. The Curie constant is calculated to $C = 0.21 \pm 0.03$ erg K/G² mol and the offset is $\chi_0 = (7.9 \pm 0.3)10^{-4}$ erg/G² mol.

In a similar approach, the orphan contribution of Cu^{2+} ions and Ir_2O_9 dimers calculated by the model 6.4 for $M(B)$ measurements can be included in the $\chi(T)$ analysis. Hence, the following model is applied to the measured $\chi(T)$ data:

$$\begin{aligned} \chi = & \frac{f_{\text{Cu}^{2+}} N_A g_{\text{Cu}^{2+}} \mu_B J_{\text{Cu}^{2+}}}{B} B_{J_{\text{Cu}^{2+}}} \left(\frac{g_{\text{Cu}^{2+}} \mu_B J_{\text{Cu}^{2+}} B}{k_B T} \right) \\ & + \frac{f_{\text{Ir}_2\text{O}_9} N_A g_{\text{Ir}_2\text{O}_9} \mu_B J_{\text{Ir}_2\text{O}_9}}{B} B_{J_{\text{Ir}_2\text{O}_9}} \left(\frac{g_{\text{Ir}_2\text{O}_9} \mu_B J_{\text{Ir}_2\text{O}_9} B}{k_B T} \right) \\ & + \frac{C}{T - \theta_W} + \chi_0 \end{aligned} \quad (6.6)$$

Here, the orphan contributions are fixed according to the results of model 6.4 to $f_{\text{Cu}^{2+}} = 4.7\%$, $J_{\text{Cu}^{2+}} = 1/2$, $g_{\text{Cu}^{2+}} = 2.24$, $f_{\text{Ir}_2\text{O}_9} = 1.00\%$, $J_{\text{Ir}_2\text{O}_9} = 1.2$ and $g_{\text{Ir}_2\text{O}_9} = 2$. The resulting curves when fitting model 6.6 to $\chi(T)$ at $B = 1$ T are shown in figure 6.9 b).

With model 6.6, the correlated part of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ is described by $\theta_W = -11 \pm 3$ K, $C = 0.21 \pm 0.03$ erg K/G² mol and $\chi_0 = (7.9 \pm 0.3)10^{-4}$ erg/G² mol.

The results obtained by including one orphan part (model 6.5) or two orphan parts (model 6.6) lead to the same parameters of the AFM correlated spin system in $\text{Sr}_3\text{CuIr}_2\text{O}_9$. This reflects how similar the orphan contribution is described by both approaches. Comparing to the high temperature Curie-Weiss model, the orphan models estimate smaller Weiss temperatures and smaller Curie constants. Although the measured data is described well by the orphan models, these models contain a Curie-Weiss component, which is a high temperature approximation. Consequently, the models are only valid at higher temperatures and the results need to be regarded with care.

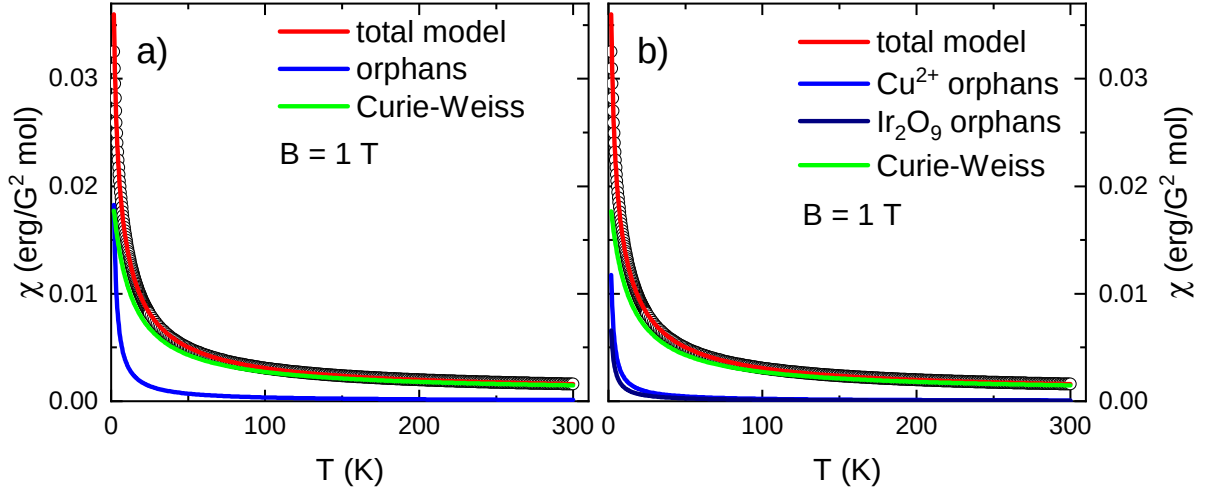


Figure 6.9: Magnetic susceptibility χ at $B = 1$ T are depicted in black circles. In **a)** the model according to 6.5 is drawn as red line. In blue the orphan contribution and in green the Curie-Weiss contribution of the model are illustrated. Similarly, the red line in **b)** shows the model 6.6. The Curie-Weiss component (green), and orphan components (Cu^{2+} in blue, Ir_2O_9 in dark blue) are plotted along.

6.3 Heat capacity

Specific heat data in zero field and $B = 14$ T from $T = 1.8$ K up to 200 K are plotted in figure 6.10. The zero field data and in field data differ only below $T \approx 35$ K. At higher temperatures both measurements show phonon like behavior, indicating that the heat capacity of the lattice dominates. There are no signs of phase transitions in the specific heat in both measurements.

To estimate the lattice specific heat, a phonon model consisting of a combination of one Debye and two Einstein functions was fitted to the zero field measurement:

$$C_{\text{lattice}} = C_{\text{D}} + \sum_{i=1}^2 C_{\text{E}, i} \quad (6.7)$$

At some temperatures the measured data show small variations from the lattice specific heat. These regions were excluded from the phonon fit in order to obtain a reasonable lattice contribution and a positive non-lattice contribution. The excluded temperature regions are:

1.8 K $\rightarrow$ 32 K
 34 K $\rightarrow$ 47 K
 52 K $\rightarrow$ 90 K
 105 K $\rightarrow$ 161 K

Fitting the phonon model to the data in the remaining temperature region leads to parameters listed in table 6.1. In figure 6.10 the model is drawn as blue line.

