

Doping Studies of Frustrated Magnets



Hajime Shinohara

Cavendish Laboratory, Department of Physics

University of Cambridge

This dissertation is submitted for the degree of

Doctor of Philosophy

Jesus College



2018

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other University. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration, except where specifically indicated in the text. This dissertation contains less than 65,000 words including appendices, bibliography, footnotes, tables and equations and has less than 150 figures.

Hajime Shinohara

2018

Acknowledgements

I would like to acknowledge Dr. Siân Dutton for giving me the opportunity to work in the Quantum Matter group and for all she has taught me over the last few years.

I would like to thank to my second supervisor Dr. Nalin Patel especially about organizing my project efficiently. In terms of my English, Dr. Rupert Brown who taught me intensively in the university language centre.

I would like to thank to all Quantum Matter group members especially Paromita Mukherjee who kindly proofread my poor English persistently countless times. Indy Liu also kindly helped me to check my English. Dr. Suchitra Sebastian intensively taught me for presentations for outreach base on this thesis.

I also would like to thank to technicians Doug Astill and Adam Brown for everyday facility maintenances.

I would also like to thank to the Winton Programme for the Physics of Sustainability, Funai Foundation for Information Technology, British Council Japan Association, International Training Programme in Japan Society for the Promotion of Science and Jesus College for providing financial support to the project.

I would like to thank to the member of Jesus College, especially Jesus MCR, and Cambridge University Korfbal Club for kind support and improving my English skill.

Finally, I would like to thank to my parents Takeshi Shinohara and Kazumi Shinohara and my sister Natsumi Shinohara for their continual support.

Doping Studies of Frustrated Magnets

Hajime Shinohara

Doping nonmagnetic materials is known as an effective way of investigating the properties of frustrated magnets.

LiCuSbO_4 is one of the simplest quasi-one dimensional spin-1/2 magnets which can be modelled with ferromagnetic(FM) nearest neighbour and antiferromagnetic (AFM) next nearest neighbour interactions. Here, doping with both non-magnetic ions, Zn, Mg, and magnetic ions, Co, is investigated. $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($\text{M}=\text{Mg, Zn, Co}$ $0 \leq x \leq 0.1$) samples were synthesized by a ceramics process. At higher doping levels ($x \geq 0.04$), paramagnetic Curie features are observed below 4 K, however the broad peak characteristic of short range ordering at 6 K is retained. Isothermal magnetization indicates that the critical field found at 12 T in LiCuSbO_4 was shifted by Zn and Mg doping. While the field is increased as the amount of Mg doping, it was increased as Zn doping in the range of $0 \leq x \leq 0.02$ but decreased by $x \geq 0.04$. The trend in critical field is observed to follow that of the c lattice parameter for both Zn and Mg doping. On doping with Co^{2+} ($S = 3/2$), a low temperature Curie feature was observed from $x=0.02$. The value of the critical field increased on doping from ($x=0$) 12 T for 13.5 T ($x=0.10$). As for non-magnetic doping the trend in H_c has the same behaviour as the lattice parameter.

The effect of doping on the pyrochlore spin ice $\text{A}_2\text{B}_2\text{O}_7$ is also explored. The effect of oxygen vacancies induced by the aliovalent substitution on the B site on the crystal electric field was explored in the ceramic solid solutions. The effect of aliovalent doping on the pyrochlore $\text{A}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($\text{A}=\text{Ho}$ and Dy $0 \leq x \leq 0.10$) $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($\text{B}=\text{Sn}$ and Ti $0 \leq x \leq 0.05$) were studied. While no dramatic changes of the saturation value of isothermal magnetization and heat capacities was observed in $\text{Dy}_2\text{Sn}_2\text{O}_7$ by Sc doping in the range of $0 \leq x \leq 0.1$, the saturation value of isothermal magnetization and magnetic entropy in $\text{Ho}_2\text{Sn}_2\text{O}_7$ was clearly increased by Sc doping more than $x=0.05$. This difference could be from the difference of Kramer's and non-Kramer's spins between Dy and Ho, as while Dy is a Kramer's ion and its ground state is protected, Ho is a non-Kramer's ion and its ground state could be split.

While $\text{Tb}_2\text{Sn}_2\text{O}_7$ is known as quantum spin ice, $\text{Tb}_2\text{Ti}_2\text{O}_7$ is known as spin liquid. A peak at 6 K of heat capacity, which is assigned as being due to a crystal electric field excitation to an excited doublet in $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ was observed in the $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ sample. However in $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ it was not observed. This indicates that the increased strain in the ceramic solid solution has a larger impact on the crystal electric field.

Contents

Contents	vii
Chapter 1 Introduction.....	1
1.1 Magnetic Materials Research	1
1.2 Atoms and spins	1
1.3 Crystals.....	2
1.4 Doping.....	2
1.5 Crystal electric fields (CEF) and Jahn-Teller effect.....	3
1.6 CEF of Lanthanides.....	6
1.7 Magnetic Interactions	7
1.7.1 Bohr magnetization and effective magnetic moments	7
1.7.2 Dipolar interactions.....	7
1.7.3 Direct exchange interaction	7
1.7.4 Superexchange interactions	8
1.7.5 Goodenough Kanamori rules	8
1.8 Magnetic models	10
1.9 Magnetic Ordering	11
1.9.1 Magnetic susceptibility	11
1.9.2 Paramagnetism (PM)	12
1.9.3 Ferromagnetism (FM).....	12
1.9.4 Antiferromagnetism (AFM).....	13
1.9.5 Frustration	13
1.10 Theoretical Bethe Ansatz methods and quantum criticality of Heisenberg $S=1/2$ one dimensional spin chains	16
1.11 Spin Ice.....	18
1.11.1 Pyrochlore structure	20
1.11.2 Research in spin ice	20
1.12 Structure of the thesis	21
Chapter 2 Experimental Techniques.....	22
2.1 Synthesis.....	22
2.2 Characterization	23
2.2.1 X-ray Diffraction	23
2.2.2 Powder X-ray diffraction	24
2.2.3 X-ray pattern Intensities:.....	25

2.2.4	Experimental conditions	26
2.2.5	Qualitative analysis	26
2.2.6	Rietveld Analysis	27
2.3	Physical Properties	29
2.3.1	Magnetic Properties Measurements	29
2.3.2	Magnetic Susceptibility	31
2.3.3	Diamagnetic correction	31
2.3.4	Heat Capacity	33
2.3.5	Schottky type specific heat	35
2.3.6	Helium-3 option for lower temperature	36
2.3.7	Heat capacity He-3 setting	36
Chapter 3	Doping with non-magnetic ions in the one-dimensional $S = 1/2$ magnet	
LiCuSbO ₄	38	
3.1	Introduction	38
3.2	Experimental	41
3.3	Results	42
3.3.1	Structural Chemistry	42
3.3.2	Magnetic Properties	47
3.4	Discussion	60
3.4.1	Structure	60
3.4.2	Magnetic properties	61
3.4.3	Difference between Zn and Mg doping	65
3.5	Conclusions	67
Chapter 4	Doping magnetic materials on one-dimensional quantum frustrated	
magnets:LiCuSbO ₄		68
4.1	Introduction	68
4.1.1	Magnetic Doping on LiCuSbO ₄	68
4.2	Sample preparation	68
4.3	Results	69
4.3.1	Structural Chemistry	69
4.3.2	Bulk Magnetic Properties	73
4.4	Discussion	83
4.4.1	Structure	83
4.4.2	Magnetic Properties	84
4.5	Conclusion	88
Chapter 5	Effect of doping in spin ice materials $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($A=\text{Dy, Ho}$)	89
5.1	Introduction	89

5.2	Sample preparation.....	91
5.3	Results	91
5.3.1	Structural Chemistry	91
5.3.2	Magnetic properties	95
5.3.3	Heat capacity.....	104
5.4	Discussion	105
5.4.1	Structure.....	105
5.4.2	Magnetic properties	106
5.4.3	Heat capacity.....	108
5.5	Conclusions	110
Chapter 6	Effect of doping in Quantum Spin Ice /Liquid Materials $Tb_2B_{2(1-x)}Sc_{2x}O_{7-x}$ ($B=Sn, Ti, 0 \leq x \leq 0.05$).....	112
6.1	Introduction	112
6.1.1	$Tb_2Sn_2O_7$ and $Tb_2Ti_2O_7$	112
6.2	Sample preparation.....	114
6.3	Results	114
6.3.1	XRD	114
6.3.2	Bulk magnetic properties	118
6.3.3	Heat Capacity.....	123
6.4	Discussion	126
6.4.1	Structure.....	126
6.4.2	Magnetic Properties	127
6.4.3	Heat Capacity.....	127
6.5	Conclusions	129
Chapter 7	Summary	130
7.1	One-dimensional spin chains $LiCu_{1-x}M_xSbO_4$ ($M=Mg, Zn, Co$).....	130
7.2	Pyrochlore Spin ice $A_2B_2O_7$ ($A=Ho, Dy, Tb, B=Sn, Ti$)	132
7.2.1	$A_2Sn_{2(1-x)}Sc_{2x}O_{7-x}$ ($A=Ho, Dy, 0 \leq x \leq 0.1$)	132
7.2.2	$Tb_2B_{2(1-x)}Sc_{2x}O_{7-x}$ ($B=Sn$ and $Ti, 0 \leq x \leq 0.1$).....	133
7.3	Summary	134
Chapter 8	References.....	136
Appendix		1

Chapter 1 Introduction

In this thesis, the phenomena of frustration in magnetic systems and its effects are investigated. Doping is an effective method for investigating and modifying materials properties. Though there are theoretical descriptions available, the interactions of spins in frustrated magnets are complicated and experimental studies are required to improve our understanding of the properties of frustrated magnets.

1.1 Magnetic Materials Research

A tremendous variety of materials are known and extensively studied and yet materials research continues to reveal new phenomena and improved enable to understand their properties. Materials with magnetic properties are the focus of this thesis. One of the key areas of study is quantum frustrated magnets, which have recently gathered increasing interest for their exotic magnetic properties¹⁻⁵.

The origins of the magnetic properties in materials are from the spins of atoms or ions and their interactions. In this thesis, frustrated magnets are experimentally realized in solid state oxide materials containing magnetic transition metal ions or magnetic rare earth ions.

1.2 Atoms and spins

The properties of atoms are dependent on their electronic orbitals, which are filled with electrons as described by Hund's rules^{6,7}. The same considerations apply to charged ions. Hund's rules are;

1. Arrange the electronic wave function so as to maximize S.
2. The next step is, given the wave function determined by the first rule, to maximize L.

3. Finally the value of J is found using $J=|L-S|$ if the shell is less than half full and $J=|L+S|$ if it is more than half full.

S , L and J are known as spin angular momentum, orbit angular momentum and total angular momentum, respectively.

The rules explain that electrons fill the orbitals from lower energy to higher energy in order to make the total energy as low as possible. Also, an electron is a Fermion and follows Fermi-Dirac statistics, which requires that no two fermions can be in the same energy state. This means that two electrons cannot have all four quantum numbers equal and so if they occupy the same orbital, their spins must be anti-parallel⁸. This is known as Pauli's exclusion principle⁸.

There are four types of electronic orbitals, s orbital, p orbital, d orbital and f orbital⁹. The s and p orbitals are of lower energy and so are filled first and then d orbitals are filled. For higher number, some overlaps happened such as $4s$ orbital was filled before $3d$ orbitals due to the order of energy levels of orbitals¹⁰. In the materials investigated in this thesis the s and p orbitals are fully filled and do not contribute to the magnetic properties. Therefore, only electrons in the d or f orbitals contribute to the magnetic properties.

1.3 Crystals

A crystal is a collection of atoms, molecules or ions assembled in a characteristic regular pattern⁹. Crystalline systems may be single crystals or polycrystalline in nature⁹. Single crystals are better for analysing the physical properties of a particular material as a single crystal allows for the properties as a function of crystallographic direction to be measured⁹. However, it can often be hard to synthesize single crystals. In this thesis, the samples which are investigated are polycrystals. Polycrystals consist of a combination of smaller crystals.

1.4 Doping

Doping as discussed in this thesis is the chemical substitution of ions within a solid solution, $A_{1-x}B_x$ ¹¹. The nominal amount of doping is the amount of x in the chemical when the materials are synthesized. However, some of the dopants can appear in sites different to the initially targeted sites. This means that the actual crystal structure can be different from that expected,

due to the dopants are doped in different sites. It is needed that designing and producing materials to minimize this difference. For example, there is a tendency that transition metals can be doped into transition metal sites. In this thesis, the amount of x in the chemical equation is the nominal amount unless otherwise written. For magnetic materials, even a small amount of doping can significantly alter the magnetic properties of the materials system^{3,12,13}. In this thesis, the doping effects on various types of frustrated magnetic oxide materials are investigated.

1.5 Crystal electric fields (CEF) and Jahn-Teller effect

Each material has unique electorical energy levels for their atoms due to the different orbitals. When atoms or ions constitute crystals, other interactions occur which alters the energy levels. The energy states of orbitals are changed by Coulomb forces between neighbouring ions in a crystal. The electrostatic energy is given by the following equation:

$$E \propto \frac{q_1 q_2}{r} \quad (1.1)$$

where, E is the bond energy between the charges, q_1 and q_2 are the charges of the interacting ions, and r is the distance between q_1 and q_2 . In $3d$ orbitals, there are five orbitals described as d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . When ions are isolated, these five orbitals have the same energy (Figure 1.1).

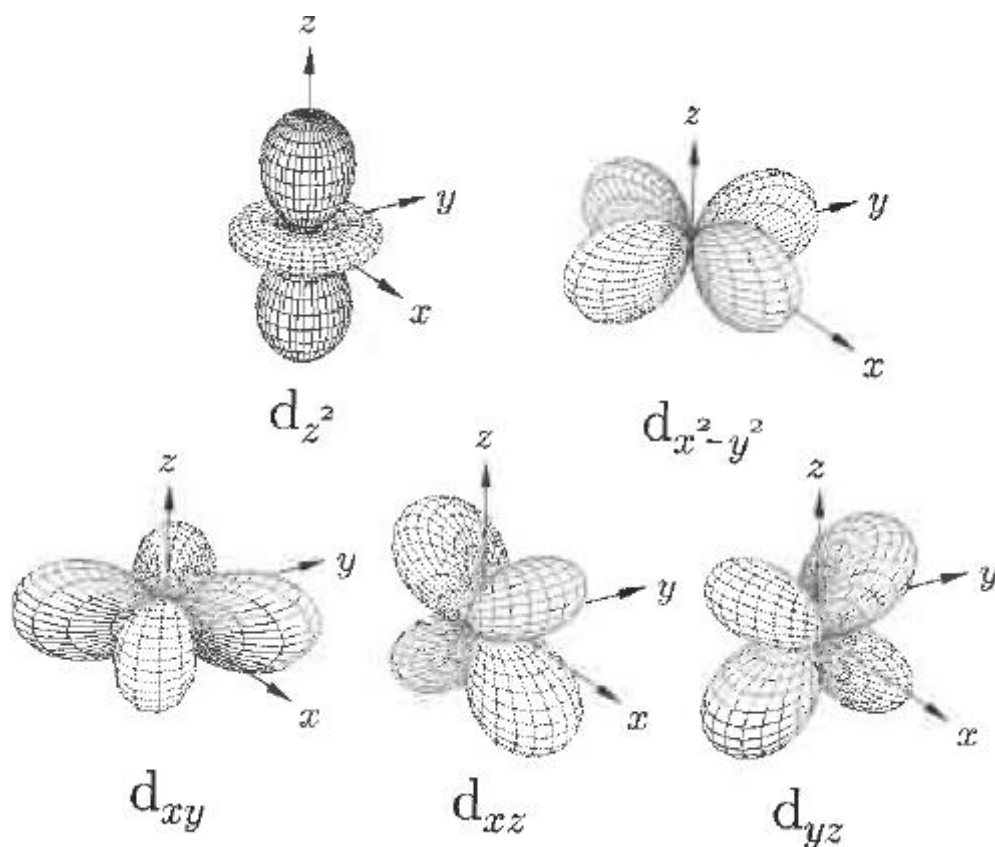


Figure 1.1 Five d orbitals, d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} , the idea of the image taken from an article¹⁴

However, once ions are coordinated by anions within the crystal structure the degeneracy of the orbitals is lifted. Here the case of Cu^{2+} in a square planar configuration will be discussed. A square planar configuration can be considered to be a distorted octahedral coordination. In an octahedral crystal field the five degenerate orbitals split into lower energy t_{2g} (d_{xy} , d_{yz} , d_{zx}) and higher energy orbitals e_g ($d_{x^2-y^2}$ and d_{z^2}), see Figure 1.2. For d^9 Cu^{2+} filling of the d orbitals in an octahedral field results in a singly filled e_g orbital. It is therefore possible to reduce the energy of the ion through a distortion of the crystal field, via a Jahn-Teller distortion¹⁵. In Cu^{2+} the Jahn-Teller distortion results in an elongation along the z axis to form a square planar configuration. The degeneracy of the orbitals is further lifted, with orbitals with a z component being lowered in energy (d_{xz} and d_{z^2}) whereas those orientated in the xy plane are raised in energy (d_{xy} , d_{yz} , and $d_{x^2-y^2}$), see Figure 1.2. As the highest energy orbital is only singly occupied this results in a lowering of the total energy of the ion.

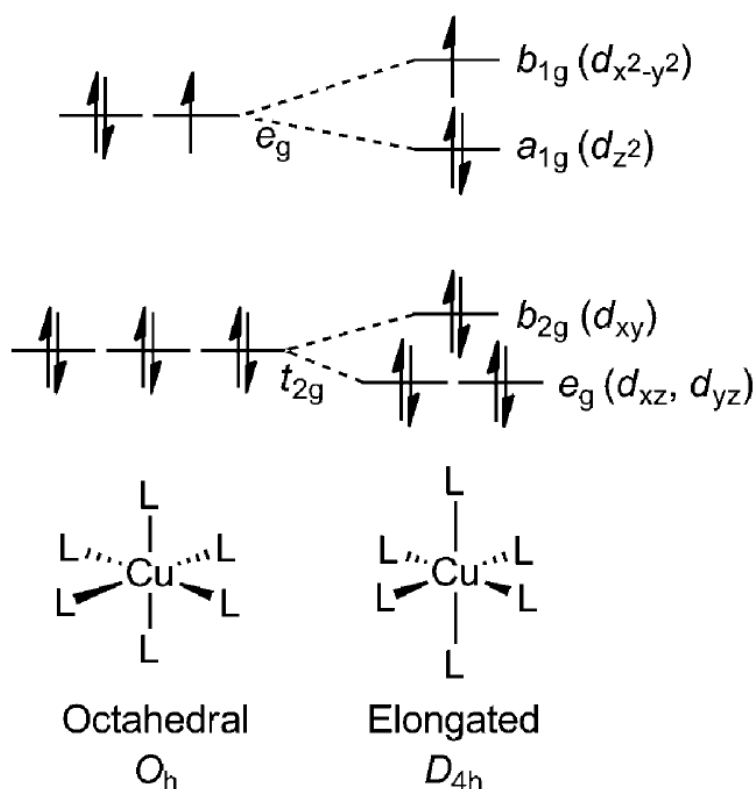


Figure 1.2 The Cu^{2+} configuration and energy level caused by Jahn-Teller distortion. Figure taken from an article¹⁶.

For $3d$ orbitals, when the crystal field splitting energy between e_g and t_{2g} (Δ_o) is smaller than the spin pairing energy⁸, the next electron occupies the e_g state as this is more stable than pairing with one of the electrons in the t_{2g} state. This is known as the high-spin state, as shown in Figure 1.3. When crystal field splitting, Δ_o , is larger than the pairing energy, electrons will populate the t_{2g} state first and this is referred to as the low-spin configuration. Many first row transition metals are found to adopt both high and low spin electronic configurations depending on the local environment, for example Co^{2+} which will be discussed in Chapter 3 can be either low spin or high spin¹⁴.

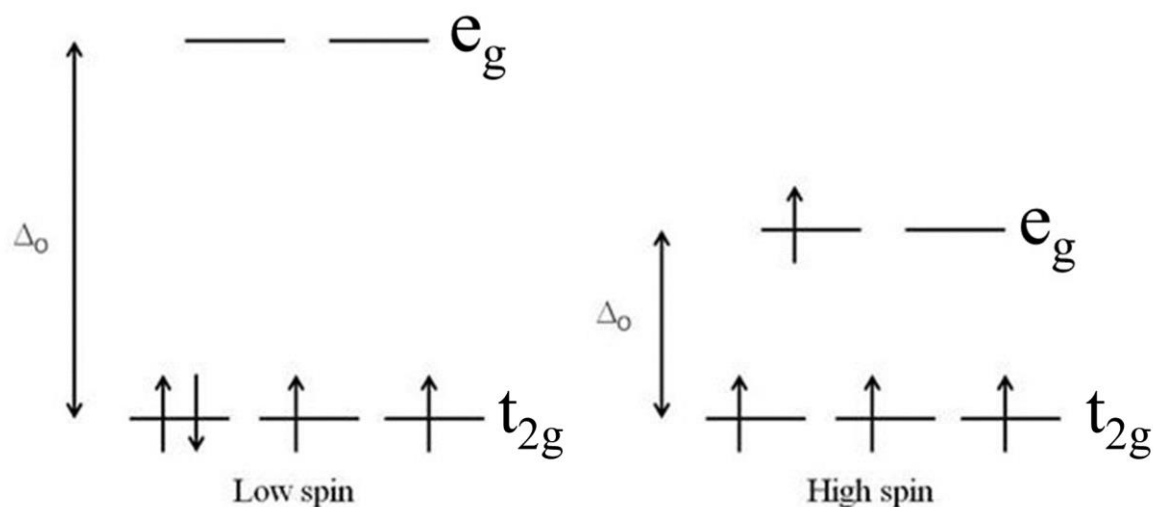


Figure 1.3 A Schematic image of low spin and high spin states. When Δ_o is larger than the pairing energy, the spins fill the t_{2g} levels first and form a low spin state. When Δ_o is smaller and an electron can fill the e_g stage before filling all of the t_{2g} state leading to a high spin state.

1.6 CEF of Lanthanides

As discussed above the CEF is determined by the coordination of ions in a structure. In lanthanide ions the CEF are highly dependent on the local site symmetry this is due to the complexity of f orbitals. The complexity of the CEF effects in Ln^{3+} ions can result in low lying excited CEF fields, the population of which can be tuned by temperature¹⁷, magnetic field¹⁸, or doping¹⁹.

1.7 Magnetic Interactions

There are several types of interactions between spins. The key magnetic interactions relevant for this thesis are described in this section.

1.7.1 Bohr magnetization and effective magnetic moments

The magnitude of magnetic moment is defined in units of the Bohr magneton which is described by the following equation:

$$\mu_B = \frac{e\hbar}{2m_e} \quad (1.2)$$

where m_e is the electron mass, e is the elementary electron charge and μ_B is the Bohr magneton. Magnetic moments of the materials are described as a unit of μ_B .

1.7.2 Dipolar interactions

The magnetic dipolar interactions are a through space interaction between dipolar spins, the dipolar interaction is described by:

$$H = -\frac{\mu_0}{4\pi|r|^3} (3(S_1 \cdot \hat{r})(S_2 \cdot \hat{r}) - S_1 \cdot S_2) \quad (1.3)$$

Where, μ_0 is the permeability of free space, r is the distance between two spins S_1 and S_2 . In the dipolar interaction, it is likely to be AFM interactions. Dipolar interactions are highly dependent on the distance between spins and typically have values of a few K in most transition-metal and lanthanide oxides.

1.7.3 Direct exchange interaction

The exchange interaction is a quantum mechanical effect. The effect is due to the overlapping of the wave function of magnetic atoms. This is called direct exchange interaction due to the

fact that no intermediate ions are needed for this interaction and the magnetic atoms are directly interacted¹⁰. Direct exchange requires a sufficiently short distance between ions for the orbitals to interact directly this is not the case for any of the materials discussed in this thesis.

1.7.4 Superexchange interactions

Superexchange interactions between spins involve interactions via intermediate ions such as oxygen ions²⁰. The Hamiltonian for the super-exchange interaction is described as:

$$H = -2JS_1 \cdot S_2 \quad (1.4)$$

Where J is the scale of the super-exchange interaction between spins S_1 and S_2 . If $J > 0$, the super-exchange is ferromagnetic whereas if $J < 0$, the super-exchange is antiferromagnetic. For 3d ions the sign of the superexchange interactions can be predicted using the Goodenough Kanamori rules. The magnitude of the superexchange interaction, J , depends on the degree of overlap between orbitals, typically for 3d ions J is on the order of 10s or 100s K whereas for the more localised 4f orbitals J is no more than a few K. A direct consequence of this is that for 3d ions the dipolar term is much smaller than J , such that it is negligible, whereas for 4f ions $J \sim D$ and so both must be considered.

1.7.5 Goodenough Kanamori rules

Whether the superexchange interaction J is positive or negative depends on the angles between the magnetic ions and the negatively charged ligands in the material, the stability of the structure of orbitals depends on the oxygen atoms coordination of magnetic ions and their relative positions in a crystalline solid. The specific case of Cu^{2+} is discussed where the unpaired electrons are in $d_{x^2-y^2}$ orbitals, shown in Figure 1.4 and Figure 1.5.

When the magnetic ions and the mediating ligand are in a one dimensional line, i.e. the Cu-O-Cu bond angle is 180° , as shown in Figure 1.4 the exchange is negative ($J < 0$) which corresponds to antiferromagnetic interactions²¹ as there is only one $2p$ orbital which can contribute to the exchange interaction. When the angle between two magnetic ions and the mediating ligand is 90° as shown in Figure 1.5, the exchange is positive ($J > 0$) which

corresponds to ferromagnetic interactions as two $2p$ orbitals can contribute to the exchange interaction. These rules are called Goodenough-Kanamori rules²⁰

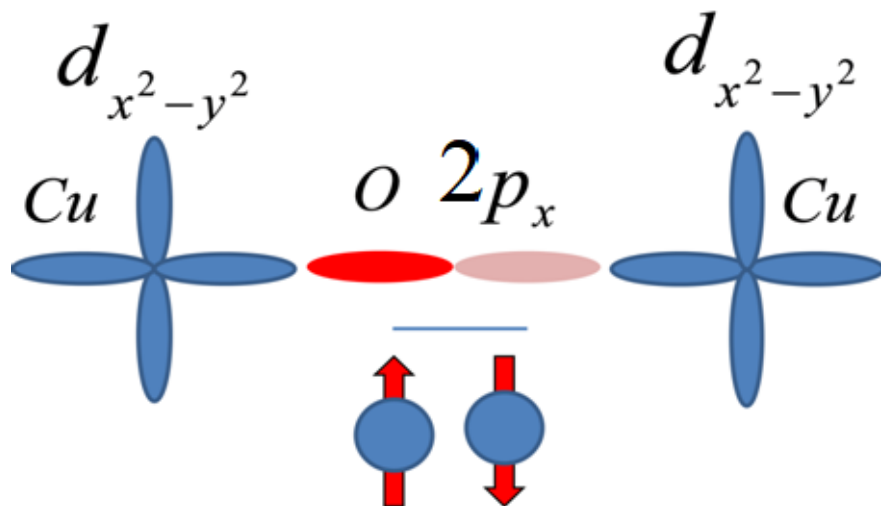


Figure 1.4 The relation between the angles of magnetic atoms and an oxygen atom based on the Goodenough-Kanamori rules. When the angle is near 180 degrees, the super-exchange is negative. This means that the interaction is antiferromagnetic.

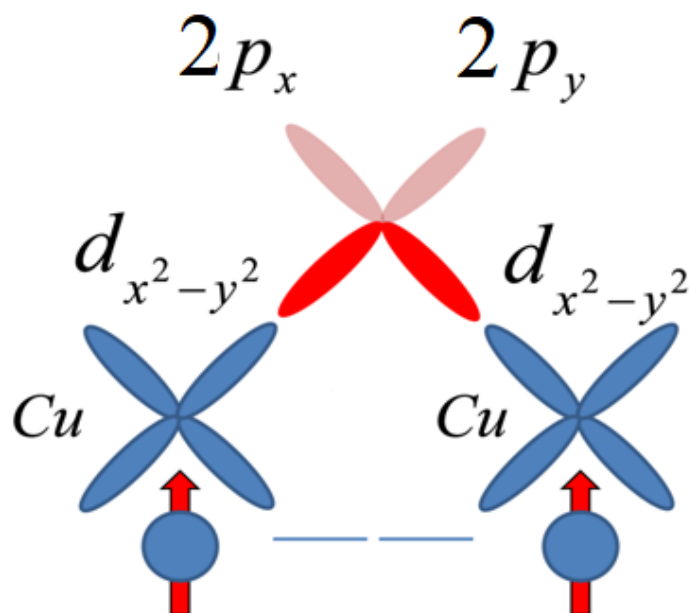


Figure 1.5 The relation between the angles of magnetic atoms and an oxygen atom based on the Goodenough-Kanamori rules. When the angle is near 90 degrees, the super-exchange is positive. This means that the interaction is ferromagnetic.

1.8 Magnetic models

In this section, several different magnetic models will be introduced as doping in pyrochlore structures in Chapter 5 and 6 can alter the model which best describes the magnetic system. The nature of the spin isotropy is highly dependent on the CEF shown in section 1.5.

1.8.1.1 Heisenberg model and Brillouin function

The Heisenberg model describes the behaviour of spins that are isotropic in three-dimensions. The Brillouin function^{9,22} can be used to model the isothermal magnetisation for non-interacting Heisenberg spins. The equation is described as follows:

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right) \quad (1.5)$$

where, J is the total angular quantum number which can be an integer or a half integer. The net magnetization is described as follows:

$$M = Ng\mu_B JB_J(x) \quad (1.6)$$

where, N is the number of atoms per unit volume, g is the atomic g factor, μ_B is the Bohr magneton. x is the ratio of the Zeeman energy of the magnetic moments in the external field to the thermal energy $k_B T$ and described as follows:

$$x = \frac{g\mu_B JB}{k_B T} \quad (1.7)$$

Where, k_B is the Boltzmann constant and T is the temperature.

1.8.1.2 Ising model

In the Ising model, spins can have only two states, up and down^{23,24}. Classical spin ice can be described by a two level Ising model. The powder averaged magnetization for Ising spins along the $\langle 111 \rangle$ direction is given by the expression^{25,26}:

$$M = \frac{\langle \mu \rangle}{2} = \frac{\langle k_B T \rangle^2}{g H^2 S} \int_0^{\frac{g \mu_B H^2 S}{k_B T}} x \tanh(x) dx \quad (1.8)$$

Where, $\mu_0 H$ is the external field and S is the spin quantum number.

1.8.1.3 Anisotropy and the transformation of models

The crystal fields of the magnetic ions can change anisotropy of the magnetic ions. The anisotropy of the magnetic ions potentially transform the model such as from Ising to Heisenberg or XY model when their environments are changed such as by doping. XY model is a model than spin can rotate in a two dimensional plane rather than spin can rotate three dimensionally. Unlike Heisenberg and Ising spins there are no analytical expression for the change in magnetisation with applied field in the literature.

1.9 Magnetic Ordering

Magnetic ordering may be long-range or short-range in nature⁹. Long-range order is characterised by a periodic arrangement of spins over the entire crystal structure⁹. Short range order refers to the ordering of spins over a short distance, usually within one or two unit cells. However, this regularity does not persist over the entire crystal structure²⁷.

1.9.1 Magnetic susceptibility

In order to quantify the magnetic properties of materials, it is useful to define the magnetic moment M per unit per mass or volume. M varies as a function of applied external magnetic field, H and this relationship is given by the magnetic susceptibility, χ . The relation between M , H and χ is as follows;

$$\chi = \frac{dM}{dH} \quad (1.9)$$

In the low regime where $M(H)$ is linear, c can be approximated by:

$$M = \chi H \quad (1.10)$$

1.9.2 Paramagnetism (PM)

Paramagnetic materials have spins that align in parallel as an applied external field¹⁰. When there are no external fields, the spins are randomly aligned due to thermal disorder. Thermal fluctuations of spins are dominant in paramagnetic materials. The magnetic susceptibility (χ) of paramagnetic materials is inversely proportional to the temperature (T) and is described by the Curie Weiss Law:

$$\chi = \frac{C}{T - \theta_p} \quad (1.11)$$

where C is called the Curie constant and determines the size of magnetic moments and θ_p is the Weiss temperature. C is described as the following equation:

$$C = \frac{1}{k_B} N \mu_0 \mu^2 \quad (1.12)$$

Where, k_B is Boltzmann constant, N is the number of magnetic atom, $\mu_0 = 4\pi \times 10^{-7}$ (H/m) is vacuum permeability, and μ is the effective magnetic moment.

1.9.3 Ferromagnetism (FM)

Ferromagnetic materials have spins aligned in the same direction below the critical temperature, T_c ²⁸. The relation between the magnetic susceptibility and temperature of ferromagnetic material is described in Curie-Weiss law in equation (1.10). For a ferromagnet, $\theta > 0$.

1.9.4 Antiferromagnetism (AFM)

In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules, align such that neighbouring spins point in opposite directions. This can be also considered as two FM aligned sublattices which are oriented in opposite directions²⁸. Since the neighbouring spins align in opposite directions, the system has no net magnetic moment²⁸. The temperature at which the antiferromagnetic transition happens is called the Néel temperature, T_N . For an antiferromagnet, $\theta_N < 0$.

1.9.5 Frustration

Frustrated magnets have been reported to exhibit both long range order and short range order²⁹. However, the unique magnetic phenomena observed in frustrated magnets are often a result of short range magnetic correlations. In systems with interacting spins, sometimes there is more than one minimum energy state in the system²⁹. An example of a frustrated system is a triangular lattice. When there are two AFM spins shown in Figure 1.6 (a), the spin configuration is stable if the spins are aligned antiparallel to each other. When there is an antiferromagnetic spin on each vertex of an equilateral triangle, all three spins cannot be aligned antiparallel to each other simultaneously. On the other hand, in Figure 1.6 (b) case, the spins cannot be satisfied to be aligned in antiparallel. This type of frustration is called geometrical frustration.

Competing antiferromagnetic and ferromagnetic interactions can also cause frustration⁴. In one dimensional frustrated magnets, also called spin chains, these interactions happen between nearest neighbour and the next nearest neighbour spins shown in Figure 1.7.

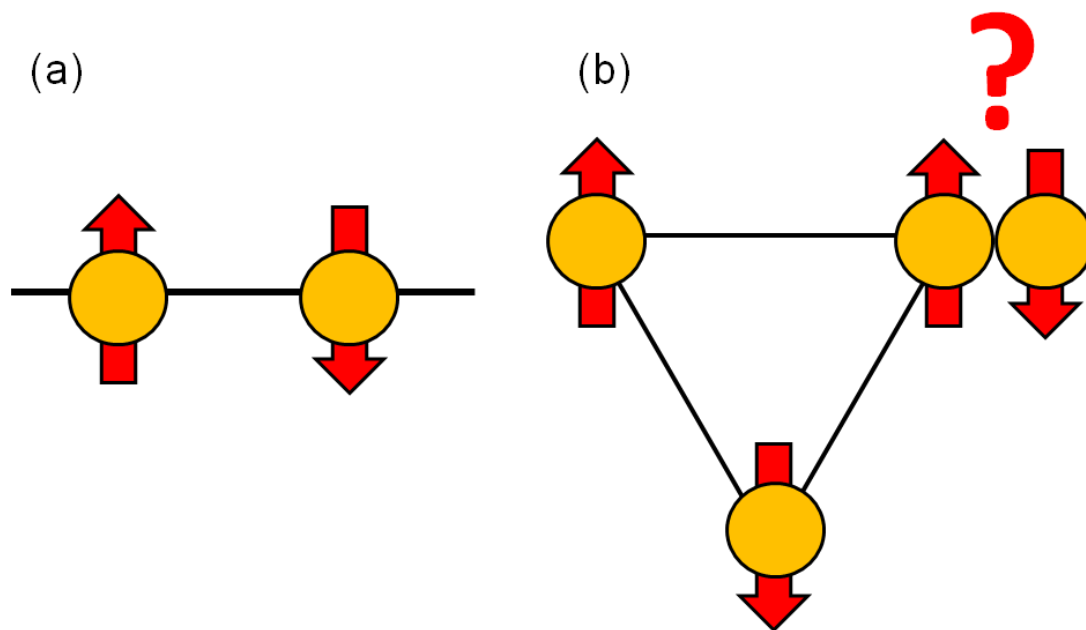


Figure 1.6 Spin is usually represented by an arrow. (a) If the spin configuration is stabilised by aligning the spins in opposite directions, two spins can be stable (b) Three spins on the triangle cannot be stable at the same time. For example, when the left one and bottom one are stable as shown, the right one cannot be stable.

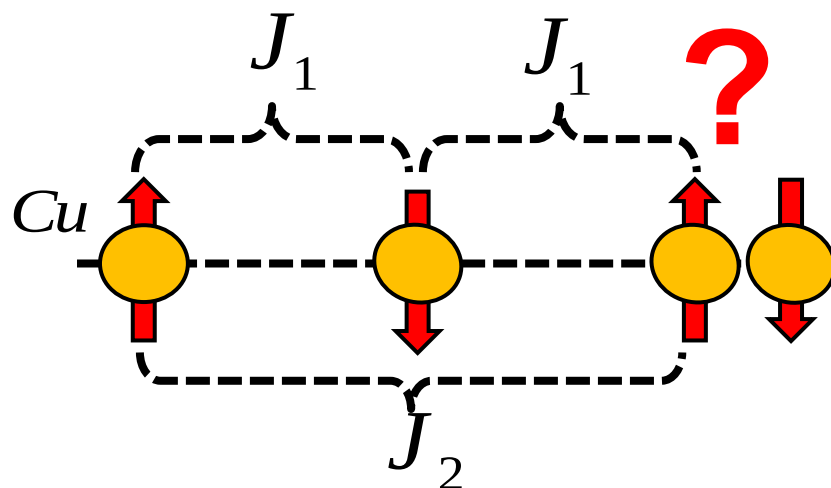


Figure 1.7 Schematic image of one dimensional spin chain. The competition between the nearest neighbour interaction (J_1) and the next nearest neighbour (J_2) determine the state.

In order to evaluate a frustration state, frustration factor described as f , is one of the methods³⁰.

$$f = \frac{\theta_{CW}}{T_C} \quad (1.13)$$

Where θ_{CW} is Curie-Weiss temperature and T_c is a critical temperature below which the material exhibits magnetic ordering features. Typically, a system is frustrated if $f > 10$.

1.9.5.1 Spin Liquid

Frustrated magnets can host spin liquid states³¹. A spin liquid can be considered as a unique strongly correlated state of matter³². The state is referred to as a "liquid" as it is a disordered state in comparison to a ferromagnet much in the way liquid is in a disordered state compared to a crystalline solid³¹. For an ideal spin liquid, $f = \infty$.

Quasi-one dimensional spin chain are a type of spin liquid.³³ One dimensional Heisenberg $S = 1/2$ spin chain model is a typical model of quantum spin chain. The competition between the nearest neighbour interaction (J_1) and the next nearest neighbour (J_2) determines the ground state as shown in Figure 1.7⁴. LiCuSbO_4 satisfies this model as it contains one dimensional Cu^{2+} chains in the crystal structure⁴. The details of LiCuSbO_4 are in Chapter 3 and Chapter 4.

1.9.5.2 Spin Glass

Spin glass is another type of system that can exhibit frustration. As the name suggests, spin glass has an 'amorphous' arrangement of spins like the amorphous glass phase of SiO_2 ⁹. Below a specific temperature called freezing temperature, the spins 'freeze' into some random configuration which has short range but no long range order.

1.10 Theoretical Bethe Ansatz methods and quantum criticality of Heisenberg $S=1/2$ one dimensional spin chains

A simple model for 1D spin chains was first generated by Bethe Ansatz. This is a method for finding the exact solutions of one-dimensional quantum many-body models with only nearest neighbour interactions³³. A more realistic model for 1D $S=1/2$ chains is one in which J_1 and J_2 are considered, a phase diagram showing how the properties change as a function of $\alpha = J_2/J_1$ is shown in Figure 1.8. The value of α and anisotropy (Δ) determine the ground state of spin-chain. More recent analytical models have included such as interchain coupling, J_3 ³⁴, and external field³⁴. In other models, extended J interactions are included^{13,35}. When an interchain J_3 term is included, the dimensionality of the magnetic interactions increases, this is found to result in an increase in the critical field (H_c)³⁴.

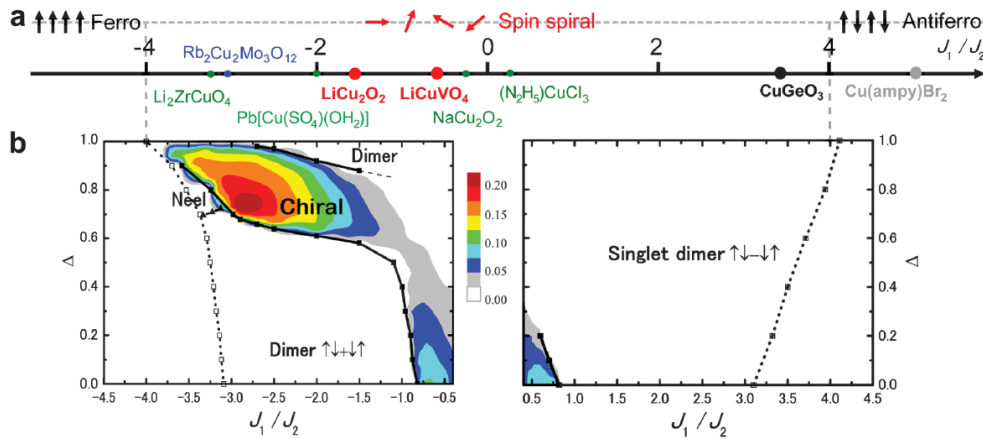


Figure 1.8 Ground-state phase diagram of the spin-chain model Heisenberg one dimensional systems (a) the classical phase diagram and relevant quantum one dimensional spin- $1/2$ materials. The materials shown in green exhibit an antiferromagnetic LRO. (b) The quantum phase diagram and the map of the chiral order parameter for $S=1/2$. The horizontal axis $J_1=J_2$ is the same as in the panel (a). The figure is taken by an article³⁶

Theory indicates a quantum critical point (QCP) which is a point in the phase diagram of a material where a continuous phase transition takes place at absolute zero. As the behaviour of materials changes dramatically around QCP, the research for QCP is an attracted research field in condensed matter physics³⁷. For Heisenberg one dimensional spin chain would be around $\alpha_c = -0.25$, $\Delta = 1$, which separates a gapless FM state ($\alpha > \alpha_c$) from a short-range ordered (SRO) phase with a small finite gap ($\alpha < \alpha_c$)^{36,38}. In terms of LiCuSbO_4 as a quantum one

dimensional Heisenberg spin chain, it is ferromagnetic interaction due to the amount that $\alpha = -0.45$ and $\Delta = 0.83^4$, if $\alpha > 0$, it would be antiferromagnetic as shown in the Figure 1.8. The value of the $\alpha = -0.45$ and $\Delta = 0.83$ in LiCuSbO_4^4 would be one of the nearest to the QCP compared to other Cu $S=1/2$ one dimensional Heisenberg spin chains such as LiCuVO_4 which has $\alpha = -0.75^3$ which will be discussed in Chapter 3 and Chapter 4.

The ratio of magnetization and the saturation value of magnetization (M_{sat}) and α is a way of evaluating frustrated magnets. Figure 1.9 shows the phase diagram of the frustrated ferromagnetic chains in the relation of M/M_{sat} as a function of α . There are several phases were reported depends on the ratios. Multipolar phases which are caused by the spin-orbit interactions and introduced to the systems when the total angular momentum quantum number J_2 is larger than $1/4$ and $S=1/2^{37}$. Spin Density Wave (SDW) is a spontaneously generated periodic oscillated static magnetization¹⁰ which looked as a wave. For example, quadrupolar phase has four spins to consist the most stable phase. The number of the spins which consist of the state for multipolar phase depends on the interactions of the spins in the system.

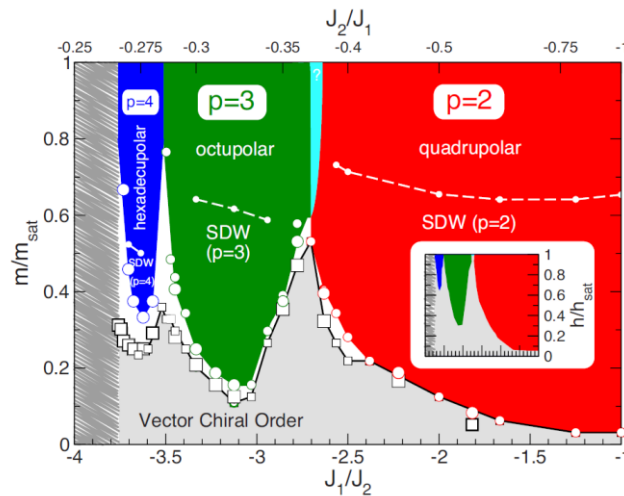


Figure 1.9 Phase diagram of the frustrated ferromagnetic chain in the J_1/J_2 vs m/m_{sat} plane. The gray low- m region exhibits vector chiral long range order. The colored regions denote spin-multipolar Luttinger liquids of bound states of $p=2,3,4$ spin flips. Close to saturation the dominant correlations are multipolar, while below the dashed crossover lines, the dominant correlations are of SDW. The cyan colored region corresponds to an incommensurate $p=2$ phase. The white region denotes a metamagnetic jump. Finally the scribbled region close to the transition $J_1/J_2 \rightarrow -4$ has not been studied here, but consists most likely of a low field vector chiral phase, followed by a metamagnetic region extending up to saturation magnetization. The inset shows the same diagram in the J_1/J_2 vs h/h_{sat} plane. The figure is taken from an article³⁷.

1.11 Spin Ice

The name of spin ice comes from the fact that it is the magnetic analogue of water ice³⁹. There are various water ice crystal structures⁴⁰. Currently, seventeen phases have been discovered and identified in “water ice” including those under high pressure⁴⁰. Among the seventeen phases, the hexagonal phase (I_h) phase has a tetrahedral structure which consists of two water molecules³⁹. Each water molecule consists of one Oxygen (O) atom and two Hydrogen (H) atoms. There are two types of O-H bonds in water ice: the covalent bond and the hydrogen bond. The covalent bond is stronger than the hydrogen bond, giving rise to the ice rules such that each O is covalently bonded to 2 protons (2 ‘short’ bonds) and hydrogen bonded to 2 protons (2 ‘long’ bonds). The protons which form hydrogen bonds with a particular oxygen ion are covalently bonded to a different oxygen ion. The relation of the O-H bonds in water ice map on to the arrangement of ‘2 in 2 out’ spin configurations in spin ice, Figure 1.10 (a)¹.

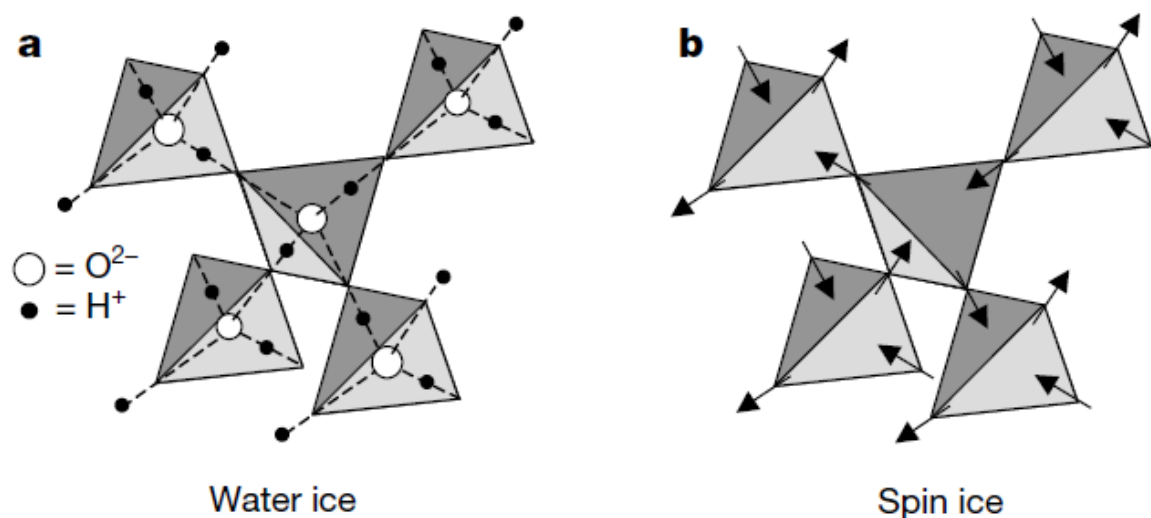


Figure 1.10 Schematic representation of frustration in water ice and spin ice. A, In water ice, each hydrogen ion is close to one or the other of its two oxygen neighbours, and each oxygen must have two hydrogen ions closer to it than to its neighbouring oxygen ions. B, In spin ice, the spins point either directly toward or away from the centres of the tetrahedra, and each tetrahedron is constrained to have two spins pointing in and two pointing out.

Figure taken from an article¹.

Spin ice is a type of frustrated magnet in three dimensions¹. Spin ice is found on pyrochlore lattices formed of corner sharing tetrahedra. Spin ice requires FM Ising spins which are

orientated either in or out of the tetrahedra. In this scenario the lowest energy state has local ordering on tetrahedra with two spin pointing in and 2 spins pointing out, the so called 2in2out configuration, however there is no LRO.

The ‘ice rule’ correlations in spin ice are a short range effect and no long range magnetic ordering is observed in spin ice¹. The presence of SRO in the absence of LRO resulted in a residual entropy at zero temperature, this can be derived analytically by considering the ordering in spin-ice. Considering Ising spins on the vertices of a tetrahedron, there are $2^4=16$ possible combinations of magnetic moment orientations due to the four spins, each able to be in two states. However, only $4C_2 = 6$ combinations satisfy the spin ice state with the two-in two-out spin configuration. For N magnetic ions in the pyrochlore structure, only $N/2$ tetrahedra exist considering the symmetry. Therefore, the number of states which satisfy the ‘ice rules’ is given by the following equation:

$$W = 2^N \left(\frac{6}{16} \right)^{\frac{N}{2}} \quad (1.14)$$

Therefore, the residual entropy (S_0) in spin ices is described as follows:

$$S_0 = k_B \ln W = k_B \ln 2^N \left(\frac{6}{16} \right)^{\frac{N}{2}} = \frac{Nk_B}{2} \ln \left(\frac{3}{2} \right) \quad (1.15)$$

Where k_B is Boltzmann constant. Therefore, the residual entropy of the spin ice can be calculated with the spin ice model and “ice rule”⁴¹. As $R=Nk_B$, a magnetic entropy of a spin ice system is given by⁴²:

$$\Delta S = S - S_0 = R \left(\ln 2 - \frac{1}{2} \ln \left(\frac{3}{2} \right) \right) \quad (1.16)$$

1.11.1 Pyrochlore structure

Pyrochlore is a type of crystal structure which can host the spin ice state⁴¹. Pyrochlore structure is described by the general formula $A_2B_2O_7$ ⁴¹ shown in Figure 1.11. Both A site and B sites consist of interpenetrating corner-sharing tetrahedral networks. In lanthanide pyrochlores the pyrochlore A site contains rare earth ions surrounded by eight oxygen ions. Six oxygen ions have longer bonds to the rare earth ion and two oxygen ions are shorter bonds to the rare earth. Each rare earth spin sits on the vertex of a tetrahedron. B site has octahedral coordination with oxygen ions. The materials discussed in Chapter 5 and 6 are based on this pyrochlore structure.