	Debye	Einstein	
n	4.3	5.8	7.6
$\theta_{\text{D/E}}$ (K)	193	326	837

Table 6.1: Parameters of the phonon model describing the lattice specific heat in $\text{Sr}_3\text{CuIr}_2\text{O}_9$. $\theta_{\text{D/E}}$ represents the Debye or Einstein temperature of the according functions. The weighting of the Debye and Einstein functions are given as n .

Besides the excluded temperature regions the specific heat is described well by the phonon model. The weightings n of the Debye and Einstein functions add up to 17.7 which is close to the total number of ions per formula unit in $\text{Sr}_3\text{CuIr}_2\text{O}_9$.

The inset of figure 6.10 shows C/T as function of temperature. Clearly, for $T \leq 35$ K the zero field and $B = 14$ T measurement bifurcate. In zero field the right flank of a hump is visible at lowest temperatures. Applying a field $B = 14$ T, this hump moves slightly to higher temperatures. From this observation, a Schottky contribution to specific heat is expected.

Below 35 K the measured specific heat is significantly larger than the phonon model. By

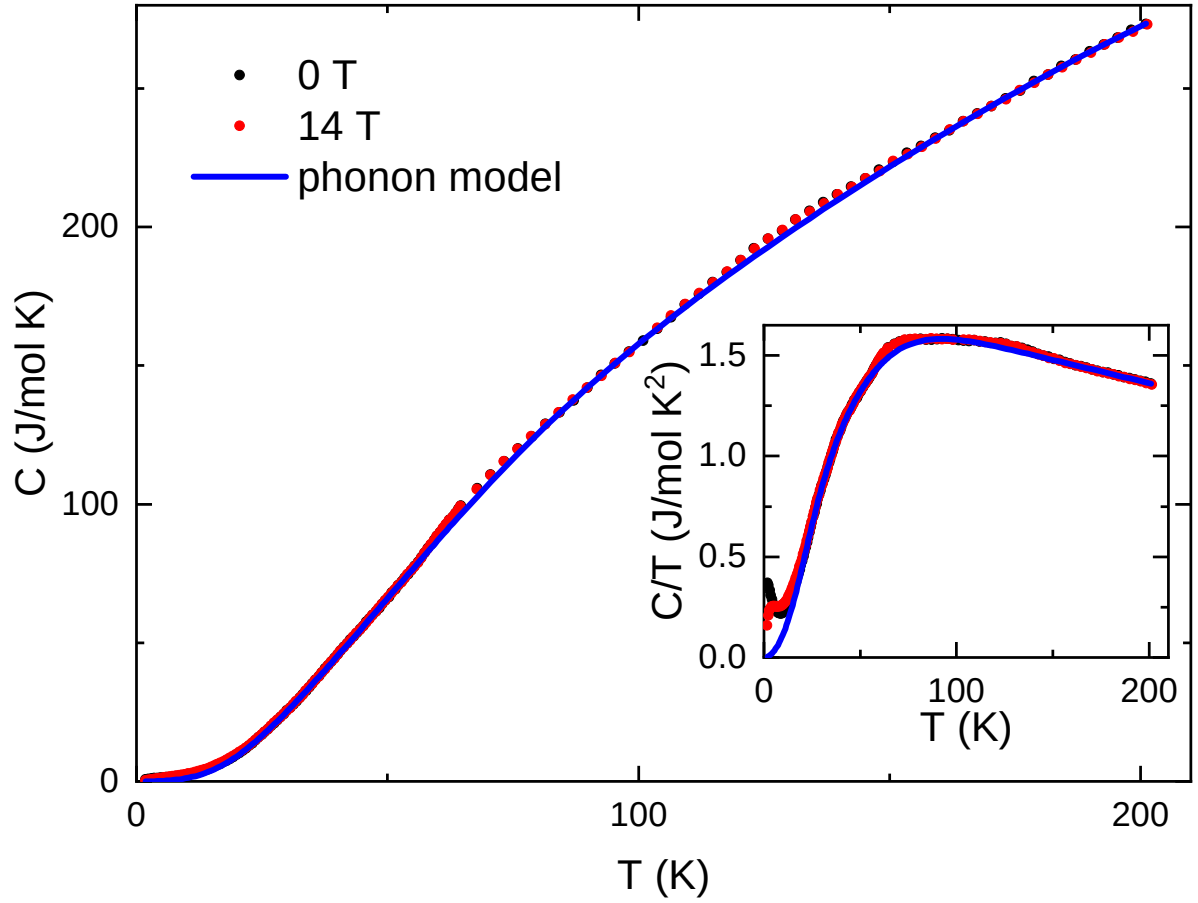


Figure 6.10: Specific heat in zero field (black dots) and in $B = 14$ T (red dots) is shown from 1.8 K up to 200 K. The blue line represents a phonon model consisting of one Debye function and two Einstein functions. **Inset:** Specific heat over temperature is plotted against temperature. Below ~ 35 K the zero field and 14 T measurement bifurcate.

subtracting the phonon specific heat from both measurements the non-lattice specific heat $C_{\text{non-lattice}}$ is calculated.

To determine the Schottky contribution in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ the difference $\Delta C_{\text{non-lattice}} = C_{\text{non-lattice}}(B) - C_{\text{non-lattice}}(B = 0)$ is considered. Using the model 4.7, already applied in previous chapters, a two level Schottky specific heat is fitted to the measured data. In figure 6.11 $\Delta C_{\text{non-lattice}}/T^2$ is plotted with the respective model. As result of the fit, the energy splitting between the two levels in zero field and in $B = 14$ T were calculated to $\Delta(B=0)/k_B = 4.72 \pm 0.03$ K and $\Delta(B=14 \text{ T})/k_B = 27.7 \pm 0.3$ K. The fraction of formula units holding this Schottky contribution is $f = 10.67 \pm 0.03$ % and a small offset between both measurements of $C_0 = (2.2 \pm 0.5) 10^{-4} \text{ J/mol K}^3$ was found.