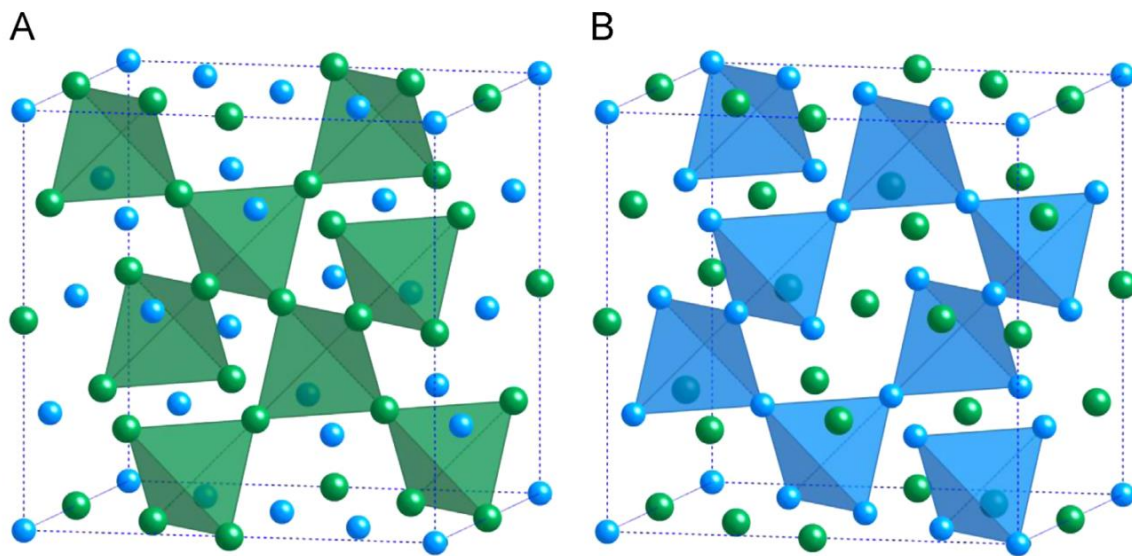


Figure 1.11 Pyrochlore structure showing the corner-sharing tetrahedral networks of A-cations (green) and B-cations (blue). Oxygen anions are not shown. Figure taken from an article⁴³.

1.11.2 Research in spin ice

Spin ice was realized in the pyrochlore structure and discovered experimentally for $\text{Dy}_2\text{Ti}_2\text{O}_7$ ⁴⁴. Their residual entropy obeys the theoretical calculation, as described in section 1.11, as a spin ice has two-in two-out states in the structure and its magnetic properties are suppressed. However, once a spin which is on a shared corner of two tetrahedra flipped, there is a pair of three-in, one out and one-in, three-out tetrahedra appear and they are as if positively charged and negatively charged tetrahedra. As a set of three-in, one-out and one-in three-out tetrahedra, can exist remotely in the system, each of can be looked as a magnetic monopole⁴⁵. Between the two magnetic monopoles, there are divergence free “flux” which is called coulomb phase

where coulomb force which obeys to the pass for the magnetic monopoles^{46,47}. An elastic neutron scattering results in the $\text{Nd}_2\text{Zr}_2\text{O}_7$, showed that pinch points which are good experimental result for existing spin ice rule was observed and after the appearance of the the magnetic monopoles, the disappearance of the pinch points were observed⁴⁸.

Doping on spin ice is an effective method to investigate the properties of spin ice¹⁸. By dilution on A site which non magnetic atoms are doped in magnetic atom site, the total amount of the zero point entropy of the spin ice were suppressed in as $\text{Dy}_{2-x}\text{M}_x\text{Ti}_2\text{O}_7$ ($M=\text{Y}$ and Lu) or $\text{Ho}_{2-x}\text{Y}_x\text{Ti}_2\text{O}_7$ ^{18,49,50}. B site doping could change the oxidation coordination reported as $\text{Pb}_2\text{M}_2\text{O}_{7-x}$ ($M = \text{Ru}, \text{Ir}$)⁵¹, $\text{Y}_2\text{Ti}_2\text{O}_{7-x}$ ⁵², $\text{Dy}_2\text{Ti}_2\text{O}_{7-x}$ ⁵² and the CEF of the magnetic ion could be affected. In this thesis, the difference of the effect of Sc doping on B site for spin ices $\text{Dy}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Sn}_2\text{O}_7$ with Kramer-ion Dy , and non-Kramer ion Ho , are discussed in Chapter 5.

1.12 Structure of the thesis

In this thesis, the effects of doping on frustrated magnets are investigated. In Chapter 1, the basic background of magnetism and frustration is explained with specific focus on the materials being investigated in this thesis. The experimental and analysis techniques for the investigation are described in Chapter 2.

The effect of doping in the one-dimensional frustrated magnet: LiCuSbO_4 are investigated in Chapter 3 and Chapter 4. In Chapter 3, non-magnetic ions Mg^{2+} and Zn^{2+} are doped on Cu^{2+} site in LiCuSbO_4 . In Chapter 4, magnetic ions Co^{2+} are doped on Cu^{2+} site in LiCuSbO_4 .

The effects of doping in frustrated pyrochlore magnets are described in Chapter 5 and Chapter 6. In Chapter 5, Sc^{3+} doping on Sn^{4+} site on $\text{Dy}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Sn}_2\text{O}_7$ which are both known as classical spin ice materials are investigated. In Chapter 6, Sc^{3+} doping on Sn^{4+} site in $\text{Tb}_2\text{Sn}_2\text{O}_7$ (which has been reported as ‘ordered’ spin ice) and $\text{Tb}_2\text{Ti}_2\text{O}_7$ (which has been reported as a spin liquid candidate) are investigated.

The conclusions of this thesis are reported in Chapter 7.

Chapter 2 Experimental Techniques

2.1 Synthesis

All materials discussed in this thesis were synthesized by a ceramic method. In a ceramic or solid state synthesis, the reaction occurs at high temperature via solid-state diffusion. In ceramic synthesis, stoichiometric amounts of starting materials, typically binary oxides or carbonates, are weighed to a precision of $\pm 0.1\text{mg}$ and mixed well using agate mortars and pestles. To increase the diffusion of the starting materials, pellets are made before heating. Pellets are made by pressing the mixed powder in pellet die under pressure, typically about 0.5 tons. The powder or pressed pellet is then placed in an alumina (Al_2O_3) crucible and heated. The time, temperature and reaction atmosphere of the heating can be used to control the final product. Samples can be exposed to reducing (5% H_2 in Ar) inert (Ar) or oxidising (O_2) atmospheres. In some cases reagents are initially exposed to lower temperatures, which allows for pre-reactions and decomposition of reagents, e.g. Li_2CO_3 to LiO and CO_2 .

Often only heating once is not sufficient to synthesize the target materials. In such cases, the heated pellets are ground again and reformed into pellets to ensure a homogeneous mixture and to facilitate the reaction. This process is called intermediate grinding.

For one dimensional frustrated magnet material series such as $\text{LiCu}_{1-x}\text{MSbO}_4$ ($M=\text{Mg}$, Zn and Co , $0 \leq x \leq 0.1$), samples were heated under 800°C for 12 hours during a preheating step the samples are the repeatedly heated, under 1050°C for 24 hours, until a phase pure product obtained.

For pyrochlore materials, such as $\text{Ho}_2\text{Sc}_{2x}\text{Sn}_{2(1-x)}\text{O}_{7-x}$, $\text{Dy}_2\text{Sc}_{2x}\text{Sn}_{2(1-x)}\text{O}_{7-x}$, and $\text{Tb}_2\text{Sc}_{2x}\text{Sn}_{2(1-x)}\text{O}_{7-x}$, samples were heated under 800°C for pre-heating and heated under 1400°C for a range of timescales. The exact details will be given in each Chapter.

2.2 Characterization

To evaluate the reaction, the structure of the heated samples must be explored. This was carried out using powder X-ray diffraction. Quantitative analysis of the crystal structure(s) was carried out using Rietveld analysis⁵³.

2.2.1 X-ray Diffraction

For solid state synthesis, whether target materials have been synthesized or whether they have impurity phases is investigated by X-ray diffraction experiments. Powder X-ray diffraction method (P-XRD) is one of the typical analytical techniques for evaluating crystal structures. In P-XRD, elastic scattering is considered where the energy of the incoming and reflected beams are the same. XRD patterns are obtained by irradiating the samples with X-rays.

Bragg's law is the fundamental theory underlying diffraction. When materials are irradiated by a beam, Bragg's law⁵⁴ gives the relationship between wavelength of the beams and the differences of the pathways of the beams:

$$2d_{hkl} \sin \theta = m\lambda \quad (2.1)$$

Where, m is an integer, d_{hkl} , λ and θ stand for the interplanar spacing of the lattice, wavelength of the X-ray, and the scattered angle respectively. Only when the spacing and the angle satisfies the Bragg's equation, does any intensity from elastic scattering appear. Bragg's law shows that there is diffracted intensity when the difference in path length of the X-rays is an integer number of wavelengths. A visual representation of Bragg's law is shown in Figure 2.1

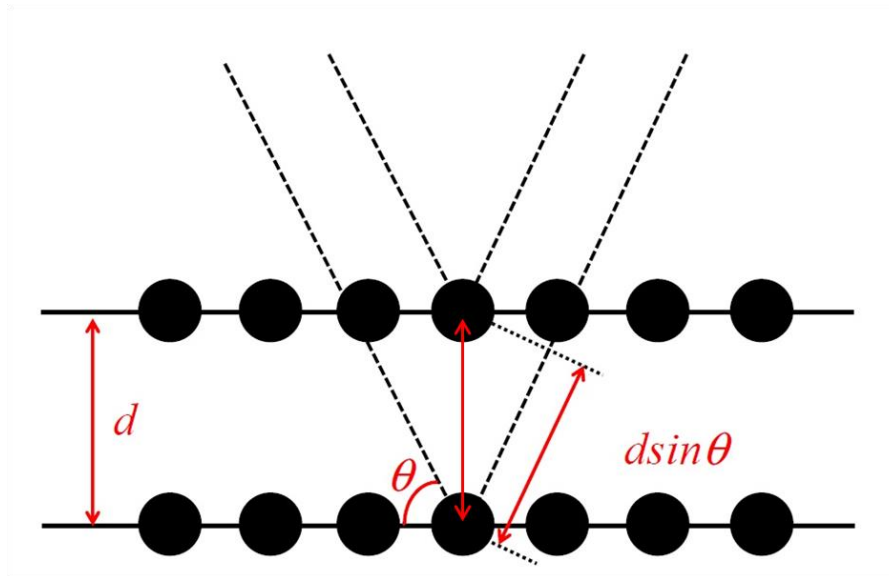


Figure 2.1 - Schematic image of Bragg's scattering. Black circles and black solid lines stand for atoms and crystal planes, respectively. Dotted lines stand for paths of X-rays. The path length difference is shown as $2d\sin\theta$.

2.2.2 Powder X-ray diffraction

Powder samples are categorized as polycrystalline materials which are comprised of individual crystallites that are oriented randomly. This means that for any set of planes, hkl , there are crystallites with the correct orientation for Bragg diffraction to occur. X-rays are detected on the circle from $2\theta=0^\circ$ to $2\theta=180^\circ$ and the scattering angle and intensity recorded are shown as Figure 2.2.

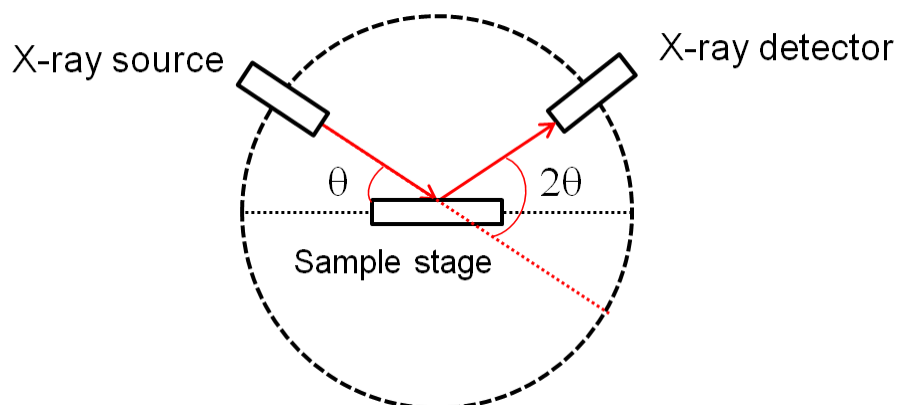


Figure 2.2 Schematic image of powder XRD. The X-ray reflected by the sample is detected by a CCD detector. The X-ray source and the X-ray detector move on a circle.

The spacing of the lattice planes d_{hkl} are described by lattice constant and the miller indices, h , k and l . For the simplest structure, a cubic lattice with $a=b=c$ and $\alpha=\beta=\gamma=90^\circ$, d_{hkl} is described as follows:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.2)$$

2.2.3 X-ray pattern Intensities:

The intensity of a diffraction peak, I_{hkl} , is determined by a number of factors:

$$I_{hkl} = sL(\theta)p(\theta)A(\theta)mF_{hkl}^2e^{-2M} \quad (2.3)$$

Where, s is a scale factor, $L(\theta)$ is the Lorentz geometric correction, $p(\theta)$ is the polarisation correction $A(\theta)$ is an absorption correction, e^{-2M} is a term modelling atomic displacement, and F_{hkl} the structure factor. The exponential term for the atomic displacement is given by:

$$M = \frac{8\pi^2 U_{iso} \sin^2 \theta}{\lambda^2} = \frac{B_{iso} \sin^2 \theta}{\lambda^2} \quad (2.4)$$

Where

$$B_{iso} = 8\pi^2 U_{iso} \quad (2.5)$$

Where B_{iso} is the isotropic displacement.

The structure factor is described as follows:

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (2.6)$$

j is the ordinal number of atoms. f_j is for the structure factor for j th atom. x_j, y_j, z_j are the positions of j th atoms.

The intensities of the reflection patterns, I_{hkl} , are proportional to the square of F_{hkl} ,

$$I_{hkl} \propto |F_{hkl}|^2 \quad (2.7)$$

A diffraction pattern is unique to a material, with the unit cell encoded in the position of the reflections and the atomic coordinates in the relative intensities.

2.2.4 Experimental conditions

The X-ray diffractometers which were used for this thesis are the Panalytical Empyrean XRD and the Bruker D8 Powder XRD. Both XRDs have CuK α X-ray sources whose wavelengths are CuK α 1 λ_1 and CuK α 2 $\lambda_2 = 1.54$ Å. There are two wavelengths from different Cu source. The irradiated X-rays are detected by a Charge Coupled Device (CCD) camera which transform light signal to electrical signal and whose outputs are linearly proportional to the strength of the X-ray. The configuration of the XRD was Bragg–Brentano theta-theta configuration in which sample position is fixed while the X-ray tube and the detector are rotated around it.

The angle ranges for measurements were $10^\circ \leq 2\theta \leq 120^\circ$ degrees. In order to minimize the effects from orientations of crystals, the sample stage was rotated during measurement. In general, 10 minute scans were conducted for qualitative analysis of the samples and long scan, typically, for several hours, are collected to evaluate them quantitatively.

2.2.5 Qualitative analysis

Before starting quantitative analysis, qualitative analyses are conducted to estimate which materials and phases are contained in the patterns. For qualitative analysis, high score plus which is a database for XRD pattern is used. As each material has a unique pattern, the

materials are identified qualitatively. Based on the qualitative analysis result, quantitative analysis will be conducted.

2.2.6 Rietveld Analysis

Rietveld analysis is a least squared method for analysing XRD data. In Rietveld analysis⁵³, the experimental XRD patterns are fitted by refining a theoretical model. By observing the difference between the experimental results and the theoretical data, a structural model for the crystal structure can be generated. These analyses are conducted using a software called FULLPROF Suite⁵⁵.

In Rietveld analysis, experimental data are fitted to theoretical structural models by refining the properties of materials such as lattice parameters, site occupancies and atomic displacement parameters. If more phases are found in materials, additional phases are also analysed in the same manner. The qualities of fitting are evaluated by the least square fit between the experimental pattern and standard models.

The quality of the fits of the fitting are determined by χ , R_p , R_{wp} and R_{exp} is the expected residual value, whereas R_{wp} is the residual taking into account variations in intensity. They are defined as:

$$R_p = \left\{ \frac{\sum_{i=1}^n [y_i - f_i(x)]^2}{\sum_{i=1}^N y_i^2} \right\}^{\frac{1}{2}} \quad (2.8)$$

$$R_{wp} = \left\{ \frac{\sum_{i=1}^n w_i [y_i - f_i(x)]^2}{\sum_{i=1}^N w_i y_i^2} \right\}^{\frac{1}{2}} \quad (2.9)$$

$$R_{\text{exp}} = \left\{ \frac{N - P}{\sum_{i=1}^n w_i y_i^2} \right\}^{\frac{1}{2}} \quad (2.10)$$

Where, y_i is the intensity of each point, i numbers between 1 and n , n is the number of data w_i is the weighted function $1/y_i$, $f_i(x)$ is the calculated intensities for i . N is the number of points and P is the number of parameters. The relation between R_{wp} and R_{exp} is:

$$\chi^2 = \left(\frac{R_{\text{wp}}}{R_{\text{exp}}} \right)^2 \quad (2.11)$$

In Rietveld analysis, fittings by the least squares are done by minimizing χ^2 . For a perfect fit,

$$R_{\text{wp}} = R_{\text{exp}} \quad (2.12)$$

and,

$$\chi^2 = 1 \quad (2.13)$$

Each material has a different diffraction pattern. By analyzing the relative intensities of contribution from each phase, the phase fraction can be determined. Peak widths are determined both by the experimental conditions (i.e. instrumental resolution) but may also be broadened by crystallites with reduced size or strain. The resolution of the instrument is described by a pseudo-Voigt function⁵⁶ which is a weighted function of Gaussian and Lorentzian.

The size of crystallites is described as the following Scherrer equation⁵⁷:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (2.14)$$

Where, t is the size of ordered crystals, K is structure factor (typically 0.9; dependent on the structure), λ is the wavelength of X-ray, β is the Full Width Half Maximum (FWHM) of the Bragg peak at the Bragg angle θ . When materials are strained, Bragg peaks become asymmetrical. By fitting the XRD patterns, how the extent of the strain can be evaluated.

In addition to elastic scattering from the sample, small amounts of inelastic scattering and in some cases fluorescence contribute to a non-zero angular dependent background. They are from facilities and sample stages and add intensities to the background. The background is obtained by interpolation of the experimental XRD pattern.

2.3 Physical Properties

After successfully synthesizing the materials, the physical properties of the materials are investigated. In this thesis, the magnetic properties and heat capacity are measured. The combined information obtained from these measurements provide new insight about the thermo-magnetic properties of the synthesized materials.

2.3.1 Magnetic Properties Measurements

The magnetic properties were explored as a function of temperature and magnetic field using a Superconducting Quantum Interference Device (SQUID)⁵⁸.

SQUIDS are comprised of two Josephson junctions^{59,60} linked to form a ring. Each Josephson junction comprises of two superconductors separated by a thin insulating layer. Electrical transport across the junction occurs via quantum tunneling through the insulating layer and as such is therefore dependent on the surrounding electromagnetic fields. In a SQUID, the magnetic flux is inferred measuring out changes in the induced voltage when a magnetic sample is moved through the device.

There is a phase difference in the superconducting ring caused by the Josephson junctions.

$$\Delta\phi(B) = 2\pi \frac{\Phi_a}{\Phi_0} \quad (2.15)$$

with a periodicity,

$$\Delta\phi(B) + 2\Delta\phi(i) = n2\pi \quad (2.16)$$

As the DC currents are described as wave functions, the maximum of the current is described as:

$$I_{\max}(\Phi) = 2I_0 \left| \cos \pi \frac{\Phi}{\Phi_0} \right| \quad (2.17)$$

The maxima of the currents form a periodic function. Therefore, the SQUID can detect very small magnetization.

For a measurement in a SQUID magnetometer samples, are positioned in a plastic capsule within a brass rod. If the sample is a powder, it is wrapped by cling films before putting in the capsules. Typically, ~20 mg of samples were used for measurements. However, this was adjusted based on the expected signal from the sample to ensure that the maximum detectable value, 4.5 emu was not exceeded during the measurement.

There are two types of bulk magnetic measurements discussed in this thesis. One is $M(T)$ measurement, which is magnetization measured as a function of temperature. In these measurements, a constant magnetic field is applied and the magnetic moment as a function of temperature is recorded. The other type of measurement is $M(H)$, which is magnetizations as a function of applied fields at constant temperature.

2.3.2 Magnetic Susceptibility

The molar magnetization, M_m , can be calculated from the data obtained from DC magnetic measurements and the mass of the samples. The magnetic susceptibility, which is the molar magnetization divided by magnetic field (H), can be calculated:

$$\chi_m = \frac{dM_m}{dH} \quad (2.18)$$

2.3.3 Diamagnetic correction

Magnetic susceptibility has two parts, one is temperature dependent and the other is temperature-independent. The χ_{meas} is described as:

$$\chi_{meas} = \chi_m + \chi_{dia} \quad (2.19)$$

For magnetic properties analysis, the diamagnetic part, which is temperature-dependent, caused by all materials including non-magnetic materials must be subtracted, in order to evaluate χ_m ⁶¹. In experiments, small magnetic moments from cling films, plastic capsule are included in χ_{meas} .

$$\chi_m = \chi_{meas} - \chi_{dia} \quad (2.20)$$

In temperature dependent data, one can fit the data to Curie-Weiss law⁹ to obtain the Curie constant (C) and Weiss temperature (θ):

$$\chi_m = \chi_{meas} - \chi_{dia} = \frac{C_m}{T - \theta} \quad (2.21)$$

In order to obtain these values from experimental results of χ - T curve, $1/\chi$ - T curve is used.

$$\frac{1}{\chi_m} = \frac{1}{C_m}(T - \theta) \quad (2.22)$$

In this figure, the slope of the line is $1/C_m$ and the x intercept is θ/C_m . The Curie-Weiss law assumes that there are no long or short range magnetic fluctuations (i.e. $T > \theta$).

From mean field theory, it can be shown that the Curie constant is directly related to the effective magnetic moment⁶² μ_{eff} , as follows:

$$C_m = \frac{N_A \mu_B^2 \mu_{\text{eff}}^2}{3k_B} \quad (2.23)$$

where

$$\mu_{\text{eff}} = g_J \sqrt{J(J+1)} \quad (2.24)$$

and

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (2.25)$$

and N_A is Avogadro's number, μ_B is the Bohr magneton, μ_{eff} is the effective magnetic moment, k is the Boltzmann constant, g is the Lande g value, J is the total angular momentum, L is the orbital angular momentum and S is the intrinsic spin angular momentum. For transition metal ions, spin-orbit coupling can be assumed to be negligible and the effective magnetic moment can be approximated by the spin only magnetic moment μ_{so} :

$$\mu_{\text{so}} = g \sqrt{S(S+1)} \quad (2.26)$$

and $g=2$, since $L=0$ and $J=S$

In order to evaluate the effect of doping, a dimensionless variant of the Curie-Weiss law can be plotted^{63 64}.

$$\frac{C_m}{|\theta|\chi_m} = \frac{T}{|\theta|} + 1 \quad (2.27)$$

This description allows samples with significant differences in their magnetic susceptibility to be compared directly. In this form, perfect Curie–Weiss behaviour results in a slope of 1 with a y-intercept of 1 for $\theta < 0$ (-1 for $\theta > 0$). Positive deviations from Curie–Weiss behaviour indicate enhanced antiferromagnetic type fluctuations or short-range order and negative deviations indicate ferromagnetic fluctuations or short-range order. The normalized temperature, T/θ , plotted on the x-axis, is scaled relative to the magnitude of the internal magnetic interactions and is the inverse of the frustration index, $f = \theta/T_N$.

2.3.4 Heat Capacity

Heat capacity is a physical property which describes how much energy is required to change the sample temperature. Heat capacity is a probe of changes in entropy associated with phase transitions. In this thesis it is primarily used to explore magnetic phases.

The heat capacity, C_p can be defined as the amount of energy which is required to change the sample temperature.

$$C_p = \frac{dQ}{dT} \quad (2.28)$$

The heat capacity can be divided into two components, $C_p = C_{\text{Latt}} + C_m$. One is heat capacity from phonons (C_{latt}); the other one is magnetic heat capacity (C_m). Phonons are from the vibrations in lattices and arise from all the atoms in the material. In other words, they are from their physical thermal energy because of the lattices. The heat capacity from the lattice vibrations are modelled by the Einstein-Debye model⁶⁵.

The equation of the Debye model is described as follows:

$$C_v = \frac{9rNkT^3}{\theta_D^3} \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (2.29)$$

At temperatures lower than the Debye temperature such as $T < \theta_D/10$, C_v can be simplified to:

$$C_v = \frac{12}{5} rR\pi^4 \left(\frac{T}{\theta} \right)^3 \quad (2.30)$$

At intermediate temperatures $\theta_D/10 < T < \theta_D/2$, the Debye function must be evaluated numerically. In this thesis, the complete Einstein-Debye model was used to subtract the lattice heat capacity and isolate the magnetic heat capacity, C_m .

From the magnetic heat capacity, C_m , the change in magnetic entropy, ΔS_m , can be calculated using Maxwell's equation⁴²:

$$\Delta S_{mag} = \int_{T_1}^{T_2} \frac{C_{mag}}{T} dT \quad (2.31)$$

The entropy S is described as follows:

$$S = k_B \ln W \quad (2.32)$$

where W is the number of states. For saturating, magnetic entropy,

$$\Delta S = R \ln(2J + 1) \quad (2.33)$$

However, in a system with Ising spins this is reduced to

$$\Delta S_M = R \ln 2 \quad (2.34)$$

2.3.5 Schottky type specific heat

When the temperature is near to the energy level of crystal field energy gap, Schottky anomalies are observed^{66,67}. This can be caused by nuclear and unpaired electrons. The equation for the effect is as follows:

$$C_{Schottky} = R \left(\frac{\Delta}{T} \right)^2 \frac{e^{\frac{\Delta}{T}}}{\left[1 + e^{\frac{\Delta}{T}} \right]^2} \quad (2.35)$$

where R is gas constant and Δ is an energy gap of a crystal field. In spin ice, these peaks appear around 1-2 K.

Heat Capacity (HC) measurements were carried out using the HC option on a Quantum Design Physical Property Measurement System (PPMS) from 1.8-30 K in fields of 0-14 T. In order to make materials thermally conducting at low temperature, samples were mixed with the same weight of silver powder and pressed into pellets. A small piece of the pellet about 2mg is cut off and placed in the sample puck which has four wires to apply heat and measure the thermal response. Apievon-N Grease is applied on the stage to improve thermal contact between the sample and the stage.

When the sample is set in the puck, the heat capacity has the contribution from the sample, N grease and the sample stage. In order to obtain the sample heat capacities only, the heat capacities for the sample stage and the grease must be subtracted. A background Addenda measurement is carried out to allow for this subtraction. The measurement process is by the two tau model to measure the heat capacity of the sample when a heat pulse applied to the sample on the platform produces a temperature difference between the two. The 2-tau model simulates the effect of heat flowing between the platform and the sample, and the effect of heat flowing between the sample platform and puck.

After this, the heat capacity contribution from the silver must be taken out so as to be able to evaluate the heat capacity of samples themselves:

$$C_{total} = C_{sample} + C_{silver} \quad (2.36)$$

where, C_{total} , C_{sample} and C_{silver} are the total heat capacity which is experimentally obtained by the PPMS measurement, contributions to heat capacity from sample and contribution to heat capacity from the silver, respectively.

Since the heat capacity of the silver is well known from the literature⁶⁸ C_{sample} is calculated by subtracting C_{silver} from the literature from C_{total} .

2.3.6 Helium-3 option for lower temperature

While Helium-4 is used for the standard He measurements on the MPMS and PPMS in the temperature range from 1.8 to 300 K, the Helium-3 option is used for very low temperature measurements down to 0.35 K. When using Helium-3 additional probe has to be attached to MPMS and PPMS.

2.3.7 Heat capacity He-3 setting

The Helium-3 system expands the temperature range of the PPMS below the standard 1.9 K temperature limit with a closed-cycle 3He probe installed into the sample space of the PPMS. To simplify operation, the system comes from the factory pre-charged with 3He without the need for any assembly or connection of any pumping lines. The Helium-3 System has a continuously circulating system which implements a return line that allows 3He to continuously flow back into the reservoir. Therefore, regeneration time is not required to maintain uninterrupted operation at low temperatures.

The base of the 3He-refrigerator probe plugs into a 12-pin connector that provides electrical access to the measurement hardware at the bottom of the PPMS sample chamber. Thermal anchoring baffles along the probe assist in cooling and maintaining the probe at a base temperature of 0.4 K. Two gas-handling lines run through the length of the probe: the pump line and the return line. 3He gas flows down the return line and condenses into the reservoir in the base of the probe. A turbo pump mounted at the top of the insert pumps on the liquid 3He via the pump line, reducing the temperature. This reservoir is thermally linked to the sample

stage that houses a thermometer, heater, and the interface for the sample mounting platforms. Samples are mounted on measurement-specific sample mounts that plug into the sample stage.

After a sample is mounted to the sample stage and the refrigerator is subsequently inserted into the sample chamber, the PPMS cools the sample chamber to 1.9 K. Once the sample chamber is cold, the ^3He refrigerator is automatically activated and begins to condense ^3He . Since ^3He is constantly recycling, there is no limitation on how long the refrigerator will stay cold.

Chapter 3 Doping with non-magnetic ions in the one-dimensional $S = 1/2$ magnet LiCuSbO_4

3.1 Introduction

In this chapter the effect of replacing $S=1/2$ Cu^{2+} ions with non-magnetic Mg^{2+} and Zn^{2+} in $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M = \text{Mg, Zn}$, $0 \leq x \leq 0.1$) is discussed.

As has already been discussed in the introduction, despite their apparent simplicity the properties of one-dimensional (1D) magnets are complex³. In the simplest case a 1D magnet can be described by two interactions: the Nearest Neighbour interaction (J_1) and the Next Nearest Neighbour interaction (J_2) between two spins. The schematic of these super-exchange interactions are shown in Figure 1.7. In the case of quantum spin $1/2$ chains theoretical simulations predict a rich phase diagram depending on the ratio of the strength of the J_1 and J_2 interactions, denoted by $\alpha = J_1/J_2$ ⁴. While J_2 is AFM, J_1 becomes either FM or AFM because of the Kanamori-Goodenough rule²⁰. The competition between J_1 and J_2 determines the magnetic properties of the system.

Materials containing chains of $S=1/2$ Cu^{2+} ions are experimental realisations of such systems, with the sign of the J_1 interactions determined by the O-Cu-O bond angle. LiCuVO_4 has one-dimensional Cu spin chains with FM J_1 interactions and $\alpha = -0.75$ ^{3,35,69-72}. However, intra-chain interactions result in the formation of a long-range ordered state at 2.1 K. There are other systems of quasi-one dimensional frustrated magnets such as $\text{Cu}_3\text{Mo}_2\text{O}_9$ ¹³, $\text{SrCu}_{1-x}\text{Ni}_x\text{O}_2$ ⁷³, LiCu_2O_2 ⁷⁴ NaCu_2O_2 ⁷⁵, $\text{Li}_2\text{CuZrO}_4$ ²¹ and $A_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ ($A = \text{Rb, Cs}$)^{76, 77}.

LiCuSbO_4 is another example of a one-dimensional frustrated magnet. Compared to LiCuVO_4 , LiCuSbO_4 has much weaker intra-chain interactions and no signatures of 3D ordering have been observed, $T > 0.1$ K.⁴ Figure 3.1 shows the crystal structure of LiCuSbO_4 . The CuO_4 square share edges forming chains which propagate along the a direction of the orthorhombic unit cell. Each Cu atom is surrounded by six O atoms. Four O atoms are in ab plane and two O are vertical to the plane shown in Figure 3.2. The Cu-spin chain is supported by oxygen bonds.

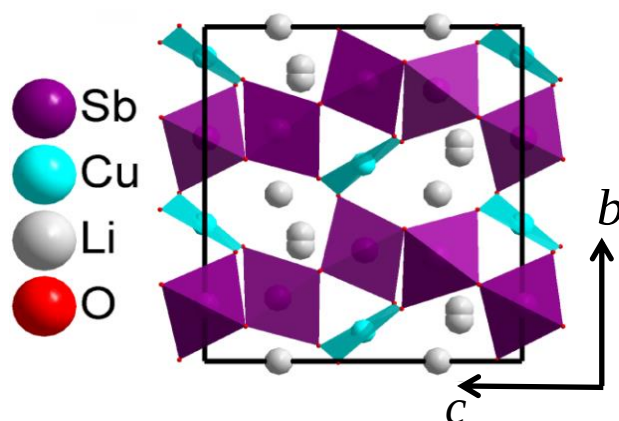


Figure 3.1 Crystal structure of LiCuSbO_4 . Purple, light blue, white, and red spheres stand for Sb, Cu, Li and O, respectively. Figure is taken from an article⁴.

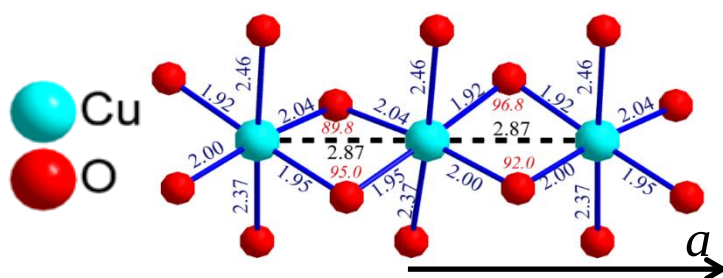


Figure 3.2 Cu chains supported by Oxygen atoms along z axis Ball and stick model showing the connectivity of the Cu chains in LiCuSbO_4 . Cu-Cu-and Cu-O bond lengths are black and blue, respectively, and Cu-O-Cu bond angles are red. Figure is taken from an article⁴.

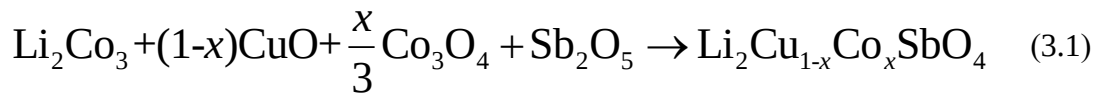
Doping on frustrated magnets is a typical method to investigate the properties of the frustrated magnets. Doping one-dimensional spin-1/2 magnets is often difficult and doping studies have only been reported for a limited number of systems^{13,35,78}. Studies on the effect of non-magnetic and magnetic doping have been previously carried out for LiCuVO₄ by substituting with Zn (non magnetic ion) and Mn and Co (magnetic ions with $S=5/2$ and $S=3/2$, respectively)⁶. The doping level for all samples was $x=0.05$ (5%)³⁵. On Zn doping in LiCuVO₄, the magnetic moments were decreased but at low temperatures, the magnetization was slightly increased³⁵. By doping Co which has larger spin quantum number than Cu, the magnetization was increased while Mn doping made the ferromagnetic interaction stronger³⁵.

In order to achieve a comprehensive understanding of the changes in the magnetic properties on doping, it is more instructive to examine several doping levels instead of only one doping level. Doping on quasi-one dimensional materials, systematic non magnetic materials Zn on Cu₃Mo₂O₉ was reported¹³. Increasing of the magnetic susceptibility at low temperature ($T<5$ K) by Zn doping was observed. However, because of the large number of parameters in Cu_{3-x}Zn_xMo₂O₉, it was hard to estimate the effect of doping¹³.

LiCuSbO₄ is a relatively simple system for the purposes of theoretical modelling⁴; however the effects of introducing different dopants as well as various percentages of doping have not been explored. Such an investigation would provide invaluable information about the impact of doping on the magnetic properties of one-dimensional frustrated magnets. In this dissertation, different levels of both non-magnetic and magnetic substituents have been successfully introduced in the LiCuSbO₄ structure and the bulk properties have been studied using magnetic susceptibility and isothermal magnetisation measurements. In this chapter, the effect of partially replacing Cu²⁺ with non-magnetic Zn²⁺ and Mg²⁺ ions in LiCuSbO₄ is discussed.

3.2 Experimental

Synthesis of the $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ series $0 \leq x \leq 0.10$, $M=\text{Mg, Zn}$, was carried out using a ceramic synthesis method. The chemical equation for this synthesis is shown in the following equation:



The starting materials were Li_2CO_3 , (99.998%, Alfa Aesar), CuO (99.995% Alfa Aesar), Co_3O_4 (99.985%, Alfa Aesar) and Sb_2O_5 (99.998%, Alfa Aesar).

Stoichiometric amounts of starting materials were intimately ground and pressed into pellets prior to firing for 12 hours under air at 800°C . The pellets were reground, mixed and made into pellets again. The pellets were then heated to 1000°C in air for 24 hours. Immediately after firing, the samples were taken out from the furnaces to quench the samples. The heated pellets were ground and made into powder. The powders were evaluated using XRD. This process was repeated with intermediate grinding until XRD indicated the formation of a phase pure product.

3.3 Results

3.3.1 Structural Chemistry

$\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M = \text{Zn}$ and Mg , $x=0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$) were successfully synthesized. All samples were measured by XRD and the structure quantitatively analysed using the Rietveld method⁵³. A typical refinement is shown in Figure 3.3. The refinements for other samples can be found in Appendix 1-15. Small amounts of LiSbO_3 , Sb_2O_3 and CuO impurity phases are detected in some samples. However as none of these are magnetic it can be assumed that the magnetic properties observed will be intrinsic to the sample. The summary of the data of the lattice parameters and impurity phases of Zn and Mg doping are shown in Appendix 23 and 24, respectively.

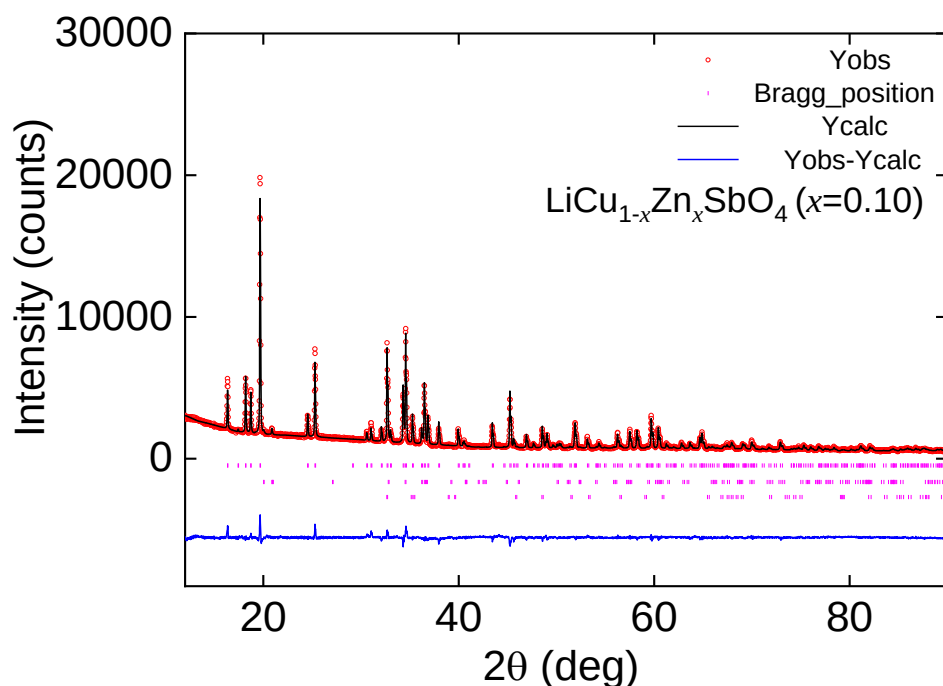


Figure 3.3 X-ray diffraction pattern for $\text{LiCu}_{0.9}\text{Zn}_{0.1}\text{SbO}_4$ series. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.

The graphs of the lattice parameters and volume as a function of Zn and Mg doping are shown in Figure 3.4 and Figure 3.5, respectively. The lattice parameter a was increased as doping in both Zn and Mg cases respectively while b was decreased with both Zn and Mg doping. While c increased with Zn doping, it decreased on Mg doping. This is the main structural difference between Zn and Mg doping. As Zn atoms are potentially tetrahedrally coordinated, it would cause the local distortions. This would be the difference of the c axis tendency as a function of Zn and Mg doping. The volume ($V=abc$) slightly decreased as a function of doping but did not have a clear systematic dependence, for either dopant.

Considering the symmetry, there are two types of Cu-O bonds: Cu-O long which are along c axis and perpendicular to the other four oxygen atoms. Cu-O short bonds are in the ab plane. Relevant bond lengths are shown in Figure 3.6 and Figure 3.7 for samples doped with Zn and Mg respectively. The bond lengths of Cu-Cu atoms, Cu-O short in ab plane and Cu-O long alongside to c axis were changed linearly. The linear changes by doping suggested that the Mg and Zn replaced Cu ions in the structure.

The general tendencies of bond and lattice lengths as a function doping are the similar in both Zn and Mg doping. Cu-Cu bond were linearly increased as a function of doping. Cu-O long bonds were linearly decreased as a function of doping. Cu-O short bond were increased as a function of doping. This suggested the structure has become more isotropic because of the amounts of Cu which were active for Jahn-Teller distortions were suppressed. The ionic radius of Zn (VI) and Mg (VI) are 0.74 Å and 0.72 Å, respectively. The ionic radius of Cu (VI) is 0.73 Å. Therefore, while the ionic radius of Zn (VI) is larger than that of Cu (VI), the ionic radius of Mg (VI) is smaller than that of Cu (VI). While Cu is active for Jahn-Teller distortion because of the electron configuration, Zn and Mg are not Jahn-Teller active. This is consistent with the reduction in the axial elongation of the Cu-O bonds on doping.

The average angles of Cu-On-Cu ($n=1,2,3,5$) are shown in Figure 3.8 (a) and Figure 3.8 (b) for Zn and Mg doping, respectively. The changes of Zn doping are more than Mg doping. This tendency is also consistent with the preference of Zn to adopt a tetrahedral co-ordination.

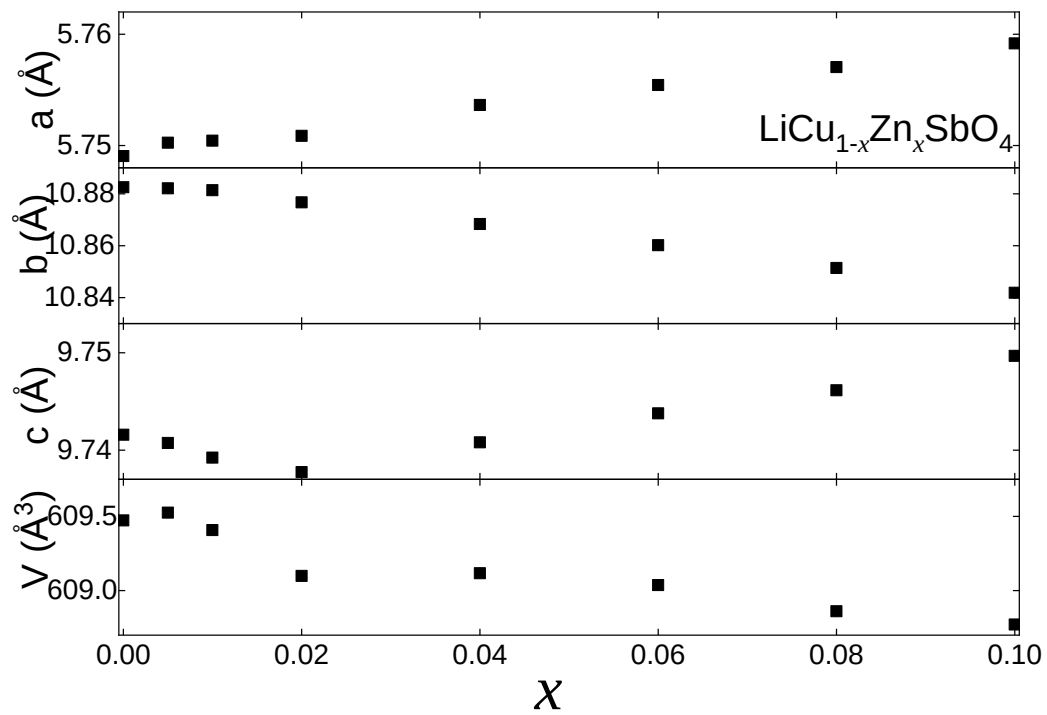


Figure 3.4 The lattice parameters a , b and c , and volume V as a function of the Zn doping. The sizes of error bars are smaller than the plots.

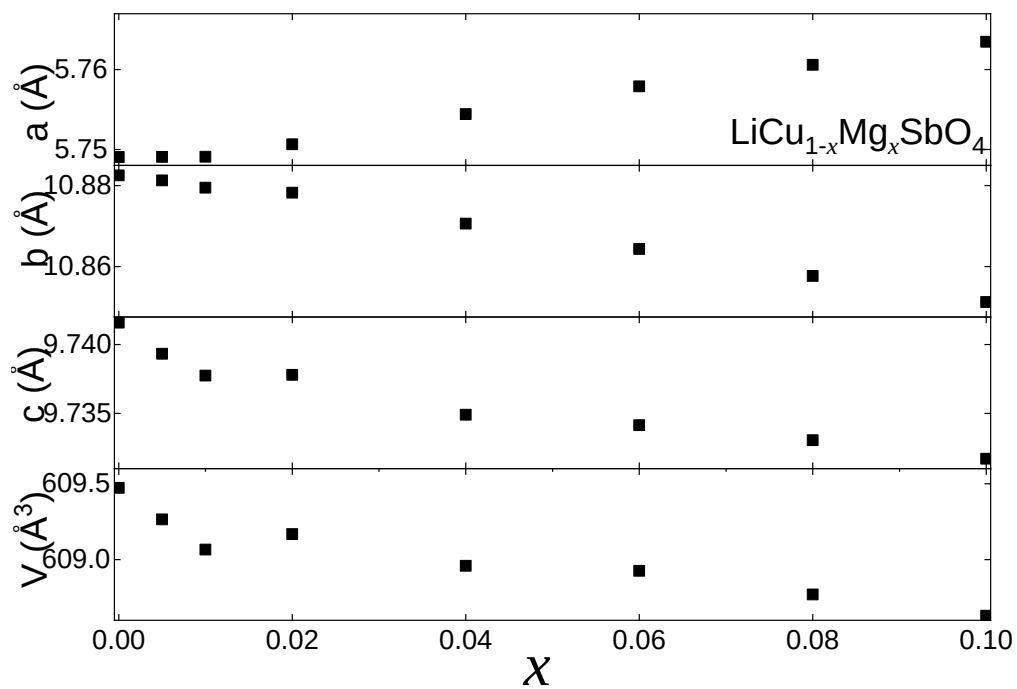


Figure 3.5 The lattice parameters a , b and c , and volume V as a function of the Mg doping. The sizes of error bars are smaller than the plots.

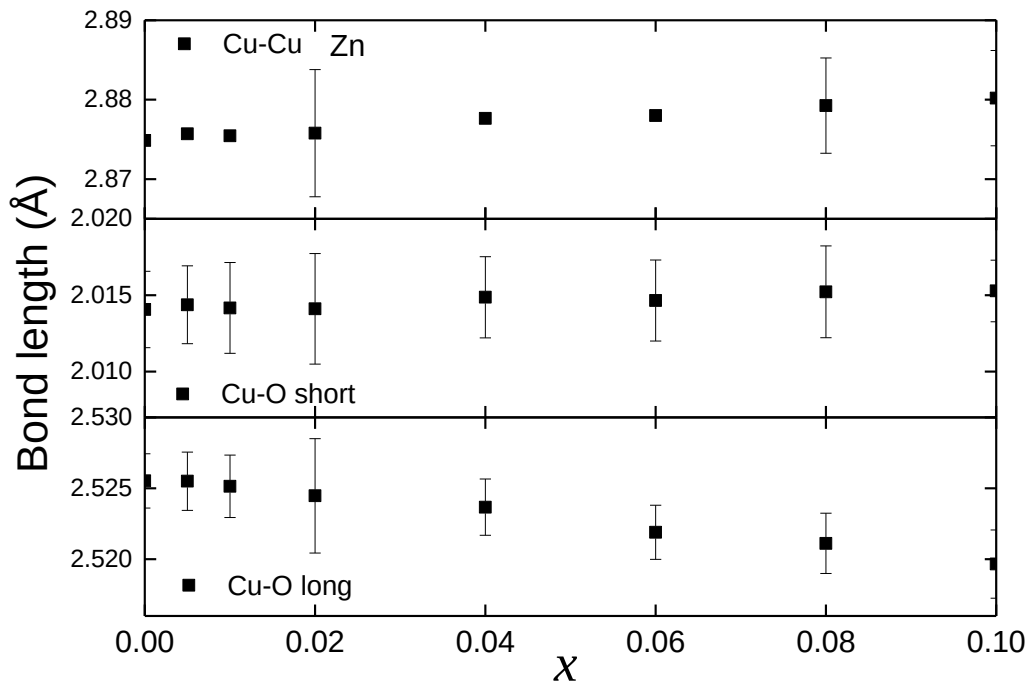


Figure 3.6 The distance between Cu atoms as a function of doping (up). The higher doping they are, the longer bond length they are. The size of error bar is smaller than plots. The bond length between Cu atoms and O atoms in the ab plane (middle). The lengths are linearly decreasing as a function of doping. The bond length between Cu and O alongside of c axis as a function of doing (down). The higher doping levels they are the shorter bond length they become.

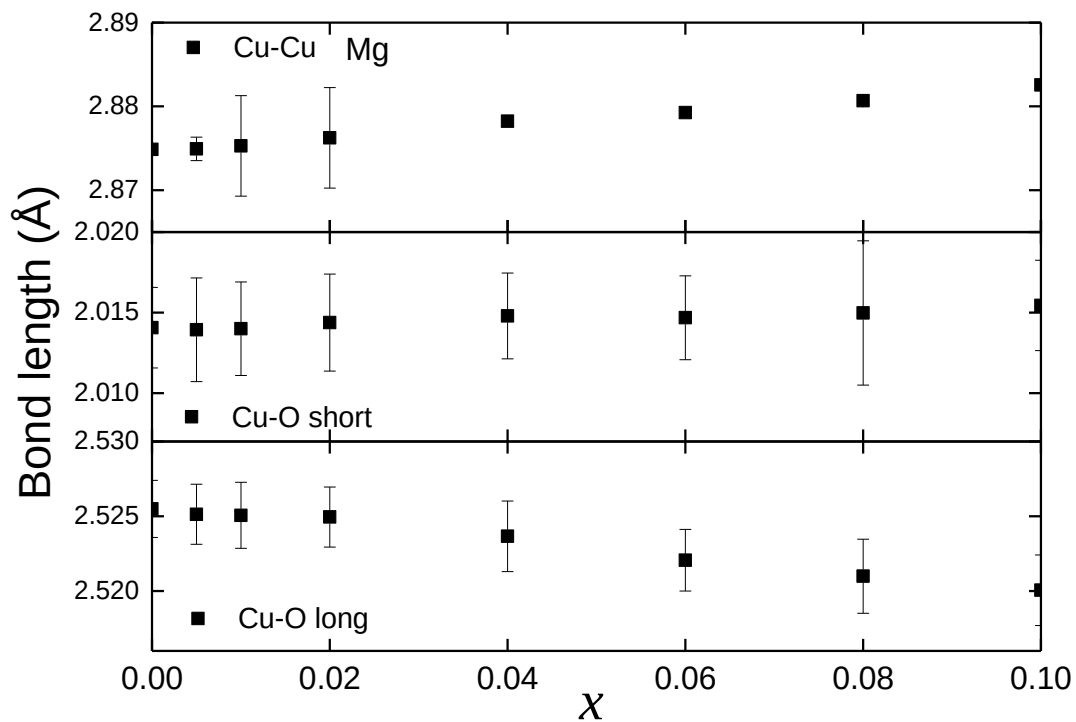


Figure 3.7 The distance between Cu atoms as a function of doping (top). The bond length between Cu atoms and O atoms in the ab plane (middle). The bond length between Cu and O alongside of c axis as a function of doping (down).

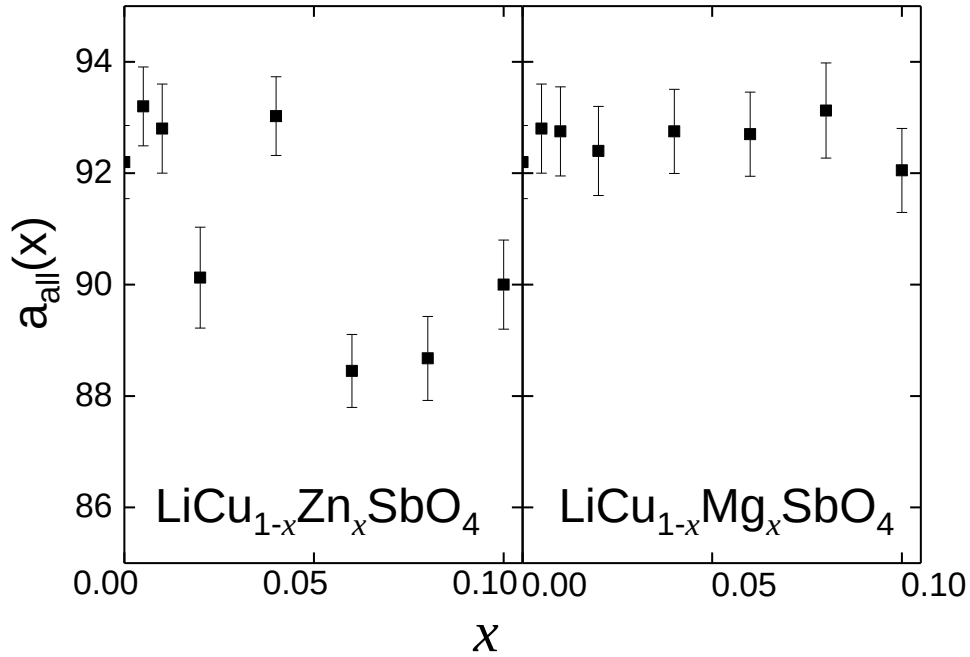


Figure 3.8 The average of angles Cu-On-Cu ($n=1,2,3,5$) of the amount of (a) Zn doping and (b) Mg doping.

3.3.2 Magnetic Properties

3.3.2.1 DC Magnetic Susceptibility, $\chi(T)$

The Zero Field Cooled (ZFC) magnetic susceptibility, $\chi(T)$ was measured in an applied field of 100 Oe. The inset of Figure 3.9 (a) and Figure 3.9 (b) show the magnetic susceptibility of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($0 \leq x \leq 0.1$) for $M=\text{Zn}$ and $M=\text{Mg}$, respectively. The magnetic properties of all samples showed similar behaviour over 30 K and can be fit to the Curie-Weiss law⁶². $1/\chi-T$ curves shown in Figure 1.47 were utilized for obtaining Curie temperatures, and Curie constants. The Curie Weiss fit is carried out between 150 and 300 K as the $1/\chi-T$ curves were linear above 150 K. Diamagnetic corrections using Pascal's constants were carried out prior to the Curie-Weiss analysis. The Curie constant, Curie-Weiss temperature (θ), and effective magnetic moment is determined and tabulated in Table 3.1 and Table 3.2, for Zn and Mg doped samples respectively. In both Zn and Mg doped samples, the Curie-Weiss temperature was around 20 K. The experimental magnetic moment and theoretical moment as a function of x corresponding to Zn and Mg doping are shown in Figure 3.10 (a) and Figure 3.10 (b) respectively. The experimental effective moments per Cu^{2+} were constant with x for both Zn

and Mg doped samples, consistent with theoretical predictions. However, compared to the theoretical calculation, the experimental results had a consistently larger value regardless of the amount of doping.

Figure 3.9 (a) and Figure 3.9 (b) shows the magnetic susceptibility for $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($0 \leq x \leq 0.1$) at low temperatures 2 – 30 K in a field of 0.01 T, for $M=\text{Zn}$ and $M=\text{Mg}$ respectively. On doping with Zn and Mg, systematic changes in the magnetic susceptibility are observed. Overall, the difference between the doping level of magnetic susceptibility on Mg doped samples were smaller than that of Zn doped samples. In the undoped $x=0$ sample, namely LiCuSbO_4 , a broad feature centred at 6 K is observed. This has been assigned to short range order (SRO)⁴. For $0 \leq x \leq 0.04$ samples, the same broad feature is observed and therefore the broad anomaly at 6 K from short ranges ordering is stable on doping up to $x=0.04$ for both Zn and Mg doped samples. However, on higher doping, $x \geq 0.06$, additional features were superimposed in the magnetic susceptibilities.

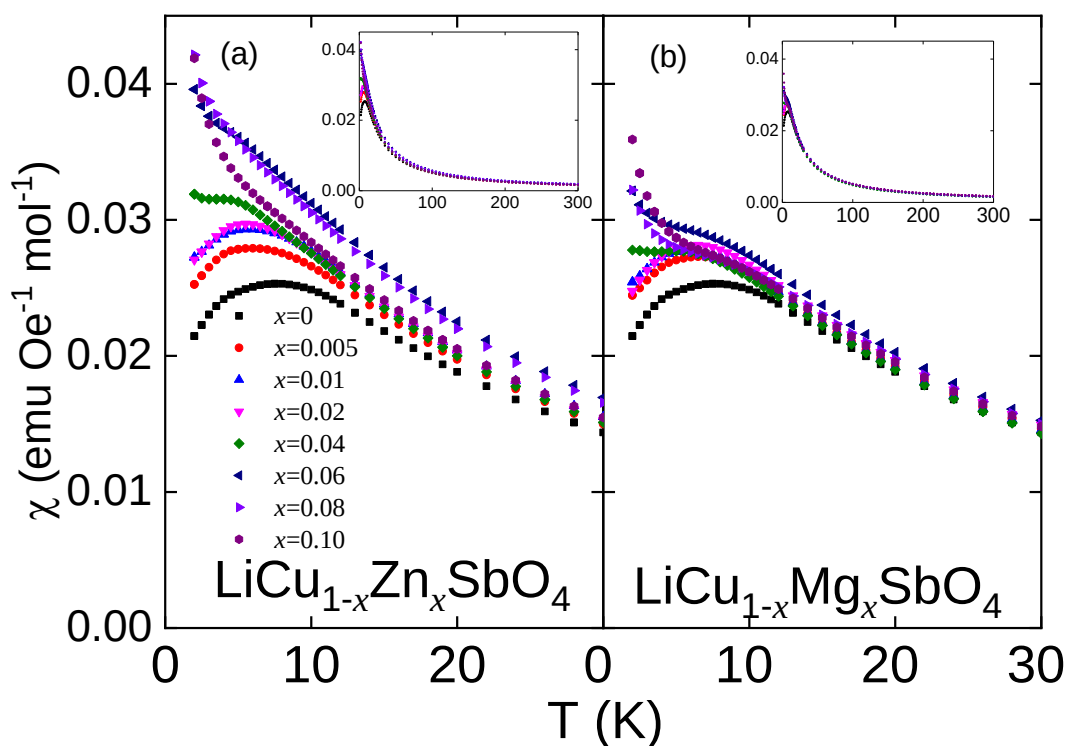


Figure 3.9 Magnetic susceptibility of (a) $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ and (b) $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ $0 \leq x \leq 0.1$ as a function of temperature from 2 to 30 K, inset for 2 to 300 K. The curvature changes from $x=0.04$. The symbols are $x=0$ (black square), $x=0.005$ (red circle), $x=0.01$ (blue up triangle), $x=0.02$ (pink down triangle), $x=0.04$ (green diamond), $x=0.06$ (navy left triangle), $x=0.08$ (violet right triangle) and $x=0.10$ (purple hexagon), respectively.

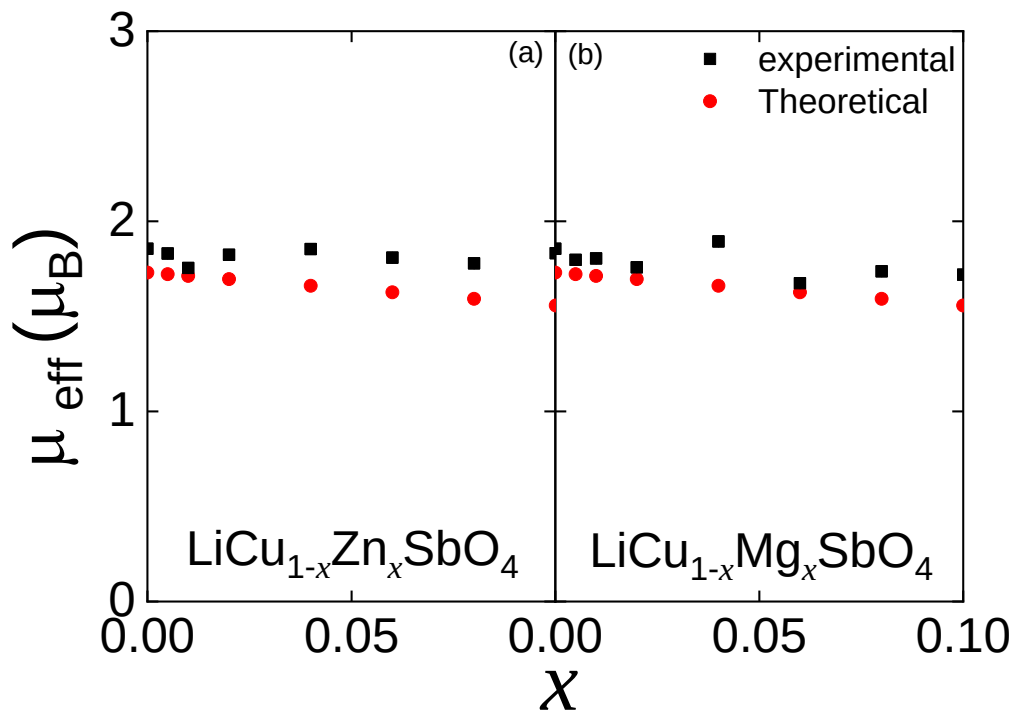


Figure 3.10 Effective magnetic moments of (a) $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ and (b) $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ as a function of doping. They are robust as a function of doping. The experimental results are continuously higher than that of theoretical calculation. The sizes of error bars are smaller than the plots.

Table 3.1 The experimental result of effective magnetic moments $\mu_{\text{eff exp}}$, the theoretical expectation of the effective the Bohr magnetization $\mu_{\text{eff the}}$ and Curie-Weiss temperature (θ) as the amount of Zn doping.

$x \text{ Zn}$	$C \text{ (emu} \cdot \text{K/mol)}$	$\theta \text{ (K)}$	$\mu_{\text{eff exp}} (\mu_B)$	$\mu_{\text{eff the}} (\mu_B)$
0	0.430(19)	22(1.0)	1.856(6)	1.73
0.005	0.419(13)	22.1(7)	1.830(5)	1.72135
0.01	0.385(11)	21.6(7)	1.754(4)	1.7127
0.02	0.416(11)	21.9(6)	1.823(4)	1.6954
0.04	0.430(15)	20.8(8)	1.854(5)	1.6608
0.06	0.4088(7)	20.1(4)	1.808(3)	1.6262
0.08	0.3952(8)	18.2(5)	1.778(3)	1.5916
0.1	0.420(6)	12(3)	1.83(19)	1.557

Table 3.2 The experimental result of effective the magnetic moments $\mu_{\text{eff exp}}$, the theoretical expectation of the effective the Bohr magnetization $\mu_{\text{eff the}}$ and Curie-Weiss temperature (θ) as the amount of Mg doping.

x Mg	C (emu $\cdot$ K/mol)	θ (K)	$\mu_{\text{eff exp}}$ (μ_B)	$\mu_{\text{eff the}}$ (μ_B)
0.005	0.403(11)	22.4(6)	1.796(4)	1.72135
0.01	0.407(15)	21.6(8)	1.805(5)	1.7127
0.02	0.3860(9)	21.0(5)	1.757(3)	1.6954
0.04	0.448(17)	24.9(9)	1.894(6)	1.6608
0.06	0.3504(9)	15.6(6)	1.674(4)	1.6262
0.08	0.377(11)	23.4(7)	1.737(4)	1.5916
0.1	0.369(12)	23.4(8)	1.719(5)	1.557

3.3.2.2 Isothermal Magnetisation, $M(H)$

Isothermal magnetisation measurements were made at selected temperatures on all samples and shown in from Figure 3.11 to Figure 3.25. In order to study the changes in the shape of the isothermal magnetisation in more detail the differential, dM/dH was considered. The plot of dM/dH as a function of field at 2 K for Zn and Mg doping series are shown in Figure 3.26 (a) and Figure 3.26 (b), respectively. At 2 K the maxima of dM/dH were increased as the amount of Mg doping. In Zn doping, they were increased until $x=0.04$ and started decreasing $0.04 \leq x$. The maximum points of dM/dH for Zn and Mg doping as a function of x are shown in Figure 3.27 (a) and Figure 3.27 (b), respectively. While $0 \leq x \leq 0.02$, the maximum point is increased and then it decreases for $0.02 \leq x$. The dM/dH curves have clear peaks around 12 T.

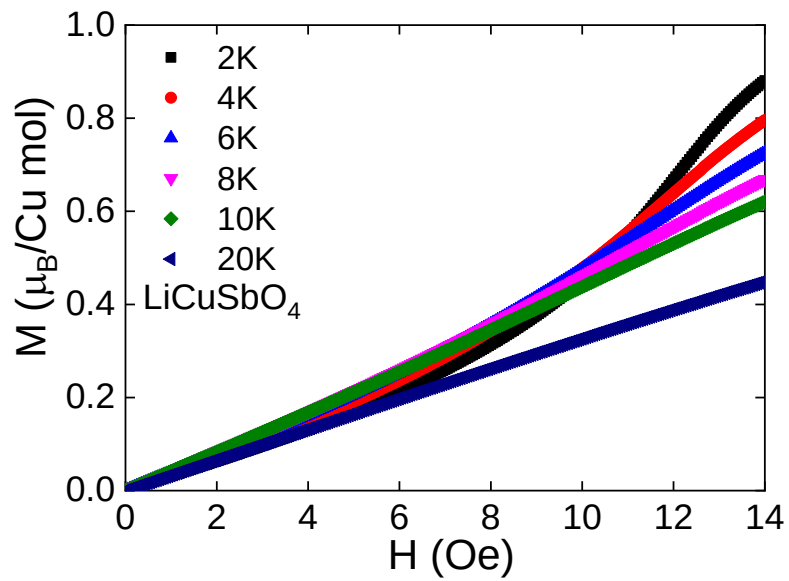


Figure 3.11 Isothermal magnetization of LiCuSbO_4 . The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

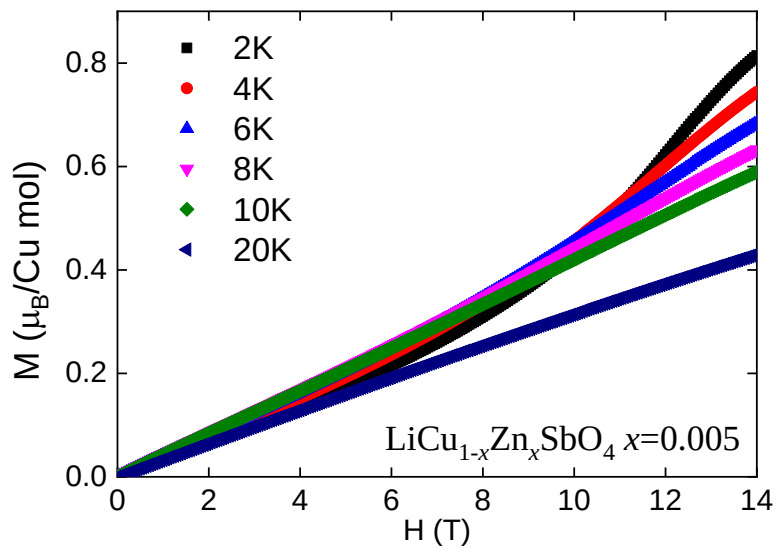


Figure 3.12 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.005$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

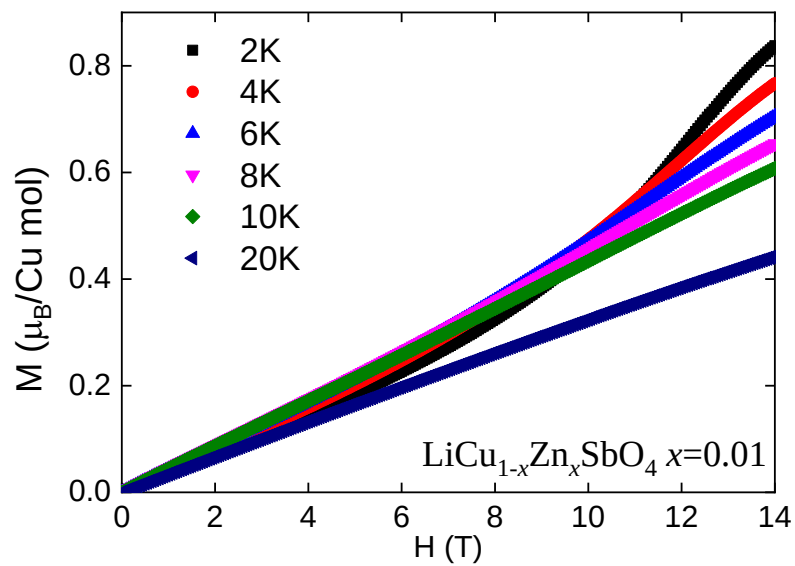


Figure 3.13 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.01$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

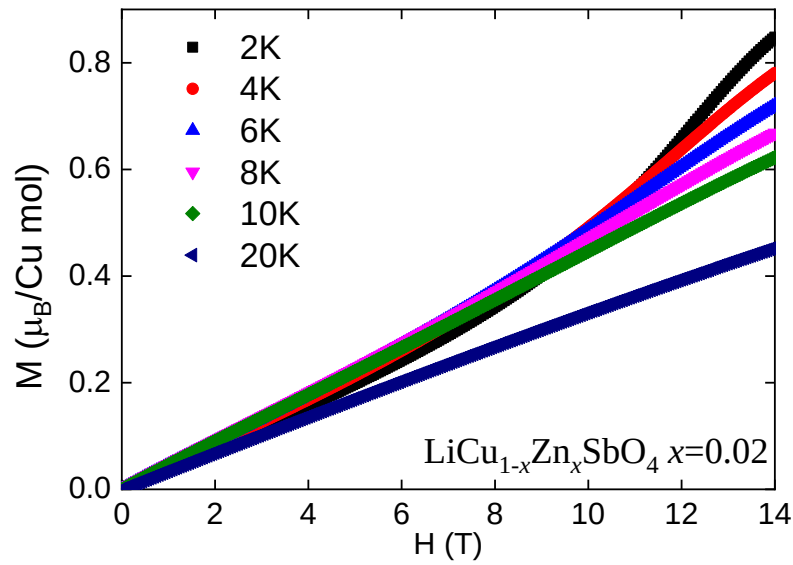


Figure 3.14 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.02$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

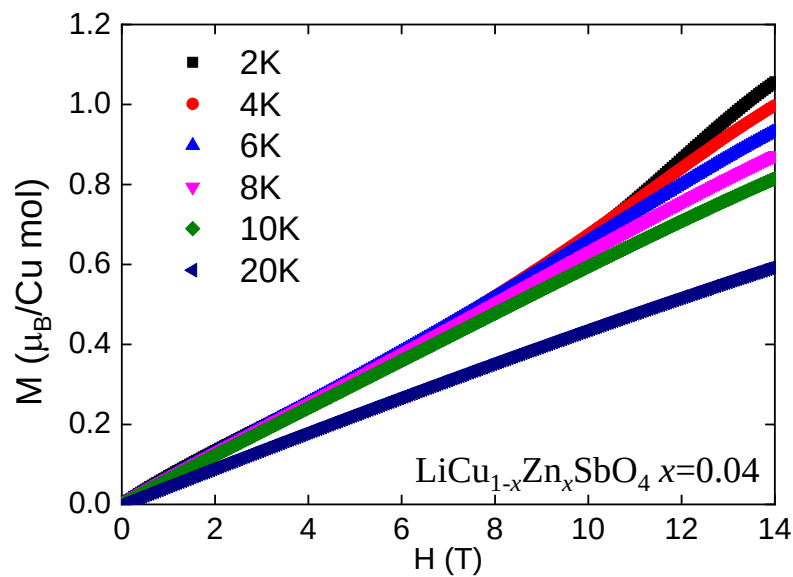


Figure 3.15 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.04$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

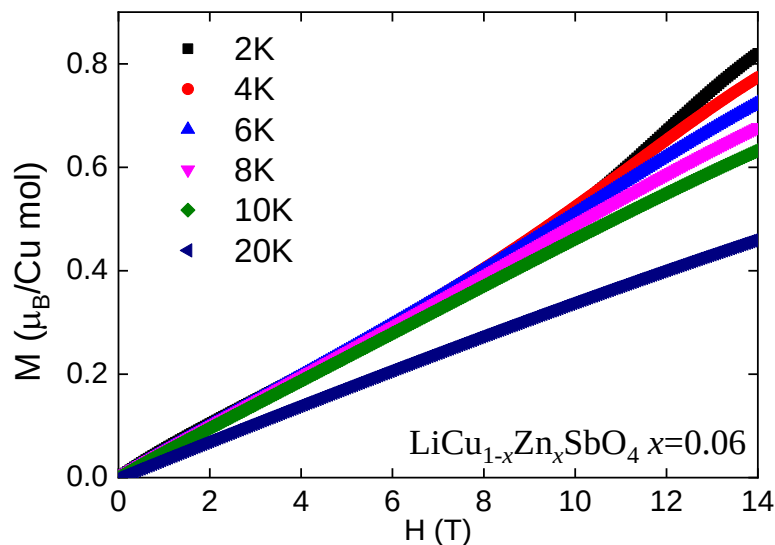


Figure 3.16 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.06$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

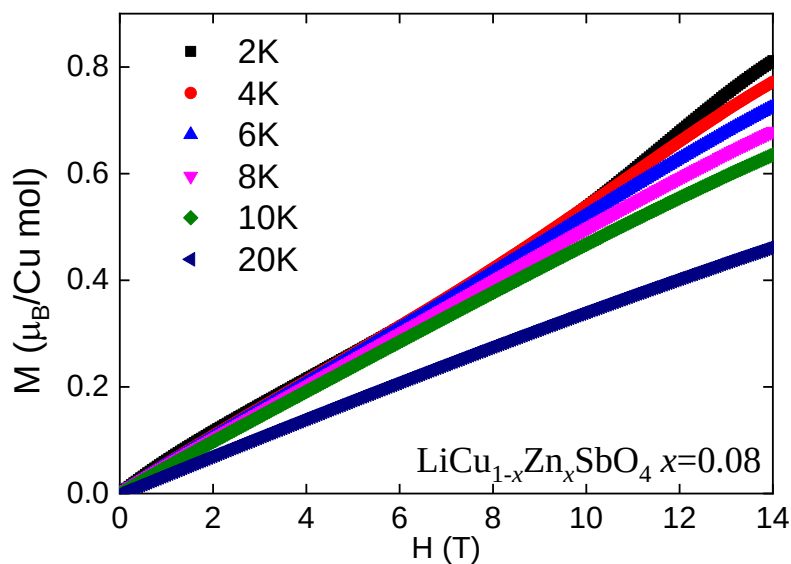


Figure 3.17 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.08$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

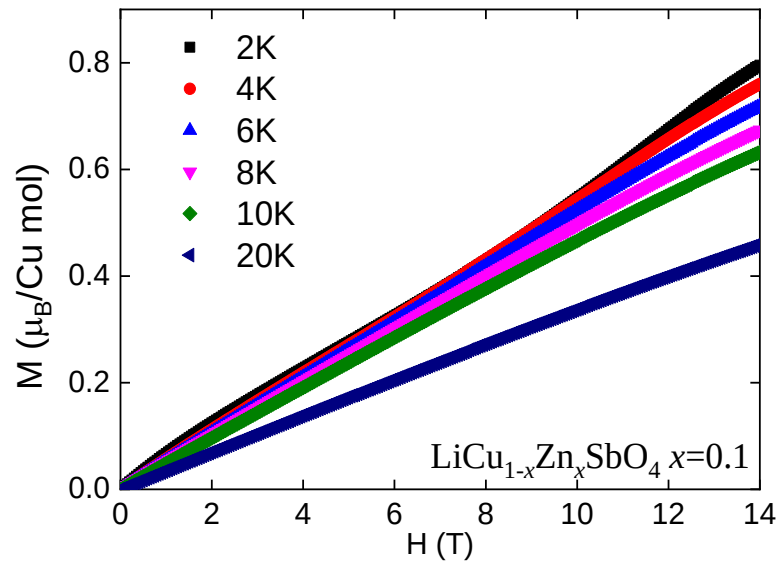


Figure 3.18 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Zn}$ $x=0.1$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

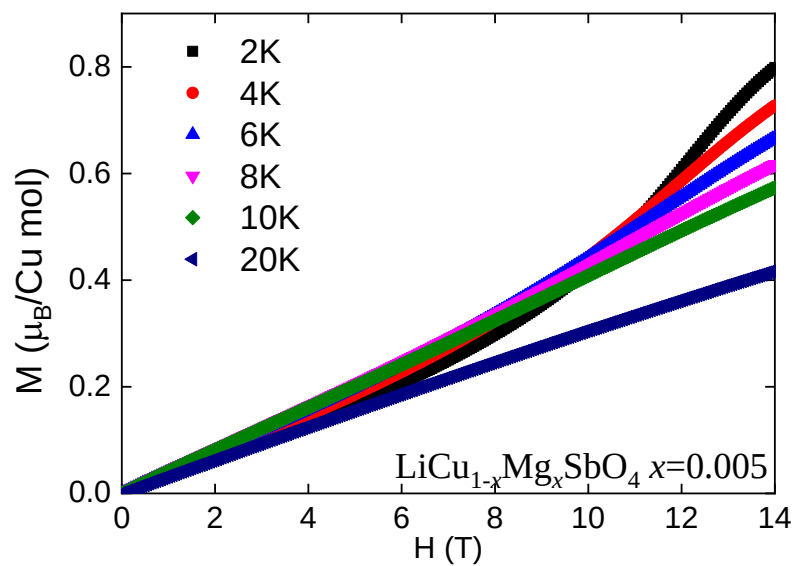


Figure 3.19 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.005$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

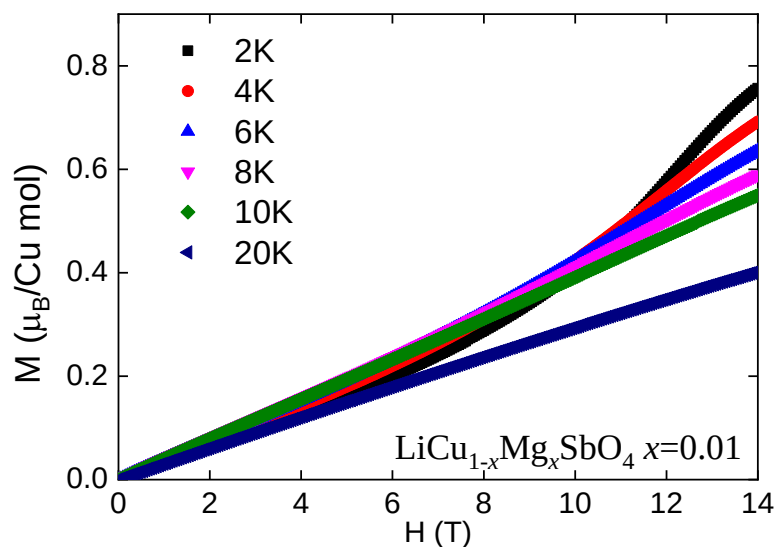


Figure 3.20 Isothermal magnetization of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.01$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

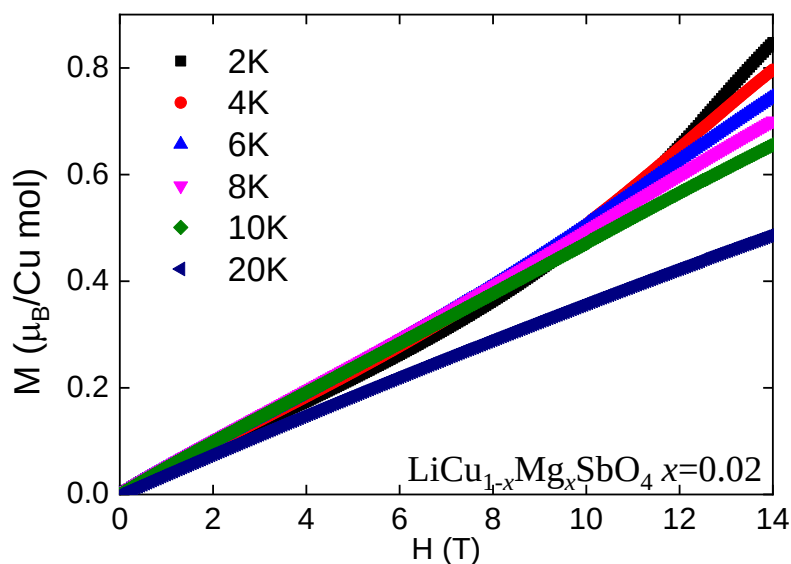


Figure 3.21 Isothermal magnetization of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.02$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

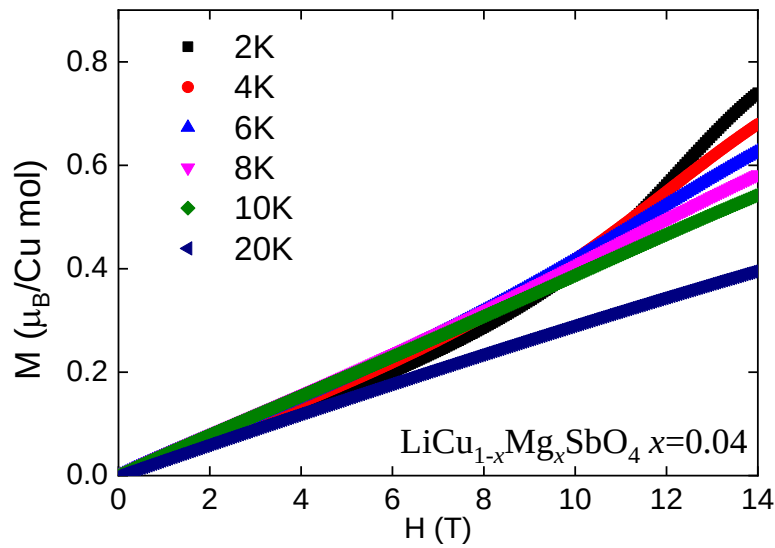


Figure 3.22 Isothermal magnetization of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.04$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

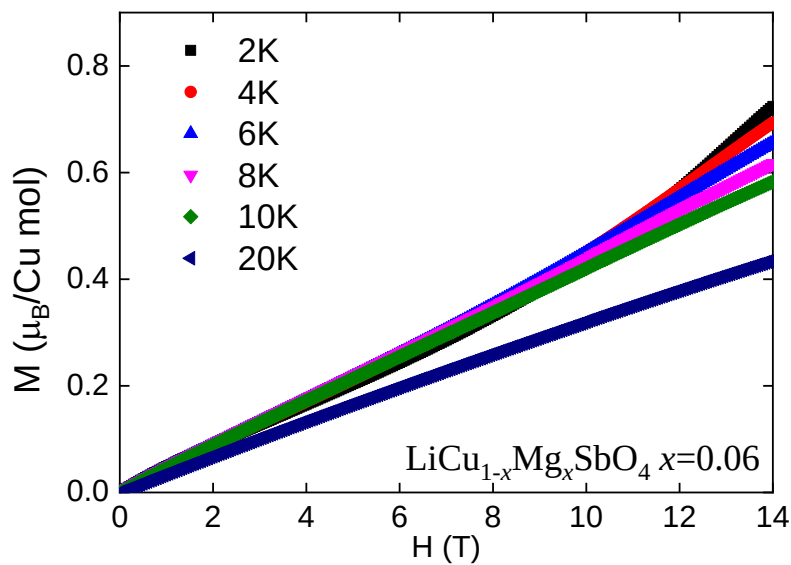


Figure 3.23 Isothermal magnetization of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.06$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

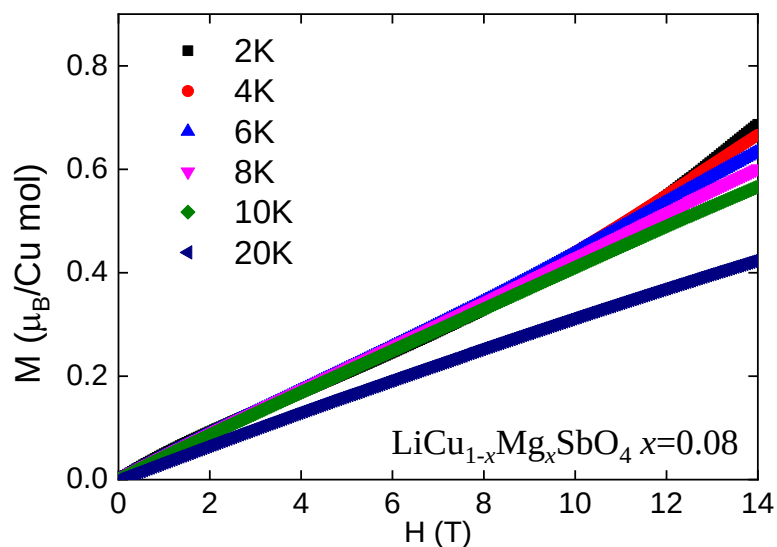


Figure 3.24 Isothermal magnetization of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.08$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

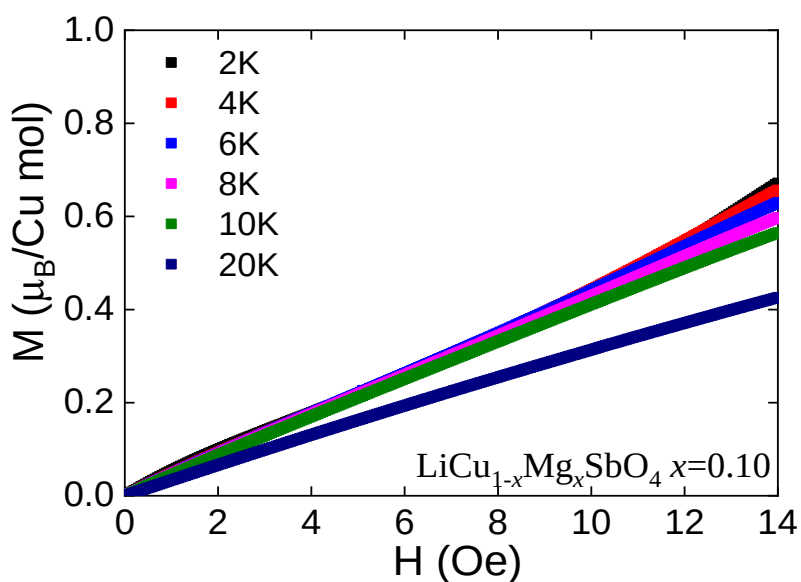


Figure 3.25 Isothermal magnetization of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($M=\text{Mg}$ $x=0.10$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

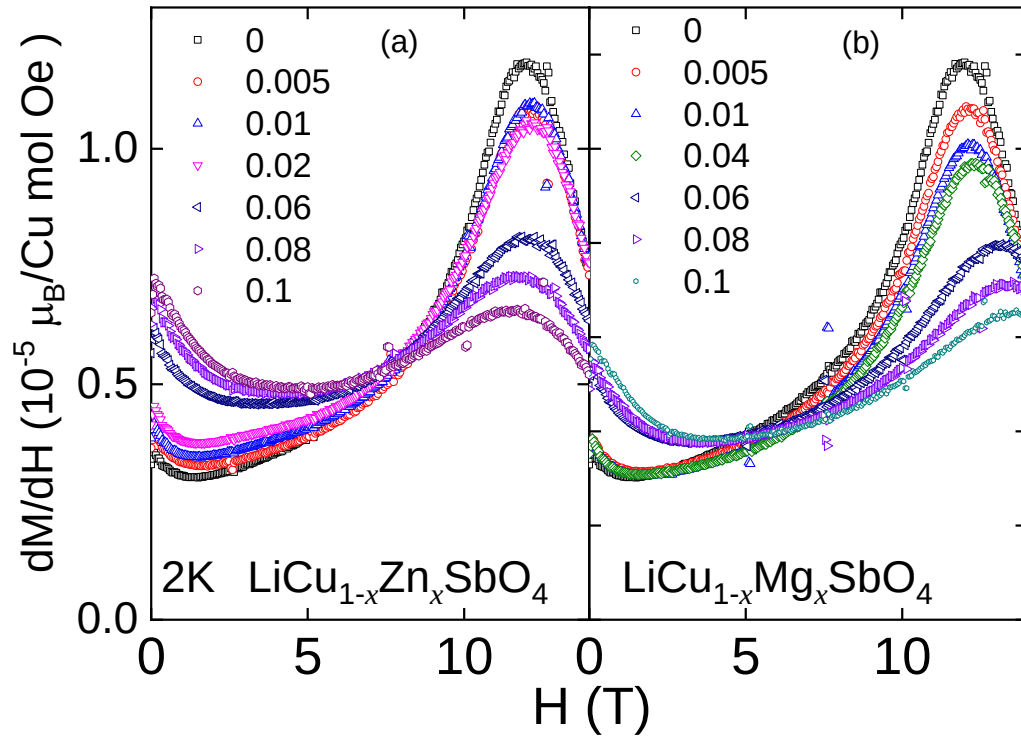


Figure 3.26 dM/dH , the differentiation of MH curve of (a) $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ and (b) $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ at 2 K. The symbols are $x=0$ (black square), $x=0.005$ (red circle), $x=0.01$ (blue up triangle), $x=0.02$ (pink down triangle), $x=0.04$ (green diamond), $x=0.06$ (navy left triangle), $x=0.08$ (violet right triangle) and $x=0.10$ (purple hexagon), respectively. While lower doping samples were lower magnetization at low field around 0-12 T, they have become higher magnetization at 14 T.

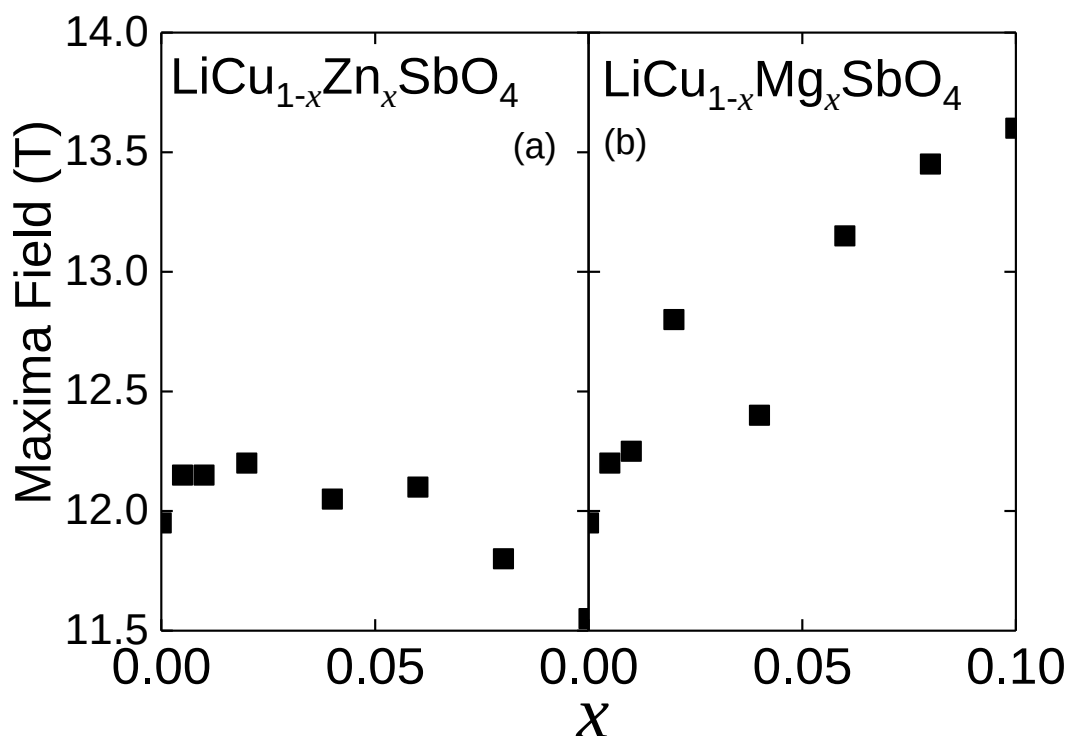


Figure 3.27 The maxima of dM/dH (a) $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ and (b) $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ at 2 K as a function of doping. While they were low doping level, they were increasing as the amount of doping, they were decreasing more than $x=0.04$.

3.4 Discussion

3.4.1 Structure

In frustrated magnets, doping is known as a typical method for investigating the properties of the frustrated magnets such as $\text{SrCr}_8\text{Ga}_4\text{O}_{19}$ ⁷⁹. For quasi-one dimensional frustrated magnets, several doping studies have been reported^{13,35}. It is mainly one level doping than systematic doping such as the comparison of $x=0$ and $x=0.05$ ⁶⁹. Zn, Co and Mn by doping, their magnetic properties especially at low temperatures were affected and features which would be from curie tail were observed in LiCuVO_4 ³⁵ and $\text{Cu}_3\text{Mo}_2\text{O}_7$ ¹³. The doping in the spin chains affected the magnetic properties of low dimensional frustrated magnets. For LiCuSbO_4 system, this is the first doping study.

XRD results are shown in Figure 3.3. No increase in the previously reported impurity phases, LiSbO_3 and CuO , were observed in both Zn and Mg doping in the range $x \leq 0.10$ ⁸⁰. Doping LiCuSbO_4 with up to 10% Zn or Mg on the Cu site can therefore be considered successful. The lattice parameters and volumes for Zn and Mg doped series are shown in Figure 3.4 and Figure 3.5, respectively. In both Zn and Mg doping, a axis increased and b axis decreased as a function of doping. While c axis for Zn was increased, c axis for Mg was decreased. The overall volume decreased as Zn and Mg doping. The linear change in lattice parameters is indicative of formation of a solid solution and indicates that as expected Zn and Mg are randomly substitute Cu on Cu sites.

The angles between Cu-O-bond angles in ab plane are shown in Figure 3.8. Though the angles of Zn doped materials are more diverse than Mg doping, all angles are in the range from 88 to 94 degrees. The range of the angles implies that J_1 in the system is FM in all materials in this doping range of Zn and Mg doping $x \leq 0.1$ because of the Kanamori-Goodenough rule²⁰.

In terms of structural differences between Zn and Mg doing on LiCuSbO_4 , while the c axis increased as Zn doping, the c axis decreased as Mg doping shown in Figure 3.4 and Figure 3.5 for respectively. The ionic radius of Cu (VI), Zn (VI) and Mg (VI) are 0.73, 0.74 and 0.72 (Å), respectively. As the Zn is 0.01 Å larger than Cu and Mg is 0.01 Å smaller than Cu, it would affect the structure, particularly the local environments. Zn has a preference to be tetragonally coordinated, which might result is local tetragonal distortions around the Zn sites. Such an effect has been seen in $\text{Ln}_3\text{Zn}_2\text{Sb}_3\text{O}_{14}$ ⁸¹, but not in $\text{Ln}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ ⁸². While Cu is active for Jahn-Teller distortion, Zn and Mg are not active. This might also affect the structural and magnetic properties.

3.4.2 Magnetic properties

The magnetic properties of the parent material LiCuSbO_4 showed several key features⁴. Under the small external magnetic field 0.1 T, the broad feature at 6 K which corresponds to one dimensional SRO is observed⁴. In isothermal magnetization, a peak at 12 T which would be a critical field that the magnetic ions which are fully polarized was observed⁴ and which was not observed using bulk probes of thermodynamic properties⁸⁰.

The CW temperatures for Zn and Mg doping shown in Table 3.1 and Table 3.2, respectively were all positive in the doping range ($x \leq 0.10$), which is indicative of FM correlations. The

CW temperatures were all around 20 K. The stability of CW temperatures suggests that the magnetic properties as a system are robust to the amount of Zn and Mg doping.

The effective magnetic moment of the Zn and Mg doping materials as a function of x shown in Figure 3.10 (a) and Figure 3.10 (b) respectively obey the weighted average of the theoretical effective moment of Cu calculated by $\mu_{\text{eff}}(\text{Cu}^{2+}) = 1.79\mu_B$ $\mu_{\text{eff}}(x) = (1-x)\mu_{\text{eff}}(\text{Cu}^{2+}) = (1-x) 1.79\mu_B$. This is consistent with the fact that both Zn and Mg are not magnetic atoms and this would be consistent with Zn and Mg replacing Cu.

Magnetic susceptibility especially at low temperature which is shown in Figure 3.9 (a) and Figure 3.9 (b) as a function of temperature were affected by Zn and Mg doping. Qualitatively the changes observed are the same for both Zn and Mg substitution. From $x=0$ to $x=0.005$, a dramatic increase in the magnetic susceptibility was observed. From $x=0.005$ to 0.02 , the magnetic susceptibility increases gradually⁸³. The feature which decreases as the temperature decrease less than 4 K was the same tendency. At $x=0.04$ the feature at 2 K changed. The additional feature can be assigned as being due to a curie tail,²³ which arises due to uncompensated spins. The position of the feature at 6 K which would be from 1D SRO feature was the same position as $x \leq 0.02$. From $x=0.06$ to $x=0.10$, the intensity of the feature which would be from curie tail was increased. The position of the feature at 6 K which would be from 1D SRO feature⁴ stable as $x \leq 0.02$. This stability of the feature at 6 K by Zn and Mg doping suggests that the SRO in this system was not affected and the SRO was not fully broken by Zn and Mg doping in this doping range ($x \leq 0.10$).

The range of the temperature for the magnetic susceptibility measurements was limited to $T \geq 2$ K. The curie tail feature was observed when $x \geq 0.04$ doping. However, if the range of the temperature were lower than 2 K, the curie tail temperature is likely to be observed at lower than $x=0.02$ doping because of the Zn and Mg doping would occur the curie tail like behaviours and the temperature of the appearance would be proportional to the amount of Zn and Mg doping as the magnetic susceptibility would be the combination of the curie tails and 1D SRO shown in Figure 3.28.

By doping non magnetic materials, the Cu chain would be almost “cut” shown in Figure 3.29. As there are no magnetic interactions between the nearest neighbour of Cu on the edge of the chain and doped non magnetic materials such as Zn and Mg, the amount of the nearest neighbour interactions J_1 were decreased as the amount of non magnetic materials doping. In

addition, the next nearest magnetic interactions from the non magnetic doping are also suppressed. The interactions between the edges of the Cu spin chains which are described as J_2' are also affected by the nonmagnetic materials doping.

For the similarities and differences of the result of Zn and Mg doping, the tendency of the features which are from curie tails and 1D SRO were observed in the same Zn and Mg doping levels shown in Figure 3.9. The angles of Cu-O-Cu in the *ab* plane and the magnetic susceptibility of Zn doping are more diverse than that of Mg doping. This could be from the size and structural difference between Zn and Mg.

Applying external magnetic fields is an effective method for analysing the properties of frustrated magnets^{4,13,29}. The differentiation dM/dH are shown in Figure 3.26, show the peaks around 12 T. This peak is also consistent with the dM/dH of the non doped LiCuSbO_4 showed the peak at 12 T⁴. The size of the peak at 12 T in dM/dH becomes smaller and broader as the amount of Zn and Mg doping. While the peak position of dM/dH for Zn was decreased, the peak position of dM/dH for Mg was increased as the amount of doping shown in Figure 3.26. This difference of the dM/dH tendency could be from the structural difference of Zn and Mg, and it is worth noting that the trends in the maximum in dM/dH are the same as those observed for the changes in the *c* lattice parameter.

Compared to other quasi-one dimensional frustrated magnet systems, the same trend on Zn doping was observed as the amount of doping increased in $\text{Mo}_3\text{Cu}_2\text{O}_7$ ¹³. Compared to $\text{Mo}_3\text{Cu}_2\text{O}_7$ ¹³, the changes especially the curie tail behaviour were observed at lower doping level $x=0.04$ which is smaller than that of $x=0.12$ in $\text{Mo}_3\text{Cu}_2\text{O}_7$ ¹³ system. This tendency of the effect of doping that in LiCuSbO_4 was smaller than that of $\text{Mo}_3\text{Cu}_2\text{O}_7$ would be consistent to the fact that the number of the neighbour Cu atoms which are interacting with each other in LiCuSbO_4 which is two atoms is smaller than that of $\text{Mo}_3\text{Cu}_2\text{O}_7$ ¹³ which would be either three or six atoms depends on Cu sites⁸⁴.

Undoped LiCuSbO_4 can be fit with a theoretical calculations of 1D SRO model⁴. It was not sure for Zn and Mg doped materials. However, the 1D SRO feature which was theoretically fitted was not affected by doping as the peak position was stable. This fit suggested that the 1D SRO part in doped LiCuSbO_4 obeyed the theoretical analysis.

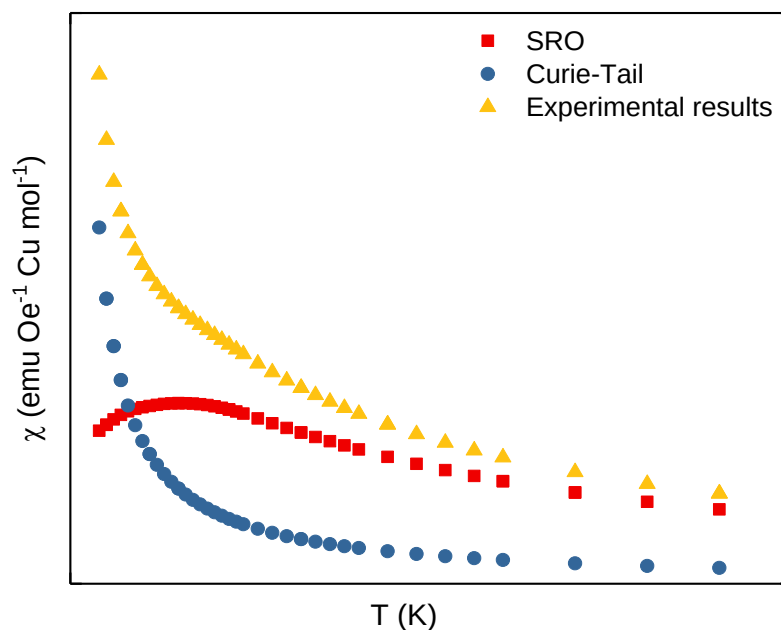


Figure 3.28 The Schematic graph of magnetic susceptibility of the combination of SRO and Curie tail. Red squares, blue circles and yellow up triangles stand for the magnetic susceptibility from 1D SRO in Cu chains, curie tail and experimental outcome.

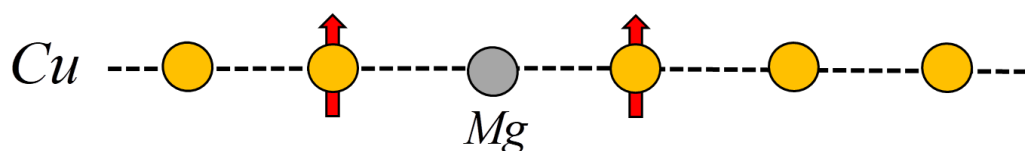


Figure 3.29 The schematic images of the edges of spins. By doping non magnetic materials, the edge of the Cu spin chain would be paramagnetic-like. However, the Cu ions on the edge could be interacting over the non magnetic ions.