Noteworthy, as seen for $\text{Sr}_3\text{CuSb}_2\text{O}_9$ and $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ in this thesis and also other compounds [34, 41], the two Schottky levels are not degenerate at zero field. Nonetheless, assuming the Zeeman effect as the driving force of the level splitting leads to:

$$\Delta(B) = \Delta(B = 0) + 2\mu_B g J B \quad (6.8)$$

With $J = 1/2$ the two level splitting predicts $g = 2.44$. This g factor is larger than the expected value for Cu^{2+} ions ($g_{\text{ESR}} = 2.24$ for $\text{Sr}_3\text{CuSb}_2\text{O}_9$ [35]). Furthermore, the Schottky analysis is built on only two measurements at different fields. The linear trend caused by the Zeeman effect needs to be confirmed by further measurements, which were not conducted in this thesis. The calculated level splittings and their expected linear relationship is depicted in the inset of figure 6.11.

The magnetic specific heat is calculated by subtracting the Schottky contribution from the non-lattice specific heat for the zero field and 14 T measurement. The resulting data is plotted in figure 6.12 a). In both magnetic fields C_{mag} is a broad peak around ~ 8 K with a slowly falling flank towards higher temperatures. At roughly 32 K C_{mag} reaches zero. Some peaks at higher temperatures are still visible after subtracting lattice and Schottky specific heat. However, these peaks are most likely artefacts or measurement errors. Magnetic specific heat is expected as a broad peak at very low temperatures [50, 35, 39]. Hence non-lattice and non-Schottky specific heat below 32 K is considered as magnetic specific heat.

The magnetic specific heat can be used to calculate the magnetic entropy S_{mag} by the following equation:

$$S_{\text{mag}} = \int \frac{C_{\text{mag}}}{T} dT \quad (6.9)$$

S_{mag} in zero field and $B = 14$ T is plotted in figure 6.12 b). Both curves roughly lie on top of each other and saturate at $S_{\text{sat}} \approx 2.3 \text{ J/mol K}$. To calculate the full magnetic entropy released at

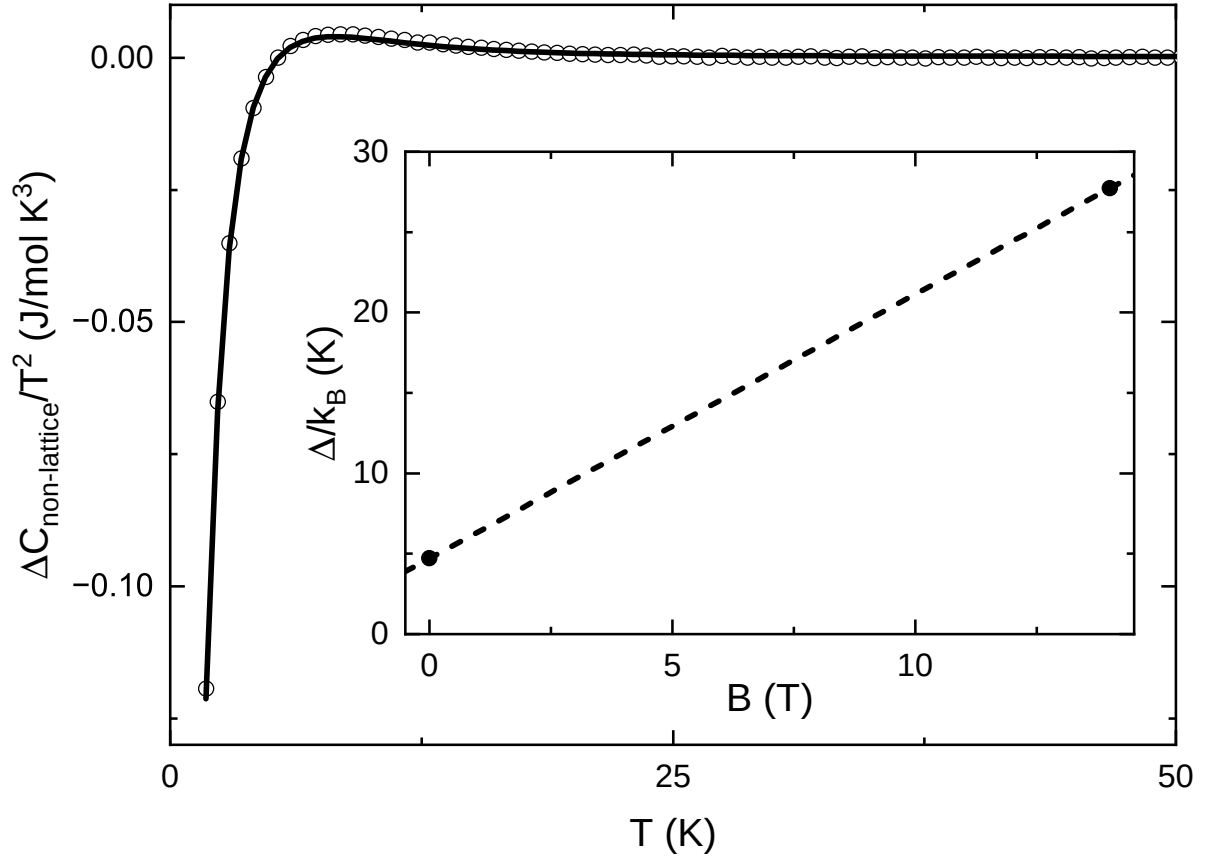


Figure 6.11: $\Delta C_{\text{non-lattice}} = C_{\text{non-lattice}}(B) - C_{\text{non-lattice}}(B = 0)$ over T^2 is plotted against temperature in black circles. The solid line represents a Schottky model fitted to the measured data. **Inset:** The calculated energy level splitting $\Delta(B)$ from the Schottky model of the zero field and 14 T measurement are illustrated as black dots. The dotted line indicates the suspected linear relationship of $\Delta(B)$.