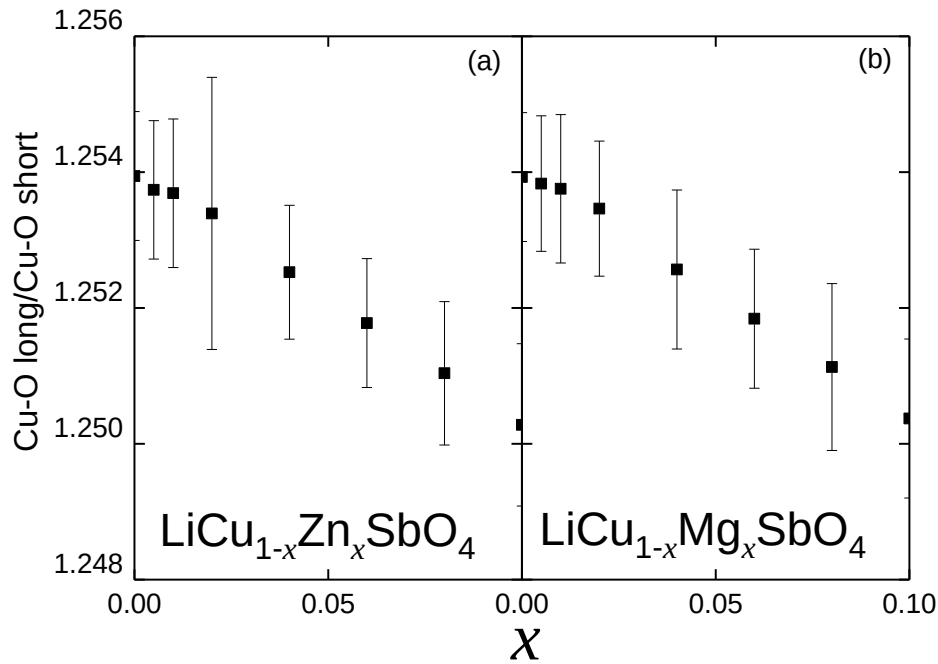


Figure 3.30 The ratio of Cu-O long divided by Cu-O short as a function for (a) $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ and (b) $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$.

The magnetic susceptibilities were started increasing around 2 K from $x=0.04$. By Zn and Mg doping, the number of Cu^{2+} atoms which are neighbour to nonmagnetic materials Zn or Mg were increased. Because of this suppression of magnetic interactions, the AFM parts especially from J_1 interactions were decreased. From about $x=0.04$, the paramagnetic like contributions which would be the effect of the edges of Cu spin chains appeared. As they were less magnetic interactions, the Cu spins on the chains would behave more paramagnetic like than that in the spin chains. The features which would be from the edges of the spins appeared from $x=0.04$. They were increased as the amount of doping.

3.4.3 Difference between Zn and Mg doping

Both Zn and Mg are non magnetic materials. However, there were differences of effects between Zn and Mg doping. The next neighbour interactions between the edges of the spins caused by Zn doping defined as $J_2'_{\text{Zn}}$ would be larger than that of Mg doping defined as $J_2'_{\text{Mg}}$.

The lattice parameters change especially in c axis as a function of doping were clearly different between Zn and Mg doping. While c axis increased by Zn doping, it decreased by Mg doping. As the crystal structure of LiCuSbO_4 shown in Figure 3.1, c axis is related to the distance of

inter Cu chains. The curvatures of $M(H)$ curve change suggest changes such as phase transitions. Figure 3.31 shows the maxima of dM/dH of Zn doping and $M(H)$ doping comparison which means the transition of the curvature of MH curve. While the maxima of Zn doping decreased as doping in higher doping, Mg doping decreased. It could be from the longer distance of c axis and the inter-Cu spin chain distances made the Zn doping sample can be broken by lower external field.

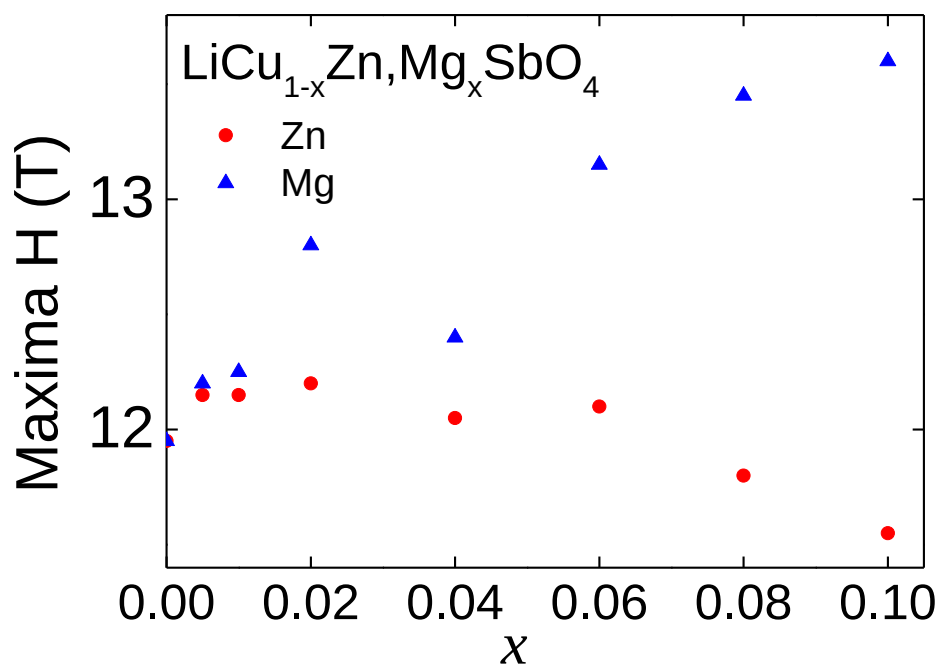


Figure 3.31 The difference of MH curve maxima of Zn and Mg doping. Red circles and Blue up triangles stand for Zn and Mg, respectively.

3.5 Conclusions

The one dimensional quantum frustrated magnets $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ series $0 \leq x \leq 0.1$, $M=\text{Mg, Zn}$ were synthesized by ceramic process. The magnetic susceptibility and MH curves were measured.

The crystal structures analysed by XRD and Rietveld analysis showed that the Zn and Mg as dopants were successfully doped in Cu sites. The results for $x=0$ which is LiCuSbO_4 had consistent results with previously reported. As the amount of doping increased, the Cu-O bond lengths which were along to c axis were suppressed because of the percentages of Cu^{2+} which were Jahn-Teller distortion active were decreased.

For small amount of doping $x \leq 0.02$, the magnetic susceptibility at low temperatures were dominated by short range order which were from Cu spin chains. From $x=0.04$, the features which would be from the edge of the Cu spins chains were observed at low temperature less than 4 K.

The edges of the Cu spin chain caused by Zn and Mg doping would behave as paramagnetic like materials. However, a simple analysis shows that the observed behaviour is more complex. This could be due to the presence of next nearest neighbour interactions are still present when Cu is replaced by Zn or Mg.

Chapter 4 Doping magnetic materials on one-dimensional quantum frustrated magnets: LiCuSbO_4

4.1 Introduction

In this chapter we investigate the effect of partial chemical substitution of cobalt for copper in LiCuSbO_4 . Comparison to the materials with non magnetic doping which were shown in Chapter 3 are also presented.

4.1.1 Magnetic Doping on LiCuSbO_4

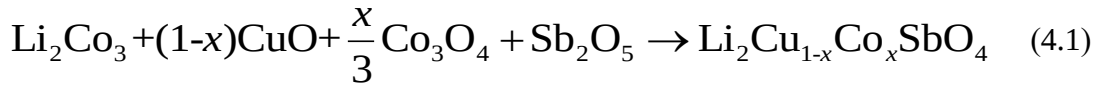
As discussed in Chapter 3, doping on frustrated magnets an effective methods of studying the variation in magnetic properties. Doping magnetic ions in the frustrated magnets can help to evaluate the magnetic properties by comparing with the non-magnetically doped analogues^{13,35}.

Compared to non magnetic ions such as Mg and Zn, the magnetic ions such as Co^{2+} have magnetic moments and still interact with other Cu^{2+} spins in Co doped LiCuSbO_4 . The comparison between the non magnetic doping and the magnetic doping can investigate the doping effect and the magnetic interaction of frustrated magnets. In one dimensional frustrated magnets, magnetic ions doping were investigated in LiCuVO_4 ³⁵. In LiCuVO_4 , 5% of Co doping on Cu site was investigated³⁵. The magnetic susceptibility was raised by Co doping.

LiCuSbO_4 is more one dimensional frustrated magnet than LiCuVO_4 , so it would be a good candidate to investigate the magnetic doping effects in a one dimensional frustrated magnets LiCuSbO_4 .

4.2 Sample preparation

Synthesis of the $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ series (for $x=0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$), was carried out using the ceramic method. The chemical equation for this synthesis is shown in the following equation:



The starting materials were Li_2CO_3 (99.998%, Alfa Aesar), CuO (99.995% Alfa Aesar), Co_3O_4 (99.985%, Alfa Aesar) and Sb_2O_5 (99.998%, Alfa Aesar).

Stoichiometric amounts of solid starting materials were intimately mixed and ground in a mortar and pestle. The samples were heated for 12 hours in air at 800°C , reground and pressed into pellets under 0.5 tons. The pellets were then heated to 1000°C in air for 24 hours. After heating, the samples were quenched by their immediate removal from the furnace. The heated pellets were ground and made into powder. The purity of powders was evaluated using XRD. This grinding, pressing pellets and heating process was repeated with intermediate grindings until XRD indicated the formation of a phase pure product.

4.3 Results

4.3.1 Structural Chemistry

Polycrystalline samples of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($0 \leq x \leq 0.1$) were successfully synthesized. All samples were measured by XRD and their structure quantitatively analysed using the Rietveld method⁵³. A typical refinement for $x=0.10$ is shown in Figure 4.1 The refinements for other samples can be found in Appendix 16-21. Small amounts of LiSbO_3 , Sb_2O_3 , CuO , $\text{Li}_3\text{Cu}_2\text{SbO}_6$ and $\text{Li}_3\text{CuSbO}_5$ impurity phases were detected in some samples. While CuO and $\text{Li}_3\text{CuSbO}_5$ are magnetic materials, their mass was around 1%. So they would not significantly affect the main phase. None of the remaining impurities are magnetic so it can be assumed that the magnetic properties observed will be unaffected by the presence of the impurities. The details of the refinement is shown in Appendix 25.

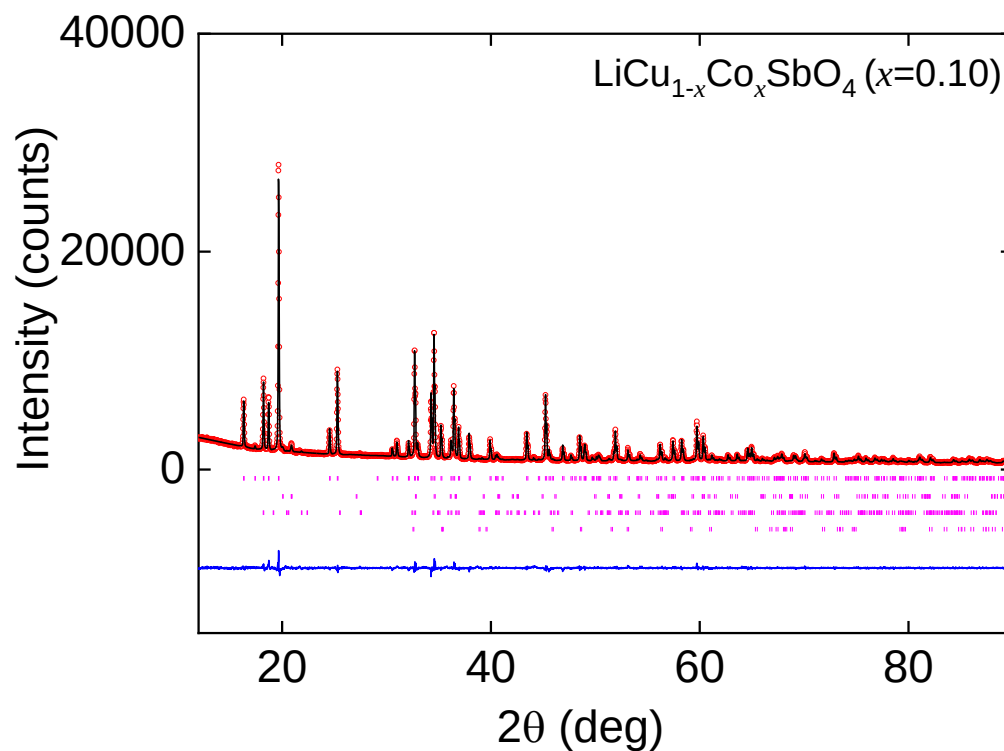


Figure 4.1 Selected X-ray diffraction data for $\text{LiCu}_{0.9}\text{Co}_{0.1}\text{SbO}_4$ series. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.

The lattice parameters and volume of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of doping level x are shown in Figure 4.2. The distances of Cu-Cu bond, Cu-O long and Cu-O short as a function of x are shown in Figure 4.3. The variation in the O-Cu-O bond angles as a function of x are shown in Figure 4.4.

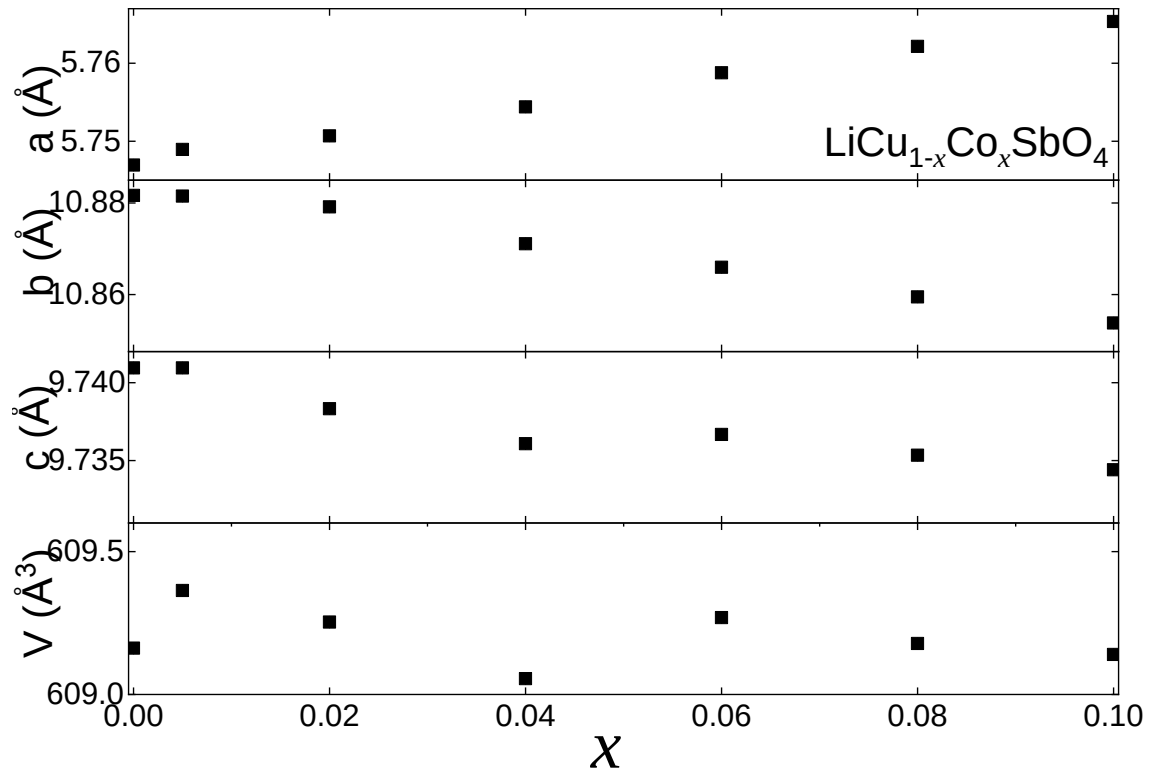


Figure 4.2 The lattice parameters a , b and c , and volume V as a function of the Co doping in $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$. The sizes of error bars are smaller than the symbols.

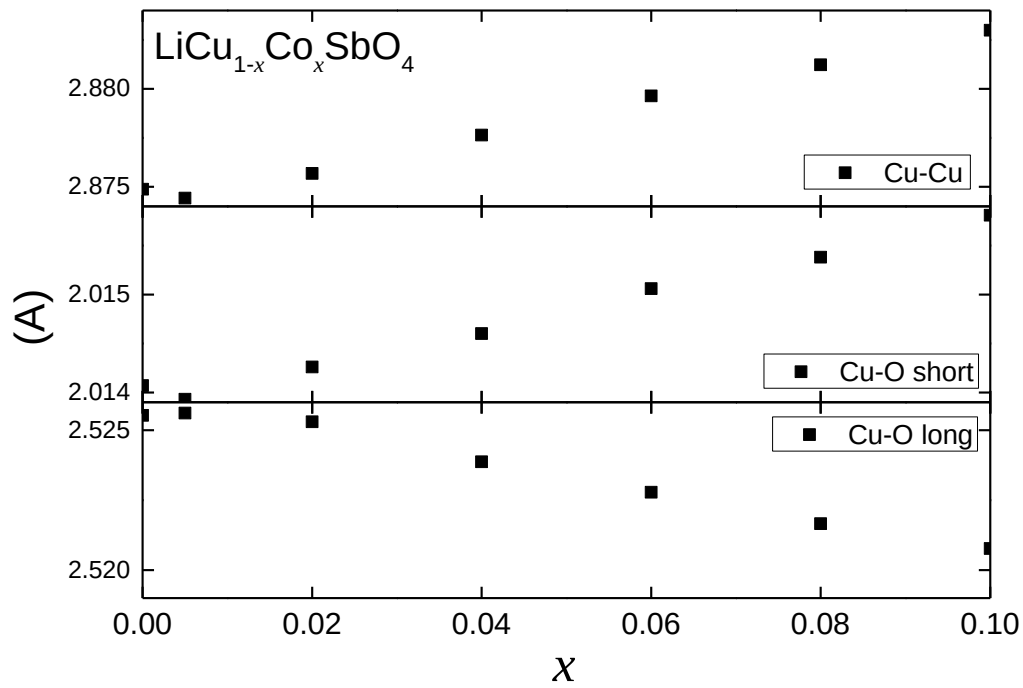


Figure 4.3 Bond length of Cu-Cu (top), Cu-O short (middle) and Cu-O long (bottom) of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of x .

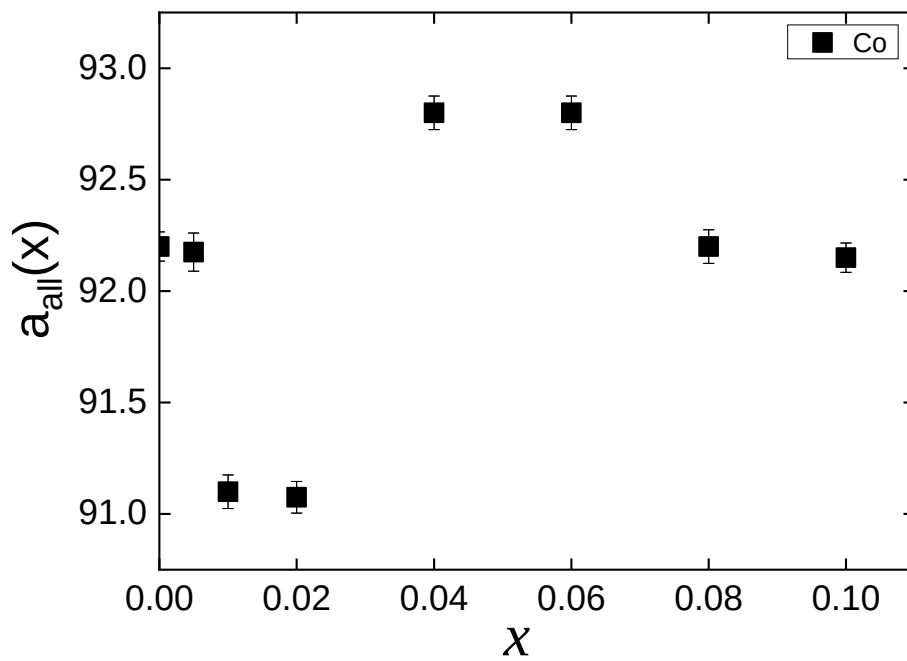


Figure 4.4 The average of angles Cu-On-Cu ($n=1,2,3,5$) of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of x .

4.3.2 Bulk Magnetic Properties

4.3.2.1 DC Magnetic Susceptibility, $\chi(T)$

The Zero Field Cooled (ZFC) magnetic susceptibility, $\chi(T)$ was measured in an applied field of 100 Oe. The doping dependence of the magnetic susceptibility of the $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ from 2 to 30 K is shown in Figure 4.5 and 2-300 K is in inset. The intensity of magnetic susceptibility was consistently proportional to the amount of Co doping even at high temperatures. This is because the fact that high spin Co^{2+} also has a magnetic moment of $S=3/2$ and so the Co^{2+} ions also contribute to the magnetic susceptibility. Therefore, the magnetic susceptibility is increased with Co doping. The magnetic susceptibility of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ had broad features around 10 K. This is from the short range order of one-dimensional frustrated Cu magnets which was described in Chapter 3. While in Mg and Zn doping, the changes on their magnetic susceptibilities were from $x=0.04$ in Co doped samples, the clear changes could be observed in the lowest doping value of $x=0.02$. In higher Co doped samples, the broad features which were from short range orders were not observed, possibly because the magnetic susceptibilities at low temperatures were increased.

The $1/\chi$ - T curves were treated by diamagnetic corrections. The magnetic susceptibility of all samples showed similar behaviour at $T > 30$ K and can be fit to the Curie-Weiss law⁶². The Curie Weiss law was carried out between 150 and 300 K as the $1/\chi$ - T curves were linear from 150 K. The Curie constant, Curie-Weiss temperature (θ), and effective magnetic moment are calculated. The properties from the Curie-Weiss fit for Co doped LiCuSbO_4 are tabulated in Table 4.1. The effective magnetic moment of the experimental results and theoretical expectation value of Co doped LiCuSbO_4 are shown in Figure 4.6.

The effective magnetic moments of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ were compared with those expected from assuming only a spin contribution. The experimental data of the effective magnetic moments of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ were consistently higher than that of theoretical calculated value. The subtraction of the magnetic moments of the theoretical calculations from the experimental results as a function of doping is shown in Figure 4.7. The subtraction of the effective magnetic moments was also linearly increasing as a function of Co doping. However, when the

contribution from Co^{2+} is deducted from the effective moment the values agree well with those observed for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$, shown in Figure 4.8.

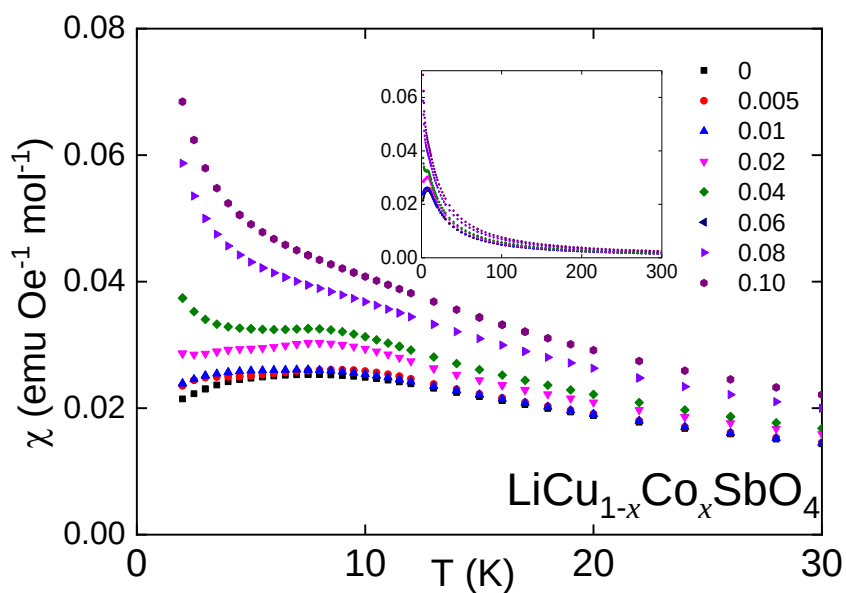


Figure 4.5 The magnetic susceptibility of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ from 2 to 30 K at 0.01 T for different doping levels. Inset for 2- 300K. The symbols are $x=0$ (black square), $x=0.005$ (red circle), $x=0.01$ (blue up triangle), $x=0.02$ (pink down triangle), $x=0.04$ (green diamond), $x=0.06$ (navy left triangle), $x=0.08$ (violet right triangle) and $x=0.10$ (purple hexagon), respectively.

Table 4.1 The summary of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$, effective the Bohr magnetization $\mu_{\text{eff exp}}$, the theoretical expectation of the effective the Bohr magnetization $\mu_{\text{eff the}}$ and Curie-Weiss temperature (θ) as the amount of Co doping.

$x \text{ Co}$	$C \text{ (emu} \cdot \text{K/mol)}$	$\theta \text{ (K)}$	$\mu_{\text{eff exp}} (\mu_B)$	$\mu_{\text{eff the}} (\mu_B)$
0	0.430(19)	22(1.0)	1.856(6)	1.73
0.005	0.4330(8)	18.1(4)	1.861(3)	1.747
0.02	0.4968(8)	12.9(3)	1.994(2)	1.798
0.04	0.573(10)	12.6(4)	2.141(2)	1.863
0.06	0.642(2)	13.6(8)	2.266(5)	1.927
0.08	0.754(5)	8(2)	2.46(10)	1.988
0.1	0.84(11)	5(3)	2.60(18)	2.047

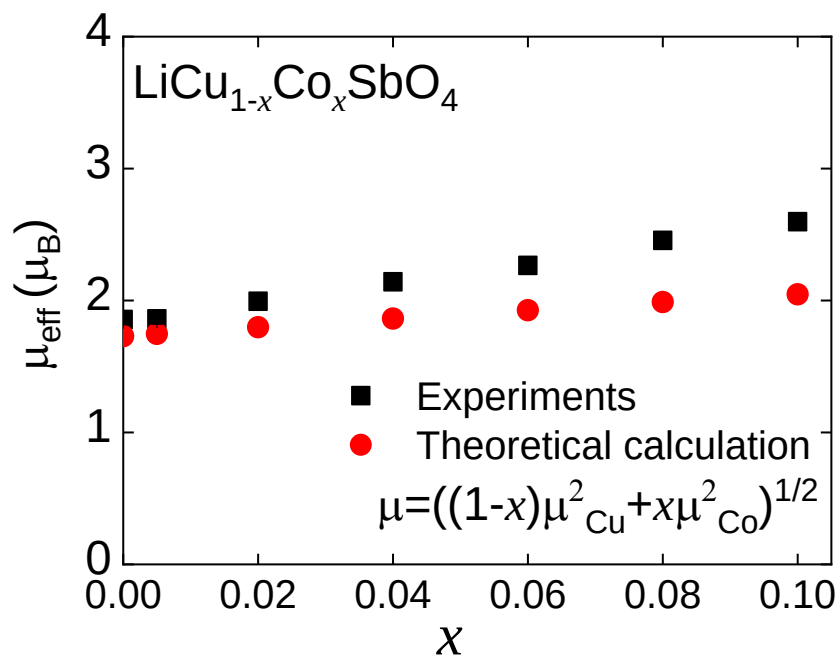


Figure 4.6 The effective magnetic moments of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of doping. Black squares and red circles stand for Experimental results and theoretical calculations, respectively. The size of the error bars is smaller than the plot sizes.

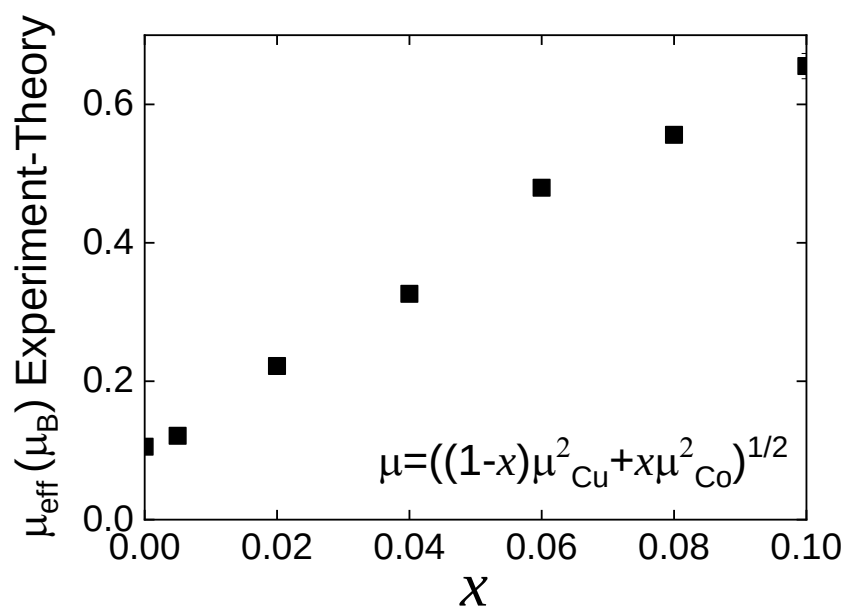


Figure 4.7 The subtraction of magnetic moments of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ from the experimental results minus the theoretical value.

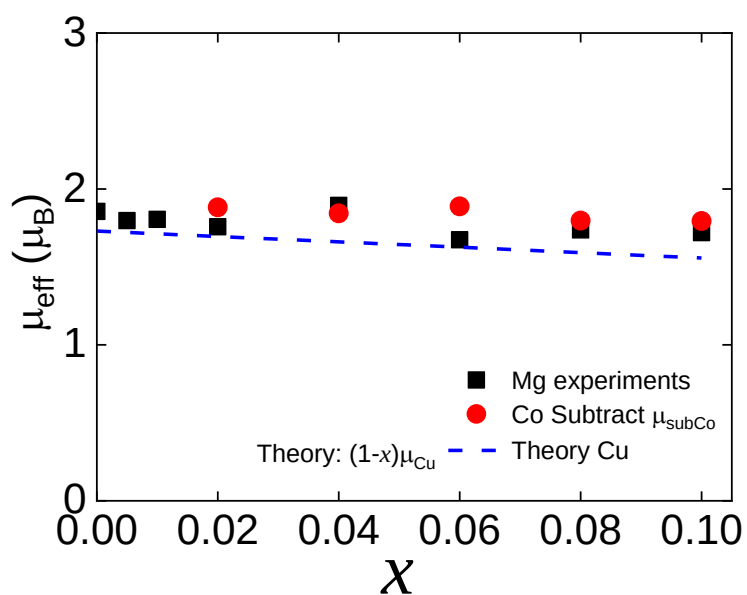


Figure 4.8 Comparison of effective moments of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of the amount of doping (x).

Black Squares, red circles, and a blue dotted line stand for the effective magnetic moments of Mg doped samples, Co doped samples and the theoretical calculation for the weighted average of the Cu ions, respectively.

4.3.2.2 Isothermal Magnetisation, $M(H)$

Temperature dependence of Isothermal magnetization of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ are shown from Figure 4.9 and Figure 4.15. Isothermal magnetization measurements of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of doping are shown in Figure 4.16. The $M(H)$ curve becomes more linear as a function of Co doping. The differential of the isothermal magnetizations of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$, dM/dH is shown in Figure 4.17. The peak shapes of dM/dH of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ are broader as a function of Co doping. The maxima of the dM/dH curves are shown in Figure 4.18. The anomalies around 12 T were observed in Co doped samples $M(H)$. As the level of Co substitution increases the maximum in dM/dH increases. The decrease in the curvature of $M(H)$ on doping results in a reduction in the magnitude of the peaks in dM/dH .

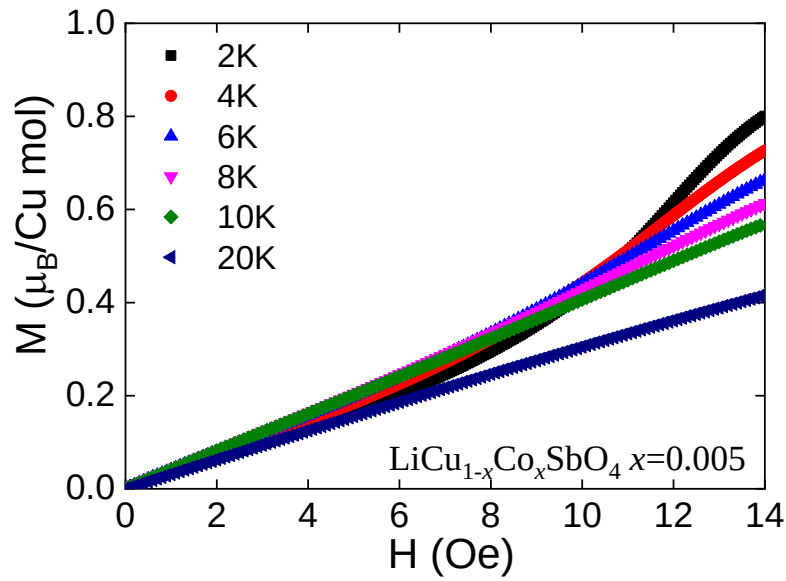


Figure 4.9 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.005$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

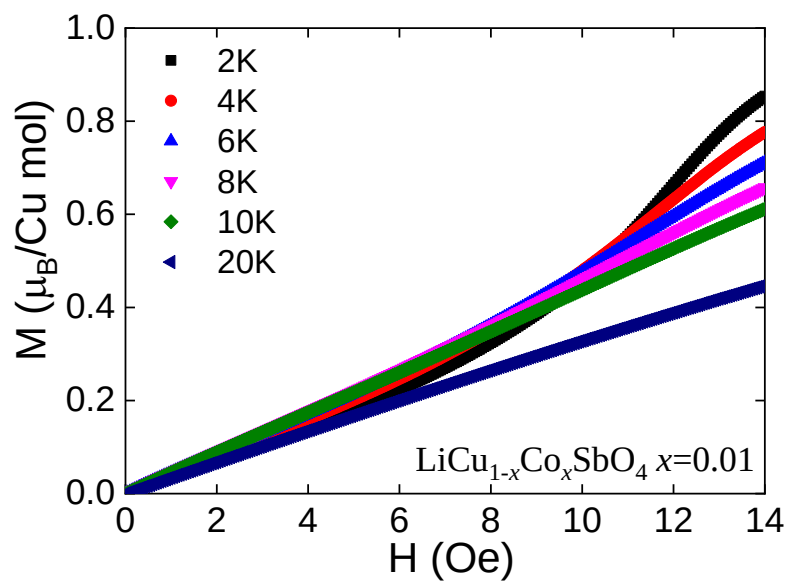


Figure 4.10 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.01$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

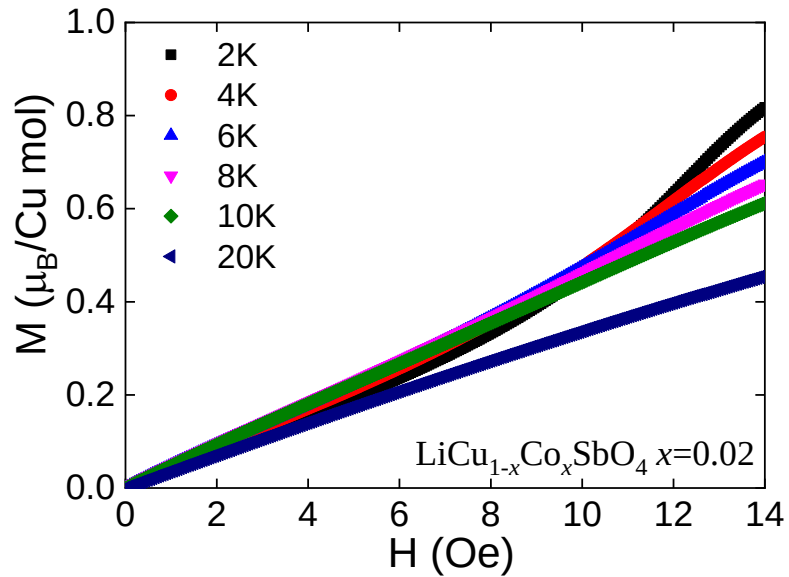


Figure 4.11 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.02$). The symbols are 2 K (black square) 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

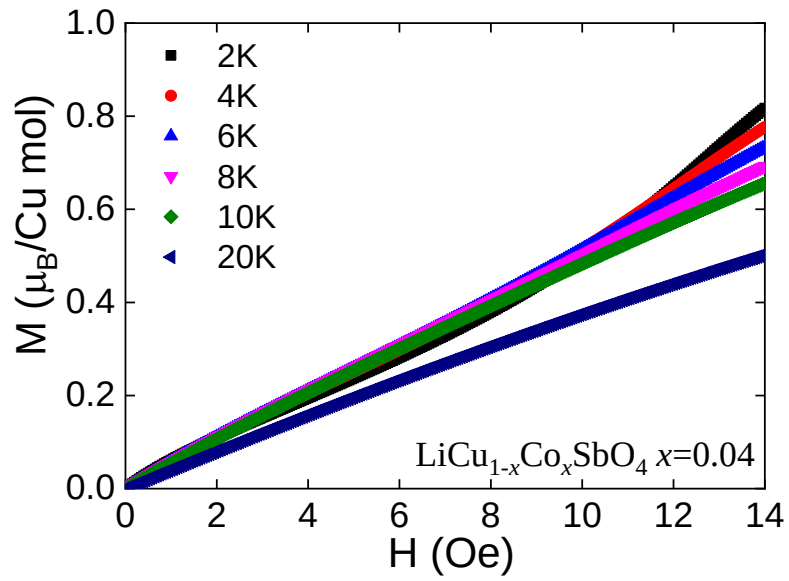


Figure 4.12 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.04$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

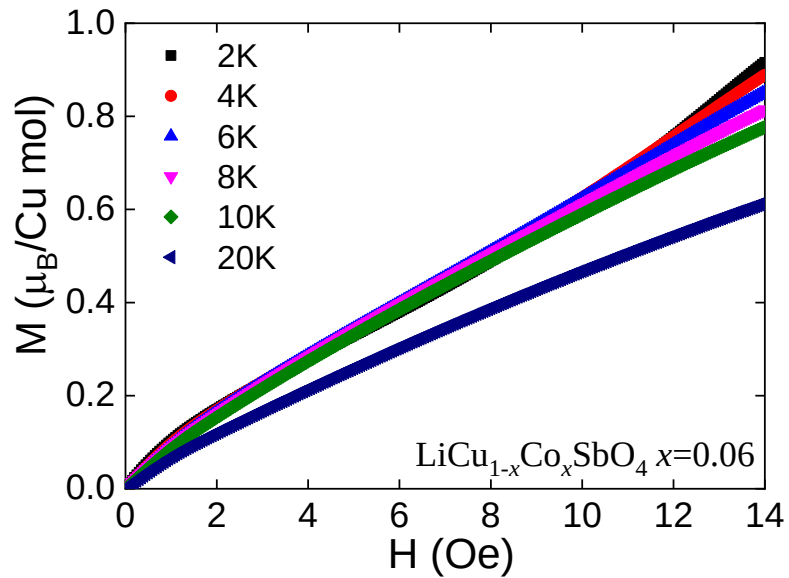


Figure 4.13 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.06$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

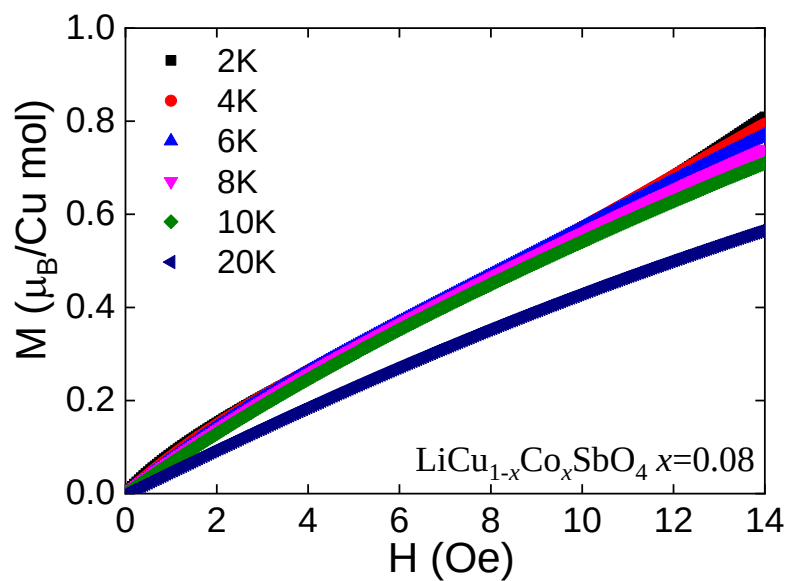


Figure 4.14 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.08$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

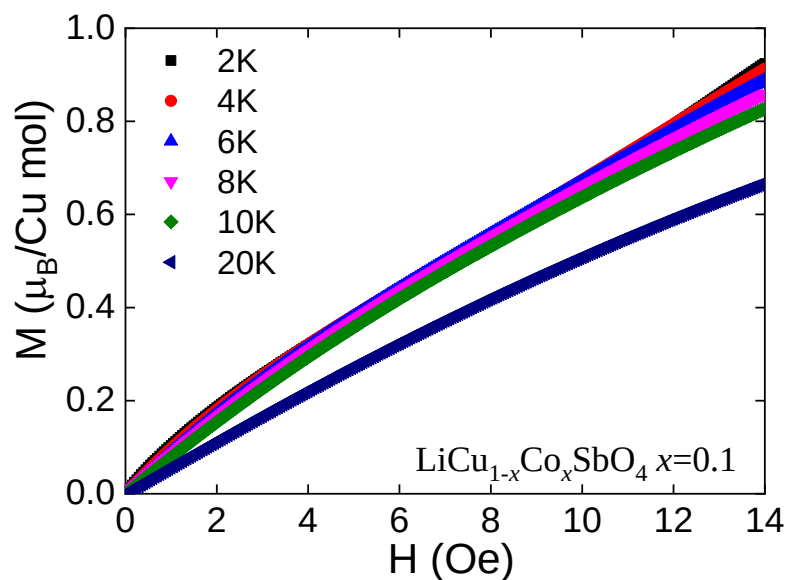


Figure 4.15 Isothermal magnetization of $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Co}$ $x=0.10$). The symbols are 2 K (black square), 4K (red circle), 6K (blue up triangle), 8K (pink down triangle), 10K (green diamond), 20K (navy left triangle), respectively. While $T=2$ K curves, higher temperatures were linear.

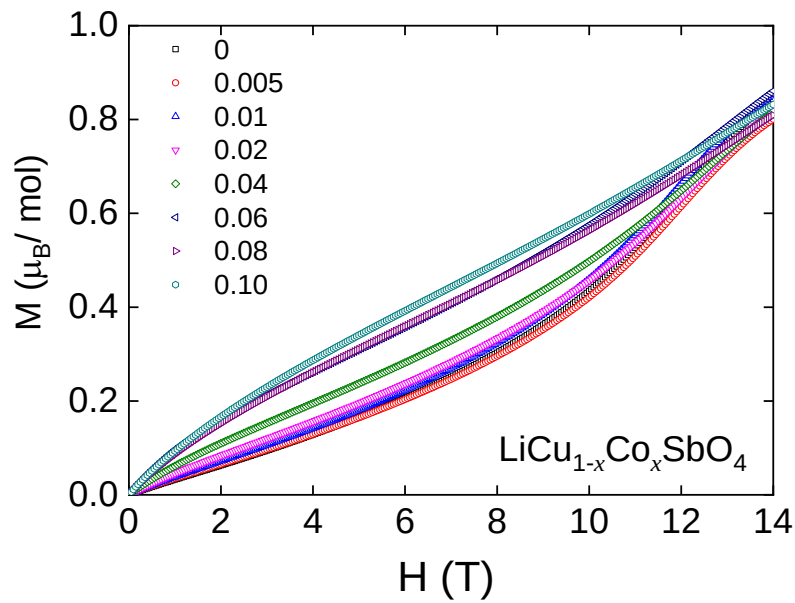


Figure 4.16 $M(H)$ curves of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$. The symbols are $x=0$ (black square), $x=0.005$ (red circle), $x=0.01$ (blue up triangle), $x=0.02$ (pink down triangle), $x=0.04$ (green diamond), $x=0.06$ (navy left triangle), $x=0.08$ (violet right triangle) and $x=0.10$ (purple hexagon), respectively.

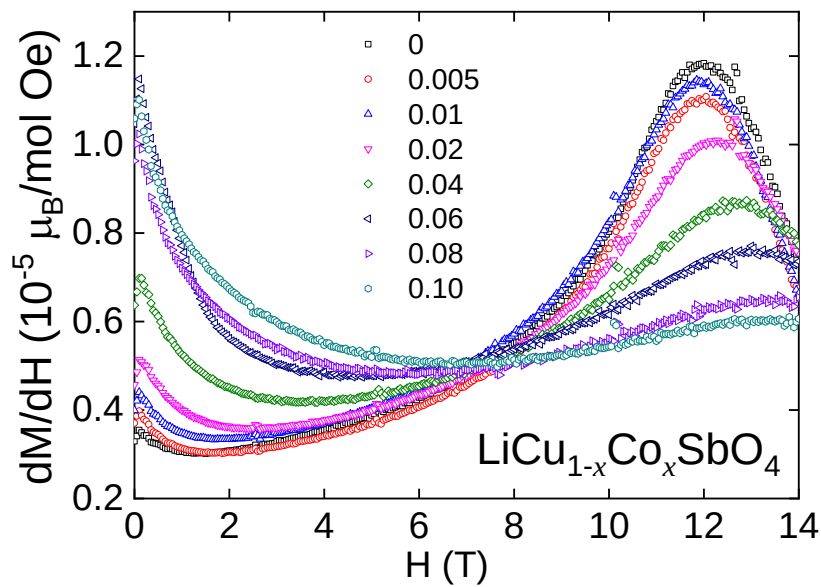


Figure 4.17 dM/dH of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ at 2 K. The symbols are $x=0$ (black square), $x=0.005$ (red circle), $x=0.01$ (blue up triangle), $x=0.02$ (pink down triangle), $x=0.04$ (green diamond), $x=0.06$ (navy left triangle), $x=0.08$ (violet right triangle) and $x=0.10$ (purple hexagon), respectively.

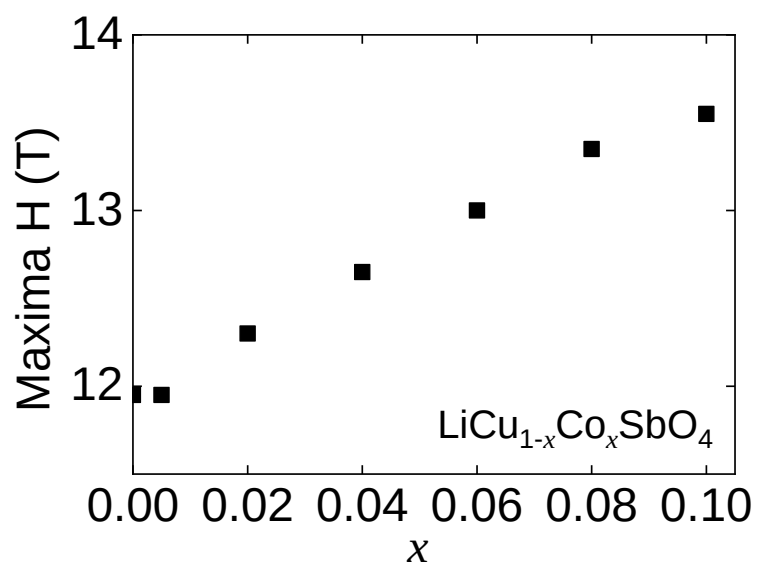


Figure 4.18 The maxima of dM/dH for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ at 2 K as a function of doping level x .

4.4 Discussion

In addition to doping non magnetic ions discussed in the previous chapter, doping magnetic ions has provided invaluable insight into the properties of frustrated systems^{13,35}. For magnetic ions doping, doped magnetic spins also interact with the magnetic ions in the parent materials and so further investigations of the properties of the frustrated system can be conducted comparing with non magnetic doping³⁵. In one dimensional frustrated systems, several investigations of magnetic ions doping have been reported such as the Mn^{2+} doping which has $S=5/2$ affected the magnetic properties of $LiCuVO_4$ which might be a FM ordering and Co doping made the intensity of the magnetic susceptibility larger at low temperature around 4 K in $LiCuVO_4$ ³⁵.

4.4.1 Structure

For $LiCuSbO_4$, this is the first investigation for the effect of partially doping Co on the Cu site. XRD results show previously reported impurity phases, $LiSbO_3$ and CuO , for Co doping in the range of $0 \leq x \leq 0.10$ ^{4,80}, however no increase in the percentage impurity was observed. No additional impurity phases are observed in the range of $0 \leq x \leq 0.10$. This suggests that the doping would be successful up to 10% Co in place of Cu.

Rietveld analysis of the XRD shows that for Co substituted samples, a increased while b and c decreased as a function of doping in the range of $0 \leq x \leq 0.10$. The overall lattice volume decreased on Co doping. The overall linear change in lattice parameters is indicative of formation of a solid solution and indicates that as expected, Co are randomly substituted on Cu sites. This changes in the lattice parameter follow the same trend as observed for Mg doped samples in chapter 3.

Co^{2+} has two types of spins; high spin and low spin. In solid state oxides, Co^{2+} are likely to be Co^{2+} high spin as in $CoNb_2O_6$ ⁸⁵ and $LiCoSbO_4$ ⁸⁶. Therefore, Co^{2+} would be expected to have a high spin configuration. The observed increase of the effective magnetic moment of the $LiCuSbO_4$ by Co doping is consistent with Co^{2+} high spin which has $S=3/2$ rather than Co^{2+} low spin which has $S=1/2$. In other materials, Co^{2+} ions are in octahedral sites including in inverse spinel structure⁸⁶, in $LiCoSbO_4$ ⁸⁶, and in $CoNb_2O_6$ ⁸⁵ which has the Columbite structure. Therefore, Co^{2+} would be likely to be seated in octahedral site.

The angles between Cu-O-bond angles in *ab* plane are shown in Figure 4.4. All the angles are in the range from 91 to 93 degrees. It is worth noting that the error associated with the bond angles is significantly smaller ($\sim 0.2^\circ$) than that observed on Zn and Mg doping ($\sim 2^\circ$). The origin of this is unclear. The range of the angles implies that J_1 in the system is FM in all materials in this doping range.

The general tendency of the structural changes of lattice by Co doping was the same as Mg doping with the same size of error. While the Cu-Cu bond lengths are increased linearly by doping and the Cu-O short bonds in *ab* plane also increase, the Cu-O long bonds along the *c* axis are decreased shown in Figure 4.3 for Co doped samples. This is the same trend as in Zn and Mg doped samples, however the magnitude of the changes in the bond lengths are significantly smaller. The Cu-O long bond lengths are caused by Cu atoms' Jahn-Teller distortion, it is consistent with the fact that Co are active but weak for the Jahn-Teller distortion and the difference between Cu-O long and Cu-O short bonds becomes smaller. They are linearly decreasing with the amount of *x*. In order to determine the relations between lattice parameters and bond lengths, taking the projections of the bond lengths along different crystallographic axes need to be considered. Cu-Cu and Cu-O short bond lengths contribute to the *a* axis direction and Cu-Cu and Cu-O short bond lengths increased so as *a* increased with doping. The Cu-O long and the Cu-O short bonds are both related to *b* and *c*. The lattice parameter *b* and *c* become shorter by Co doping as the Cu-O long and the Cu-O short changed.

The impact of such distortions on the structural properties requires further experiments such as synthesizing single crystals and XANES and PDF analysis. Once single crystals are synthesized, more detail information such as anisotropy of the oxygen coordination of the Cu sites can be investigated. XANES and PDF can investigate the local structures around the magnetic ions.

4.4.2 Magnetic Properties

The magnetic properties of undoped LiCuSbO_4 and the changes on doping with non-magnetic ions have been discussed in Chapter 3. The CW temperatures for Co doped samples shown were all positive in the doping range ($0 \leq x \leq 0.10$), indicative of FM correlations. The CW temperatures were decreasing with Co doping from 22 K ($x=0$) to 8 K ($x=0.10$). This suggests a decrease in the strength of the FM correlations on doping. The effective magnetic moment

increases with Co doping, indicative of the presence of high spin Co^{2+} , $S=3/2$. However, the increase observed is larger than would be expected. This might be due to short range magnetic correlations within the T range of the fit (150-300 K).

No significant changes in magnetic susceptibility are observed in the range of $0 \leq x \leq 0.01$ except a slight increase of a Curie-tail like peak below 4 K. The intensities of the magnetic susceptibilities of Co doped samples were increased in the whole temperature range of $4 \leq T \leq 300$ K as Co^{2+} are also magnetic ions and so the magnetic susceptibility also includes a contribution from Co^{2+} was also included in the measured magnetic susceptibility of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ in the range of $0.01 \leq x \leq 0.10$. An additional upturn at 4 K from $x=0.02$ is observed, this possibly corresponds to a Curie tail²³. However, if susceptibility measurements could be carried out below 2 K, it is expected that the Curie tail would also be observed for doping levels $0 \leq x \leq 0.01$ as the temperature at which the Curie tail is observed would be proportional to the amount of Co doping due to the expected temperature dependence for the curie tail $\chi=C/T$. A curie-tail like behaviour was also observed in Co doping in another one dimensional frustrated magnet system, LiCuVO_4 ³⁵.

The intensity of the Curie tail in Co doped samples appears larger than that of Zn or Mg doped samples as the susceptibility of the Co doped samples is larger than that of Zn and Mg doped samples. The comparison of 10 % doping of Zn, Mg and Co doped samples are shown in Figure 4.19. The general tendency was $\chi_{\text{Co}} > \chi_{\text{Zn}} > \chi_{\text{Mg}}$. However, as the experimental results of magnetic susceptibility include not only Curie tail behaviours, but also other effects such as SRO, it is difficult to quantitatively compare between different doped systems.

The feature at 6 K from 1D SRO⁴ was stable which was the same as Zn and Mg doped samples as discussed in Chapter 3. This stability of the feature at 6 K on Co doping suggests that the SRO in this system was not affected and the SRO was not fully broken by Co doping in this doping range ($0 \leq x \leq 0.10$).

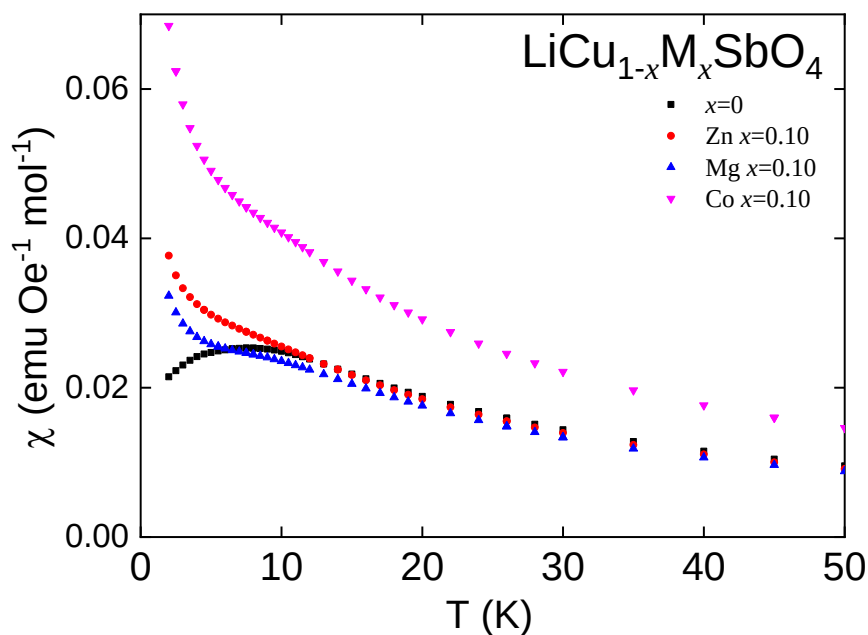


Figure 4.19 Magnetic susceptibility of LiCuSbO_4 and 10 % Zn (red), Mg (blue) and Co (pink) doped samples.

Unlike the non-magnetic doped samples discussed in the previous chapter, doping with magnetic ions is more complex as one needs to consider $J_{1\text{Co-O-Cu}}$ which is the NN interaction of Cu and Co in addition to $J_{2\text{Co-O-O-Cu}}$ and $J_{2\text{Cu-O-O-Cu}}$ which are NNN interactions via Co-O-O-Cu and Cu-O-O-Cu pathways respectively. This difference between the magnetic ions and non magnetic ions doping means that the simple orphan spin approach which was used for Zn and Mg doped samples which are non magnetic ions cannot be applied for this system in Co doping which is a magnetic ion due to the possibility that the Co^{2+} spins would interact with Cu^{2+} spins.

However, the measurements for non magnetic doped samples showed that the magnetic susceptibility of Zn and Mg doped materials was made of two components including SRO and Curie tails. In the Co doped samples, these two features are also present, and as can be seen in Figure 4.12, the Curie tail feature is more significant on Co doping when compared to Zn and Mg doping. On Co doping there may be additional contribution which cannot be resolved in the powder averaged measurements presented here. In Co doping of the 1D $S=1/2$ compounds LiCuVO_4 , the SRO peak and curie-tail like behaviours were observed and shown in the magnetic susceptibility of $\text{LiCu}_{0.95}\text{Co}_{0.05}\text{VO}_4$ ³⁵ which was consistent with the result. The Weiss temperature of LiCuVO_4 which was -21.29 K became more strongly antiferromagnetic in Co

doping which was -32.44 K in $\text{LiCu}_{0.95}\text{Co}_{0.05}\text{VO}_4$. In LiCuVO_4 , the Mn doped changed the CW temperature from minus to plus by increasing temperature³⁵. This tendency is consistent with the experimental data in LiCuSbO_4 that the higher the Co doping, the smaller the Weiss temperatures³⁵. Further analysis such as XPS was conducted for comparing magnetic Co doped LiCuVO_4 with non magnetic Zn doped LiCuVO_4 showed that no appreciable change was observed between Zn and Co doping which indicated there are no changes of oxidation state³⁵.

In LiCuSbO_4 , the dM/dH curve at 2 K for Co doped samples showed a peak at high field for all samples. This is also consistent with the dM/dH of non-doped LiCuSbO_4 which showed a peak at 12 T corresponding to the critical field H_c where all Cu^{2+} spins are fully polarized⁴. The peak becomes smaller and broader as the amount of Co doping increases. This broadening of the peak suggests a range of possible critical fields and is due to the dopant ions. For Co doping, the critical field was linearly increased with doping except $x=0.01$'s slight off reaching a maximum value of 13.5 T for $x = 0.10$. Theoretical reports have demonstrated the role of 3D ordering in the value of the critical field, with higher H_c being associated with more 3D ordering³⁴. The changes in H_c on doping can therefore be associated with changes in the degree of 3D ordering in LiCuSbO_4 . Whilst doping increases the 3D ordering it should be noted that the maximum critical field of 13.6 T is significantly smaller than the critical field of other $S=1/2$ one dimensional frustrated systems such as 40 T and 44 T for LiCuVO_4 $H||c$ and LiCuVO_4 $H||a$ and b , respectively⁸⁷. This smaller critical field suggest that even doped LiCuSbO_4 has relatively weak 3D interactions.

While the critical field of Zn doped materials were decreased for higher doping levels $x \geq 0.06$, that of Mg and Co doped materials were increased in the range $x \geq 0.06$. The structural difference along c axis could explain the differences in the behaviours of Zn, Mg and Co doped samples. While the lattice parameter c was increased by Zn doping, it was decreased by Mg and Co doping in the range of $0.04 \leq x \leq 0.10$. This tendency might be consistent with the previous result that the one dimensional frustrated magnetic chains were three dimensionally interacting as the longer c axis would suppress the inter-chain three dimensional interactions³⁴.

While the experimental data of the effective magnetic moments in Zn and Mg doped samples obeyed the theoretical weighted average of the magnetic moments of Cu, the experimental data of the effective magnetic moments in Co doped samples were constantly larger than that of the

weighted average of the theoretical effective magnetic moments of Cu^{2+} and Co^{2+} . This may be the result of short range correlations existing at higher T in Co doped samples.

Future experimental work such as heat capacity measurements, neutron scattering, ESR, NMR as well as detailed theoretical modelling is required to fully understand the impact of Co doping in LiCuSbO_4 . Magnetic heat capacity will help to understand the ensemble behaviours of magnetic properties with the amount of Co doping. Inelastic Neutron scattering will be able to investigate the local magnetic structures by investigating the magnetic interactions. ESR can investigate the behaviour of 1D Cu spin chains as well as Cu spins which are the neighbours of the doped Co^{2+} spin. Low temperature measurement with Helium-3 insert or dilution fridge can investigate the magnetic properties of low temperature $T < 2$ K. The theoretical model and fitting will make it easier for more quantitative analysis of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ systems.

4.5 Conclusion

Quasi-one dimensional frustrated magnets LiCuSbO_4 was doped magnetic Co atoms. $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($0 \leq x \leq 0.10$) were synthesized by a ceramics process. The magnetic properties including magnetic susceptibility and isothermal magnetizations were measured. At smaller doping level ($x \leq 0.01$), their behaviours of magnetic properties were the same tendency as that of the parent material LiCuSbO_4 . Also, SRO feature which was also reported for parent material was observed. Once the doping level were higher ($x \geq 0.04$), Curie tail like behaviours in their magnetic susceptibility at low temperatures around 4 K were observed. The results imply that the magnetic Co doping would also be partly “cut” the one dimensional Cu chain and the Cu atoms on the edges of the chains would behave as “orphan” spins as non magnetic doped samples such as Zn or Mg doped samples discussed in Chapter 3.

In isothermal magnetization, the peaks around 12 T which were reported as a phase transition were observed in Co doping in the range of $0 \leq x \leq 0.10$. The critical field was increased as Co doping which would the same tendency that of Mg doping. This 3D ordering in Mg doping might be smaller than that of Zn doping.

Chapter 5 Effect of doping in spin ice materials

$A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($A=\text{Dy}, \text{Ho}$)

5.1 Introduction

In this chapter, the synthesis and behaviour of the spin ice materials, $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ have been investigated. The structure of $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ are pyrochlore which has a cubic unit cell and chemical formula described as $A_2B_2\text{O}_6\text{O}'^{88}$. Both A and B form interpenetrating networks of corner sharing tetrahedra. Each A site is surrounded by eight oxygen atoms. Six oxygen atoms are described as O (or O1) and two oxygen atoms are described as O' (or O2)⁸⁹. The bond length between the A atoms are described as $A\text{-O1}$ and $A\text{-O2}$ respectively. The B site has octahedral coordination and is surrounded by 6 O atoms⁸⁹. The O co-ordination of the A site is shown in Figure 5.1.

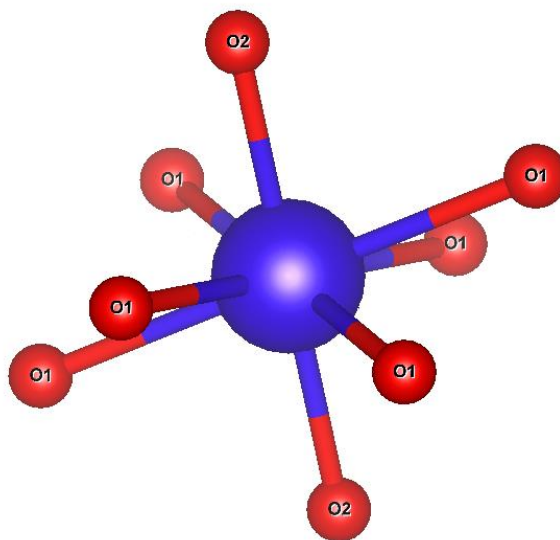


Figure 5.1 rare earth atom on A site (blue) which is surrounded by eight oxygen atoms (red), Six O1s and Two O2s.

Usually, in the lanthanide pyrochlores, magnetic lanthanide ions are seated on A sites and non-magnetic ions are seated on B sites. The O co-ordination of the rare earth ions results in strong local $\langle 111 \rangle$ Ising anisotropy when $A = \text{Ho, Dy}$ and at low temperatures around 1 K, a spin-ice configuration was observed to form^{1,39}. The heat capacities of $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ which will be discussed in this chapter have also been reported⁸⁸. The magnetic heat capacity showed the peak around 2 K which was known as the peak of dipolar spin ice⁴¹. The magnetic entropy of the spin ice is suppressed because of the residual entropy⁴¹. The value of the suppression of the magnetic entropy is calculated by the “ice rules” discussed in section 1.11. However in both $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ which behave very similarly to $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$, a divergence in the ZFC and FC susceptibility is observed below 0.7 K, this is ascribed to spin freezing²³.

Doping is an effective method to analyse frustrated magnets^{12,49,90,91}. It is also true for investigating the properties of spin ice. As the magnetic ions are located in A sites, the magnetic lattice is affected directly for A site doping^{90,92,18}. There are two types of doping; magnetic doping and non-magnetic doping. Nonmagnetic doping is usually known as magnetic dilution as the nonmagnetic ions do not have magnetic spins and the intensity of the effective magnetic moment of the system is reduced. In pyrochlores, A sites dilution of magnetic ions such as $\text{Dy}_{2-x}\text{M}_x\text{Ti}_2\text{O}_7$ ($M = \text{Y and Lu}$) or $\text{Ho}_{2-x}\text{Y}_x\text{Ti}_2\text{O}_7$ has been carried out and the changes in their zero point entropy have been explored^{18,49,50}. Once the spin ices were diluted by doping on A site, their saturation value of magnetic entropy was suppressed, as was their zero point entropy. This suppression is observed even at the minimum dilution level of 5 %.

On the other hand, doping on the B site which is usually occupied by a non magnetic cation affects the properties of lanthanide pyrochlores differently. The mixed B site pyrochlores such as $\text{Tb}_2\text{Sn}_x\text{Ti}_{2-x}\text{O}_7$ showed ground states different from $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ and this unique state suggested that in $\text{Tb}_2\text{Sn}_x\text{Ti}_{2-x}\text{O}_7$ series, the CF effect is highly dependent on the local structure. This is in part due to the ground state of Tb^{3+} not being constrained to be doubly degenerate from Kramer’s theorem. It was postulated that the ionic radii difference between Ti^{4+} and Sn^{4+} ions and the fact that the O atom positions are also slightly changed, effects the observed magnetic properties¹⁹.

Doping magnetic atoms on B site has been shown to induce spin glass like behaviours when V is doped on Ti site in $\text{Dy}_2\text{Ti}_{2-x}\text{V}_x\text{O}_7$ ⁹³ ($0 \leq x \leq 0.5$). An increase in the freezing temperature, T_f , is observed as x increases until $x=0.4$, no freezing is observed when $x=0.5$. In pyrochlore

$\text{Ho}_2\text{CrSbO}_7$ system, ferromagnetic order at 10 K is reported⁴³. This is discussed in relation to ferromagnetic interactions between Cr^{3+} and Ho^{3+} resulting in ordering.

As can be seen doping on the B site can play critical roles in the nature of the ordering in rare earth pyrochlores. In this chapter, the systematic removal of the coordinated oxygen atoms for $A=\text{Ho}$ and $A=\text{Dy}$ in pyrochlore spin ices will be investigated by doping Sc^{3+} for Sn^{4+} in the B site. As Sn has 4+, Sc has 3+ charge half an equivalence of O is also removed to ensure charge balance. Therefore, by doping a Sc^{3+} atom, half an O^{2-} ion would be removed to maintain the charge balance. As the rare earth atoms are surrounded by O ions, the removal of the O ions would affect the magnetic properties of spin ices on A sites by changing the crystal fields. In this chapter, the effects of Sc doping on B site to change the environments of spins on spin ice materials $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($A=\text{Dy}$ and Ho) and the difference in the effect of doping between $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ spin ices series is discussed.

5.2 Sample preparation

Synthesis of the $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series ($x=0, 0.025, 0.05, 0.075, 0.10$ $A=\text{Ho}, \text{Dy}$) was carried out using a ceramic synthesis method. The starting materials were Ho_2O_3 (99.995%, Alfa Aesar), Dy_2O_3 (99.99%, Alfa Aesar), Sc_2O_3 (Alfa Aesar), and SnO_2 (99.995%, Alfa Aesar).

Stoichiometric amounts of solid starting materials were intimately ground prior to firing as pellets for 12 hours under air at 800 °C. The pellets were then ground, mixed well and re-made into pellets. The pellets were then heated to 1400 °C in air for 24 hours. The structure of the resultant powder was evaluated using XRD. Heating was continued until a phase pure product was formed. Typically, samples were heated for 196 hours.

5.3 Results

5.3.1 Structural Chemistry

$A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series ($x=0, 0.025, 0.05, 0.075, 0.10$ $A=\text{Ho}, \text{Dy}$) were successfully synthesized and found to adopt the cubic pyrochlore structure. Attempts to synthesise samples with $x > 0.1$ resulted in the additional phase formation of $A_3\text{Sc}_5\text{O}_{12}$ ($A=\text{Ho}, \text{Dy}$) garnet impurities. All samples were measured by XRD and the structure quantitatively analysed using

the Rietveld method⁵³. A typical refinement is shown in Figure 5.2. The refinements for other samples can be found in Appendix 30-39.

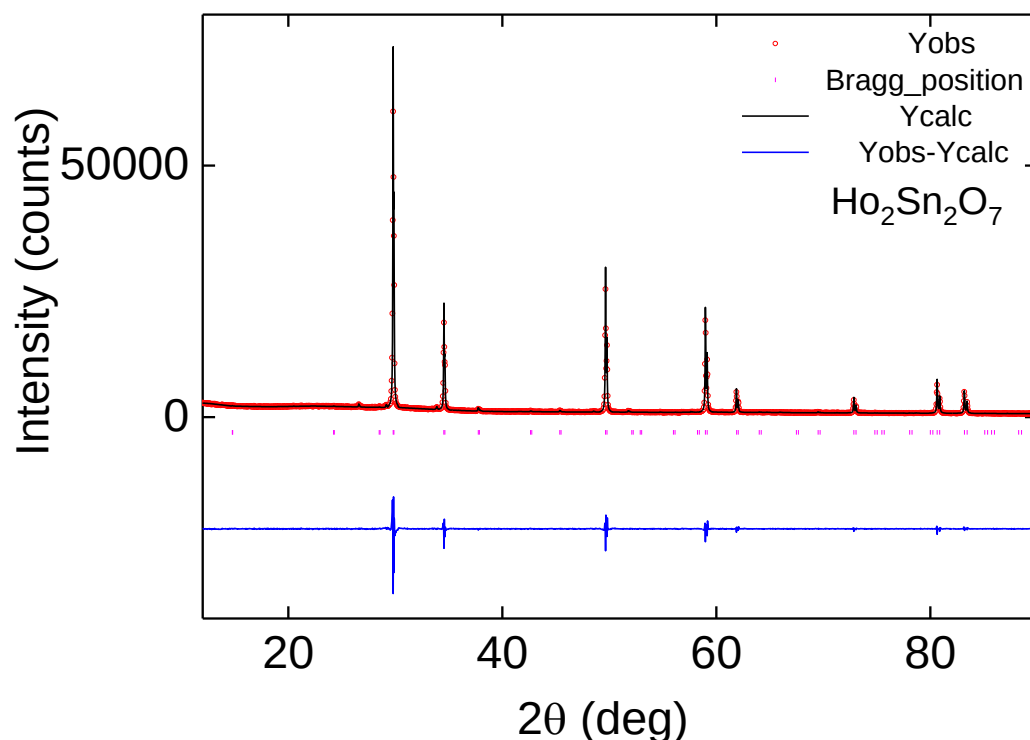


Figure 5.2 X-ray diffraction data for the $\text{Ho}_2\text{Sn}_2\text{O}_7$. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.

The lattice parameter a decreased linearly in Ho series as a function of Sc doping. In Dy doping, from $x=0$ to $x=0.025$ it decreased significantly and then from $x=0.025$ to $x=0.10$ it did not change dramatically. The lattice parameters as a function of doping in $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 5.3 (a) and Figure 5.3 (b), respectively. The RE-On ($n=1,2$) bond lengths of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ for Ho and Dy are shown in Figure 5.4 (a) and Figure 5.4 (b), respectively. Details of the refinements and selected bond lengths are summarized in Table 5.1 and Table 5.2 for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ respectively.

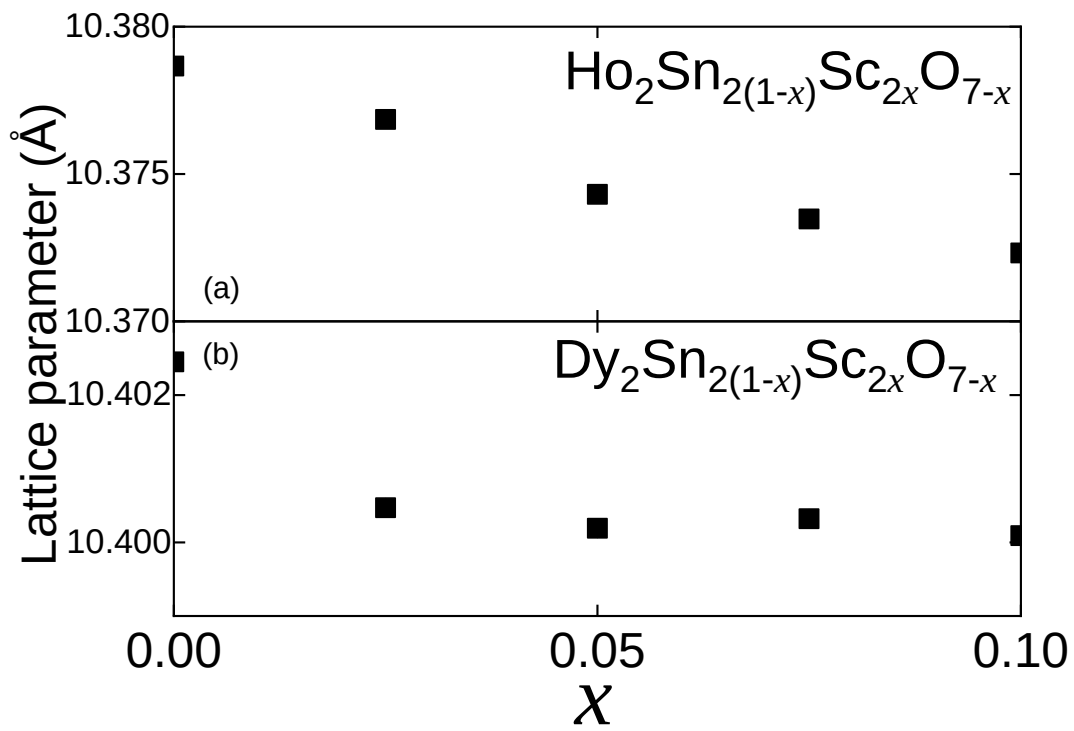


Figure 5.3 Lattice parameter of (a) $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and (b) $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of doping x .

Table 5.1 Summary of lattice parameters and bond lengths for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ B_{iso} was fixed to 0.5.

x		0	0.025	0.05	0.075	0.1
a (Å)		10.37866(4)	10.37685(5)	10.37473(7)	10.37345(5)	10.37232(6)
R_p		4.1	3.55	3.95	4.2	6.94
R_{wp}		6.52	5.46	7.06	6.57	9.85
R_{exp}		2.58	2.56	2.53	2.5	2.64
χ^2		6.4	4.55	7.77	6.92	13.9
O1	x	0.3400(12)	0.3368(13)	0.334(2)	0.3415(11)	0.3408(13)
Ho_2O_3	wt%	0.95(12)	0.84(14)	-	1.17(12)	1.28(10)
SnO_2	wt%	1.07(11)	0.06(11)	-	-	-
Bond length(Å)	Ho-O1	2.475(9)	2.497(8)	2.505(9)	2.463(7)	2.468(8)
Bond length (Å)	Ho-O2	2.24705(0)	2.24665(0)	2.24611(0)	2.24592(0)	2.24567(0)

Table 5.2 Summary of lattice parameters and bond lengths for $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ B_{iso} was the fixed to 0.5.

x		0	0.025	0.05	0.075	0.1
a (Å)		10.40245(4)	10.40047(4)	10.40019(5)	10.40033(4)	10.40009(5)
R_p		6.66	6.22	5.69	6.21	5.45
R_{wp}		9.3	8.61	7.71	8.58	7.35
R_{exp}		4.63	4.61	4.62	4.5	4.62
χ^2		4.03	3.49	2.78	3.63	2.53
O1	x	0.33901(11)	0.3376(10)	0.33406(9)	0.33788(8)	0.33982(8)
Bond length (Å)	Dy-O1	2.487(6)	2.497(6)	2.521(5)	2.494(5)	2.481(5)
Bond length (Å)	Dy-O2	2.25220(0)	2.25177(0)	2.25171(0)	2.25174(0)	2.25169(0)

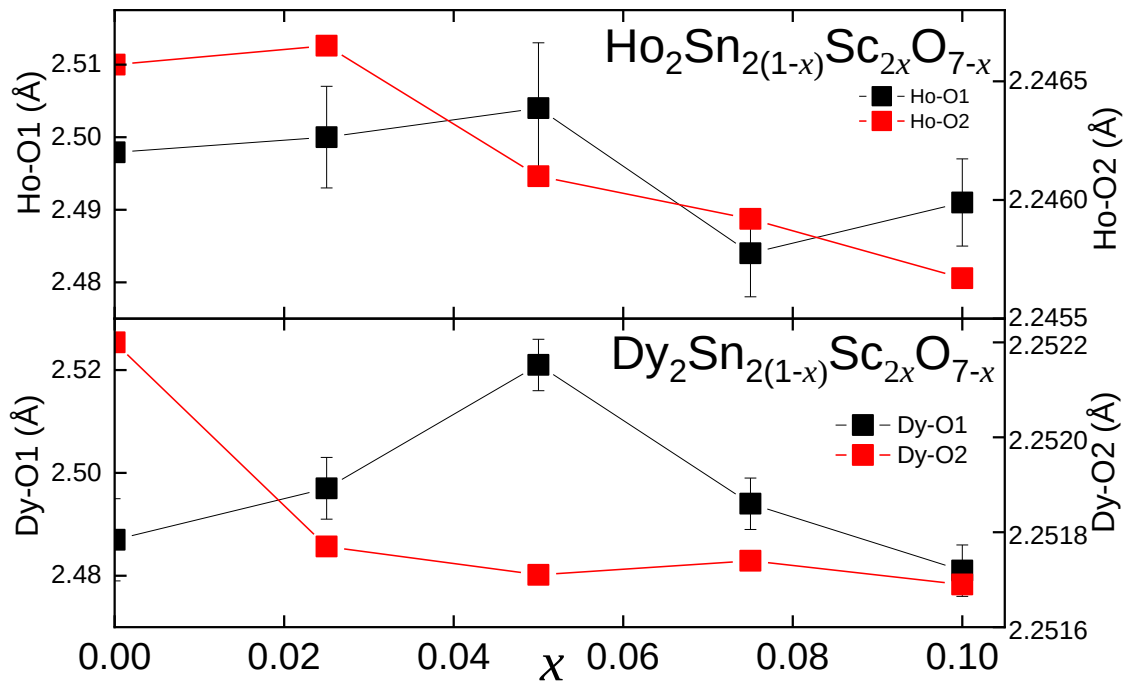


Figure 5.4 Bond lengths of (a) $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of doping x with error bars. Black squares and red circles stand for $A\text{-O1}$ and $A\text{-O2}$, respectively. For $A\text{-O2}$ bonds the error is smaller than the data point.

5.3.2 Magnetic properties

5.3.2.1 Isothermal Magnetisation, $M(H)$

Temperature dependence of the isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown from Figure 5.5 to Figure 5.14. The isothermal magnetisation of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ at 5 K are shown in Figure 5.15 and Figure 5.16, respectively. In Dy series, no change was observed in the isothermal magnetization as a function of Sc doping. On the other hand, in the Ho series, there was a large difference in the saturation value of the isothermal magnetization. This is more clearly seen when considering $M_{2K,5T}$ as a function of x as shown in the inset of Figure 5.15.

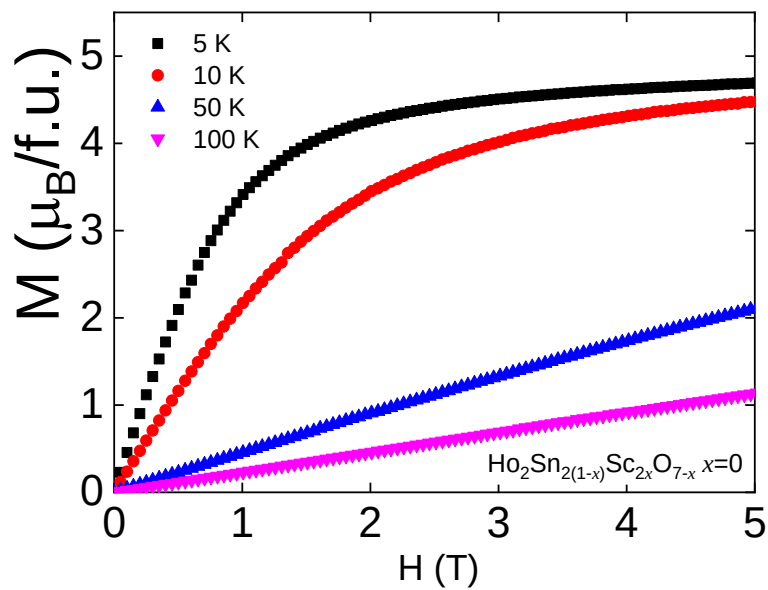


Figure 5.5 Temperature dependence of isothermal magnetization of $\text{H}_2\text{Sn}_2\text{O}_7$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

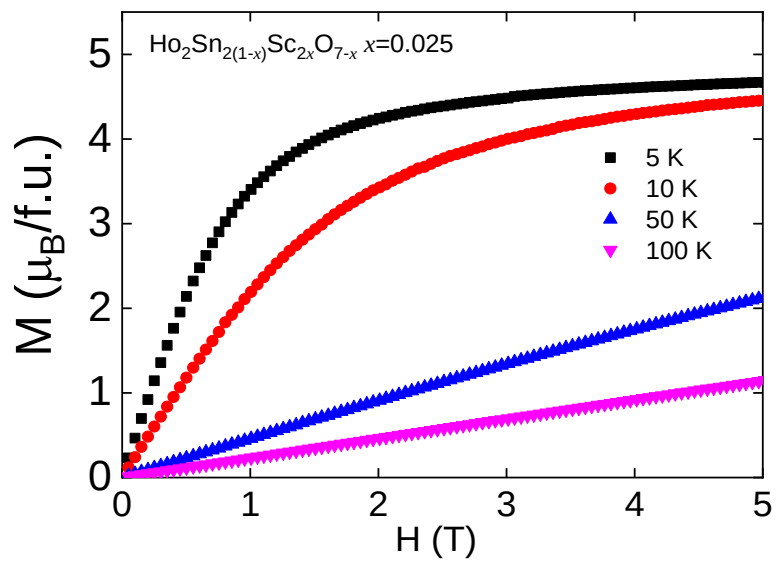


Figure 5.6 Temperature dependence of isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.025$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

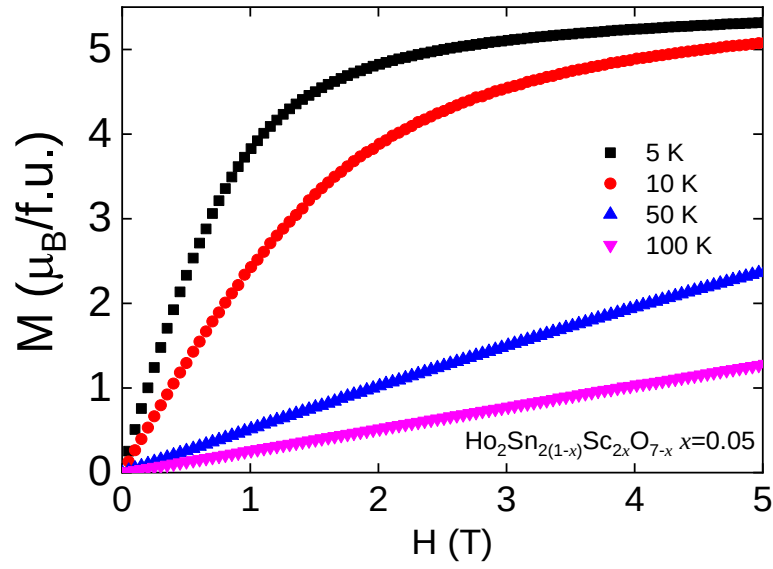


Figure 5.7 Temperature dependence of isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.05$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

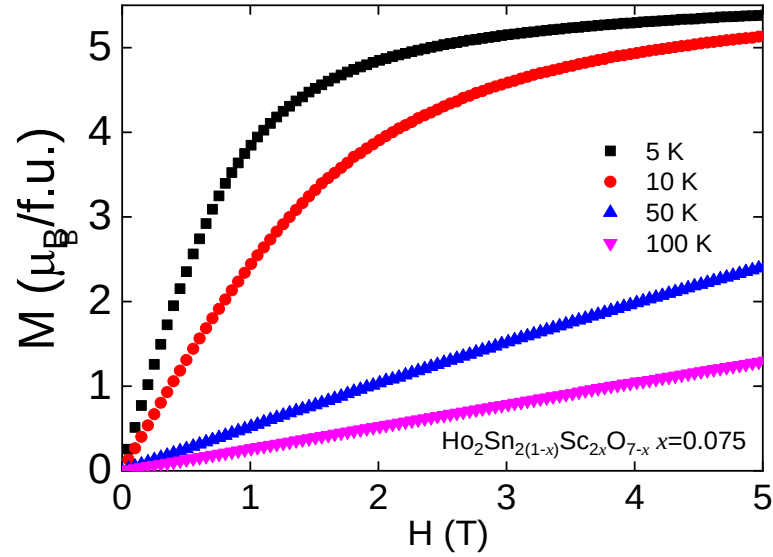


Figure 5.8 Temperature dependence of isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.075$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

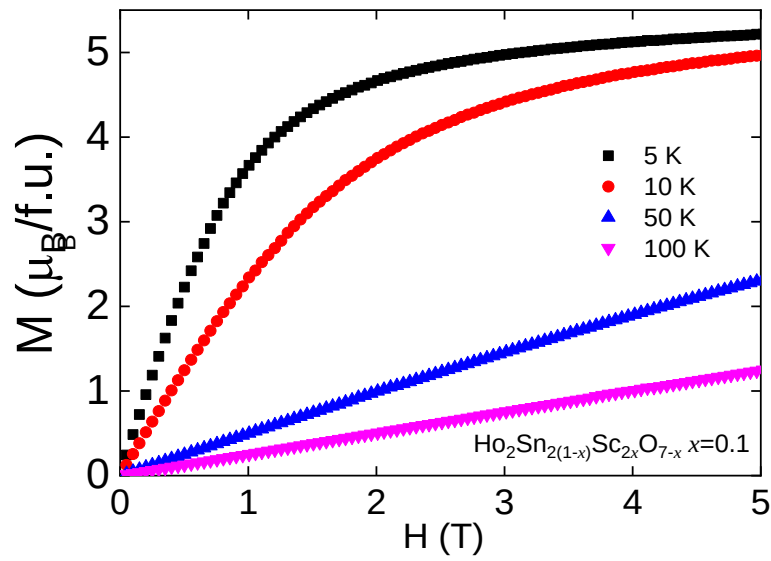


Figure 5.9 Temperature dependence of isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.10$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

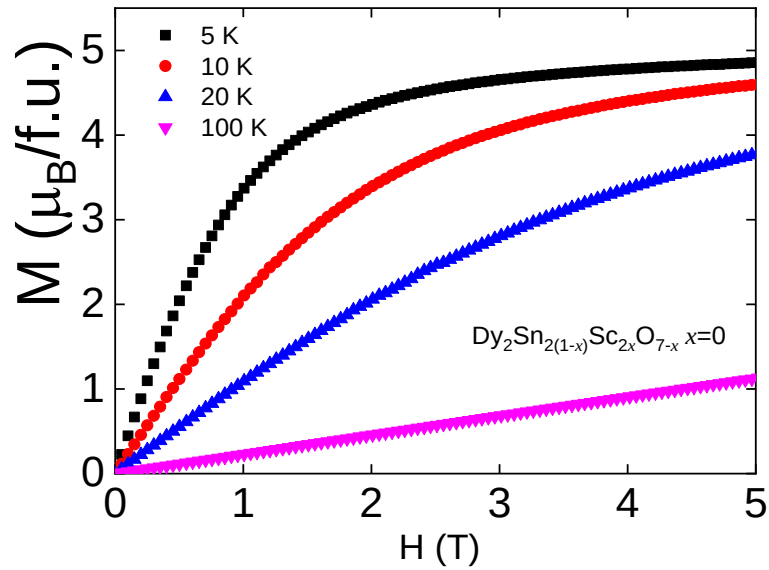


Figure 5.10 Temperature dependence of isothermal magnetization of $\text{Dy}_2\text{Sn}_2\text{O}_7$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

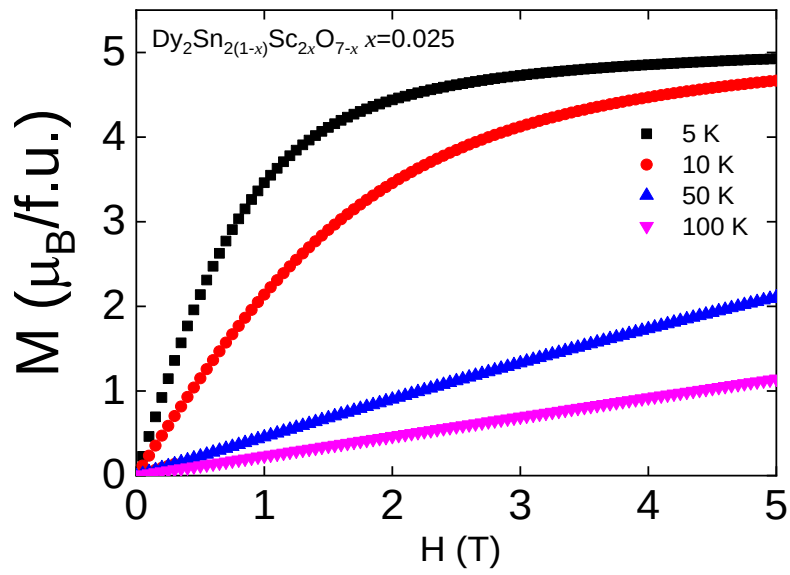


Figure 5.11 Temperature dependence of isothermal magnetization of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.025$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

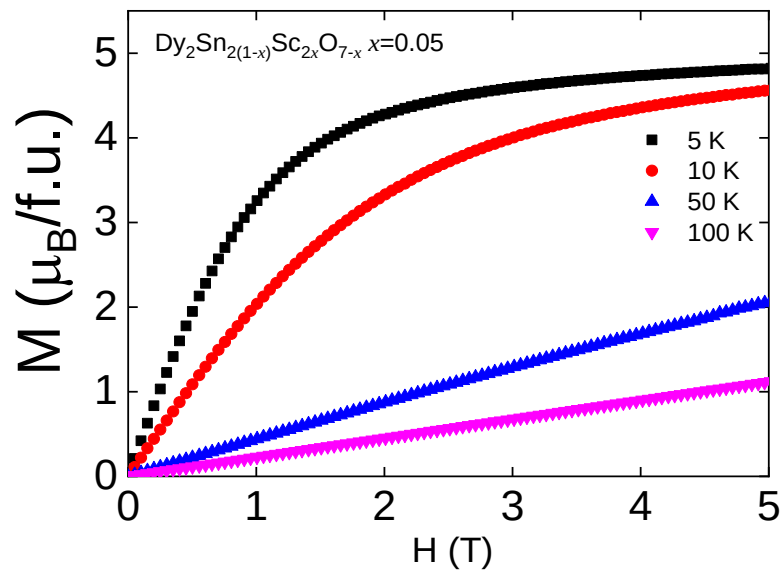


Figure 5.12 Temperature dependence of isothermal magnetization of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.05$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

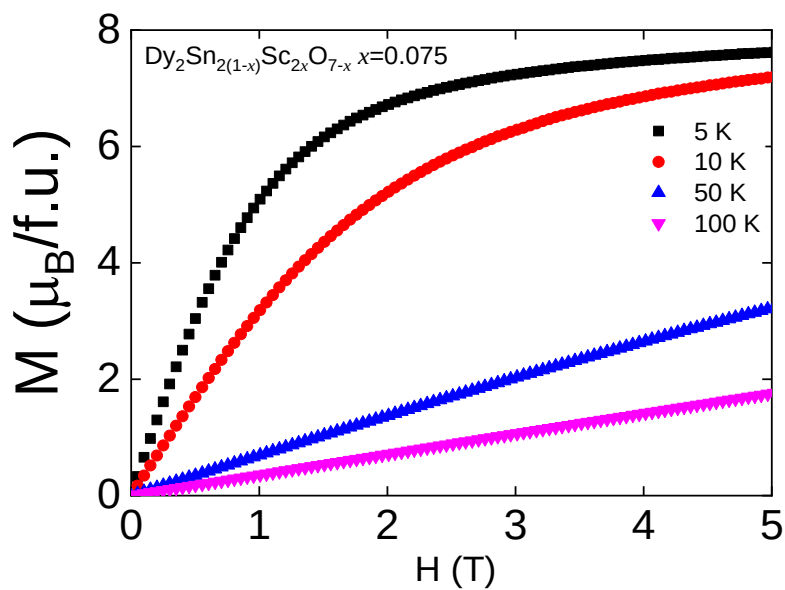


Figure 5.13 Temperature dependence of isothermal magnetization of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.075$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

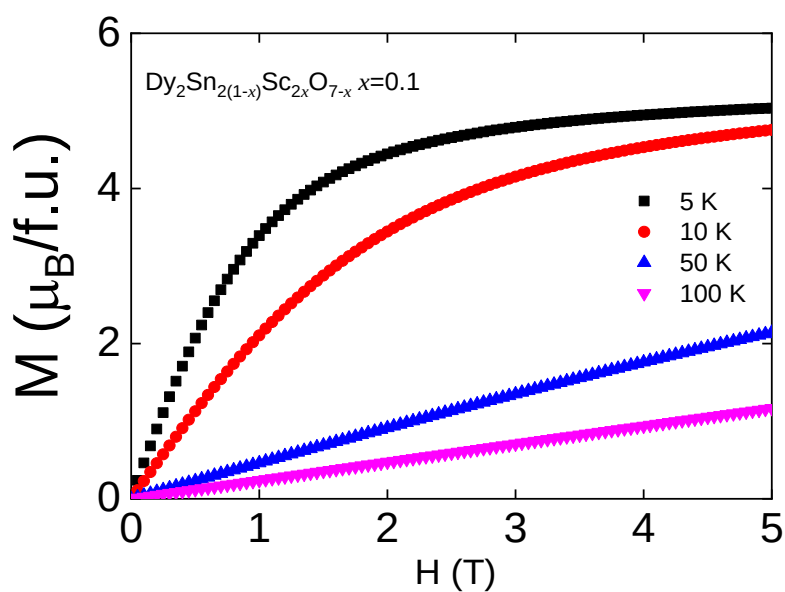


Figure 5.14 Temperature dependence of isothermal magnetization of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.1$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

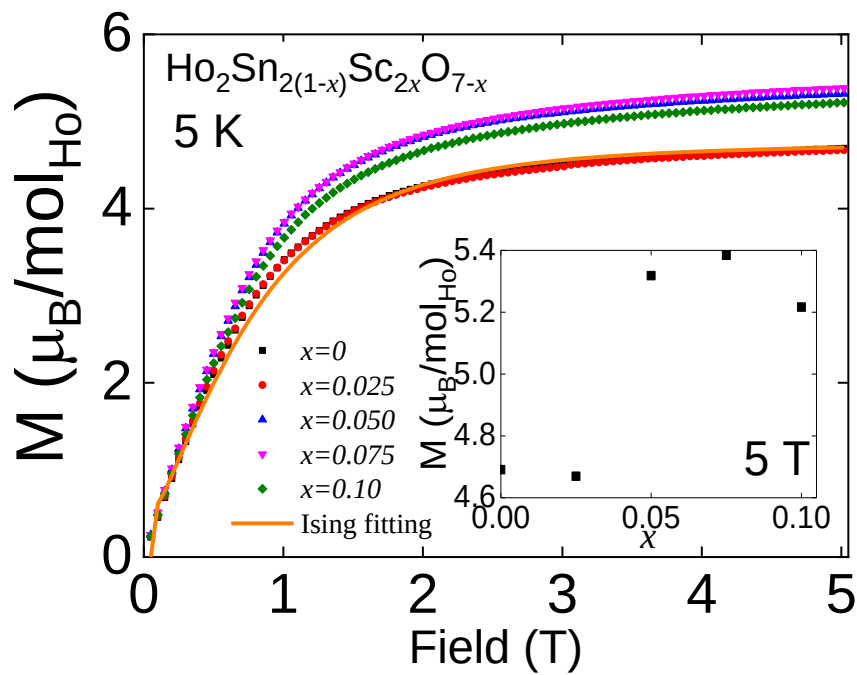


Figure 5.15 Isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ at 5 K for the different doping levels of x . black, red, blue, pink and green square stand for $x=0.00, 0.025, 0.050, 0.075$ and 0.100 respectively. Orange line is for the Ising model shown in equation with $g=19$. Inset was for the isothermal magnetization at 5 T, 5 K as a function of x .

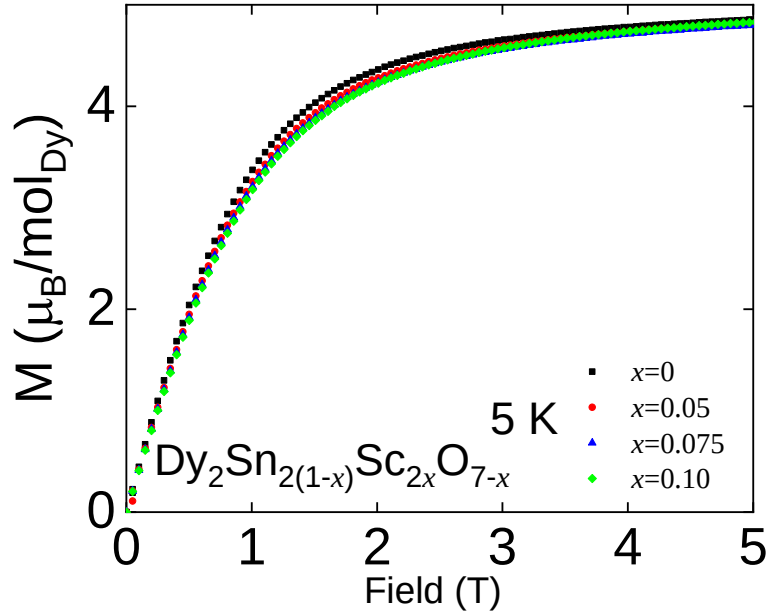


Figure 5.16 Isothermal magnetization of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ at 5 K for the different doping levels of x . black, red, blue and green square stand for $x=0.00$, 0.050 , 0.075 and 0.100 respectively.

5.3.2.2 DC Magnetic Susceptibility, $\chi(T)$

Figure 5.17 (a) and Figure 5.17 (b) show the magnetic susceptibility of $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($0 \leq x \leq 0.1$) from 2-300 K for $A=\text{Ho}$ and $A=\text{Dy}$, respectively. No significant changes in the magnetic susceptibility were observed with the amount of doping under low magnetic field 0.01 T. The inverse magnetic susceptibility for $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($0 \leq x \leq 0.1$) from 2-300 K for $A=\text{Ho}$ and $A=\text{Dy}$ are shown in inset of Figure 5.17 (a) and Figure 5.17 (b), respectively. Fits to the Curie-Weiss law were carried out in the range of $150 \leq T \leq 300$ K and the results are summarized in Table 5.3 and Table 5.4 for $A=\text{Ho}$ and $A=\text{Dy}$, respectively. The Curie constants and effective magnetic moments were not significantly changed as a function of Sc doping.

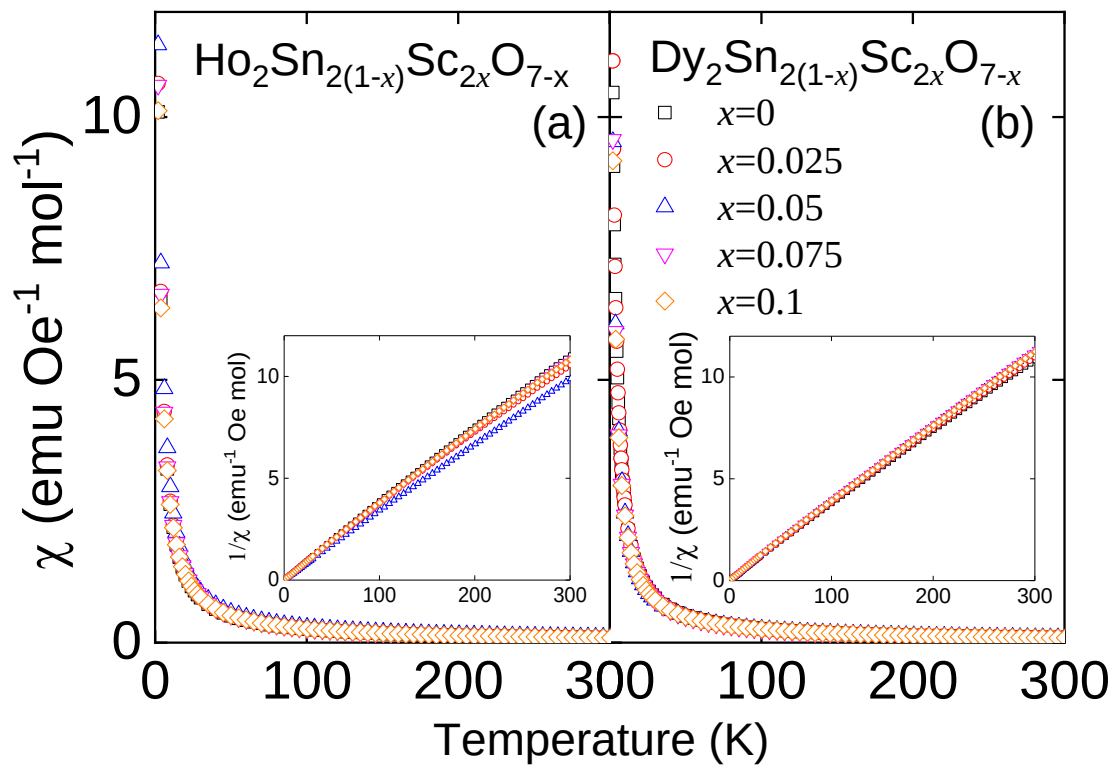


Figure 5.17 Magnetic susceptibility of (a) $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and (b) $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of temperature $2 \leq T \leq 300$ K in a field of 0.01 T. Black squares, red circles, blue up triangle, pink down triangle and orange diamond stand for $x=0.00, 0.025, 0.050, 0.075$ and 0.10 respectively. Inset is for inverse magnetic susceptibility.