~ 35 K, the contribution below 1.8 K needs to be estimated. At 1.8 K the magnetic specific heat is $C_{\text{mag}}(T = 1.8 \text{ K}) = 0.28 \text{ J/mol K}$. By extrapolating the magnetic specific heat linearly from 1.8 K to zero the magnetic entropy can be calculated:

$$S_{\text{ext}} = \int_0^{1.8} \frac{0.28 T}{1.8 T} \text{ J/mol K}^2 dT = 0.28 \text{ J/mol K} \quad (6.10)$$

Adding the extrapolated magnetic entropy to the measured saturation value leads to $S_{\text{max}} = S_{\text{ext}} + S_{\text{sat}} \approx 2.6 \text{ J/mol K}$. Comparing this result with the theoretical magnetic entropy of a spin $1/2$ system $S_{\text{theory}} \approx 5.76 \text{ J/mol K}$, $\text{Sr}_3\text{CuIr}_2\text{O}_9$ releases only 45 % of the theoretical magnetic entropy. Besides the $J = 1/2$ Cu^{2+} ions also near $J = 0$ Ir_2O_9 dimers should contribute to magnetic entropy. Consequently, even higher magnetic entropy is expected in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ than in spin $1/2$ systems. The lack of entropy detected by heat capacity measurements could hint on a highly degenerate ground state, supporting the hypothesis of a QSL. However, the subtraction of lattice specific heat highly influences the calculation of magnetic entropy. Improvements in the estimate of the phonon contribution are needed to manifest the observations in magnetic entropy.

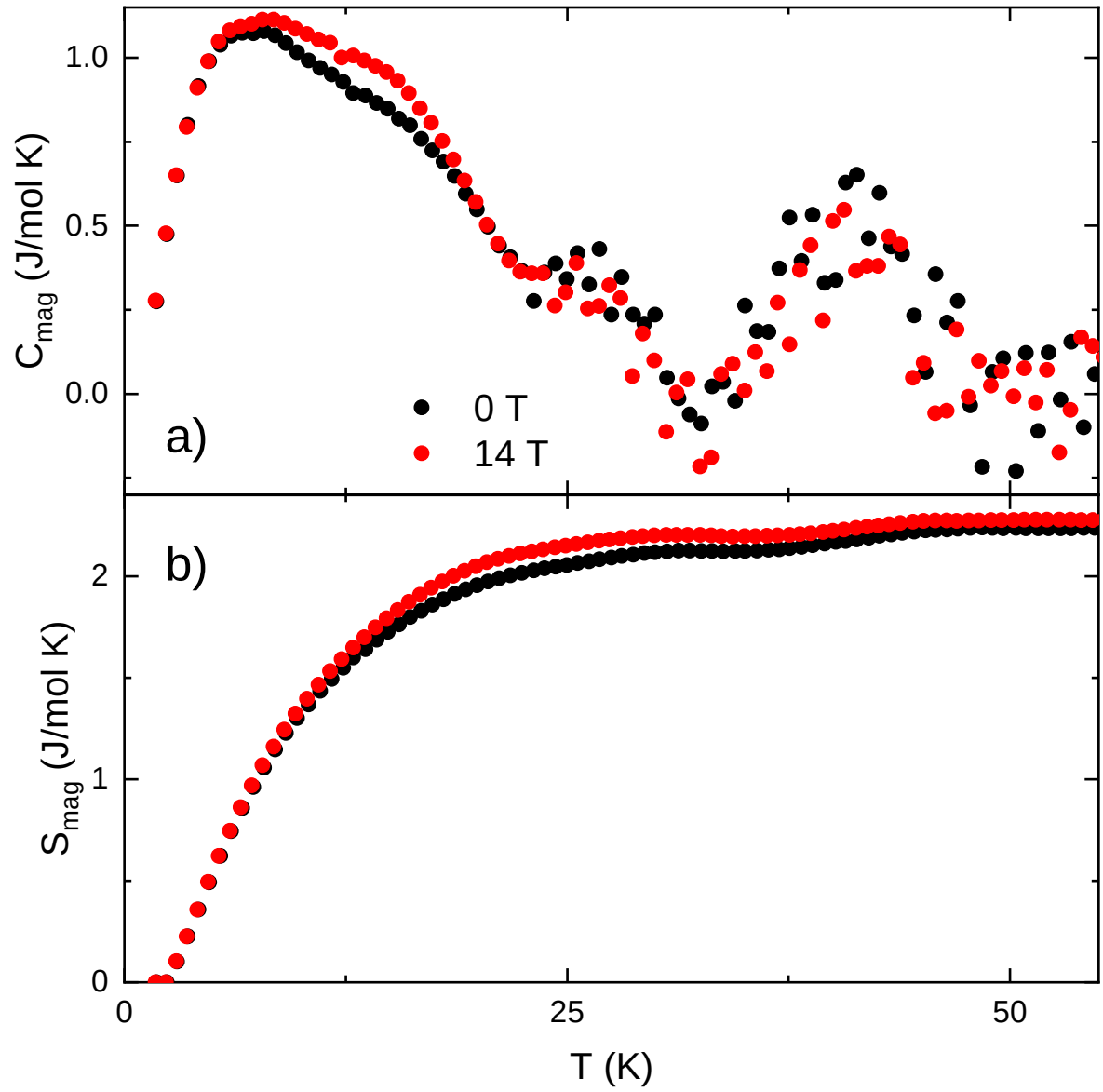


Figure 6.12: **a)** Magnetic specific heat in zero field (black) and $B = 14$ T (red) against temperature. Non-zero signals above ~ 32 K are artefacts or measurement errors and not considered as magnetic specific heat. **b)** Magnetic entropy is plotted over temperature. It saturates for zero field and $B = 14$ T at roughly 2.3 J/mol K .

Conclusions

In this thesis magnetization and heat capacity measurements of the three quantum spin liquid candidates $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ and $\text{Sr}_3\text{CuIr}_2\text{O}_9$ have been studied. Measurements were performed in the temperature range from 1.8 K up to 300 K and in magnetic fields up to 14 T using Quantum Designs devices MPMS and PPMS. Much results concern the size of the magnetic interactions, the presence of orphan spins and conclusions on the possible ground states in the compounds.

$\text{Sr}_3\text{CuSb}_2\text{O}_9$

For $\text{Sr}_3\text{CuSb}_2\text{O}_9$, magnetization was measured at various magnetic fields and temperatures. No magnetic phase transition is observed down to the lowest temperature measured of 1.8 K. Furthermore, no hysteresis is detected. The field dependence of the magnetization of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ at $T = 1.8$ K shows a Brillouin-like contribution from orphan spins and a linear contribution from correlated spins in the bulk of the material. Modeling the Brillouin like contribution leads to two different approaches with individual problems:

A first description of $M(B)$ at $T = 1.8$ K with a Brillouin function representing orphan spins and a linear function for the correlated spins does not match the measured data well. The best fit of this model to the measurement estimates a fraction of $f = 4.03 \pm 0.07$ % orphan spins per unit cell with total angular momentum $J = 1.04 \pm 0.02$. In contrast, for Cu^{2+} orphan spins total angular momentum $J = 1/2$ is expected.