Table 5.3 Summary of Curie constant, Curie-Weiss temperature and effective magnetic moments of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series

x Ho	C (emu $\cdot$ K/mol)	θ (K)	$\mu_{\text{eff exp}} (\mu_B)$
0	28.15(5)	-11.6(4)	15.005(3)
0.025	30.17(7)	-19.2(6)	15.538(5)
0.05	31.11(2)	-7.50(17)	15.775(15)
0.075	28.08(3)	-7.2(3)	14.989(2)
0.10	28.75(7)	-12.6(6)	15.166(5)

Table 5.4 Summary of Curie constant, Curie-Weiss temperature and effective magnetic moments of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series.

x Dy	C (emu $\cdot$ K/mol)	θ (K)	$\mu_{\text{eff exp}} (\mu_B)$
0	28.65(2)	-11.0(5)	15.138(4)
0.025	28.30(14)	-10.8(11)	15.046(10)
0.05	27.25(3)	-7.9(2)	14.764(2)
0.075	27.20(2)	-8.8(2)	14.750(17)
0.10	27.37(2)	-8.1(2)	14.797(17)

5.3.3 Heat capacity

The zero field heat capacity of the Ho and Dy series were measured in the temperature range of $0.4 \leq T \leq 20$ K. The magnetic heat capacity (C_{mag}) of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 5.18 (a) and Figure 5.18 (b), respectively. In both cases in $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, a sharp peak around 2.0 K is observed. this has been reported as being due to the short range dipolar spin ice correlations in $\text{Dy}_2\text{Ti}_2\text{O}_7$ ⁹⁰. While the peak in Dy series slightly increased by Sc doping from 1.2 K to 1.3 K from $x=0$ to $x=0.10$ ⁹⁰, the peak in Ho series was dramatically decreased by Sc doping from 2.0 to 0.5 K from $x=0$ to $x=0.05$ ⁸⁸ and is not observed above 0.4 K for $x=0.10$ which was the limiting temperature of the measurement.

C_{mag}/T of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 5.18 (c) and Figure 5.18 (d), respectively. The tendency of C_{mag}/T at high temperatures is consistent with previous work^{2,3}. The magnetic entropy (ΔS) of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 5.18 (e) and Figure 5.18 (f), respectively.

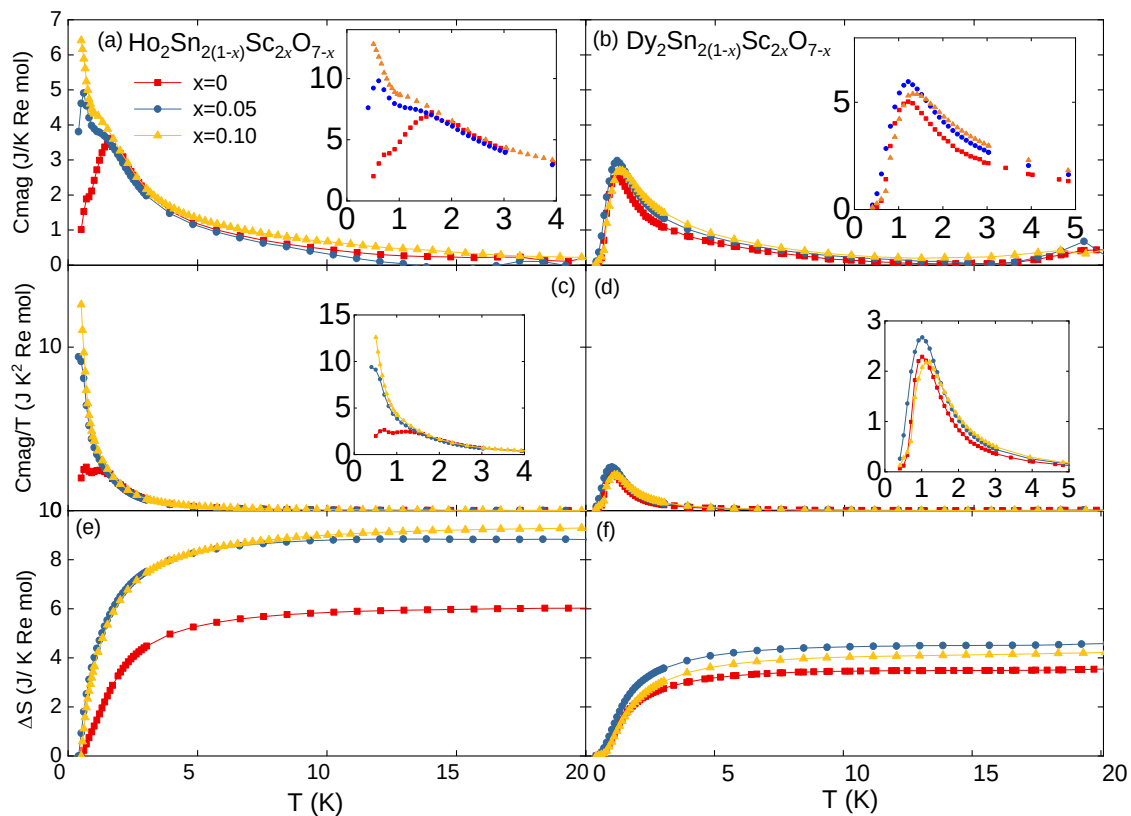


Figure 5.18 The summary of the results of heat capacity for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ (left) and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ (right). (a) and (b) for C_{mag} , (c) and (d) for C_{mag}/T inset are for low temperature, and (e) and (f) for magnetic entropy, respectively. Red squares, Blue circles and yellow up triangles stand for $x=0$, $x=0.05$, and $x=0.10$, respectively.

5.4 Discussion

5.4.1 Structure

For Ho and Dy series of spin ices, the effect of partially doping Sc on the Sn site has been investigated for the first time in the ceramics solid solution. XRD results show no impurity was observed by Sc doping in the range $0 \leq x \leq 0.10$. Therefore, the doping is successful up to 10% Sc in place of Sn. At high doping levels of more than 10% doping, a garnet impurity phase, $A_3\text{Sn}_5\text{O}_{12}$ ($A = \text{Ho}, \text{Dy}$), was formed and so will not be discussed further.

The ionic radii of Sn^{4+} and Sc^{3+} are 0.69 and 0.745 Å, respectively and so an increase in the lattice parameter might be expected on substitution, however this is not observed. Rather in the $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series, the lattice parameter, a , is linearly decreased by Sc doping in the

range of $0 \leq x \leq 0.10$. In $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series on the other hand, the lattice parameter a is significantly decreased by Sc doping in the range of $0 \leq x \leq 0.025$, then it decreases slightly in the range of $0.025 \leq x \leq 0.10$. The addition of O vacancies into the pyrochlore structure may also have an impact on the size of the lattice. It is speculated that these two competing effects result in the observed changes in the lattice parameter.

On doping with Sc, half an equivalent O ion is removed from the structure. Oxygen deficient pyrochlores are well documented, with the structure able to accommodate vacancies of all the O2 sites in $\text{Dy}_2\text{Ti}_2\text{O}_{7-x}$ ⁵². Previous reports of oxygen removal in $\text{Dy}_2\text{Ti}_2\text{O}_7$ by heating under vacuum assigns vacancies to the O2 sites. In XRD analysis it is assumed that all vacancies are located on the O2 sites. In other pyrochlores, O2 are more likely to be removed than O1 such as $\text{Pb}_2\text{M}_2\text{O}_{7-x}$ ($M = \text{Ru}, \text{Ir}$)⁵¹, $\text{Y}_2\text{Ti}_2\text{O}_{7-x}$ ⁵², $\text{Dy}_2\text{Ti}_2\text{O}_{7-x}$ ⁵². Therefore, it is postulated that the O2 would be also removed in these Sc doped systems. However, the XRD measurements are not sensitive to this and NMR, PDF or XANES are required to confirm this hypothesis.

The A -O2 bond length became shorter on Sc doping. The tendency is the same as the lattice parameter since the A -O2 bond length and the lattice parameter are related to each other. On the other hand, A -O1 bond length has large error bar than that of A -O2 and the bond length were not significantly changed by Sc doping. This indicated on Sc doping, the anisotropy might impact the crystal field of the rare earth ions for both Ho and Dy series.

5.4.2 Magnetic properties

The magnetic susceptibility of Ho and Dy series are not observed to change on Sc doping in the range of $0 \leq x \leq 0.10$ and in the range of $2 \leq T \leq 300$ K as shown in Figure 5.17 (a) and Figure 5.17 (b), respectively. This suggests that no significant change of phase or SRO were induced by Sc doping in the range of $0 \leq x \leq 0.10$. The Curie constant, Curie-Weiss temperature and effective magnetic moments are stable on Sc doping for both Ho and Dy series and the values were consistent with previous works¹⁷.

The temperature dependence of the isothermal magnetizations of $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ was similar to each other. At 5 K the curvature of the isothermal magnetization is consistent with Ising spins and can be described by equation in Chapter 1^{95,25}. The changes in the isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of Sc doping at 5 K are quite different. In $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, the saturation value of the isothermal magnetization for more than $x=0.05$ is $5.3 \mu_B/\text{mol}_{\text{Ho}}$ which is much larger than that of the $x=0$ and $x=0.025$

samples, $4.8 \mu_B/\text{mol}_{\text{Ho}}$. In $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, on the other hand, the saturation value of the isothermal magnetization was not changed by Sc doping and it was $4.8 \mu_B/\text{mol}_{\text{Dy}}$ for all doping levels.

In previous work on oxygen deficient $\text{Dy}_2\text{Ti}_2\text{O}_{7-x}$ ⁵², O vacancies were postulated to result in the spin isotropy changing from Ising spins to Heisenberg spins. One way to consider the changes is to assume that every O ion removed results in formation of a Heisenberg spin, the isothermal magnetisation is therefore the sum of two contributions:

$$M(H) = (1-y)M_{\text{Ising}}(H) + yM_{\text{Heisenberg}}(H) \quad (5.1)$$

Where the M_{Ising} and $M_{\text{Heisenberg}}$ are described by equation and equation respectively in chapter 1. The fitting of the Isothermal magnetization for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ at 5 K was shown in Figure 5.19. For $x=0$ and $x=0.10$, the function was well fit. Figure 5.20 shows the saturation value of the isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ at 5 K and 5 T. For the intermediate doping level such as $x=0.025$, $x=0.05$ and $x=0.075$, it is not obeyed in the fitting probably because the dramatical change of the isothermal magnetization instead of linear weighted average like. change. This can be seen in Figure 5.20, where the change in the magnetisation at 2 K and 5 T is plotted as a function of doping, and compared to the value predicted by equation (5.1).

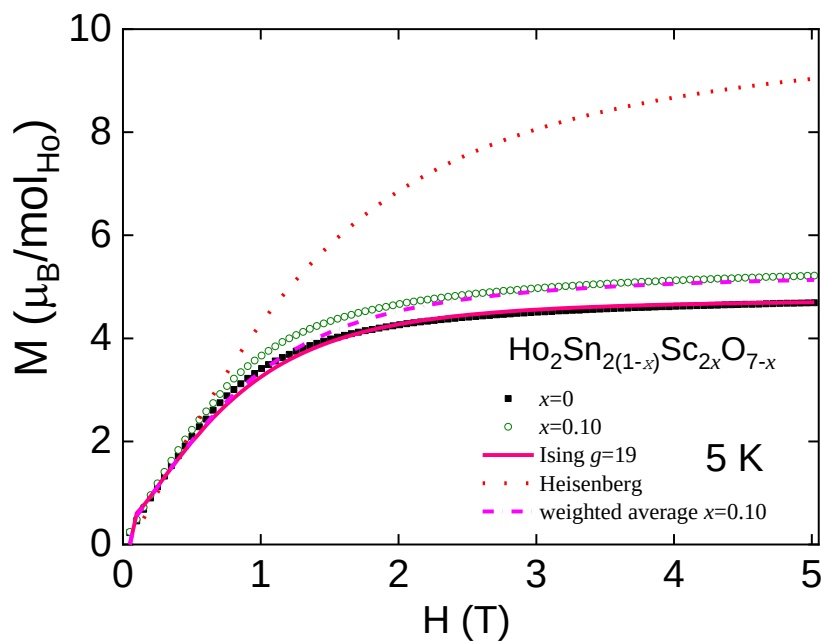


Figure 5.19 The comparisons between the experimental data and theoretical calculations at 5 K. Closed black squares and open green circles stand for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, $x=0.00$ and $x=0.10$, respectively. The pink solid line

and dotted orange line stand for Ising model $g=19$ and Heisenberg Brillouin function. The pink dashed line is a weighted average of the Ising model and Brillouin function $y=0.10$ which means 10% part of Ising model.

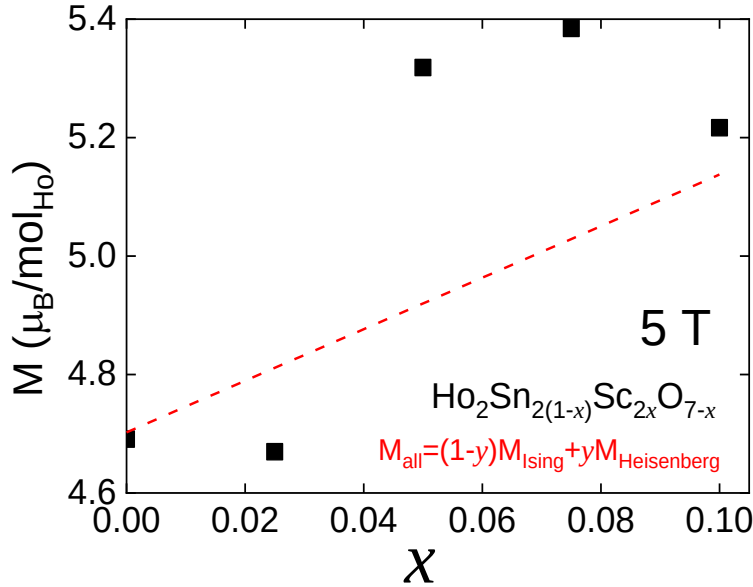


Figure 5.20 The comparisons between the experimental data and theoretical calculations of the magnetization at 5 K and 5 T as a function of x . Closed black squares stand for the experimental result of the magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, and the dotted red line stands for the weighted average of the Heisenberg model and Ising model respectively.

5.4.3 Heat capacity

In undoped $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ a peak which has previously been assigned to that of a dipolar spin ice correlations⁹⁶ is observed at 2 K. Increased Sc doping in $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series results in a shift in the peak from 2.0 ($x=0$) to 0.5 ($x=0.05$) K. At the maximum doping level of $x=0.10$, the increasing of the intensity of C_{mag} is observed down to 0.4 K, the limiting temperature of the measurement. The peak might be observed at lower temperature $T < 0.4$ K for the $x=0.10$ sample. On the other hand, for the $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series, the feature of the C_{mag} , which was assigned to dipolar spin ice model correlations⁹⁶, is not changed dramatically with only a slight increase of the peak position from 1.2 K ($x=0, 0.05$) to 1.3 K ($x=0.10$).

When the quantity C_{mag}/T is considered, further differences on doping are observed. In the Ho series an anomaly at 0.8 K ($x=0$) was shifted to 0.4 K ($x=0.05$), the peak was not observed in $x=0.10$ in the T range of our measurements, $0.4 \leq T \leq 20$ K. In the Dy series a peak around 1.2 K is observed in the range of $0 \leq x \leq 0.10$ reported for dipolar spin ice⁹⁶. The peak position of

C_{mag}/T of Dy series was practically unchanged on doping and only slight, temperature increase (0.1 K) of the peak position for $x=0.10$ was observed.

The magnetic entropies of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series were calculated by equation (2.31) in Chapter 2. The magnetic entropy of the Ho series, had a jump of the saturation value at 20 K from $6.6 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ at $x=0$ to $8.8 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ and $9.2 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ for $x=0.05$ and $x=0.10$ respectively. $x=0$ value $6.6 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ was higher than previous report which was $3.89=0.68R\ln 2 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ ⁹⁷. The value $6.6 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ is also larger than that of $R\ln 2=5.8 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$. On the other hand, the saturation value of the magnetic entropy of Dy series were around 3.5 ($x=0$), 4.5 ($x=0.05$), 4.0 ($x=0.10$) $\text{J K}^{-1} \text{ mol}_{\text{Dy}}^{-1}$ which was around the same value with previous reports of values such as $4.0 \text{ J K}^{-1} \text{ mol}_{\text{Dy}}^{-1}$ ³⁹ and $4.8 \text{ J K}^{-1} \text{ mol}_{\text{Dy}}^{-1}$ ⁵⁰. The clear jump which was observed in Ho series from 6.6 ($x=0.025$) to 9.2 ($x=0.05$) $\text{J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ was not observed in the Dy series.

The error size of the magnetic entropy would be at least about $0.8 \text{ J K}^{-1} \text{ mol}_{\text{Ho}}^{-1}$ due to the difference of the previous works^{39,50} and this is larger than that of the difference between the magnetic entropy of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ results. However, the difference between $x=0.0$ and $x=0.05$ for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series would be large enough compared to the difference. This indicates that the magnetic entropy of the $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ was increased by 5% Sc doping, while that of $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ was not changed.

While, the saturation values of both isothermal magnetization and magnetic entropy of $\text{Ho}_2\text{Sn}_2\text{O}_7$ had a dramatic change on Sc doping from $x=0$ to $x=0.050$, no notable amount of change was observed on $\text{Dy}_2\text{Sn}_2\text{O}_7$ by Sc doping in the range of $0 \leq x \leq 0.10$. The reasons of the increase of the saturation values of the isothermal magnetizations in Ho series would be due to a change from Ising anisotropy to one with reduced spin anisotropy. The increased magnetization on Sc doping is consistent with this hypothesis. However, the system could not be modelled as a simple, such as the average of the Ising and Heisenberg magnetization as this might only be from the local effect of doping.

The reason for the difference of the behaviours of the Ho and Dy series when O ions are removed is discussed below. One possible explanation could be the robustness of the CEF levels of the rare earth ions to the introduction of O defects. The results in this research suggested that the $A=\text{Ho}$ is more susceptible to changes than $A=\text{Dy}$. This could be due to the difference between Kramers and non-Kramers ions. In undoped, $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$, the

ground state of the rare earth ions at low temperatures is a doubly degenerate effective $S=1/2$ doublet. On Sc doping, due to the introduction of O defects, the CEF levels could change and the degeneracy might be lifted in the case of non-Kramers Ho^{3+} ions. Such differences in CEF levels of Ho^{3+} reported in the formation of non magnetic singlet states in HoBO_3 ⁹⁸ and $\text{Ba}_2\text{HoSbO}_6$ ⁹⁹. This arises due to Ho occupying a low symmetry site and results in a broad feature in the magnetic susceptibility at ~ 5 K corresponding to van Vleck paramagnetism⁹⁸. This absence of such a feature in $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ suggests this is unlikely, however the low percentage of lower symmetry ions may mean that it cannot be detected in these measurements.

As the feature of the isothermal magnetisation curve is changed by Sc doping for Ho series, the g factor might be also changed. It would be hard to evaluate the quantitative change of the g factor by Sc doping, though it may be possible using ESR. In Dy series, it appears that g is unchanged as the isothermal magnetization was not changed by Sc doping.

The impact of Sc doping on the structural properties requires further experiments such as synthesizing single crystals and XANES and PDF analysis. XANES and PDF can investigate the local structures around the magnetic ions. It also may be possible to prepare higher Sc doped samples by alternative synthesis methods to investigate the $\text{Dy}_2\text{Sn}_2\text{O}_7$ series. Neutron scattering will be able to investigate the local spin-spin correlations the systems. NMR can investigate the microscopic properties of spin systems to know the crystallographic positions of nuclei. Low temperature measurement with dilution Helium refrigeration can Bulk magnetic measurements using a dilution refrigerator can be used to investigate the magnetic properties of below 0.4 K.

5.5 Conclusions

$\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $0 \leq x \leq 0.10$ were synthesized and their bulk magnetic properties and heat capacities were measured. No significant changes were observed in magnetic susceptibility as a function of Sc doping in the range of $2 \leq T \leq 300$ K in both Ho and Dy series. While the saturation values of the isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ were increased at 5 T for higher doping level in the range of $0.05 \leq x \leq 0.10$, no change was observed in $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ in the range of $0 \leq x \leq 0.10$. The sudden change of the saturation value of the isothermal magnetization of $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ was observed between $0.025 \leq x \leq 0.05$.

The heat capacity, C_{mag} , C_{mag}/T and ΔS was measured in the range of $0.4 \leq T \leq 20$ K and compared between $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series. While the peak position of C_{mag} and C_{mag}/T which was reported to correspond to dipolar spin ice correlations⁹⁶ was shifted to lower temperatures by Sc doping in $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, no significant change was observed in $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series.

The magnetic entropy (ΔS) of Ho was clearly different between $x=0$ and $x \geq 0.05$. While the saturation value of the magnetic entropy for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ was clearly increased in Sc doping, that of Dy was not dramatically changed by Sc doping in the range of $0 \leq x \leq 0.10$. By Sc doping, the O2 atoms in the pyrochlore structures is postulated to be removed. The removal of O2 could change the CEF and remove the ground state degeneracy for non-Kramer's ion. While Ho ions are non-Kramer ions, Dy ions are Kramer ions. Therefore, for $A=\text{Ho}$, the saturation value of the isothermal magnetization and the magnetic entropy would be increased which is consistent to experimental results. On the other hand, the Dy ions are Kramer's ions, and $\text{Dy}_2\text{Sn}_2\text{O}_7$ system is not affected by Sc doping.

Chapter 6 Effect of doping in Quantum Spin Ice /Liquid Materials $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($B=\text{Sn, Ti}$, $0 \leq x \leq 0.05$)

6.1 Introduction

In the previous chapter, the effect of doping in classical spin ice materials were discussed. In this chapter, the effect of doping in another set of rare earth pyrochlore materials $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($B=\text{Sn}$ and Ti) will be discussed.

6.1.1 $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$

The behaviour of classical spin ice systems can be quantitatively described by the $\langle 111 \rangle$ Ising spin model with nearest-neighbour exchange and long-range dipolar interactions¹⁰⁰. Tb^{3+} pyrochlores have unique properties compared to other spin ice materials such as $\text{Ho}_2\text{Sn}_2\text{O}_7$ or $\text{Dy}_2\text{Sn}_2\text{O}_7$ which were discussed in Chapter 5. In other pyrochlore spin ices, the properties of stannate spin ice and titanate spin ice are similar^{23,89}. On the other hand, the properties of $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ are quite different from each other^{89,94,101–103}. $\text{Tb}_2\text{Sn}_2\text{O}_7$ is known as ordered spin ice or soft spin ice. It shows a local spin ice structure but long range magnetic order and nonzero magnetization below 1 K which is different from other spin ices such as $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ discussed in Chapter 5^{5,104,105} and additionally $\text{Tb}_2\text{Sn}_2\text{O}_7$ is reported to show quantum fluctuation¹⁰². On the other hand, $\text{Tb}_2\text{Ti}_2\text{O}_7$ shows very different and intriguing behaviour compared to $\text{Tb}_2\text{Sn}_2\text{O}_7$. $\text{Tb}_2\text{Ti}_2\text{O}_7$ has received a lot of attention for showing a spin liquid ground state stable down to very low temperatures, $T=17$ mK, despite the presence of strong antiferromagnetic correlations. It is believed that $\text{Tb}_2\text{Ti}_2\text{O}_7$ belongs to the same family of $\langle 111 \rangle$ Ising systems¹⁰⁰ as $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ but with an effective nearest neighbour AF interaction around 13 K⁹¹.

In order to investigate the difference between $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$, several studies have been conducted. Measurement of heat capacities of $\text{Tb}_2\text{Sn}_2\text{O}_7$ ¹⁰⁴ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ ¹⁰⁶ showed that the magnetic heat capacity of $\text{Tb}_2\text{Sn}_2\text{O}_7$ had a peak around 1.6 K¹⁰⁴ and that of $\text{Tb}_2\text{Ti}_2\text{O}_7$ had

two peaks at 1.5 and 6 K¹⁰⁷. The 1.5 K peak is attributed to be from a single ion ground state doublet and 6 K peak is attributed to a transition to the first excited state in their crystal fields¹⁰⁷. The saturation value of the magnetic entropy (ΔS) of Tb₂Ti₂O₇ reached around 10.5 J mol⁻¹ K⁻¹ which is higher than $R\ln 2 = 5.78$ J mol⁻¹ K⁻¹ which is expected for pyrochlore structure. This is due to the formation of a long range state which reduced the residual entropy of the low temperature phase¹⁰⁷.

The saturation value of the magnetic entropy of Tb₂Sn₂O₇ reached around 10.5 J mol⁻¹ K⁻¹ which is between $R\ln 3$ and $R\ln 4$ and is higher than $R\ln 2$ ⁹⁴. The higher saturation values of the magnetic entropy than $R\ln 2 = 5.78$ J mol⁻¹ K⁻¹ shows that Tb₂Ti₂O₇ and Tb₂Sn₂O₇ behave differently to other Ising spin-ice pyrochlores and this could be due to the quantum fluctuation of Tb³⁺ spins.

There are several theoretical proposals why Tb₂Ti₂O₇ fails to order at same temperature as Tb₂Sn₂O₇ around 1 K^{96,108} such as virtual transitions between the crystal field states where interaction-induced fluctuations among otherwise non-interacting single-ion CF states lead to a renormalization of the effective low-energy¹⁰². Another proposal is that there is a Jahn-Teller phase transition at low but finite temperature to a singlet ground state, creating a sufficiently large singlet-singlet gap such that dipolar magnetic order does not occur^{108,109}. As Tb₂Ti₂O₇ has a larger energy gap between the ground state doublet and first excited state doublet¹⁰⁸ than Tb₂Sn₂O₇, it could be one of the reasons why they behave differently.

In both scenarios, the difference between Tb₂Sn₂O₇ and Tb₂Ti₂O₇ is explained to arise from the difference in the low lying crystal fields levels^{108,19}. The environments of *B* site could be another factor. The research into the Tb₂Ti_{2-x}Sn_xO₇¹⁹ solid solution shows that materials with intermediate compositions did not show behaviour that was a weighted average of Tb₂Sn₂O₇ and Tb₂Ti₂O₇¹⁹. Rather a unique state was observed for intermediate compositions which were caused by the mixture of *B* site atoms. This was attributed to the difference in ionic radii between Ti⁴⁺ and Sn⁴⁺ atoms. The O atom positions are also slightly changed¹⁹ which could affect the CF configuration.

The unique state of the Tb₂B₂O₇ (*B* = Ti, Sn) suggested the CF configuration was not protected by Kramers theorem as discussed in Chapter 5¹⁹. Also it could be due to the fact that Tb³⁺ behaves like a quantum spin which has quantum fluctuation¹⁰².

The study of off stoichiometry compositions of $\text{Tb}_2\text{Ti}_2\text{O}_7$, $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$, shows that the spin liquid state in $\text{Tb}_2\text{Ti}_2\text{O}_7$ becomes a quantum spin liquid state with quadrupole order of Tb^{3+} spins¹². Here, in this chapter, the effect of doping, non magnetic Sc^{3+} on the B site in the materials $\text{Tb}_2\text{B}_2\text{O}_7$ ($B = \text{Ti}, \text{Sn}$) will be discussed. This changes the coordination of oxygen ions for Tb^{3+} and impacts the structure and magnetic properties.

6.2 Sample preparation

Synthesis of the $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series $B=\text{Sn}, \text{Ti}$ for $x=0, 0.025, 0.05$ was carried out using a ceramic synthesis method. The starting materials were Tb_4O_7 (99.9%, Alfa Aesar), Sc_2O_3 (Alfa Aesar), TiO_2 (99.99%, Alfa Aesar) or SnO_2 (99.995%, Alfa Aesar). Stoichiometric amounts of starting materials were ground and fired as pellets for 12 hours in air at 800 °C. The pellets were then reground and made into pellets again. The pellets were then heated to 1400 °C in air for 24 hours. The heated pellets were then evaluated using XRD. This process was repeated with intermediate grindings until XRD indicated the formation of a phase pure product. Typically, samples were heated for 196 hours.

6.3 Results

6.3.1 XRD

The $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series ($x=0, 0.025, 0.05$ $B=\text{Sn}, \text{Ti}$) were successfully synthesized at higher doping levels other phases were detected and so will not be discussed further. All samples were measured by XRD and the structure was quantitatively analysed using the Rietveld method⁵³. A typical refinement of the XRD pattern of the $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ materials is shown in Figure 6.1. The refinements for other samples can be found in Appendix 40-44. Relevant bond lengths are also given in Table 6.1 and Table 6.2 for samples doped with Sn and Ti, respectively.

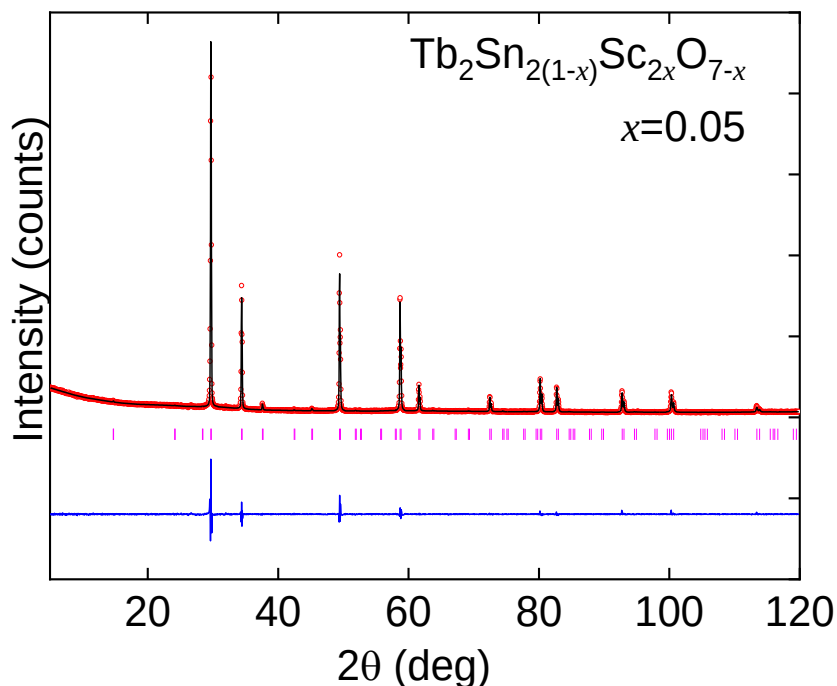


Figure 6.1 X-ray diffraction data for $\text{Tb}_2\text{Sn}_{0.9}\text{Sc}_{0.1}\text{O}_{6.95}$. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.

The lattice parameter as a function of doping for $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 6.2. While the lattice parameter increased with Sc doping in $\text{Tb}_2\text{Ti}_2\text{O}_7$, the lattice parameter decreased with doping in $\text{Tb}_2\text{Sn}_2\text{O}_7$. The bond lengths of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ between rare earth ions and O_n ($n=1,2$) are shown in Figure 6.3 (a) and Figure 6.3 (b), respectively. While the Tb-O2 bond length became longer with doping in $\text{Tb}_2\text{Ti}_2\text{O}_7$, the Tb-O2 bond length became shorter with doping in $\text{Tb}_2\text{Sn}_2\text{O}_7$.

Table 6.1 Summary of lattice parameters and bond lengths for of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ B_{iso} fixed as 0.5

x		0	0.025	0.05
a (Å)		10.43054(6)	10.4286(3)	10.42732(5)
R_p		5.07	6.39	3.5
R_{wp}		7.72	13.1	4.96
R_{exp}		3.04	2.79	2.84
χ^2		6.45	22	3.05
positions	O1 x	0.3351(14)	0.345(5)	0.3409(11)
Bond length (Å)	Tb-O1	2.522(8)	2.45(4)	2.480(7)
	Tb-O2	2.25828(0)	2.25837(0)	2.25758(0)

Table 6.2 Summary of lattice parameters and bond lengths for of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ B_{iso} fixed as 0.5

x		0	0.025	0.05
a (Å)		10.15417(5)	10.15466(5)	10.16397(6)
R_p		4.71	4.26	4.58
R_{wp}		7.65	6.71	7.45
R_{exp}		2.83	2.85	2.72
χ^2		7.3	5.56	7.5
positions	O1 x	0.32024(13)	0.32204(11)	0.31932(11)
Bond length (Å)	Tb-O1	2.560(7)	2.547(8)	2.569(6)
	Tb-O2	2.19844(0)	2.19855(0)	2.20056(0)

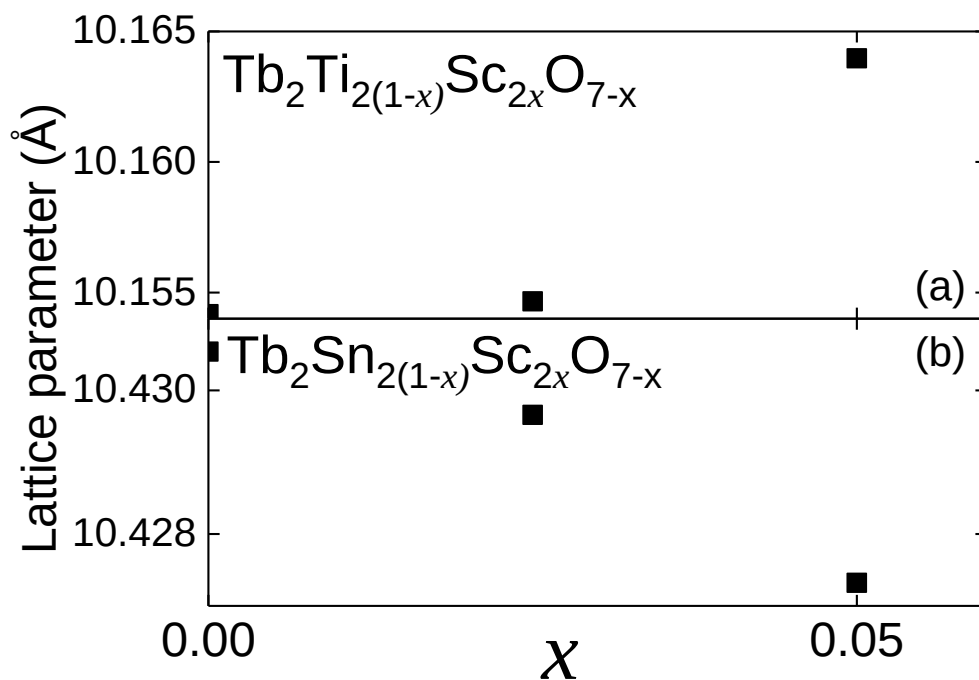


Figure 6.2 Lattice parameter of (a) $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and (b) $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of doping x . The size of the error bars are smaller than the plots.

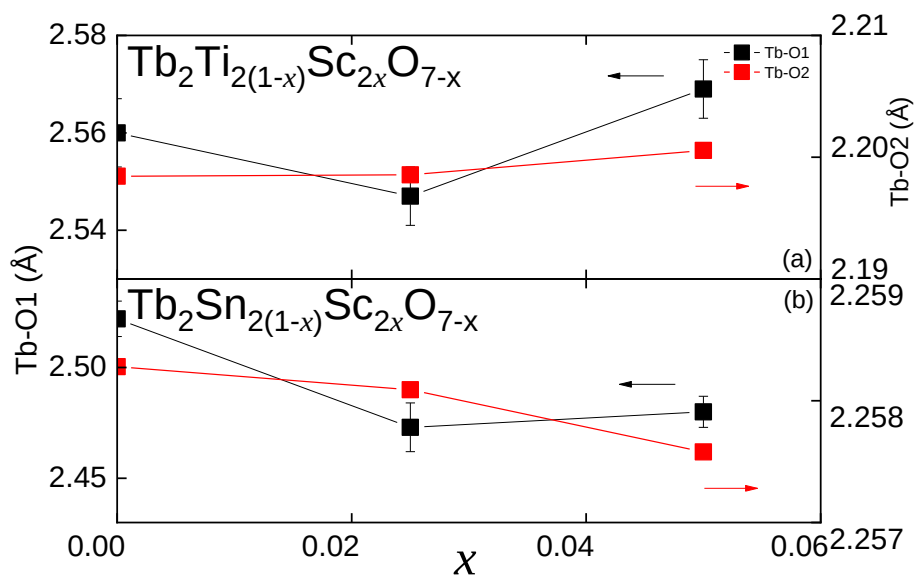


Figure 6.3 Bond lengths of (a) $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ of (b) $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of doping x with error bars. Black squares and red circles stand for Tb-O1 and Tb-O2, respectively.

6.3.2 Bulk magnetic properties

1.3.2.1 Isothermal Magnetisation, $M(H)$

Temperature dependence of isothermal magnetization of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, $\text{Tb}_2\text{Sc}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ for $x=0$ and $x=0.05$ are shown in Figure 6.4, Figure 6.5, Figure 6.6, Figure 6.7 respectively. Isothermal magnetisation curves at 5 K for $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, $\text{Tb}_2\text{Sc}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 6.8 and Figure 6.9 respectively. On Sc doping, the saturation value of the isothermal magnetization was reduced in both $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$ from 4.8 to 4.3 $\mu_B/\text{mol}_{\text{Tb}}$ for $\text{Tb}_2\text{Ti}_2\text{O}_7$ and 5.2 to 4.9 $\mu_B/\text{mol}_{\text{Tb}}$ for $\text{Tb}_2\text{Sn}_2\text{O}_7$, respectively. The isothermal magnetization curve did not agree with the Brillouin function suggesting that at 2 K the Tb^{3+} moments can no longer be approximated as free spins. The isothermal magnetization of $\text{Tb}_2\text{Ti}_2\text{O}_7$ ¹¹⁰ did not saturate until 5 T while the isothermal magnetisation for other pyrochlore spin ice materials saturated by 5 T, as seen in Chapter 5.

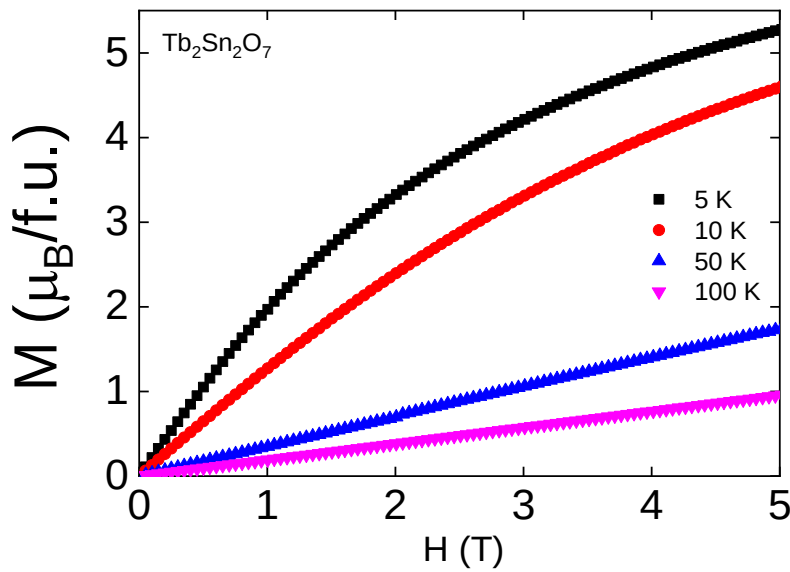


Figure 6.4 Temperature dependence of isothermal magnetization of $\text{Tb}_2\text{Sn}_2\text{O}_7$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

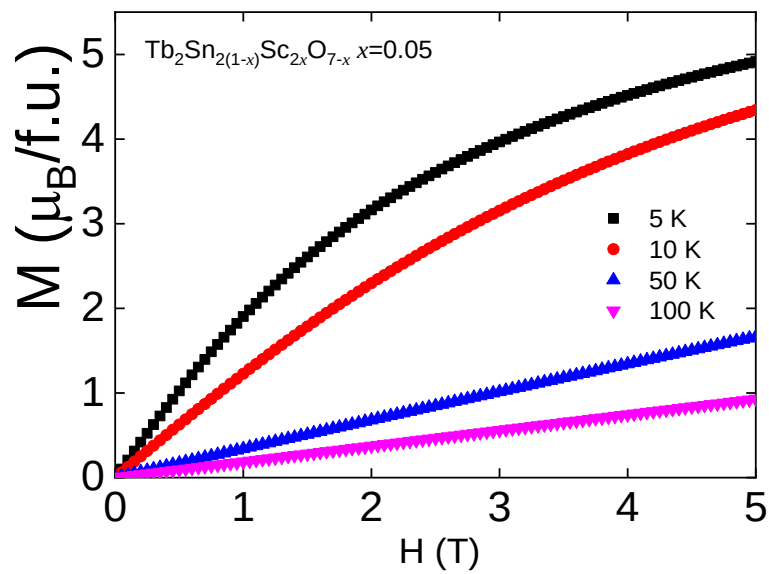


Figure 6.5 Temperature dependence of isothermal magnetization of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.05$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

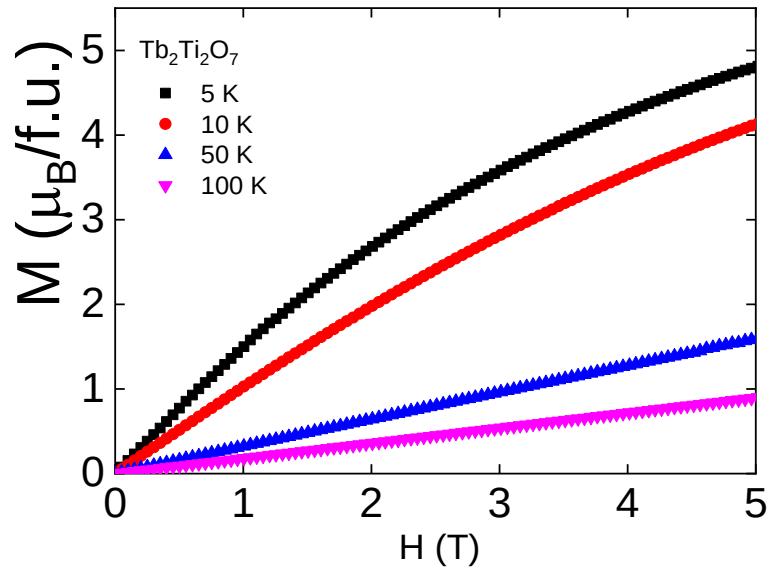


Figure 6.6 Temperature dependence of isothermal magnetization of $\text{Tb}_2\text{Ti}_2\text{O}_7$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

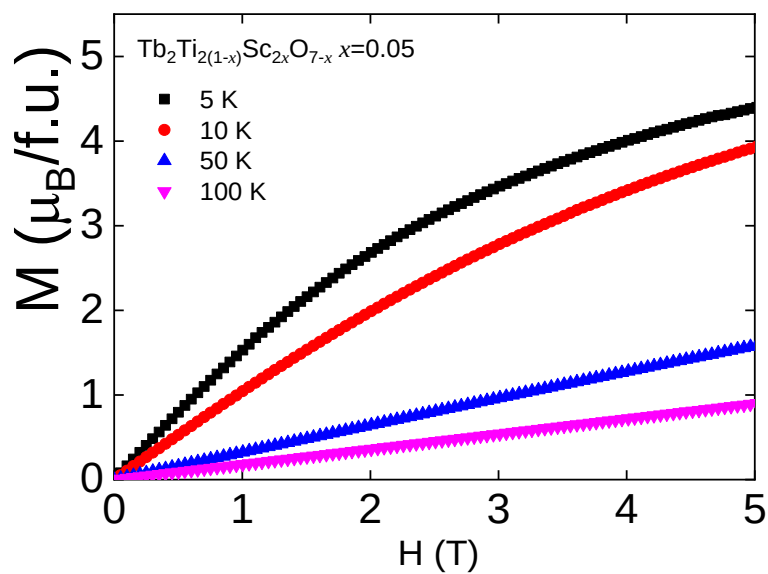


Figure 6.7 Temperature dependence of isothermal magnetization of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.05$ at black square, red circle, blue up triangle and pink down triangle stand for $T=5$ K, 10 K, 50 K and 100 K, respectively.

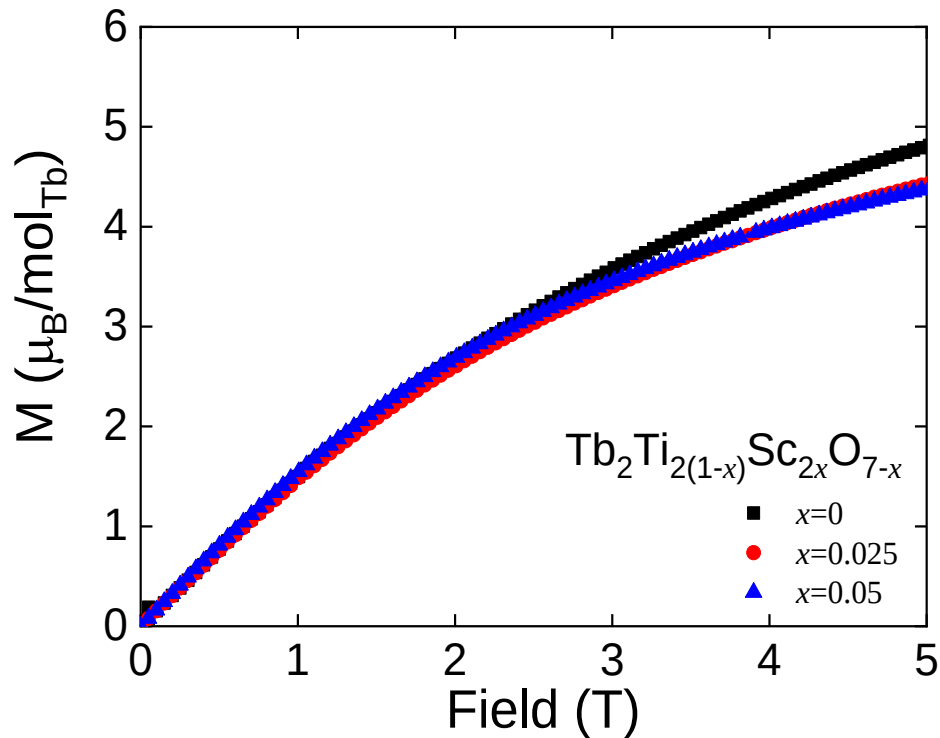


Figure 6.8 Isothermal magnetization of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Black squares, red circles, Blue triangles stand for $x=0$, $x=0.025$ and $x=0.05$, respectively.

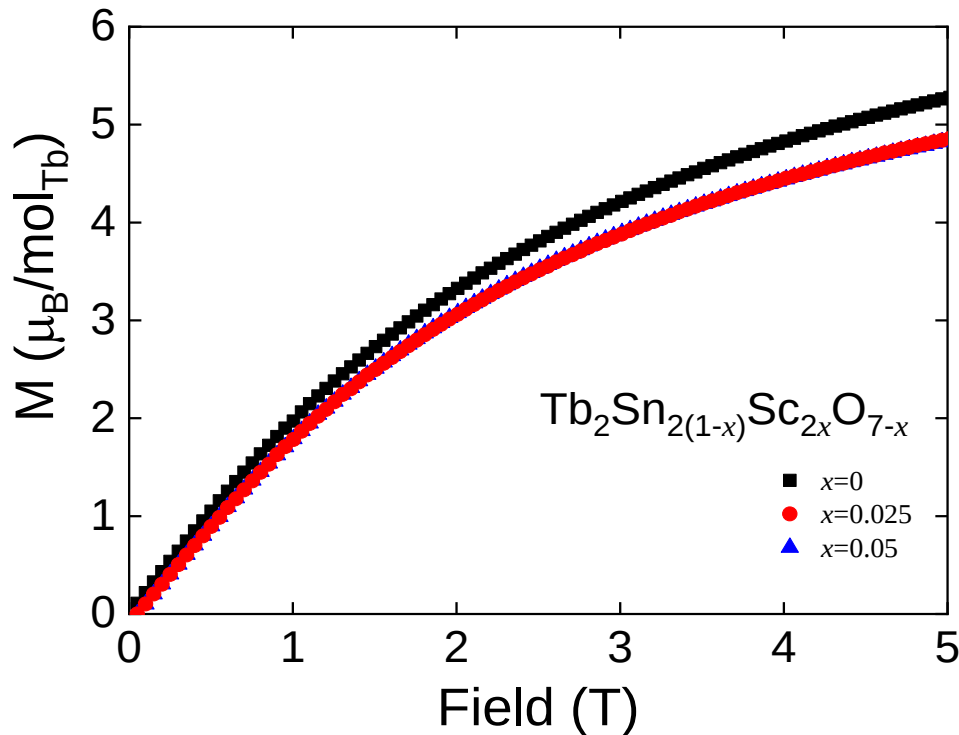


Figure 6.9 Isothermal magnetization of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Black squares, red circles, Blue triangles stand for $x=0$, $x=0.025$ and $x=0.05$, respectively.

6.3.2.1 DC Magnetic Susceptibility, $\chi(T)$

The zero Field Cooled (ZFC) magnetic susceptibility, $\chi(T)$ of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 6.10 and Figure 6.11, respectively. The inverse magnetic susceptibility is inset. No specific changes were observed with the amount of Sc doping in low magnetic field of 0.01 T in the range of 2-300 K. The Curie constant, Curie Weiss temperature and effective magnetic moments are summarized in Table 6.3 and Table 6.4 for $B=\text{Ti}$ and $B=\text{Sn}$, respectively. The Curie constants and Curie Weiss temperature were not changed by Sc doping and the value of the Curie Weiss temperature was not significantly different from previous works which was $\theta_{\text{CW}} = -18.9$ K and $\theta_{\text{CW}} = -12.48$ K for $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$, respectively⁸⁹. The effective magnetic moments were not changed by Sc doping. The effective magnetic moments were about $13 \mu_B$ which was slightly larger than that of previous works: $\mu_{\text{eff}} = 9.6 \mu_B$ and $\mu_{\text{eff}} = 9.68 \mu_B$ for $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$, respectively⁸⁹.

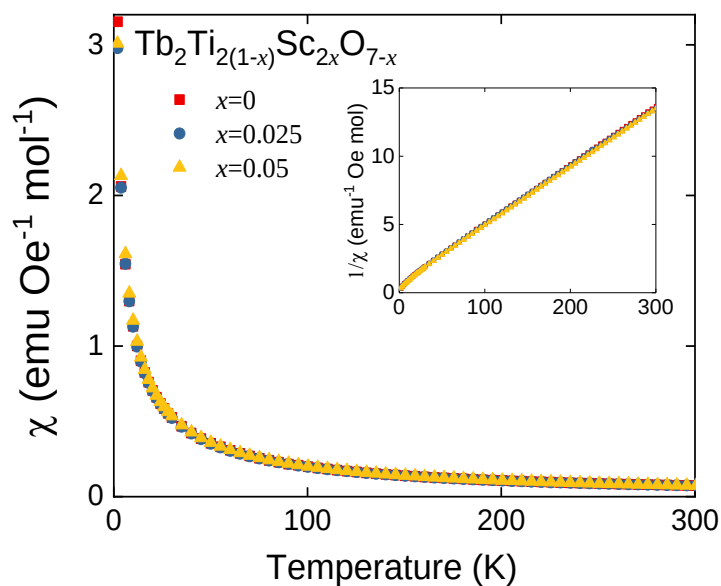


Figure 6.10 Magnetic Susceptibility of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of temperature. Red squares and blue circles and yellow triangles stand for $x=0$, $x=0.025$ and $x=0.05$, respectively. Inset is for inverse magnetic susceptibility.

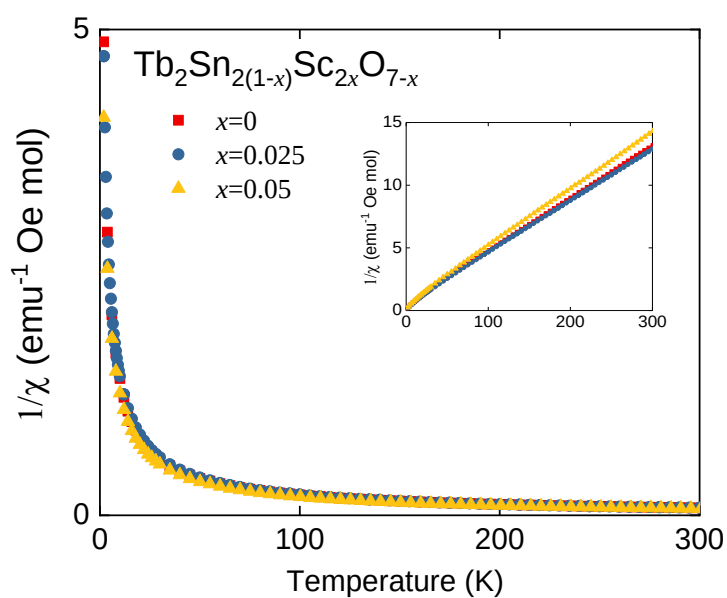


Figure 6.11 Magnetic Susceptibility of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ as a function of temperature. Red squares and blue circles and yellow triangles stand for $x=0$, $x=0.025$ and $x=0.05$, respectively. Inset is for inverse magnetic susceptibility.

Table 6.3 Summary of Curie constant, Curie-Weiss temperature and effective magnetic moments of $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series.

x Ti	C (emu $\cdot$ K/mol)	θ (K)	μ_{eff} (μ_{B})
0	23.25(17)	-17.4(17)	13.637(15)
0.025	23.64(5)	-20.4(4)	13.751(4)
0.05	23.48(19)	-16.5(19)	13.705(16)

Table 6.4 Summary of Curie constant, Curie-Weiss temperature and effective magnetic moments of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series.

x Sn	C (emu $\cdot$ K/mol)	θ (K)	μ_{eff} (μ_{B})
0	23.82(2)	-13.4(2)	13.803(2)
0.025	24.44(4)	-14.8(4)	13.982(3)
0.05	22.21(5)	-16.4(5)	13.330(4)

6.3.3 Heat Capacity

The magnetic heat capacity (C_{mag}) and C_{mag}/T of $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ are shown in Figure 6.12 and Figure 6.13, respectively. In both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$, one sharp peak around 1.0 K and one broad peak around 6 K were observed. In Sc doped materials, no sharp peak around 1.0 K was observed, while broad peaks around 3 to 6 K were observed instead. The tendency of C_{mag}/T at high temperatures shown in Figure 6.13 was consistent with previous works⁹⁴. In Sc doped samples, the intensity of the C_{mag}/T was decreased compared to $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. The magnetic entropy of (ΔS) of $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ is shown in Figure 6.14. The saturation values of the magnetic entropy were $9.8 \text{ J K}^{-1} \text{ mol}_{\text{Tb}}^{-1}$ ⁹⁴ and $8.5 \text{ J K}^{-1} \text{ mol}_{\text{Tb}}^{-1}$ ⁹⁴ for $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$, respectively. They were relatively small than previous works which reported values of $11 \text{ J K}^{-1} \text{ mol}_{\text{Tb}}^{-1}$ ⁹⁴ for both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$.

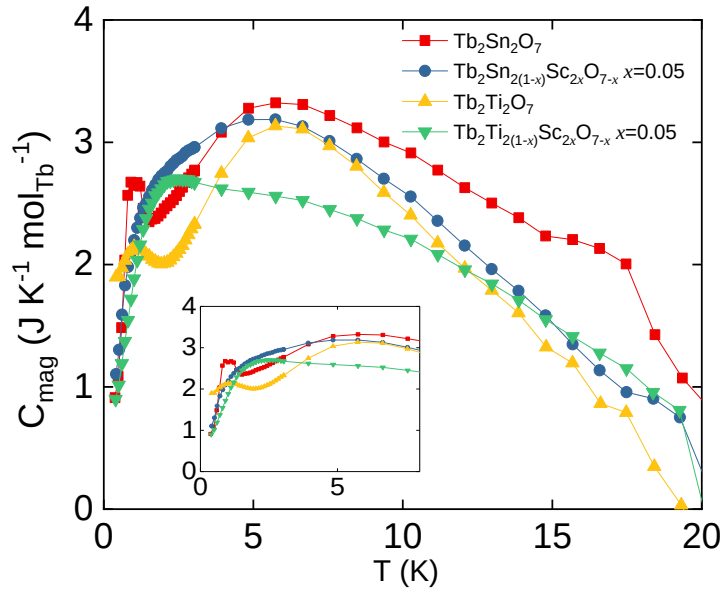


Figure 6.12 Magnetic heat capacity of $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Red squares, blue circles, yellow triangles and green down triangles stand for $\text{Tb}_2\text{Sn}_2\text{O}_7$, $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, respectively. Inset is for low temperature region.

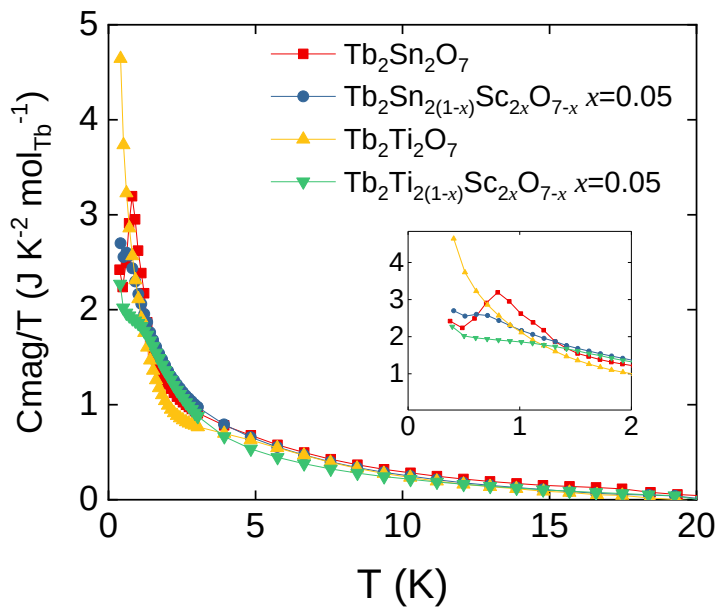


Figure 6.13 Magnetic heat capacity divided by temperature of $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Red squares, Blue circles, yellow up triangles and green down triangles stand for $\text{Tb}_2\text{Sn}_2\text{O}_7$, $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$, respectively. Inset for low temperature.

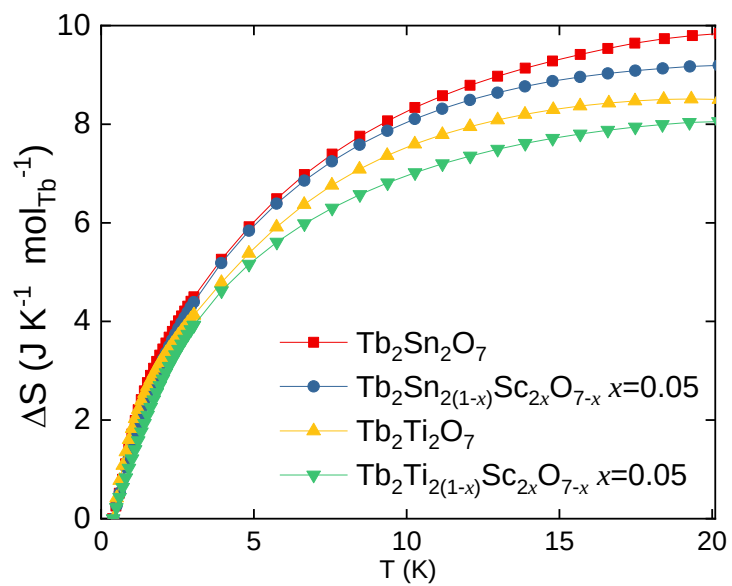


Figure 6.14 Magnetic Entropy (ΔS) of $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Red squares, Blue circles, yellow up triangles and green down triangles stand for $\text{Tb}_2\text{Sn}_2\text{O}_7$, $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.05$, $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $x=0.05$, respectively.

6.4 Discussion

6.4.1 Structure

The effect of partially doping Sc for Sn and Ti on the *B* site has been investigated for the first time in the $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ compositions. XRD results show no impurities on Sc doping in the range $0 \leq x \leq 0.05$ for $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Therefore, the doping is successful up to 5% Sc in place of Sn or Ti site. In attempts to synthesise materials with more than 5% doping, other phase appeared and so will not be discussed further in this thesis.

While in the Ti series, the lattice parameter *a* was linearly increased, it was linearly decreased by Sc doping in Sn series in the range of $0 \leq x \leq 0.05$. The ionic radii of Sn, Ti and Sc (coordination VI) are 0.69, 0.605 and 0.745 Å, respectively. If only the effect of ionic radii is considered, the lattice parameter for $\text{Tb}_2\text{Sn}_2\text{O}_7$ series would be expected to increase by Sc doping. Instead, it decreases. This could be caused by the structural change after the removal of O atoms by Sc doping.

The bond lengths of *B*-O1 and *B*-O2 were changed by Sc doping in both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. In $\text{Tb}_2\text{Ti}_2\text{O}_7$, the *B*-O2 bond lengths were increased by Sc doping. On the other hand, in $\text{Tb}_2\text{Sn}_2\text{O}_7$ series, the *B*-O2 was decreased by Sc doping. In accordance with this tendency, the ratio of *B*-O2/*B*-O1 in $\text{Tb}_2\text{Ti}_2\text{O}_7$ was increased, but that of $\text{Tb}_2\text{Sn}_2\text{O}_7$ was decreased with Sc doping in the range of $0 \leq x \leq 0.05$ shown in Figure 6.3 (a) and Figure 6.3 (b) respectively. This difference could cause differences in the CEF between $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$. The difference of the ionic radii for Ti (0.745 Å) and Sc (0.605 Å) is larger than that of Sc (0.605 Å) and Sn (0.69 Å). While there is a strain in Ti series, there is reduced strain in Sn series¹⁹. This could be the reason for the difference in the tendency of the lattice parameter and bond length as Sc doping. The difference in ionic radii also means that more local distortions to CEF would be expected on Sc doping in Ti series than that of Sn series. In addition to the structural difference between Sn and Ti, oxygen vacancies were induced by Sc doping. This could also induce changes in the CEF and single-ion anisotropy. As the difference between first excited state and ground state in $\text{Tb}_2\text{Ti}_2\text{O}_7$ is larger than $\text{Tb}_2\text{Sn}_2\text{O}_7$ ^{108,19}, Sc doping could make the difference even larger.

6.4.2 Magnetic Properties

The magnetic susceptibilities of Sn and Ti series were not changed by Sc doping in the range of $0 \leq x \leq 0.05$ and in the range of $2 \leq T \leq 300$ K. The absence of the significant changes suggests that the no phase transition or SRO were induced by Sc doping in the range of $0 \leq x \leq 0.05$. The effective magnetic moments were not changed by Sc doping. The values of effective moment were consistent with the previous works^{89,110}. This is also consistent with the results in $A_2\text{Sn}_{2(1-x)}\text{Sn}_{2x}\text{O}_{7-x}$ ($A=\text{Ho}, \text{Dy}$) discussed in Chapter 5.

The intensity of the isothermal magnetization at 5 T for $\text{Ho}_2\text{Sn}_2\text{O}_7$ was increased by Sc doping on the Sn site and that of $\text{Ho}_2\text{Sn}_2\text{O}_7$ was not changed in the range of $0.05 \leq x \leq 0.10$ and $0 \leq x \leq 0.10$, respectively. No change was observed in $\text{Dy}_2\text{Sn}_2\text{O}_7$ in the range of $0 \leq x \leq 0.10$. On the other hand, the isothermal magnetization at 5 T of both $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$ were decreased by Sc doping in the range of $0 \leq x \leq 0.05$. It was not observed in other pyrochlore spin ices that the saturation value of the isothermal magnetization was decreased by doping on *B* sites than pristine spin ice materials.

6.4.3 Heat Capacity

In C_{mag} , a peak at 1.5 K which was observed in a previous work of $\text{Tb}_2\text{Ti}_2\text{O}_7$ ¹⁰⁷ is related to the ground state doublet was also observed at 1.5 K in both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. The peak was not observed on 5% Sc doping in both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. This indicated that the ground doublet state in both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ was affected by 5% Sc doping.

On the other hand, the broad features around 6 K which is from the first excited state doublet¹⁰⁷ was observed in both $\text{Tb}_2\text{Sn}_2\text{O}_7$, $\text{Tb}_2\text{Ti}_2\text{O}_7$ and also Sc doped $\text{Tb}_2\text{Sn}_2\text{O}_7$. However, the 6 K peak was not observed in Sc doped $\text{Tb}_2\text{Ti}_2\text{O}_7$. This difference indicated that the first excited states in $\text{Tb}_2\text{Ti}_2\text{O}_7$ could be affected by Sc doping, but the first excited states in $\text{Tb}_2\text{Sn}_2\text{O}_7$ was not affected by Sc doping in the range of $0 \leq x \leq 0.05$.

The saturation value of the magnetic entropy (ΔS) $\text{Tb}_2\text{Sn}_2\text{O}_7$ was $8.5 \text{ J mol}^{-1} \text{ K}^{-1}$ which was slightly smaller than that of the previous work which was 10.5 ¹⁰⁷ $\text{J mol}^{-1} \text{ K}^{-1}$. Both values are larger than that of the predicted maximum value for pyrochlore $R\ln 2 \div 5.78 \text{ J mol}^{-1} \text{ K}^{-1}$. The reported saturation values of the magnetic entropy of $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ lie between $R\ln 3$ and $R\ln 4$ which are much larger than that of the ideal spin ices probably because of other interactions such as quantum fluctuations⁹⁴.

In both $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$, the saturation value was decreased by Sc doping, as shown in Figure 6.14 (a) and (b), respectively. This suggests that both Sc doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ could have more residual entropy than non doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. It also could indicate that Sc doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ could have more degenerate states than that of non doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$.

The impact of such distortions due to Sc doping on the structural properties requires further experiments such as synthesizing single crystals and XANES and PDF analysis. Smaller and finer Sc doped sample can be used to investigate the series. XANES and PDF can investigate the local structures around the magnetic ions. Neutron scattering will be able to investigate the local magnetic structures of the systems. NMR can investigate the microscopic properties of spin systems to know the crystallographic positions of nuclei. Low temperature measurements with a dilution fridge can be used to investigate the magnetic properties below 0.4 K.

6.5 Conclusions

$\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ $0 \leq x \leq 0.05$ were synthesized and their magnetic properties and heat capacities were measured. The linear changes of the lattice parameter a suggested that Sc is successfully doped on the B site in the pyrochlore structure.

The magnetic properties including magnetic susceptibility and isothermal magnetization was measured. No specific changes were observed on magnetic susceptibility as a function of Sc doping in the range of $2 \leq T \leq 300$ K.

The values of the magnetization were decreased at 5 T, with increased amount of Sc doping in both $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. The heat capacity including C_{mag} , C_{mag}/T and ΔS were measured in the range of $0.4 \leq T \leq 20$ K. The sharp peak of C_{mag} at 0.6 K which was observed in $x=0$ materials were not observed in $x=0.05$ materials.

The broad peak around 6 K which was observed in $x=0$ were observed in $x=0.05$ $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ but not observed in $x=0.05$ $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Both the magnetic entropy (ΔS) of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ were decreased by Sc doping.

Chapter 7 Summary

The aim of this project was to investigate the effect of doping on different types of frustrated magnets which is a classical method to investigate the properties of frustrated magnets. In this thesis, two types of frustrated magnets and their effect of doping were investigated. One dimensional spin chains; LiCuSbO_4 is one of the simplest frustrated magnets which is thus and ideal system to investigate the effect of frustrated magnets. The other system is Pyrochlore Spin ice $A_2B_2O_7$ ($A=\text{Ho, Dy, Tb}$, $B=\text{Sn, Ti}$) materials which are known to be a series of highly frustrated materials. The properties of the pyrochlore frustrated magnets are highly dependent on what atoms are in A and B sites. By doping Sc^{3+} on B sites which have either Ti^{4+} or Sn^{4+} , the effects of frustrated magnets in pyrochlore were investigated.

7.1 One-dimensional spin chains $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Mg, Zn, Co}$)

Doping of both non magnetic ions, Zn, Mg and magnetic ions Co was investigated. Polycrystalline $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Mg, Zn, Co}$, $0 \leq x \leq 0.10$) were synthesized by a ceramics process. The samples were characterized by XRD. As the level of doping M was increased the bond length between Cu atoms were linearly changed. This suggested that the dopants M were successfully doped in Cu sites.

The magnetic properties including magnetic susceptibility and isothermal magnetizations were measured. The field dependence of their magnetic properties were also investigated. At small doping levels for Zn and Mg ($x \leq 0.02$), the behaviour of the magnetic properties was similar to that of the parent material LiCuSbO_4 . Once the doping level were higher, paramagnetic like behaviours in their magnetic properties at low temperatures around 4 K were observed. The results imply that the non magnetic materials' doping would "cut" the one dimensional Cu chain and the Cu^{2+} spins on the edges of the chains would behave as paramagnetic like spins. However, the interactions of the Cu^{2+} spins over the dopants would still exist. In order to investigate the result, further research such as direct measurements of spins' behaviours by NMR will be needed.

A difference between Zn and Mg doped samples were observed. For their magnetic properties, their general tendencies by doping on LiCuSbO_4 were the same for Zn and Mg doped samples. However, the Zn doped samples results were more diverse than that of Mg doped samples. This might be from the fact that Zn was the tetragonally coordinated atom and there would be an anisotropy around Zn atoms, whereas Mg was octagonally coordinated and would not be anisotropically distorted.

While the c axis of Mg doped samples were decreased, that of Zn doped samples were increased in the lower doping level in the range of $0 \leq x \leq 0.02$, and then increased $x \geq 0.04$ in both Zn and Mg doped samples. The critical saturation magnetic field of the Mg and Zn doped samples had the tendency which might be related to the change of c axis due to the 3D inter chain interactions would be related to the lattice parameter c which is related to the inter-chain distances in LiCuSbO_4 . As the lattice parameter c changed, which might be related that the critical field of Mg doped samples were increased and that of Zn doped samples was increased at smaller doping level in the range of $0 \leq x \leq 0.02$, and then decreased $x \geq 0.04$. This could be from the inter-chain interaction which was affected by the distances which were related to the lattice parameter c .

Not only non magnetic ions, but also the effect of magnetic ion Co doping was investigated. The intensity of the magnetic susceptibility were increased as the amount of Co doping increased in any temperature from 2-30 K. Compared to Zn and Mg doped samples, the magnetic susceptibility was higher in the range of $2 \leq T \leq 30$ K due to the presence of the magnetic moments in Co^{2+} ions. The paramagnetic like behaviours were observed and suggested that the magnetic ion Co^{2+} doping would also “cut” the Cu chain. However, the interactions over the Co dopants would also still exist which would be similar to non magnetic ions doped materials. In order to investigate the result, further research such as direct measurements of spins’ behaviours on the edge of the Cu chains by NMR will be needed.

The tendency of the lattice parameters of Co doped samples would be the same as that of Mg doped samples in the range of $0 \leq x \leq 0.01$. In addition to the tendency of the lattice parameter, the tendency of the critical field in Co doped samples would be the same tendency of that of Mg doped samples. This relation between the lattice parameters and critical fields as a function of doping could indicate that the critical field could be changed by the three dimensional inter-chain interactions.

The effect of non magnetic (Zn and Mg) and magnetic (Co) atoms doping on one dimensional frustrated magnet LiCuSbO_4 were investigated. The orphan spins on the spin chains were observed in Zn, Mg and Co doping. The relation between the critical field and the inter chain distance would be observed in LiCuSbO_4 series.

7.2 Pyrochlore Spin ice $A_2B_2O_7$ ($A=\text{Ho, Dy, Tb}$, $B=\text{Sn, Ti}$)

Pyrochlore spin ice is an extensive field of research in frustrated magnetism. Doping on spin ices is also known as an effective method to investigate the properties of the spin ices. The purpose of doping on A site and B site is different. While A site doping is to investigate the effect of doping on magnetic ions directly, B site doping is to investigate the effect of doping on the environments of the magnetic ions which are usually on A site. In this thesis, doping effects on B site of the pyrochlore spin ices were investigated.

7.2.1 $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($A=\text{Ho, Dy}$ $0 \leq x \leq 0.10$)

$A_2\text{Sn}_2\text{O}_7$ ($A=\text{Ho, Dy}$) are well studied pyrochlore spin ices. For Ho and Dy series of spin ices, the effect of partially doping Sc on the Sn site has been investigated. Pyrochlore spin ice $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($A=\text{Ho, Dy}$ $0 \leq x \leq 0.10$) were synthesized by ceramics process. The residual entropy was affected by Sc doping which affects the oxygen coordination of rare earth ions which are located on A sites and which are surrounded by eight oxygen atoms in pyrochlore structure.

In $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series, the lattice parameter, a , is linearly decreased by Sc doping in the range of $0 \leq x \leq 0.10$. In $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ series on the other hand, the lattice parameter a is significantly decreased by Sc doping in the range of $0 \leq x \leq 0.025$, then it decreases slightly in the range of $0.025 \leq x \leq 0.10$. The addition of O vacancies into the pyrochlore structure may also have an impact on the size of the lattice. It is speculated that these two competing effects result in the observed changes in the lattice parameter.

The $A\text{-O}_2$ bond length became shorter on Sc doping. The tendency is the same as the lattice parameter since the $A\text{-O}_2$ bond length and the lattice parameter are related to each other. On the other hand, $A\text{-O}_1$ bond length has large error bar than that of $A\text{-O}_2$ and the bond length were not significantly changed by Sc doping. This indicated that the more Sc doping, the lesser

anisotropy of the ratio of A -O1 and A -O2 was observed. The anisotropy might be related to the crystal field of the rare earth ions for both Ho and Dy series.

While the saturation value of the peak position of the heat capacity peak at 1.5 K which was reported as dipolar spin ice was shifted, isothermal magnetizations and magnetic entropy of $\text{Ho}_2\text{Sn}_2\text{O}_7$ series were increased by Sc doping, no clear changes were observed in $\text{Dy}_2\text{Sn}_2\text{O}_7$ by Sc doping in the range of $0 \leq x \leq 0.10$.

The removal of O_2 could change the CEF and remove the ground state degeneracy for non-Kramer's ion. While Ho ions are non-Kramer ions, Dy ions are Kramer ions. Therefore, for $A=\text{Ho}$, the saturation value of the isothermal magnetization and the magnetic entropy would be increased which is consistent with the experimental results. On the other hand, the Dy ions are Kramer's ions, and $\text{Dy}_2\text{Sn}_2\text{O}_7$ system is not affected by Sc doping.

The effects of Sc doping for spin ice materials $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ were investigated. The difference of Kramer's ion (Dy) and non-Kramer's ion (Ho) would be observed in spin ice materials as reported in different systems.

7.2.2 $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($B=\text{Sn}$ and Ti $0 \leq x \leq 0.05$)

Many Pyrochlore spin ice and spin liquids have been reported, of these Terbium spin ice is a particularly interesting one due to it having some unique properties. While $\text{Tb}_2\text{Sn}_2\text{O}_7$ behave as a spin ice, $\text{Tb}_2\text{Ti}_2\text{O}_7$ is a spin liquid. The intermediate states of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Ti}_{2x}\text{O}_{7-x}$ ($0 < x < 1$) were also unique to the both pristine materials $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. In the research, the doping effects on B site were investigated.

$\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($B=\text{Sn}$ and Ti $0 \leq x \leq 0.05$) were synthesized by ceramics process. In both cases of Ti and Sn series samples, the isothermal magnetizations and heat capacities of the pyrochlores were affected by Sc doping, demonstrated by the peaks of heat capacity at 6 K which was reported as first excited states, disappearing with Sc doping. The saturation value of the magnetic entropy of both $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$ are between $R \ln 3$ and $R \ln 4$ which are higher values than that of the ideal classical spin pyrochlore which has $R \ln 2$. This could be potentially due to more degenerated states than the spin liquid and spin ice in $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$. This could be an effect from quantum spin ice.

The magnetic properties including magnetic susceptibility and isothermal magnetization was measured. No specific changes were observed on magnetic susceptibility as a function of Sc doping in the range of $2 \leq T \leq 300$ K. The values of the magnetization were decreased at 5 T, with increased amount of Sc doping in both $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. This suggests that both Sc doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ could have more residual entropy than non doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$. It also could indicate that Sc doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ could have more degenerate states than that of non doped $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$.

The heat capacity including C_{mag} , C_{mag}/T and ΔS were measured in the range of $0.4 \leq T \leq 20$ K. The sharp peak of C_{mag} at 0.6 K which was observed in $x=0$ materials were not observed in $x=0.05$ materials. The broad peak around 6 K which was observed in $x=0$ were observed in $x=0.05$ $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ but not observed in $x=0.05$ $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$. Both the magnetic entropy (ΔS) of $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ and $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ were decreased by Sc doping. This difference indicated that the first excited states in $\text{Tb}_2\text{Ti}_2\text{O}_7$ could be affected by Sc doping, but the first excited states in $\text{Tb}_2\text{Sn}_2\text{O}_7$ was not affected by Sc doping in the range of $0 \leq x \leq 0.05$ probably due to the CEF difference in $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Sn}_2\text{O}_7$.

The effects of Sc doping for $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ were investigated. The difference of CEF of $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ could be observed. This could be one of the reasons why $\text{Tb}_2\text{Sn}_2\text{O}_7$ is spin ice while $\text{Tb}_2\text{Ti}_2\text{O}_7$.

7.3 Summary

Doping is an effective method to investigate the properties of materials. In summary, there are variety of the aim and effects of doping on frustrated magnets. In this thesis, two different types of frustrated system were investigated by the systematic doping for different purposes. One is the doping non magnetic atoms and magnetic atoms to change the magnetic properties of the system directly as Zn, Mg and Co doping on Cu sites in LiCuSbO_4 . The other one is the doping change the oxidation state of magnetic atoms in frustrated magnets as Sc doping on B sites in pyrochlore spin ices and spin liquid $A_2B_2\text{O}_7$ ($A=\text{Ho, Dy, Tb}$, $B=\text{Ti, Sn}$).

I have synthesized $\text{LiCu}_{1-x}\text{M}_x\text{SbO}_4$ ($M=\text{Mg, Zn, Co}$ $0 \leq x \leq 0.1$) which is one of the simplest one dimensional frustrated magnets. I investigated the effect of non magnetic and magnetic atom doping on one dimensional frustrated magnets by measuring their magnetic properties. The orphan spins on the spin chains were observed in Zn, Mg and Co doping. The relation between the critical field and the inter chain distance would be observed in LiCuSbO_4 series.

I have synthesized $A_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($A=\text{Ho, Dy}$ $0\leq x\leq 0.1$) and $\text{Tb}_2\text{B}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($B=\text{Sn and Ti}$ $0\leq x\leq 0.05$) in which pyrochlore spin ices are well studied research areas. I investigated the effect of Sc atom doping on pyrochlore materials by measuring their magnetic properties and heat capacities. The effects of Sc doping for spin ice materials $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Dy}_2\text{Sn}_2\text{O}_7$ were investigated. The difference of Kramer's ion (Dy) and non-Kramer's ion (Ho) would be observed in spin ice materials as reported in different systems. The effects of Sc doping for $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ were investigated. The effects of Sc doping for $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ were investigated and difference of CEF of $\text{Tb}_2\text{Sn}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ could be observed. This could be one of the reasons why $\text{Tb}_2\text{Sn}_2\text{O}_7$ is spin ice while $\text{Tb}_2\text{Ti}_2\text{O}_7$.

Therefore, different effect of doping on frustrated magnets were investigated on different purposes in this thesis.

Chapter 8 References

- ¹ J. Snyder, J.S. Slusky, R.J. Cava, and P. Schiffer, *Nature* **413**, 48 (2001).
- ² S.E. Dutton, E.D. Hanson, C.L. Broholm, J.S. Slusky, and R.J. Cava, *J. Phys. Condens. Matter* **23**, 386001 (2011).
- ³ M. Enderle, C. Mukherjee, B. Fåk, R.K. Kremer, J.-M. Broto, H. Rosner, S.-L. Drechsler, J. Richter, J. Malek, A. Prokofiev, W. Assmus, S. Pujol, J.-L. Raggazzoni, H. Rakoto, M. Rheinstädter, and H.M. Rønnow, *Europhys. Lett.* **70**, 237 (2005).
- ⁴ S.E. Dutton, M. Kumar, M. Mourigal, Z.G. Soos, J.-J. Wen, C.L. Broholm, N.H. Andersen, Q. Huang, M. Zbiri, R. Toft-Petersen, and R.J. Cava, *Phys. Rev. Lett.* **108**, 187206 (2012).
- ⁵ S. Petit, P. Bonville, I. Mirebeau, H. Mutka, and J. Robert, *Phys. Rev. B* **85**, 54428 (2012).
- ⁶ F. Hund, *Zeitschrift Für Phys.* **33**, 345 (1925).
- ⁷ W. Kutzelnigg and J.D. Morgan, *Zeitschrift Für Phys. D Atoms, Mol. Clust.* **36**, 197 (1996).
- ⁸ W. Pauli, *Zeitschrift Für Phys.* **31**, 765 (1925).
- ⁹ C. Kittel, *Introduction to Solid State*, 7th ed. (John Wiley and Sons, 1966).
- ¹⁰ S. Blundell, *Magnetism in Condensed Matter* (Oxford university press, Oxford, 2001).
- ¹¹ A.H. Wilson, *The Theory of Metals* (Cambridge University Press, 1965).
- ¹² H. Takatsu, S. Onoda, S. Kittaka, A. Kasahara, Y. Kono, T. Sakakibara, Y. Kato, B. Fåk, J. Ollivier, J.W. Lynn, T. Taniguchi, M. Wakita, and H. Kadowaki, *Phys. Rev. Lett.* **116**, 217201 (2016).
- ¹³ M. Hase, H. Kitazawa, K. Ozawa, T. Hamasaki, H. Kuroe, and T. Sekine, *J. Phys. Soc. Japan* **77**, 34706 (2008).
- ¹⁴ Y. Nishida and S. Kida, *Coord. Chem. Rev.* **27**, 275 (1979).
- ¹⁵ U. Opik and M.H.L. Pryce, *Proc. R. Soc. A Math. Phys. Eng. Sci.* **238**, 425 (1957).

-
- ¹⁶ M.A. Halcrow, Chem. Soc. Rev. **42**, 1784 (2013).
- ¹⁷ K. Matsuhira, Y. Hinatsu, K. Tenya, and T. Sakakibara, J. Phys. Condens. Matter **12**, 649 (2000).
- ¹⁸ X. Ke, R.S. Freitas, B.G. Ueland, G.C. Lau, M.L. Dahlberg, R.J. Cava, R. Moessner, and P. Schiffer, Phys. Rev. Lett. **99**, 137203 (2007).
- ¹⁹ B.D. Gaulin, E. Kermarrec, M.L. Dahlberg, M.J. Matthews, F. Bert, J. Zhang, P. Mendels, K. Fritsch, G.E. Granroth, P. Jiramongkolchai, A. Amato, C. Baines, R.J. Cava, and P. Schiffer, Phys. Rev. B **91**, 245141 (2015).
- ²⁰ R. Seo, T. Ishizuka, A. A Abdel-aziz, and T. Kunieda, Prog. Theor. Phys. **42**, 6353 (2001).
- ²¹ S.-L. Drechsler, O. Volkova, A. Vasiliev, N. Tristan, J. Richter, M. Schmitt, H. Rosner, J. Málek, R. Klingeler, A. Zvyagin, and B. Büchner, Phys. Rev. Lett. **98**, 077202 (2007).
- ²² M.I. Darby, Br. J. Appl. Phys. **18**, 1415 (1967).
- ²³ H. Fukazawa, R.G. Melko, R. Higashinaka, Y. Maeno, and M. Gingras, Phys. Rev. B **65**, 7 (2001).
- ²⁴ B. Lisnyi and J. Strečka, Phys. Status Solidi **251**, 1083 (2014).
- ²⁵ S.T. Bramwell, M.N. Field, M.J. Harris, and I.P. Parkin, J. Phys. Condens. Matter **12**, 483 (2000).
- ²⁶ J.A.M. Paddison, H.S. Ong, J.O. Hamp, P. Mukherjee, X. Bai, M.G. Tucker, N.P. Butch, C. Castelnovo, M. Mourigal, and S.E. Dutton, Nat. Commun. **7**, 1 (2016).
- ²⁷ F.J. Owens and C.P.P. Jr, *The Physics and Chemistry of Nanosolids* (John Wiley & Sons., 2008).
- ²⁸ M.L. Néel, Ann. Phys. (Paris). **12**, 137 (1948).
- ²⁹ a P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994).
- ³⁰ Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. Lett. **91**, 107001 (2003).

- ³¹ L. Balents, *Nature* **464**, 199 (2010).
- ³² M. Hermele, M.P.A. Fisher, and L. Balents, *Phys. Rev. B* **69**, 064404 (2004).
- ³³ M. Jafarpour, M. Ghahramaninezhad, and A. Rezaeifard, *New J. Chem.* **38**, 2917 (2014).
- ³⁴ S. Nishimoto, S.L. Drechsler, R.O. Kuzian, J. Van Den Brink, J. Richter, W.E.A. Lorenz, Y. Skourski, R. Klingeler, and B. Buchner, *Phys. Rev. Lett.* **107**, 097201 (2011).
- ³⁵ A. Kumar, P. Kumari, A. Das, G.D. Dwivedi, P. Shahi, K.K. Shukla, K. Ghosh, K. Nigam, K.K. Chattopadhyay, and S. Chatterjee, *J. Solid State Chem.* **208**, 120 (2013).
- ³⁶ S. Furukawa, M. Sato, and S. Onoda, *Phys. Rev. Lett.* **105**, 257205 (2010).
- ³⁷ J. Sudan, A. Lüscher, and A.M. Läuchli, *Phys. Rev. B* **80**, 140402 (2009).
- ³⁸ J. Sirker, *Phys. Rev. B* **81**, 014419 (2010).
- ³⁹ A.P. Ramirez, A. Hayashi, R.J. Cava, R. Siddharthan, and B.S. Shastry, *Nature* **399**, 333 (1999).
- ⁴⁰ R. Tillner-Roth and H.D. Baehr, *J. Phys. Chem. Ref. Data* **23**, 657 (1994).
- ⁴¹ S.T. Bramwell, *Science*. **294**, 1495 (2001).
- ⁴² V.K. Pecharsky and K.A.G. Jr, *J. Appl. Phys.* **565**, (2006).
- ⁴³ M.J. Whitaker and C. Greaves, *J. Solid State Chem.* **215**, 171 (2014).
- ⁴⁴ S.T. Bramwell and M.J. Harris, *J. Phys. Condens. Matter* **10**, 215 (1998).
- ⁴⁵ C. Castelnovo, R. Moessner, and S.L. Sondhi, *Nature* **451**, 42 (2008).
- ⁴⁶ C.L. Henley, *Annu. Rev. Condens. Matter Phys.* **1**, 179 (2010).
- ⁴⁷ Y. Perrin, B. Canals, and N. Rougemaille, *Nature* **540**, 410 (2016).
- ⁴⁸ S. Petit, E. Lhotel, B. Canals, M. Ciomaga Hatnean, J. Ollivier, H. Mutka, E. Ressouche, A.R. Wildes, M.R. Lees, and G. Balakrishnan, *Nat. Phys.* **12**, 746 (2016).
- ⁴⁹ G. Ehlers, J.S. Gardner, C.H. Booth, M. Daniel, K.C. Kam, A.K. Cheetham, D. Antonio, H.E. Brooks, A.L. Cornelius, S.T. Bramwell, J. Lago, W. Häussler, and N. Rosov, *Phys. Rev.*

B. **73**, 174429 (2006).

⁵⁰ J. Snyder, B.G. Ueland, A. Mizel, J.S. Slusky, H. Karunadasa, R.J. Cava, and P. Schiffer, Phys. Rev. B **70**, 184431 (2004).

⁵¹ J.M. Longo, P.M. Raccach, and J.B. Goodenough, Mater. Res. Bull. **4**, 191 (1969).

⁵² G. Sala, M.J. Gutmann, D. Prabhakaran, D. Pomaranski, C. Mitchelitis, J.B. Kycia, D.G. Porter, C. Castelnovo, and J.P. Goff, Nat. Mater. **13**, 488 (2014).

⁵³ H.M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).

⁵⁴ H.A. Wilson, Phys. Rev. **18**, 396 (1921).

⁵⁵ J. Rodriguez-carvajal, Phys. B **192**, 55 (1993).

⁵⁶ J.J. Olivero and R.L. Longbothum, J. Quant. Spectrosc. Radiat. Transf. **17**, 233 (1977).

⁵⁷ A. Monshi, M.R. Foroughi, and M.R. Monshi, World J. Nano Sci. Eng. **2**, 154 (2012).

⁵⁸ Katila T, *Principles and Applications of SQUID Sensors* (New York: Plenum Press, 1989).

⁵⁹ B.D. Josephson, Rev. Mod. Phys., **46**, 251 (1974).

⁶⁰ B.D. Josephson, Phys. Lett. **1**, 251 (1962).

⁶¹ G.A. Bain and J.F. Berry, J. Chem. Educ. **85**, 1 (2008).

⁶² E.P.W. P. Rhodes, Proc. R. Soc. A 247 (1962).

⁶³ B.C. Melot, J.E. Drewes, R. Seshadri, E.M. Stoudenmire, and A.P. Ramirez, J. Phys. Condens. Matter **21**, 216007 (2009).

⁶⁴ S.E. Dutton, C.L. Broholm, and R.J. Cava, J. Solid State Chem. **183**, 1798 (2010).

⁶⁵ D. Peter, Ann. Der Phys. Leipzig **39**, 789 (1912).

⁶⁶ Horst Meyer and P. L. Smith, J. Phys. Chem. Solids **9**, 285 (1959).

⁶⁷ V.F.Sears, Proc. Phys. Soc. **84**, 951 (1964).

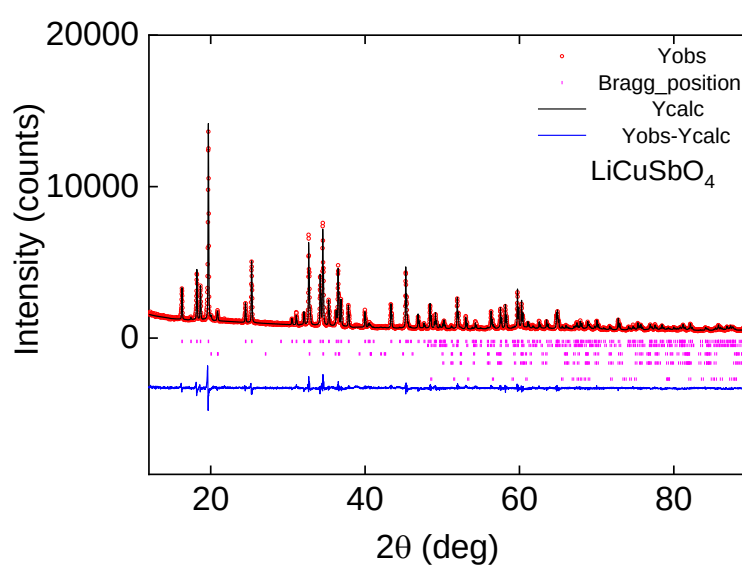
⁶⁸ D.R. Smith and F.R. Fickett, J. Res. Natl. Inst. Stand. Technol. **100**, 119 (1995).

- ⁶⁹ M. Mourigal, M. Enderle, R.K. Kremer, J.M. Law, and B. Fåk, Phys. Rev. B **83**, 100409 (2011).
- ⁷⁰ D. Dai, H.-J. Koo, and M.-H. Whangbo, Inorg. Chem. **43**, 4026 (2004).
- ⁷¹ H. -A. Krug von Nidda, L. Svistov, M. Eremin, R. Eremina, A. Loidl, V. Kataev, A. Validov, A. Prokofiev, and W. Aßmus, Phys. Rev. B **65**, 134445 (2002).
- ⁷² M. A. Lafontaine, M. Leblanc, and G. Ferey, Acta Crystallogr. Sect. C Cryst. Struct. Commun. **45**, 1205 (1989).
- ⁷³ G. Simutis, M. Thede, R. Saint-Martin, A. Mohan, C. Baines, Z. Guguchia, R. Khasanov, C. Hess, A. Revcolevschi, B. Büchner, and A. Zheludev, Phys. Rev. B **93**, 214430 (2016).
- ⁷⁴ H. Katsura, S. Onoda, J. Han, and N. Nagaosa, Phys. Rev. Lett. **101**, 187207 (2008).
- ⁷⁵ L. Capogna, M. Mayr, P. Horsch, M. Raichle, R.K. Kremer, M. Sofin, A. Maljuk, M. Jansen, and B. Keimer, Phys. Rev. B **71**, 140402 (2005).
- ⁷⁶ M. Hase, H. Kuroe, K. Ozawa, O. Suzuki, H. Kitazawa, G. Kido, and T. Sekine, Phys. Rev. B **70**, 104426 (2004).
- ⁷⁷ Y. Hoshino, S. Atarashi, T. Goto, M. Hase, and T. Sasaki, Proc. Int. Conf. Strongly Correl. Electron Syst. **14012**, 1 (2014).
- ⁷⁸ T. Hanna, Y. Muraba, S. Matsuishi, N. Igawa, K. Kodama, S. Shamoto, and H. Hosono, Phys. Rev. B **84**, 024521 (2011).
- ⁷⁹ X. Obradors, A. Labarta, A. Isalgue, J. Tejada, J. Rodriguez, and M. Pernet, Solid State Commun. **65**, 189 (1988).
- ⁸⁰ H.-J. Grafe, S. Nishimoto, M. Iakovleva, E. Vavilova, L. Spillecke, A. Alfonsov, M.-I. Sturza, S. Wurmehl, H. Nojiri, H. Rosner, J. Richter, U.K. Rößler, S.-L. Drechsler, V. Kataev, and B. Büchner, Sci. Rep. **7**, 6720 (2017).
- ⁸¹ M.B. Sanders, J.W. Krizan, and R.J. Cava, J. Mater. Chem. C **4**, 541 (2016).
- ⁸² M.B. Sanders, K.M. Baroudi, J.W. Krizan, O.A. Mukadam, and R.J. Cava, Phys. Status Solidi **253**, 2056 (2016).

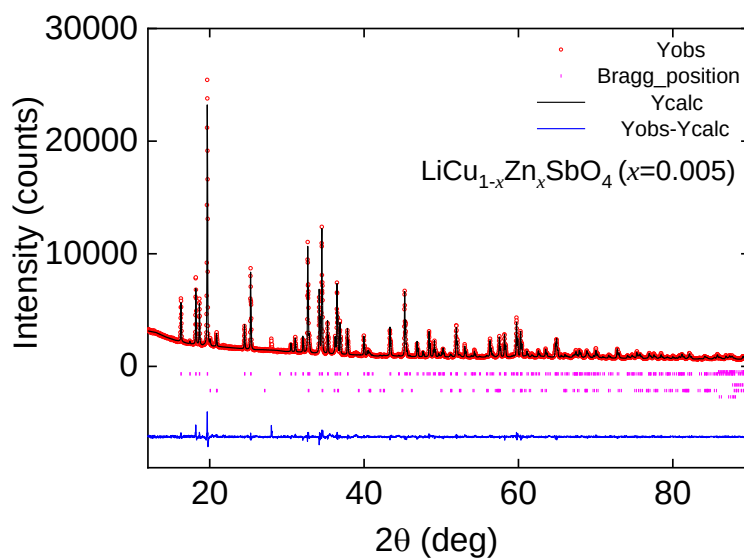
-
- ⁸³ P. Schiffer and I. Daruka, *Phys. Rev. B* **56**, 013712 (1997).
- ⁸⁴ T. Hosaka, S. Hachiuma, H. Kuroe, T. Sekine, M. Hase, K. Oka, T. Ito, H. Eisaki, M. Fujisawa, S. Okubo, and H. Ohta, *J. Phys. Conf. Ser.* **400**, 32022 (2012).
- ⁸⁵ S. Lei, C. Wang, D. Guo, X. Gao, D. Cheng, J. Zhou, B. Cheng, and Y. Xiao, *RSC Adv.* **4**, 52740 (2014).
- ⁸⁶ M. Arrabito, N. Penazzi, S. Panero, and P. Reale, *J. Power Sources* **94**, 225 (2001).
- ⁸⁷ L.E. Svistov, T. Fujita, H. Yamaguchi, S. Kimura, K. Omura, A. Prokofiev, A.I. Smirnov, Z. Honda, and M. Hagiwara, *JETP Lett.* **93**, 21 (2011).
- ⁸⁸ G. Ehlers, A. Huq, S.O. Diallo, C. Adriano, K.C. Rule, L. Cornelius, P. Fouquet, P.G. Pagliuso, and J.S. Gardner, *J. Phys. Condens. Matter* **24**, 76005 (2012).
- ⁸⁹ K. Matsuhira, Y. Hinatsu, K. Tenya, H. Amitsuka, and T. Sakakibara, *J. Phys. Soc. Japan* **71**, 1576 (2002).
- ⁹⁰ X. Ke, B.G. Ueland, D. V West, M.L. Dahlberg, R.J. Cava, and P. Schiffer, *Phys. Rev. B* **76**, 214413 (2007).
- ⁹¹ M. Wakita, T. Taniguchi, H. Edamoto, H. Takatsu, and H. Kadowaki, *J. Phys. Conf. Ser.* **683**, 12023 (2016).
- ⁹² L.J. Chang, Y. Su, Y.-J. Kao, Y.Z. Chou, R. Mittal, H. Schneider, T. Brückel, G. Balakrishnan, and M.R. Lees, *Phys. Rev. B* **82**, 172403 (2010).
- ⁹³ H. Liu, Y. Zou, L. Ling, L. Zhang, C. Zhang, and Y. Zhang, *J. Magn. Magn. Mater.* **388**, 135 (2015).
- ⁹⁴ Y. Chapuis, A. Yaouanc, P. Dalmas De Réotier, C. Marin, S. Vanishri, S.H. Curnoe, C. Vgju, and A. Forget, *Phys. Rev. B - Condens. Matter Mater. Phys.* **82**, 100402 (2010).
- ⁹⁵ C. Bansal, H. Kawanaka, H. Bando, and Y. Nishihara, *Phys. Rev. B* **66**, 052406 (2002).
- ⁹⁶ B.C. den Hertog and M.J.P. Gingras, *Phys. Rev. Lett.* **84**, 3430 (2000).
- ⁹⁷ G. Ehlers, A. Huq, S.O. Diallo, C. Adriano, K.C. Rule, a L. Cornelius, P. Fouquet, P.G. Pagliuso, and J.S. Gardner, *J. Phys. Condens. Matter* **24**, 76005 (2012).

- ⁹⁸ P. Mukherjee, Y. Wu, G.I. Lampronti, and S.E. Dutton, *Mater. Res. Bull.* **98**, 173 (2017).
- ⁹⁹ S. Calder, X. Ke, F. Bert, A. Amato, C. Baines, C. Carboni, R.J. Cava, A. Daoud-Aladine, P. Deen, T. Fennell, A.D. Hillier, H. Karunadasa, J.W. Taylor, P. Mendels, P. Schiffer, and S.T. Bramwell, *Phys. Rev. B* **81**, 064425 (2010).
- ¹⁰⁰ Y.-J. Kao, M. Enjalran, A. Del Maestro, H.R. Molavian, and M.J.P. Gingras, *Phys. Rev. B* **68**, 172407 (2003).
- ¹⁰¹ N. Hamaguchi, T. Matsushita, N. Wada, Y. Yasui, and M. Sato, *Phys. Rev. B* **69**, 132413 (2004).
- ¹⁰² H.R. Molavian, M.J.P. Gingras, and B. Canals, *Phys. Rev. Lett.* **98**, 157204 (2007).
- ¹⁰³ J.S. Gardner, S.R. Dunsiger, B.D. Gaulin, M.J.P. Gingras, J.E. Greedan, R.F. Kiefl, M.D. Lumsden, W.A. MacFarlane, N.P. Raju, J.E. Sonier, I. Swainson, and Z. Tun, *Phys. Rev. Lett.* **82**, 1012 (1999).
- ¹⁰⁴ I. Mirebeau, A. Apetrei, J. Rodríguez-Carvajal, P. Bonville, A. Forget, D. Colson, V. Glazkov, J.P. Sanchez, O. Isnard, and E. Suard, *Phys. Rev. Lett.* **94**, 246402 (2005).
- ¹⁰⁵ I. Mirebeau, I. Goncharenko, H. Cao, and A. Forget, *Phys. Rev. B* **80**, 220407 (2009).
- ¹⁰⁶ E. Lhotel, C. Paulsen, P. Dalmas de Réotier, A. Yaouanc, C. Marin, and S. Vanishri, *Phys. Rev. B* **86**, 20410 (2012).
- ¹⁰⁷ M. Gingras, B. den Hertog, M. Faucher, J. Gardner, S. Dunsiger, L. Chang, B. Gaulin, N. Raju, and J. Greedan, *Phys. Rev. B* **62**, 006496 (2000).
- ¹⁰⁸ J. Zhang, K. Fritsch, Z. Hao, B. V Bagheri, M.J.P. Gingras, G.E. Granroth, P. Jiramongkolchai, R.J. Cava, and B.D. Gaulin, *Phys. Rev. B* **89**, 134410 (2014).
- ¹⁰⁹ P. Bonville, I. Mirebeau, A. Gukasov, S. Petit, and J. Robert, *Phys. Rev. B* **84**, 184409 (2011).
- ¹¹⁰ P. Bonville, A. Gukasov, I. Mirebeau, and S. Petit, *Phys. Rev. B* **89**, 85115 (2014).