In a second approach the combination of a $J = 1/2$ orphan contribution, an impurity phase contribution and a bulk contribution are fitted to $M(B)$. The measurement is described well with this model. At 1.8 K, the fraction $f_1 = 5.21 \pm 0.03$ % of $J = 1/2$ magnetic moments are estimated per unit cell with an small interaction of $\theta = -0.774 \pm 0.015$ K. The impurity phase is present in $f_2 = 0.576 \pm 0.011$ % of unit cells and holds an angular momentum of $J_2 = 3.50 \pm 0.04$. The large amount f_2 of the impurity phase with a large angular momentum J_2 is hardly probable, hence the model is presumably inadequate.

In the temperature dependence of the magnetization Curie-Weiss behavior is observed. Using high temperature Curie-Weiss fits, the Weiss temperature is estimated to $\theta_W = -132 \pm 10$ K

which is comparable to the result in literature [35]. Further models are applied to $\chi(T)$ to gain insight on the orphan and bulk contributions to the magnetic susceptibility. These models suggest AFM super-exchange interactions of $J \approx 90$ K between correlated spins and yield roughly 15 % spin $1/2$ orphans in the $\text{Sr}_3\text{CuSb}_2\text{O}_9$ sample. The different amount of orphans calculated in the $M(B)$ analysis and $\chi(T)$ analysis might hint on a temperature dependence in orphan spin abundance. By including results from $M(B)$ measurements, most of the measured temperature regime is successfully reconstructed with a phenomenological model combining a TAFM function and Brillouin functions.

Specific heat measurements show no phase transition down to 1.8 K in $\text{Sr}_3\text{CuSb}_2\text{O}_9$. A Schottky contribution most likely caused by Zeeman splitting of $S = 1/2$ orphan spins is observed. Intriguingly, non-zero energy splitting for the Schottky levels at zero applied field is detected. A non-zero crystal field and correlations of orphan spins with their environment might cause this level splitting. The magnetic entropy is assessed to $S \approx 1.0$ J/mol K, which is ~ 17 % of the expected entropy of a spin $1/2$ system. The lack of magnetic entropy calculated from the heat capacity measurement suggests a large ground state entropy typical for QSLs.

$\text{Sr}_3\text{ZnIr}_2\text{O}_9$

In $\text{Sr}_3\text{ZnIr}_2\text{O}_9$, measurements of magnetization do not show any sign of a magnetic phase transition down to 1.8 K for $\text{Sr}_3\text{ZnIr}_2\text{O}_9$. Though the Ir^{5+} ions are nominally in a $J = 0$ state, a small magnetic moment is observed for this compound, which implies the presence of a finite paramagnetic moment with $J \neq 0$. In $M(B)$ measurements at 1.8 K a Brillouin term caused by orphan moments and a linear term are identified. Using a fit, the properties of the orphan moments are calculated to $J = 1.223 \pm 0.012$ with $g = 2$ and an abundance $f = 0.428 \pm 0.006$ % orphan moments per unit cell. Considering the temperature dependence of the magnetic susceptibility $\chi(T)$, Curie-Weiss behavior is observed in combination with a large temperature independent offset χ_0 . From a high temperature Curie-Weiss fit the Weiss temperature $\theta_W = -39 \pm 8$ K and the effective moment $\mu_{\text{eff}} = 0.85 \pm 0.09$ $\mu_B/\text{f.u.}$ are calculated. These results are similar to findings for $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [17]. The temperature independent offset in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ is surprisingly large with $\chi_0 = (1.23 \pm 0.05)10^{-3}$ erg/G² mol. Including results of the $M(B)$ analysis, $\chi(T)$ can be modeled with a combination of a Curie-Weiss function and a Brillouin function representing the orphan moments.

In measurements of heat capacity again no sign of a magnetic phase transition is detected. A Schottky contribution to specific heat is found that does not show considerable field dependence. Similar to $\text{Sr}_3\text{CuSb}_2\text{O}_9$, a non-zero energy level splitting is observed in zero magnetic field. Magnetic entropy was estimated to $S = 0.8$ J/mol K which is in the same magnitude as the magnetic entropy in the related compound $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [17].

Sr₃CuIr₂O₉

Sr₃CuIr₂O₉ combines both magnetic sources (Cu²⁺ and Ir₂O₉) of the previous compounds in one structure. Again no magnetic phase transition has been observed neither in heat capacity nor magnetization measurements down to 1.8 K. In magnetization measurements no hysteresis or features are observed in contrast to measurements published in [50]. Furthermore, a peak measured in the in-phase susceptibility χ' and out-of-phase susceptibility χ'' by [50] is not detected in measurements from this thesis. Hence, the features reported in [50] might originate from impurity phases which are not present in the samples studied in this thesis.

Analyzing the field dependence of the magnetization a Brillouin contribution associated with orphan spins and a linear part for correlated spins are identified. In a simple model the properties of the orphan spins are estimated to $J = 0.809 \pm 0.013$ with $g = 2$ and an abundance of $f = 4.81 \pm 0.11$ % per unit cell. When considering a more complex model, the orphan spins from Cu²⁺ ions and Ir₂O₉ dimers can be fitted separately. As result of this fit, $f_{\text{Cu}^{2+}} = 4.7 \pm 0.2$ % of unit cells contain Cu²⁺ orphans and $f_{\text{Ir}_2\text{O}_9} = 1.00 \pm 0.07$ % of unit cells hold Ir₂O₉ orphans.

In the temperature dependence of the magnetic susceptibility Curie-Weiss behavior is observed. A high temperature Curie-Weiss fit gives the Weiss temperature $\theta_W = -17 \pm 5$ K and an effective moment $\mu_{\text{eff}} = 1.47 \pm 0.03 \mu_B/\text{f.u.}$. Surprisingly, the effective moment is significantly smaller than the effective moment expected from a spin 1/2 system. Also comparing to results of reference [50], the magnetic moment observed in this thesis is much smaller. Furthermore the Weiss temperature estimated in this thesis is only roughly 55 % of the value from [50]. Reason for that could be a too low start temperature of the fit range for the Curie-Weiss fit. With further models including results of $M(B)$ fits, the whole measured temperature regime of $\chi(T)$ could be reconstructed, but the resulting parameters deviate even more from the expected results.

Heat capacity was measured in fields $B = 0$ T and 14 T from $T = 1.8$ K up to 200 K. A Schottky contribution to the specific heat is detected. Using a two level Schottky model the energy splitting between the two discrete states is calculated. A non-zero energy splitting $\Delta_0 = 4.72 \pm 0.03$ K in zero applied field is found. Magnetic specific heat appears in Sr₃CuIr₂O₉ up to ~ 32 K. From the magnetic specific heat the magnetic entropy S is calculated. It amounts to $S \approx 2.6$ J/mol K which is roughly 45 % of the magnetic entropy expected for a spin 1/2 system. The magnetic entropy determined in this thesis matches well with the finding in [50] of 2.9 J/mol K. Missing magnetic entropy suggests a highly degenerate ground state which implies a possible QSL ground state in Sr₃CuIr₂O₉.

Comparing the results of Sr₃CuSb₂O₉, Sr₃ZnIr₂O₉ and Sr₃CuIr₂O₉ shows, that the magnetic properties of Sr₃CuIr₂O₉ are not just the sum of the properties from Cu²⁺ spins and Ir₂O₉ moments. Magnitude and shape of $M(B)$, $\chi(T)$ and C_{mag} are different in Sr₃CuIr₂O₉ from the

sum of the quantities in $\text{Sr}_3\text{CuSb}_2\text{O}_9$ and $\text{Sr}_3\text{ZnIr}_2\text{O}_9$. This demonstrates that the magnetic processes in $\text{Sr}_3\text{CuIr}_2\text{O}_9$ are not only influenced by Cu^{2+} - Cu^{2+} and Ir_2O_9 - Ir_2O_9 interactions but also their cross correlations.

Appendix

This appendix shows complementary analyses of magnetization measurements for $\text{Sr}_3\text{CuSb}_2\text{O}_9$, $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ and $\text{Sr}_3\text{CuIr}_2\text{O}_9$ by comparing Curie-Weiss fits in different fit ranges similar to reference [49]. Therefore, a modified Curie-Weiss model according to equation 2.10 is fitted to the measured data from a temperature called T_{Fitstart} up to 300 K. The Curie-Weiss model is only valid for high temperatures, hence T_{Fitstart} should not be chosen too low. Usually, at least $T_{\text{Fitstart}} > 2\theta_{\text{W}}$ is desired to obtain trustworthy results from a Curie-Weiss model. In contrast, for large T_{Fitstart} less data is available which reduces the reliability of the fit. Furthermore, with rising temperature the measured magnetization becomes smaller and more prone to noise and measurement errors. Applying the Curie-Weiss model in different temperature ranges allows to study the dependence of the fit parameters on T_{Fitstart} . If the parameters show a constant plateau over a considerable T_{Fitstart} range and $T_{\text{Fitstart}} > 2\theta_{\text{W}}$ the obtained parameters by the fit are trustworthy.

For all three compounds studied in this thesis the temperature dependent susceptibility $\chi(T)$ measured in a FC protocol in fields $B = 1$ T, 3 T and 7 T are analyzed with different T_{Fitstart} . Additionally, for $\text{Sr}_3\text{CuSb}_2\text{O}_9$ the TAFM model was fitted analogously in different fit ranges.

For $\text{Sr}_3\text{CuSb}_2\text{O}_9$, the obtained parameters from measurements in different fields show similar dependence on T_{Fitstart} for both the Curie-Weiss and the TAFM model (see figure 7.1). For $T_{\text{Fitstart}} < 80$ K, the parameters change rapidly with T_{Fitstart} . In the range $120 \text{ K} \leq T_{\text{Fitstart}} \leq 180 \text{ K}$, the parameters are roughly constant. Although here θ_{W} has roughly the same magnitude as T_{Fitstart} this range of T_{Fitstart} seems most trustworthy to apply Curie-Weiss models and TAFM models. The variation of the parameters with T_{Fitstart} in this regime was considered in estimating the errors of the parameters of Curie-Weiss fits and TAFM fits. For $T_{\text{Fitstart}} > 180$ K the parameters of the fit begin to vary strongly with T_{Fitstart} .

In figure 7.2 the variation of parameters obtained by Curie-Weiss fits with different T_{Fitstart} for $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ are plotted. The parameters from fits applied to the 3 T and 7 T measurements are mostly close together, while the parameters of fits to the 1 T measurement deviate from the others. At $T_{\text{Fitstart}} = 250$ K a jump in all parameters is visible, most likely due to an unstable fit relying on too little data. With rising T_{Fitstart} the parameters in all three fields vary more with

T_{Fitstart} and no constant plateau can be found. In this thesis, all results found by Curie-Weiss fits for $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ should be seen as rough estimate but because of the strong variation with the fit range, no unmistakened parameters can be given.

The variation of parameters for $\text{Sr}_3\text{CuIr}_2\text{O}_9$ from Curie-Weiss fits with different T_{Fitstart} is plotted in figure 7.3. In all fields, the calculated parameters are roughly the same. Only for $T_{\text{Fitstart}} = 250$ K the parameters of different fields vary considerably. This might be caused by unstable fits with little data. For 1 T and 7 T measurements, there is a little range of constant parameters around $T_{\text{Fitstart}} \approx 180$ K. Still, all the parameters change significantly with the fit range for most of the used T_{Fitstart} . This is an unexpected observation, as the Curie-Weiss model is valid for $T_{\text{Fitstart}} \gtrsim 2\theta_{\text{W}}$, which seems to be the case for $\text{Sr}_3\text{CuIr}_2\text{O}_9$.

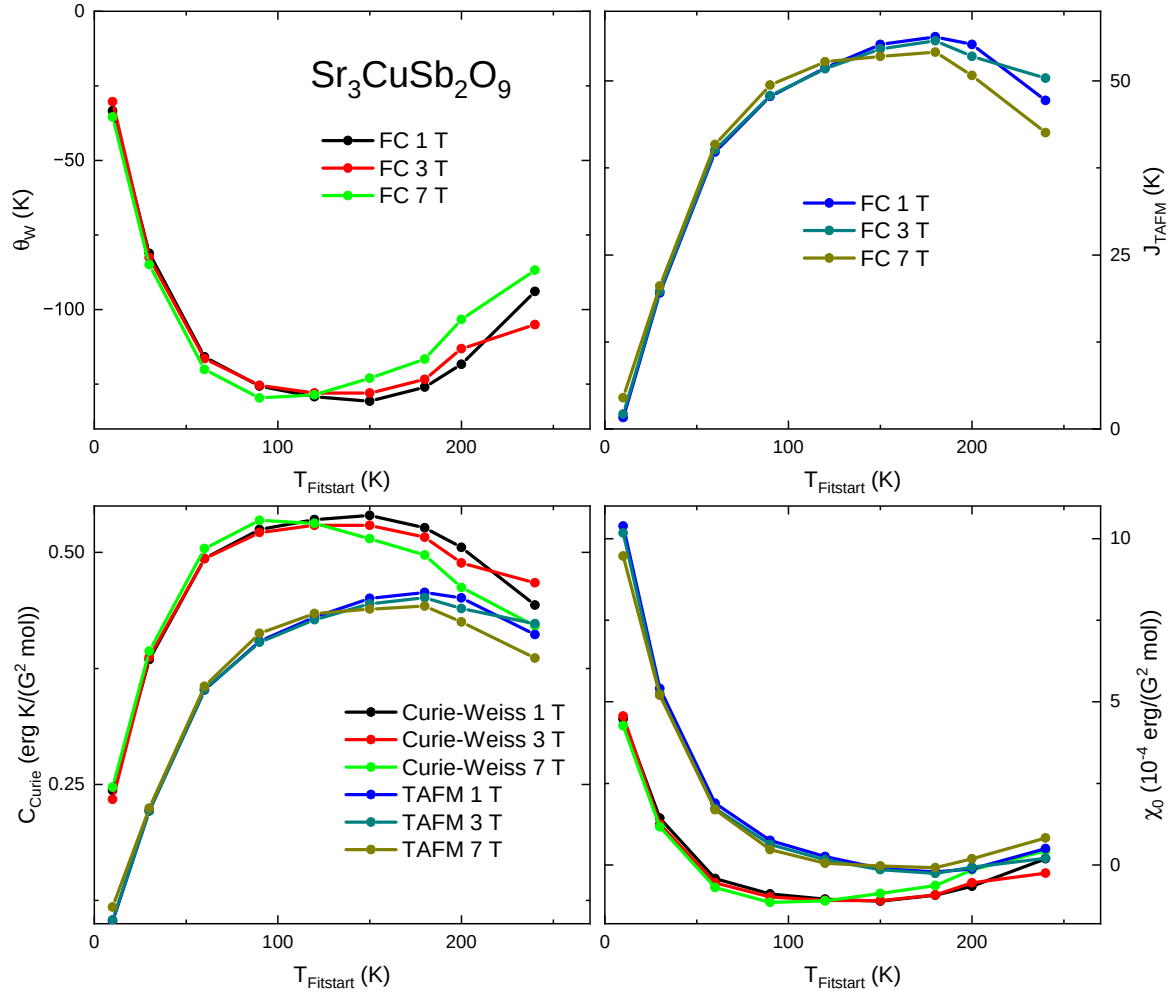


Figure 7.1: The parameters of the Curie-Weiss model (see equation 2.10) and the TAFM model applied to $\chi(T)$ data of $\text{Sr}_3\text{CuSb}_2\text{O}_9$ are plotted vs. the temperature T_{Fitstart} . Both models were applied in the temperature range $T_{\text{Fitstart}} \leq T \leq 300$ K.

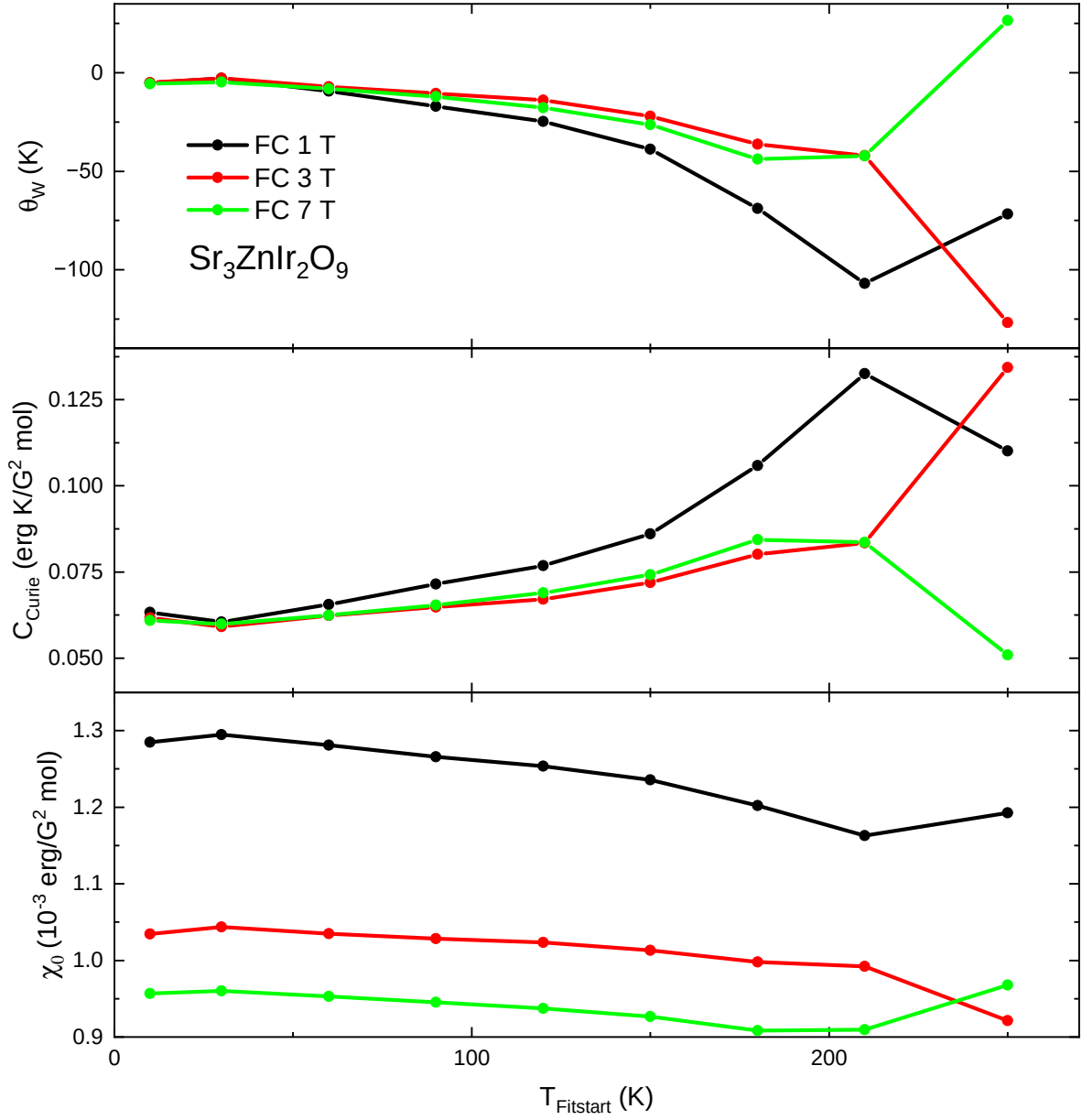


Figure 7.2: Parameters of the Curie-Weiss model (see equation 2.10) applied to $\chi(T)$ data of $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ are plotted vs. the temperature T_{Fitstart} . The Curie-Weiss model was applied in the temperature range $T_{\text{Fitstart}} \leq T \leq 300$ K.

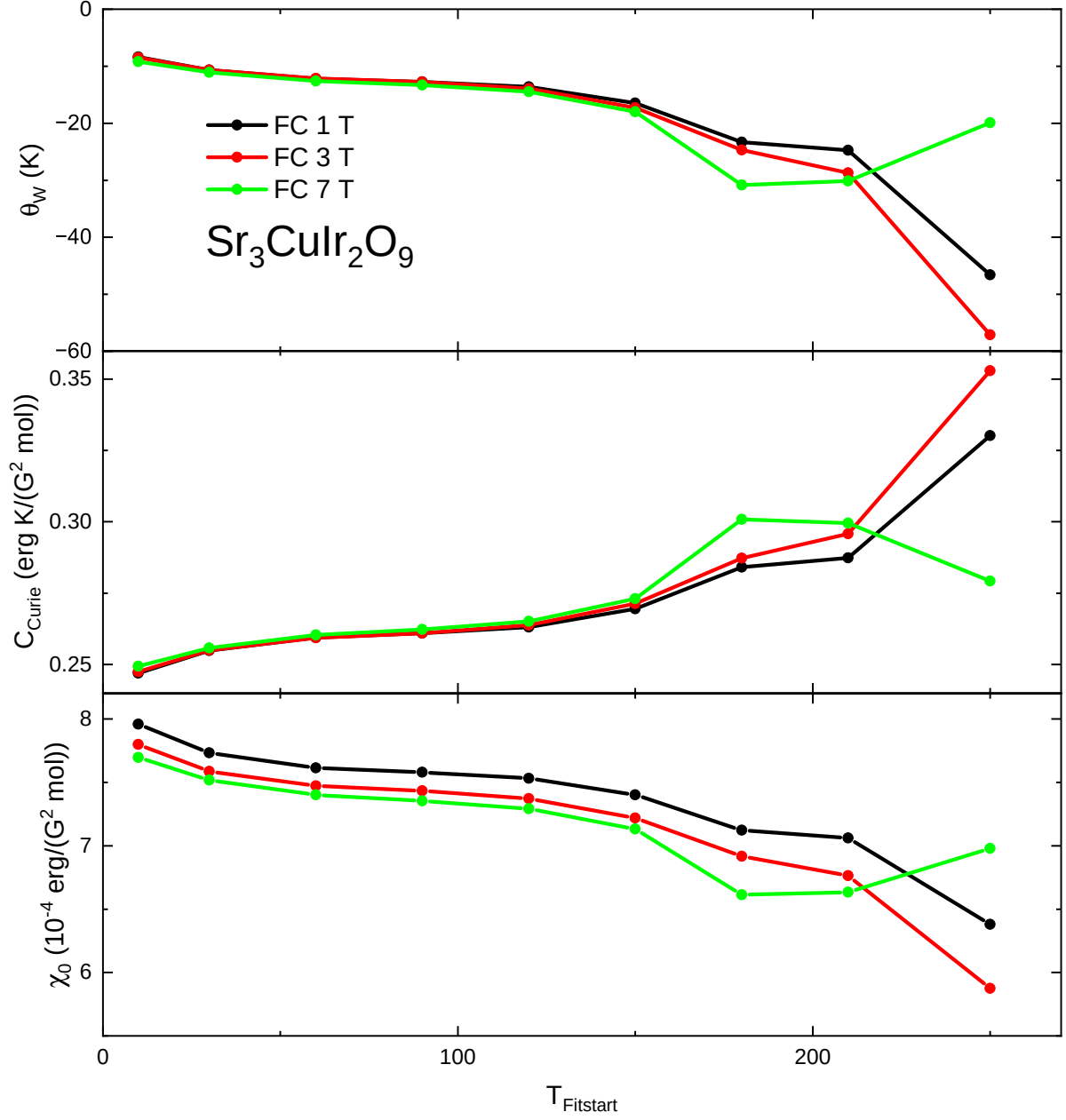


Figure 7.3: Parameters of the Curie-Weiss model (see equation 2.10) applied to $\chi(T)$ data of $\text{Sr}_3\text{CuIr}_2\text{O}_9$ are plotted vs. the temperature T_{Fitstart} . The Curie-Weiss model was applied in the temperature range $T_{\text{Fitstart}} \leq T \leq 300$ K.

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Erklärung:

Ich versichere, dass ich diese Arbeit selbstständig verfasst habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Heidelberg, den

15.03.2024 Timo Kleinbohl
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