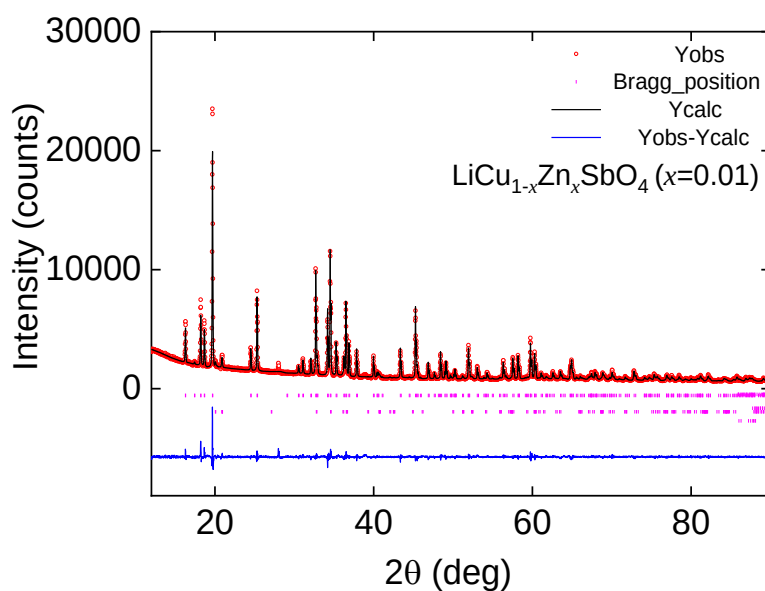
Appendix



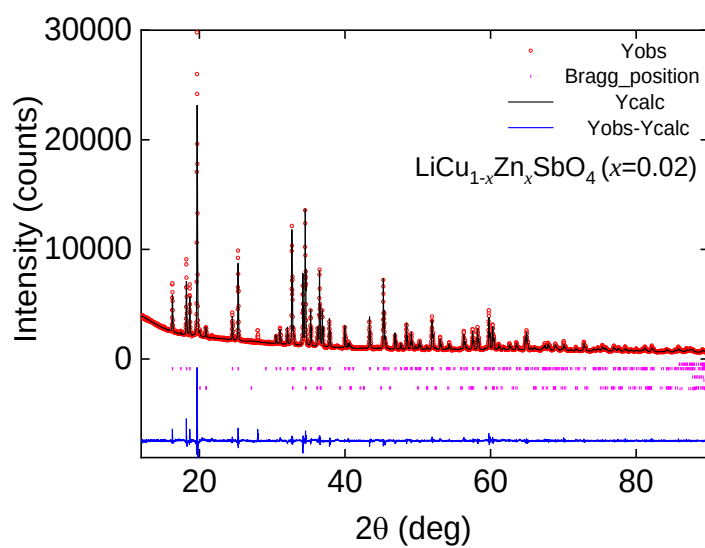
Appendix 1 X-ray diffraction pattern for LiCuSbO_4 . Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



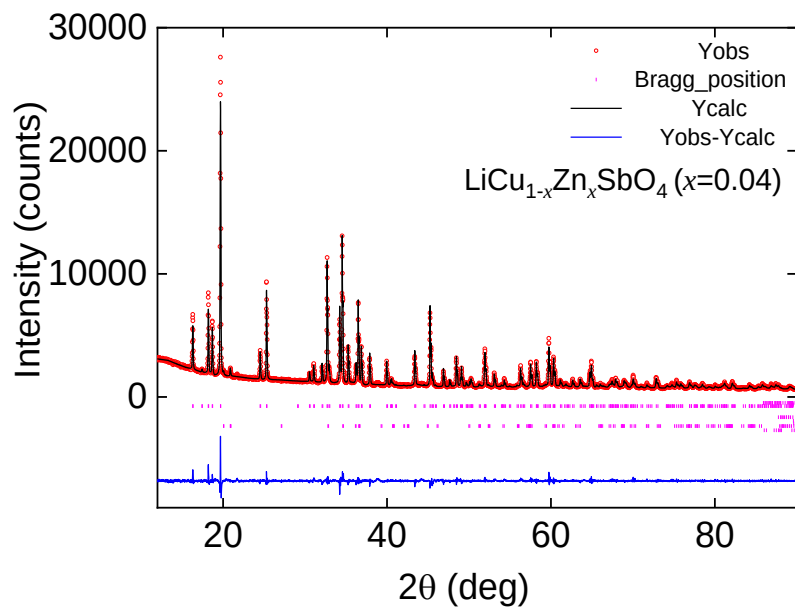
Appendix 2 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ ($x=0.005$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot



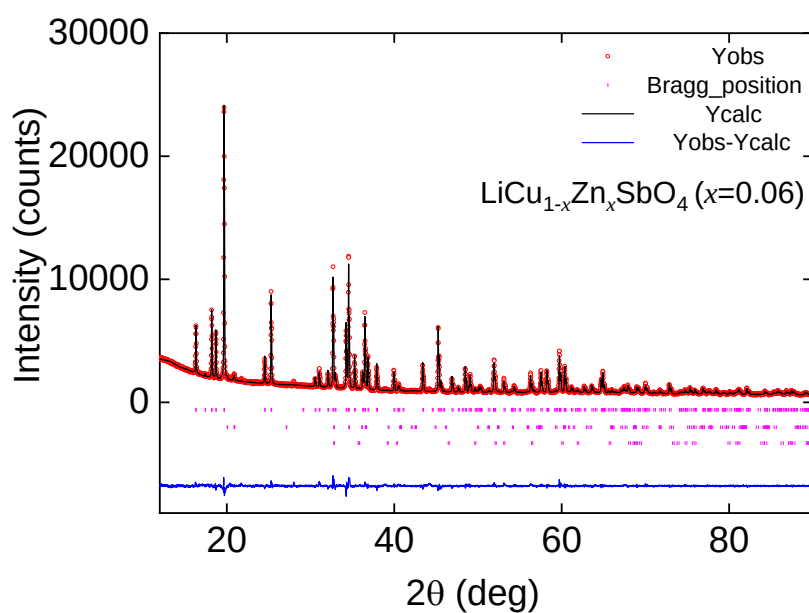
Appendix 3 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ ($x=0.01$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



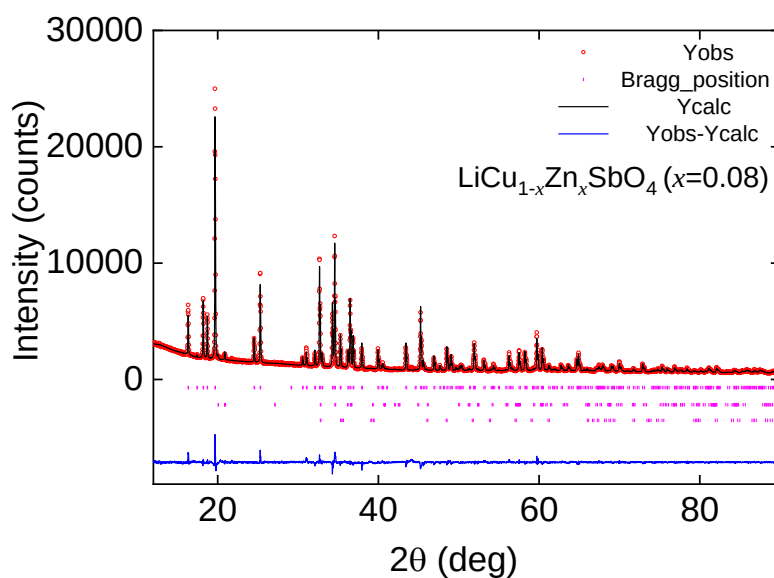
Appendix 4 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ ($x=0.02$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



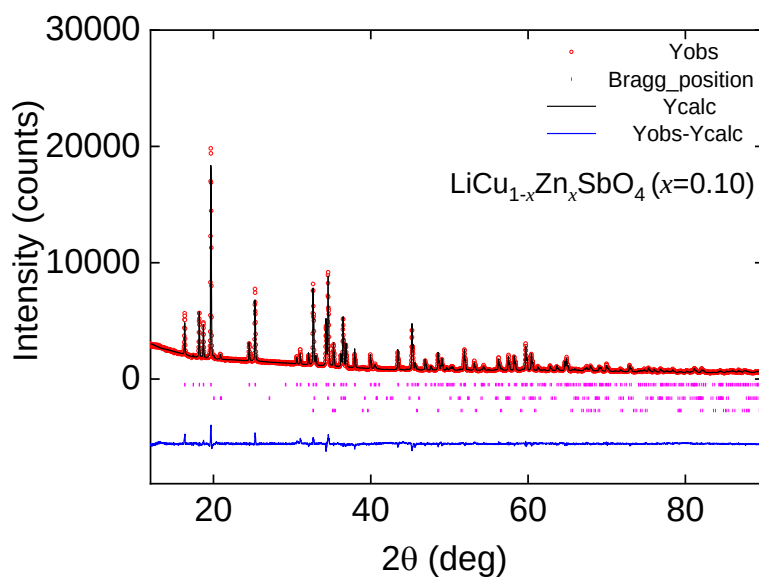
Appendix 5 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ ($x=0.04$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



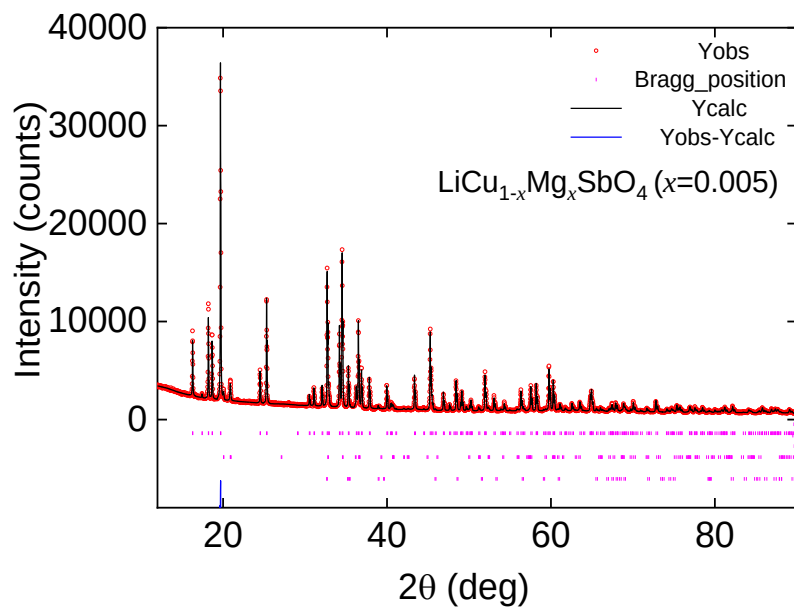
Appendix 6 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ ($x=0.06$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



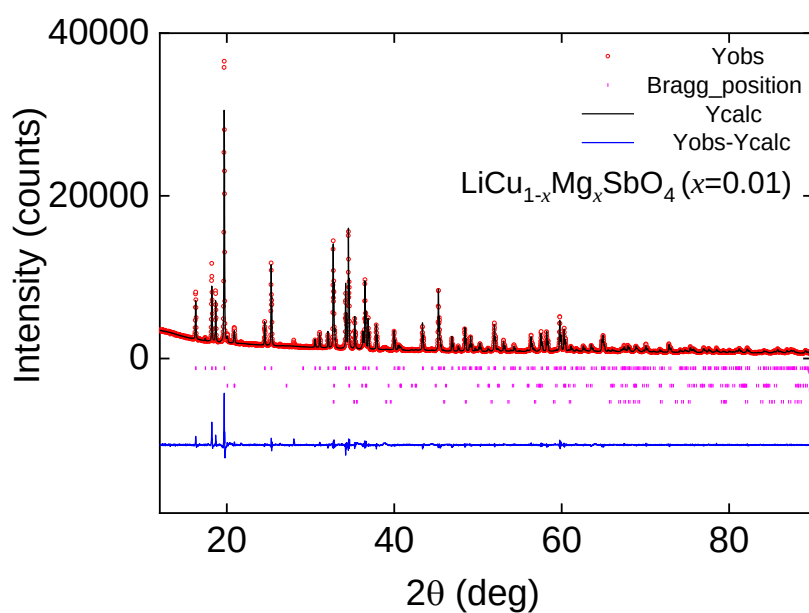
Appendix 7 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$ ($x=0.08$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



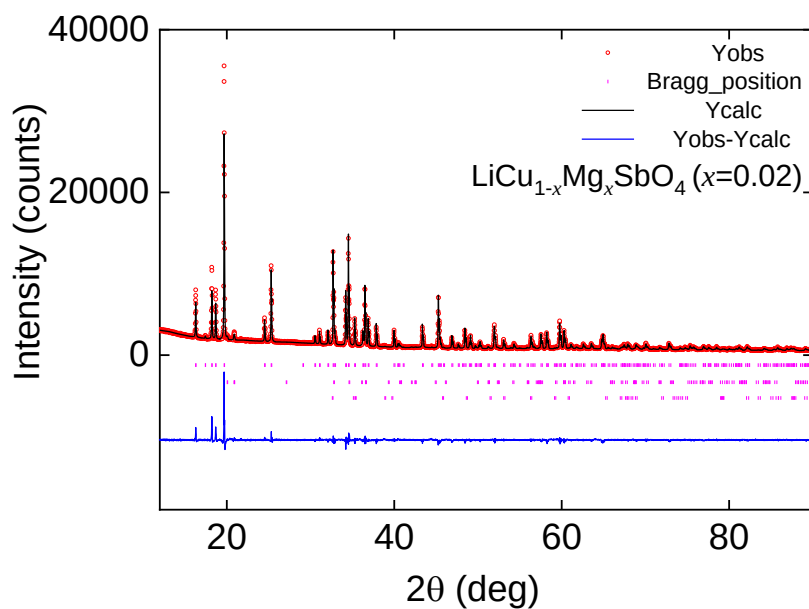
Appendix 8 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$. ($x=0.10$) Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



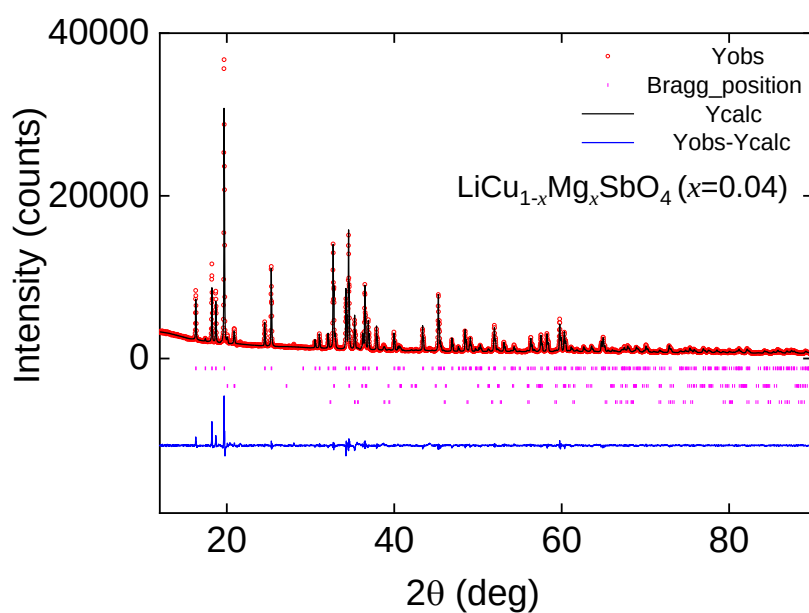
Appendix 9 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.005$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



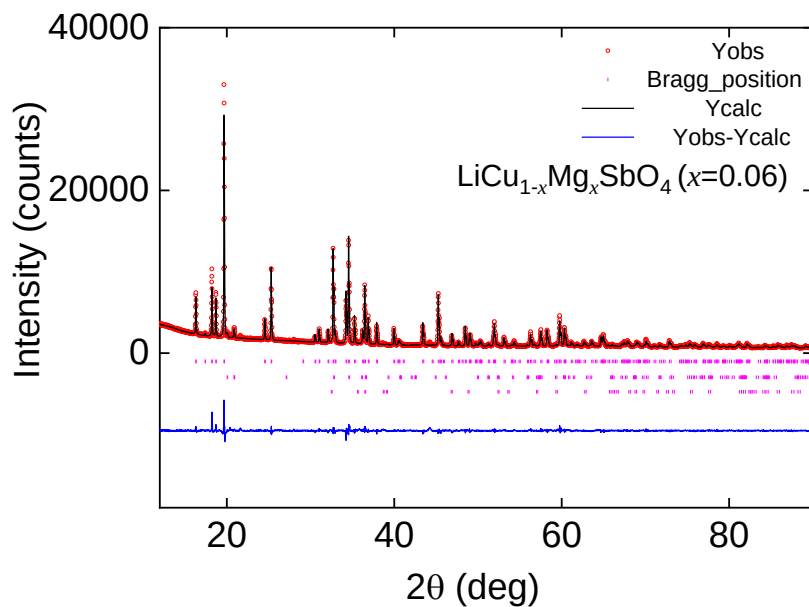
Appendix 10 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.01$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



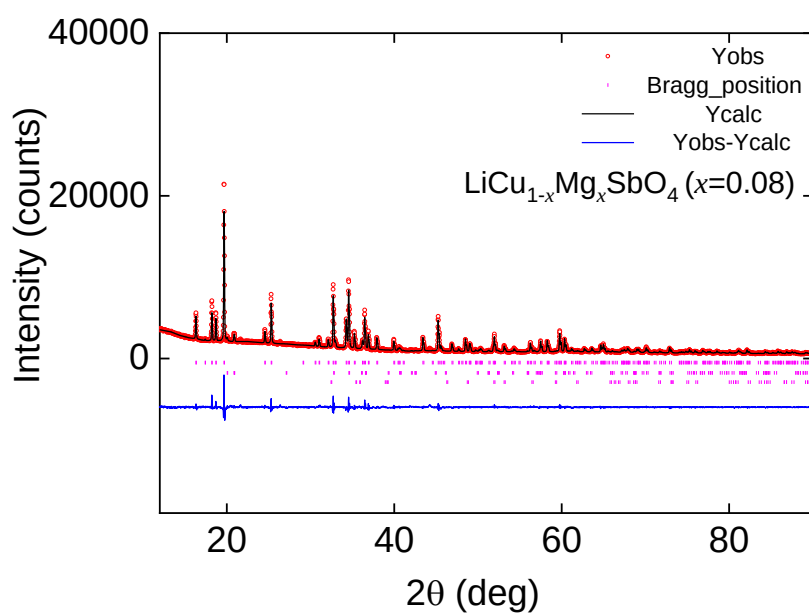
Appendix 11 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.02$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



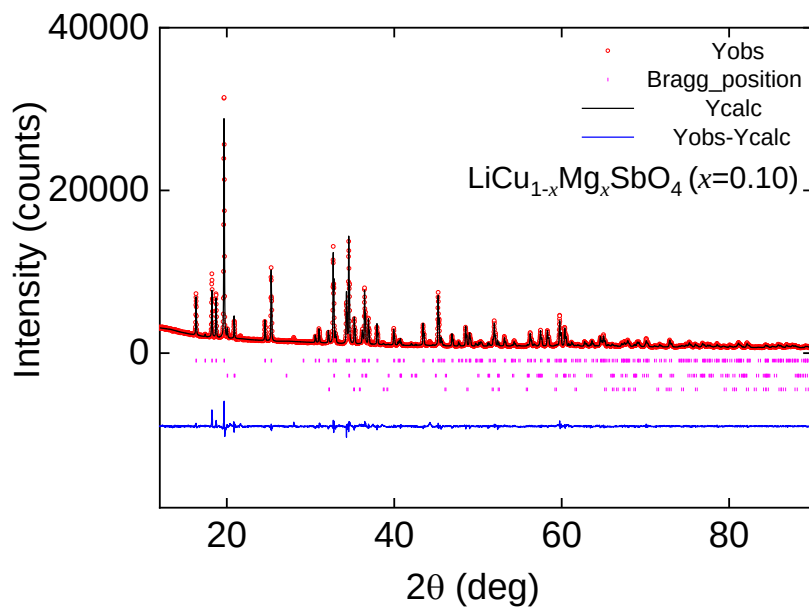
Appendix 12 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.04$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



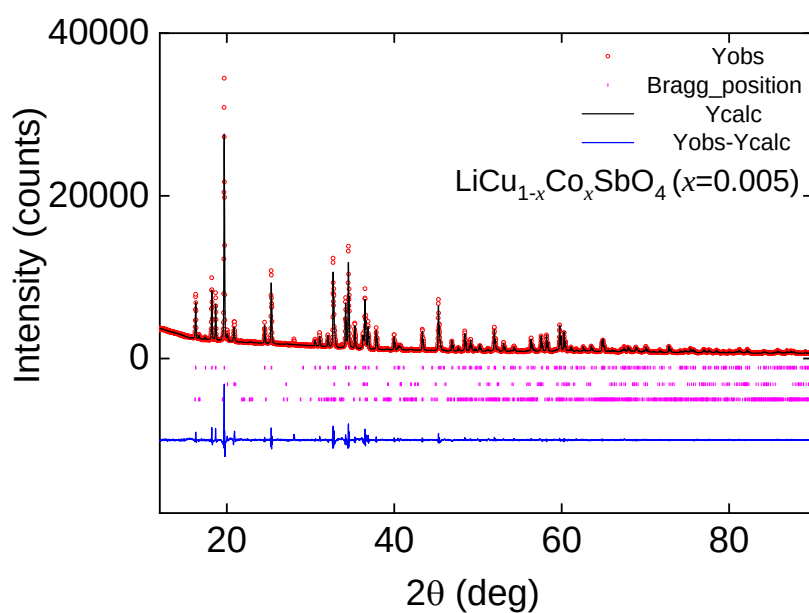
Appendix 13 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.06$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



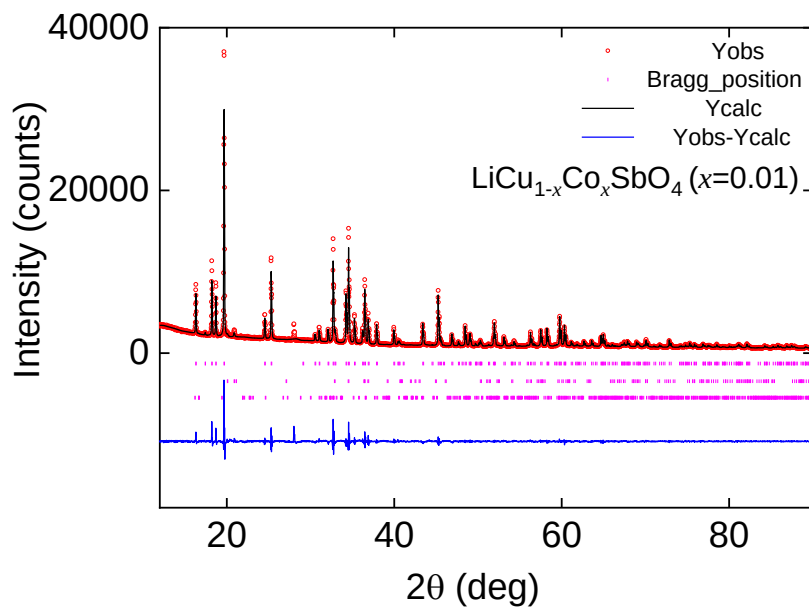
Appendix 14 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.08$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



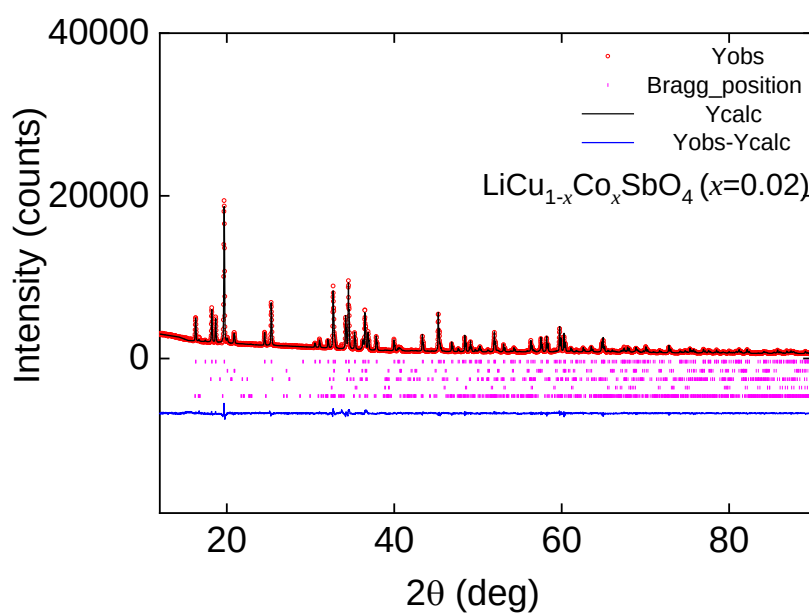
Appendix 15 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$ ($x=0.1$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



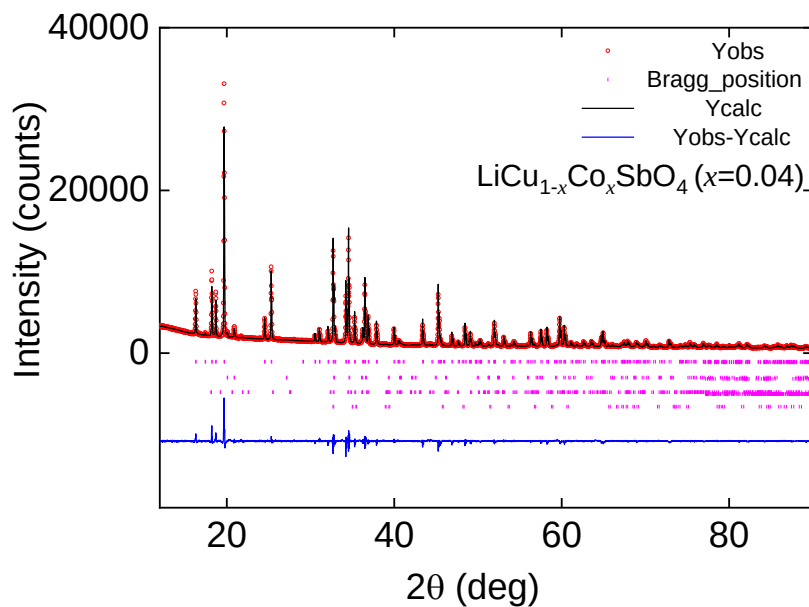
Appendix 16 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.005$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



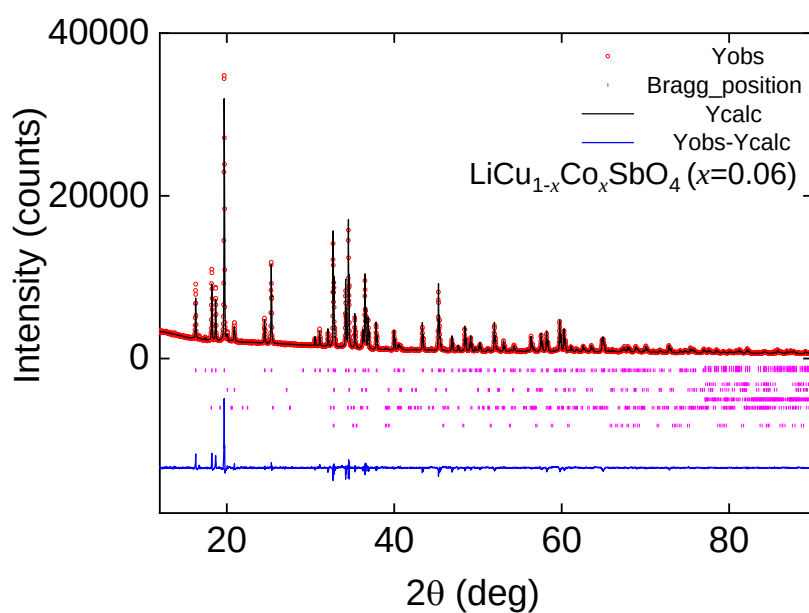
Appendix 17 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.01$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



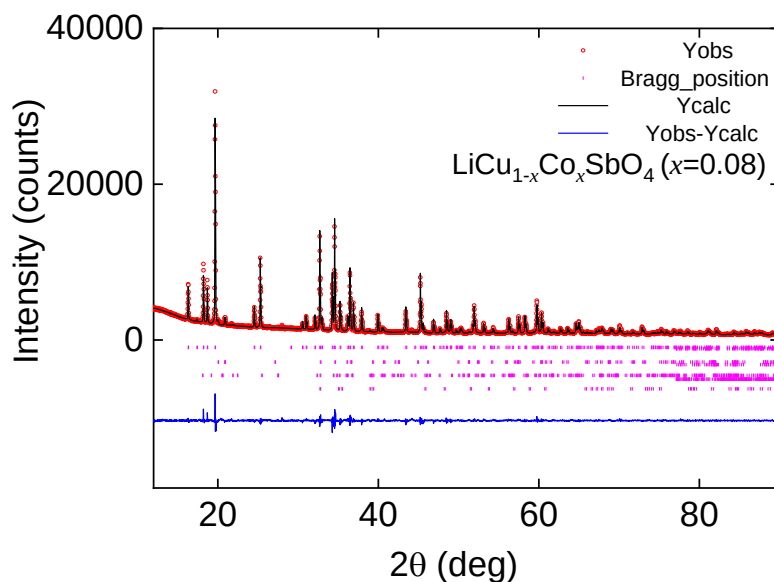
Appendix 18 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.02$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



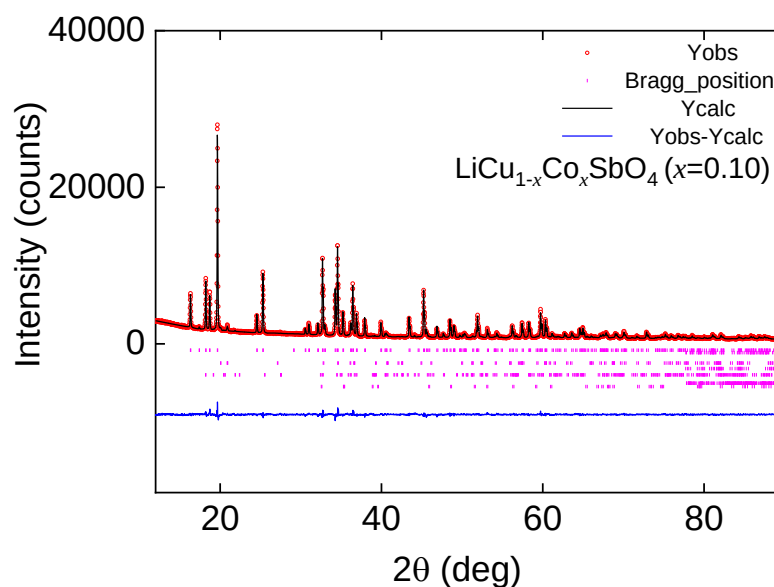
Appendix 19 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.04$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



Appendix 20 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.06$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



Appendix 21 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.08$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot



Appendix 22 X-ray diffraction pattern for $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ ($x=0.1$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.

Appendix 23 Summary of XRD refinement of $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$

	x	0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
a		5.74905(3)	5.75026(3)	5.75044(3)	5.75087(4)	5.75365(4)	5.75544(3)	5.75704(3)	5.75917(4)
b		10.88251(5)	10.88211(5)	10.88134(6)	10.87668(7)	10.86833(6)	10.86021(5)	10.85141(6)	10.84188(8)
c		9.74158(4)	9.74073(5)	9.73923(5)	9.73774(6)	9.74079(6)	9.74377 (5)	9.74613(6)	9.74967(7)
V		609.473(8)	609.526(9)	609.408(9)	609.10(12)	609.12(11)	609.037(9)	608.86(10)	608.77(12)
Rp		3.33	3.28	3.18	3.81	3.77	3.32	3.86	3.53
Rwp		4.33	4.33	4.31	5.39	5.08	4.29	5.05	4.62
Rexp		2.71	2.75	2.66	2.69	2.72	2.77	2.86	2.8
χ^2		2.55	2.49	2.62	4.01	3.5	2.4	3.11	2.72
positions	Sb1 y	0.31056(2)	0.31106(2)	0.31085(2)	0.31036(3)	0.31242(2)	0.31389(2)	0.31507(2)	0.31177(3)
	Sb1 Z	0.27072(4)	0.27064(5)	0.26962(5)	0.27269(8)	0.26965(5)	0.27412(4)	0.27309(5)	0.26823(6)
	Sb2 y	0.16785(2)	0.16746(2)	0.16692(3)	0.16686(4)	0.16877(2)	0.16977(2)	0.17147(3)	0.16837(3)
	Sb2 Z	-0.00393(5)	-0.00450(5)	-0.00547(5)	-0.00337(7)	-0.00542(5)	-0.00219(4)	-0.00291(5)	-0.00729(6)
	Cu y	0.41007(3)	0.41062(3)	0.41059(3)	0.41264(5)	0.41013(3)	0.40889(3)	0.40742(3)	0.41013(3)
	Zn y	0.41007(3)	0.41062(3)	0.41059(3)	0.41264(5)	0.41013(3)	0.40889(3)	0.40742(3)	0.41013(3)
	Li1 y	0.34296(0)	0.31157(0)	0.35758(0)	0.35192(7)	0.34296(0)	0.16884(0)	1.00262(0)	0.95966(0)
	Li1 Z	0.69726(0)	0.67543(0)	0.72595(0)	0.73587(0)	0.69726(0)	0.52845(0)	1.19164(0)	0.79135(0)
	Li2 y	0.37860(0)	0.34690(0)	0.35394(0)	0.37501(0)	0.37860(0)	0.57431(0)	-0.08411(3)	0.12627(0)
	Li2 z	0.69726(0)	0.74916(0)	0.67807(0)	0.65977(1)	0.69726(0)	0.35789(0)	1.06874(4)	0.49248(0)
	Li3 x	0.02534(0)	0.06945(0)	0.06418(0)	0.03721(0)	0.02534(0)	0.04643(0)	0.16765(14)	-4.50620(0)
	Li3 y	-0.00012(0)	0.01734(0)	-0.00012(0)	-0.00847(11)	-0.00012(0)	0.01144(0)	0.08246(8)	0.15093(0)
	Li3 z	0.26558(0)	0.25713(0)	0.23239(0)	0.27116(2)	0.26558(0)	0.22990(0)	0.18604(9)	0.20974(0)
	O1 y	0.00517(17)	0.00239(19)	0.00777(2)	0.01814(3)	0.00292(19)	-0.00240(2)	-0.00196(2)	-0.00375(2)
	O1 z	0.08601(17)	0.07817(17)	0.07275(19)	0.06944(3)	0.07705(18)	0.08543(17)	0.08926(2)	0.09016(2)
	O2 y	0.32321(2)	0.32635(2)	0.32318(3)	0.32079(3)	0.32121(2)	0.33191(2)	0.33937(2)	0.31008(3)
	O2 z	0.89397(15)	0.90031(16)	0.89898(18)	0.88615(3)	0.90149(15)	0.87453(15)	0.87808(2)	0.90160(2)
	O3 y	0.46054(2)	0.46016(2)	0.46577(2)	0.47736(4)	0.46631(2)	0.47006(19)	0.46259(2)	0.47325(2)
	O3 z	0.14366(16)	0.13966(17)	0.13387(18)	0.13523(2)	0.13956(17)	0.14541(16)	0.14491(2)	0.13781(2)
	O4 x	0.24186(14)	0.23581(15)	0.22818(16)	0.23439(2)	0.23634(15)	0.24812(14)	0.24199(18)	0.21505(18)
	O4 y	0.22062(12)	0.22254(13)	0.22468(14)	0.23362(3)	0.22302(13)	0.21519(11)	0.21606(14)	0.21829(15)
	O4 z	0.14060(14)	0.13310(16)	0.13052(18)	0.12163(3)	0.14102(15)	0.14461(15)	0.14409(17)	0.13177(2)
	O5 y	0.15476(19)	0.15785(19)	0.16115(2)	0.15103(3)	0.16107(2)	0.17239(19)	0.18739(2)	0.16797(3)
	O5 z	0.37705(15)	0.37981(15)	0.38059(17)	0.37064(2)	0.38530(15)	0.36100(14)	0.36482(19)	0.36823(2)

	O6 x	0.72932(3)	0.72507(3)	0.75484(5)	0.73297(4)	0.73057(4)	0.71259(3)	0.70416(3)	0.79420(3)
	O6 y	0.40509(11)	0.40156(11)	0.39627(11)	0.39391(14)	0.39523(10)	0.40496(11)	0.39928(12)	0.39354(13)
	O6 z	0.36900(14)	0.37192(15)	0.36484(15)	0.36417(19)	0.37708(14)	0.37751(14)	0.39012(16)	0.35991(17)
phases	LiCuSbO4	96.4(6)	96.1(3)	96.5(4)	97.0(7)	98.5(3)	97.6(4)	98.4(4)	98.3(4)
	LiSbO3	3.0(11)	2.98(8)	2.65(8)	2.2(14)	1.37(7)	1.59(8)	1.32(7)	1.5(10)
	Li3Cu2SbO6	-	-	-	-	-	-	-	-
	CuO	-	-	-	-	-	0.53(9)	0.18(0)	0.14(0)
	Sb2O3	0.67(4)	0.90(5)	0.81(5)	0.86(7)	0.13(4)	0.33(4)	0.15(5)	0.07(5)

Appendix 24 Summary of refinement of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$

	x	0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
a		5.74905(3)	5.74907(2)	5.74908(3)	5.75064(3)	5.75443(3)	5.75789(3)	5.76059(5)	5.76348(4)
b		10.88251(5)	10.88127(4)	10.87947(5)	10.87828(6)	10.87060(6)	10.86434(6)	10.85767(9)	10.85123(7)
c		9.74158(4)	9.73933(4)	9.73774(5)	9.73779 (5)	9.73491(5)	9.73415(5)	9.73306(8)	9.73172(6)
V		609.473(8)	609.265(7)	609.066(9)	609.168(9)	608.96(10)	608.926(9)	608.77(15)	608.63(12)
Rp		3.33	3.61	3.7	3.92	3.79	3.52	3.85	3.88
Rwp		4.33	4.86	5.06	5.35	5.13	4.81	5.38	5.32
Rexp		2.71	2.58	2.6	2.73	2.64	2.66	2.74	2.66
χ^2		2.55	3.55	3.79	3.85	3.78	3.28	3.86	4
positions	Sb1 y	0.31056(2)	0.31041(19)	0.31086(0)	0.31015(3)	0.31153(2)	0.31194(2)	0.31174(3)	0.31232(2)
	Sb1 Z	0.27072(4)	0.26860(3)	0.26886(0)	0.26986(6)	0.27131(5)	0.27041(5)	0.27050(7)	0.27055(5)
	Sb2 y	0.16785(2)	0.16644(0)	0.16657(10)	0.16635(3)	0.16820(3)	0.16764(2)	0.16772(3)	0.16791(3)
	Sb2 Z	-0.00393(5)	-0.00599(0)	-0.00516(4)	-0.00604(6)	-0.00406(5)	-0.00468(5)	-0.00494(7)	-0.00488(6)
	Cu y	0.41007(3)	0.41108(2)	0.41069(3)	0.41076(4)	0.41029(3)	0.41150(0)	0.41118(4)	0.41128(4)
	Mg y	0.41007(3)	0.41108(2)	0.41069(3)	0.41076(4)	0.41029(3)	0.41150(0)	0.41118(4)	0.41128(4)
	Li1 y	0.34296(0)	0.35104(0)	0.35367(13)	0.35658(0)	0.41028(0)	0.34653(0)	0.34296(0)	0.34296(0)
	Li1 Z	0.69726(0)	0.72910(0)	0.72379(14)	0.85366(0)	0.83127(0)	0.73322(0)	0.69726(0)	0.69726(0)
	Li2 y	0.37860(0)	0.37639(0)	0.36249(12)	0.35116(0)	0.37760(0)	0.35442(0)	0.37860(0)	0.37860(0)
	Li2 z	0.69726(0)	0.68367(0)	0.65847(15)	0.78221(0)	0.77209(0)	0.66158(0)	0.69726(0)	0.69726(0)
	Li3 x	0.02534(0)	0.05243(0)	0.03943(2)	-0.04549(0)	-0.42503(0)	0.03642(0)	0.02534(0)	0.02534(0)
	Li3 y	-0.00012(0)	0.01556(0)	0.01728(5)	-0.03493(0)	-0.12312(0)	-0.01081(0)	-0.00012(0)	-0.00012(0)
	Li3 z	0.26558(0)	0.28231(0)	0.28584(8)	0.14810(0)	0.28980(0)	0.23208(0)	0.26558(0)	0.26558(0)
	O1 y	0.00517(17)	0.00759(16)	0.00707(2)	0.01812(2)	0.01516(2)	0.01401(18)	0.01037(3)	0.01620(2)
	O1 z	0.08601(17)	0.07587(16)	0.07256(19)	0.07438(2)	0.07883(17)	0.07080(17)	0.07406(2)	0.07049(19)
	O2 y	0.32321(2)	0.31594(2)	0.31371(2)	0.30807(3)	0.31931(2)	0.32283(2)	0.32955(3)	0.32555(2)
	O2 z	0.89397(15)	0.90780(16)	0.90750(19)	0.91465(2)	0.90102(18)	0.90172(17)	0.89803(19)	0.89626(18)
	O3 y	0.46054(2)	0.46099(2)	0.46393(2)	0.46786(2)	0.47544(2)	0.46751(2)	0.47213(3)	0.47070(2)
	O3 z	0.14366(16)	0.13704(15)	0.13947(2)	0.12329(2)	0.11974(15)	0.13637(16)	0.13633(2)	0.13522(17)
	O4 x	0.24186(14)	0.22421(15)	0.22551(17)	0.20617(19)	0.22605(16)	0.23049(15)	0.23961(2)	0.23480(16)
	O4 y	0.22062(12)	0.22533(12)	0.22692(15)	0.22826(18)	0.23483(17)	0.22763(14)	0.22513(18)	0.22992(16)
	O4 z	0.14060(14)	0.13007(14)	0.13138(18)	0.11462(19)	0.13032(18)	0.13021(17)	0.13130(0)	0.12675(19)
	O5 y	0.15476(19)	0.16328(18)	0.16004(2)	0.16150(2)	0.14878(2)	0.15770(2)	0.15832(0)	0.15536(2)
	O5 z	0.37705(15)	0.38486(14)	0.38461(17)	0.38046(18)	0.37607(16)	0.38236(16)	0.38285(5)	0.37648(18)

	O6 x	0.72932(3)	0.74294(4)	0.73929(4)	0.78318(4)	0.72425(4)	0.73593(4)	0.72653(6)	0.73474(4)
	O6 y	0.40509(11)	0.39431(9)	0.39562(11)	0.38875(11)	0.39458(11)	0.39678(10)	0.39746(15)	0.39689(11)
	O6 z	0.36900(14)	0.37115(14)	0.37352(17)	0.35776(15)	0.37488(15)	0.37837(16)	0.37140(18)	0.37705(17)
phases	LiCuSbO4	96.4(6)	94.8(3)	95.0(4)	97.0(4)	92.5(4)	96.6(4)	96.5(5)	94.6(4)
	LiSbO3	3.0(11)	4.04(7)	4.13(8)	2.58(9)	3.77(8)	2.92(8)	3.4(11)	3.92(8)
	CuO	-	0.96(9)	0.32(0)	0.41(0)	3.4(14)	0.3(10)	0.00(0)	1.1(12)
	Sb2O3	0.67(4)	0.21(4)	0.53(4)	0.04(5)	0.35(4)	0.21(4)	0.15(7)	0.46(4)

Appendix 25 Summary of the crystal structure parameters from Rietveld refinement of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$

	x	0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
a		5.74905(3)	5.74787(4)	5.75786(4)	5.75128(3)	5.75440(3)	5.74769(3)	5.76180(3)	5.76597(3)
b		10.88251(5)	10.88121(7)	10.86632(7)	10.88108(5)	10.87282(5)	10.88187(5)	10.85966(5)	10.85641(5)
c		9.74158(4)	9.73967(6)	9.73509(6)	9.73901(5)	9.73641(5)	9.73875(4)	9.73444(5)	9.73551(4)
V		609.473(8)	609.15(12)	609.09(12)	609.469(9)	609.1749(9)	609.116(8)	608.096(9)	608.421(8)
Rp		3.33	4.04	4.03	3.29	3.31	3.57	3.55	3.04
Rwp		4.33	5.82	5.82	4.32	4.52	4.67	4.7	3.91
Rexp		2.71	2.58	2.6	2.76	2.57	2.59	2.63	2.75
c2		2.55	5.1	5.02	2.45	3.09	3.23	3.2	2.02
positions	Sb1 y	0.31056(2)	0.30984(4)	0.31153(3)	0.31094(2)	0.30930(2)	0.30914(2)	0.31214(2)	0.31242(18)
	Sb1 Z	0.27072(4)	0.26934(7)	0.27054(8)	0.27114(5)	0.26897(5)	0.26745(5)	0.27031(5)	0.27044(4)
	Sb2 y	0.16785(2)	0.16924(4)	0.16874(3)	0.16769(3)	0.16659(3)	0.16626(3)	0.16824(3)	0.16807(2)
	Sb2 z	-0.00393(5)	-0.00549(8)	-0.00382(7)	-0.00405(5)	-0.00636(5)	-0.00636(5)	-0.00481(5)	-0.00389(4)
	Cu y	0.41007(3)	0.41123(4)	0.41001(4)	0.41072(3)	0.41156(3)	0.41096(3)	0.41010(3)	0.41068(2)
	Co y	0.41007(3)	0.41123(4)	0.41001(4)	0.41072(3)	0.41156(3)	0.41096(3)	0.41010(3)	0.41068(2)
	Li1 y	0.34296(0)	0.39695(0)	0.50248(0)	0.34296(0)	0.34296(0)	0.34296(0)	0.34296(0)	0.34296(0)
	Li1 Z	0.69726(0)	0.70534(0)	0.41655(0)	0.69726(0)	0.69726(0)	0.69726(0)	0.69726(0)	0.69726(0)
	Li2 y	0.37860(0)	0.35571(0)	0.35074(0)	0.37860(0)	0.37860(0)	0.37860(0)	0.37860(0)	0.37860(0)
	Li2 z	0.69726(0)	0.68694(0)	0.64673(0)	0.69726(0)	0.69726(0)	0.69726(0)	0.69726(0)	0.69726(0)
	Li3 x	0.02534(0)	0.04537(0)	0.03465(0)	0.02534(0)	0.02534(0)	0.02534(0)	0.02534(0)	0.02534(0)
	Li3 y	-0.00012(0)	-0.00806(0)	0.00128(0)	-0.00012(0)	-0.00012(0)	-0.00012(0)	-0.00012(0)	-0.00012(0)
	Li3 z	0.26558(0)	0.26615(0)	0.25312(0)	0.26558(0)	0.26558(0)	0.26558(0)	0.26558(0)	0.26558(0)
	O1 y	0.00517(17)	0.00676(3)	-0.00355(3)	0.00746(2)	0.01918(2)	0.01088(2)	0.00372(2)	0.00148(15)
	O1 z	0.08601(17)	0.07381(2)	0.08360(2)	0.07950(18)	0.06923(17)	0.07166(17)	0.08011(17)	0.08336(14)
	O2 y	0.32321(2)	0.32503(4)	0.31482(3)	0.32626(2)	0.32073(2)	0.31203(2)	0.32446(2)	0.32361(19)
	O2 z	0.89397(15)	0.89290(2)	0.89459(2)	0.88823(17)	0.90426(18)	0.91484(17)	0.89372(17)	0.89706(13)
	O3 y	0.46054(2)	0.46766(3)	0.46278(3)	0.46789(2)	0.46021(2)	0.45935(2)	0.46640(2)	0.46139(18)
	O3 z	0.14366(16)	0.13907(3)	0.15421(2)	0.13630(17)	0.13534(17)	0.13752(17)	0.13936(17)	0.14400(14)
	O4 x	0.24186(14)	0.23584(2)	0.23308(2)	0.24141(16)	0.21894(16)	0.20363(16)	0.23701(15)	0.23561(12)
	O4 y	0.22062(12)	0.22925(2)	0.21873(18)	0.22282(14)	0.23063(15)	0.22966(15)	0.22548(14)	0.22572(10)
	O4 z	0.14060(14)	0.13879(2)	0.14474(2)	0.13712(17)	0.12450(17)	0.12552(18)	0.13651(17)	0.14005(13)
	O5 y	0.15476(19)	0.15366(3)	0.16032(3)	0.15954(2)	0.16095(2)	0.16517(19)	0.15414(2)	0.15623(16)
	O5 z	0.37705(15)	0.37791(2)	0.38251(2)	0.37317(17)	0.38641(15)	0.38561(14)	0.37637(16)	0.37687(13)
	O6 x	0.72932(3)	0.73993(6)	0.73653(6)	0.73543(4)	0.77401(4)	0.78505(3)	0.73226(4)	0.73006(3)

	O6 y	0.40509(11)	0.39970(15)	0.39857(14)	0.40025(12)	0.39401(11)	0.38957(10)	0.40196(11)	0.40136(9)
	O6 z	0.36900(14)	0.36394(2)	0.38150(2)	0.36662(15)	0.36258(14)	0.36219(15)	0.37319(16)	0.37394(12)
phases	LiCuSbO4	96.4(6)	92.1(5)	97.2(5)	92.9(4)	94.7(4)	93.8(4)	93.1(3)	96.4(5)
	LiSbO3	3.0(11)	5.2(11)	1.6(10)	4.60(9)	3.8(14)	5.2(13)	5.10(1)	1.69(5)
	Li3Cu2SbO6	-	2.2(16)		0.20(9)	0.52(9)	0.36(8)	0.41(0)	1.01(7)
	CuO	-			0.5(12)	0.8(12)	0.7(11)	1.15(0)	0.80(9)
	Li3CuSbO5			0.2(15)	1.6(18)	-	-		
	Sb2O3	0.67(4)	0.47(5)	1.05(5)	0.13(5)	0.21(4)	-	0.30(4)	0.10(3)

Appendix 26 Bond lengths and bond angles of $\text{LiCu}_{1-x}\text{Zn}_x\text{SbO}_4$

x		0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
lengths	Cu-Cu	2.87487(0)	2.87571(0)	2.87545(0)	2.876(8)	2.87765(0)	2.878 (0)	2.879(6)	2.880(6)
	Cu-O1	1.902(12)	1.909(13)	1.921(14)	1.96(3)	1.911(14)	1.921(14)	1.929(15)	1.899(15)
	Cu-O2	2.008(13)	1.964(13)	1.986(18)	2.07(3)	1.982(14)	2.065(13)	2.026(14)	2.07(2)
	Cu-O3	2.081(13)	2.051(13)	2.032(14)	2.07(2)	2.071(13)	2.126(13)	2.121(15)	2.110(15)
	Cu-O4	2.476(14)	2.424(15)	2.392(17)	2.28(4)	2.455(15)	2.532(14)	2.507(16)	2.456(18)
	Cu-O5	2.000(12)	1.998(12)	2.006(13)	2.030(17)	1.978(12)	2.164(13)	2.188(16)	2.084(19)
	Cu-O6	2.385(13)	2.399(14)	2.480(14)	2.487(17)	2.434(13)	2.357(13)	2.367(14)	2.546(16)
angles	Cu-O1-Cu	98.2(4)	97.7(4)	96.9(4)	94.5(5)	97.7(4)	97.0(4)	94.4(4)	95.3(4)
	Cu-O2-Cu	91.4(3)	94.1(4)	92.8(4)	87.9(5)	93.1(4)	88.3(3)	92.5(4)	91.2(4)
	Cu-O3-Cu	87.3(3)	89.0(3)	90.0(4)	88.0(4)	88.0(3)	85.2(3)	87.2(4)	88.8(4)
	Cu-O5-Cu	91.9(3)	92.0(3)	91.5(4)	90.1(4)	93.3(3)	83.3(3)	80.6(3)	84.7(4)

Appendix 27 Bond lengths and bond angles of $\text{LiCu}_{1-x}\text{Mg}_x\text{SbO}_4$

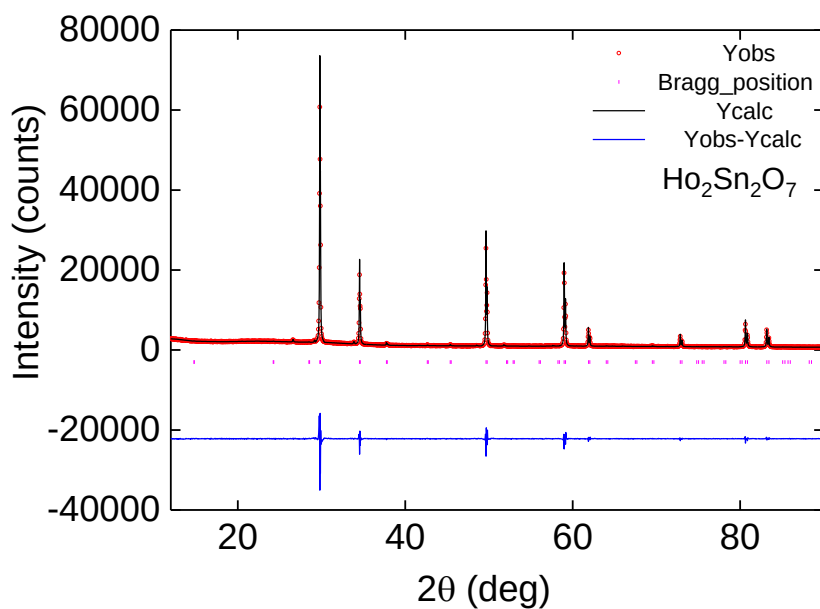
x		0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
lengths	Cu-Cu	2.87487(0)	2.875(14)	2.875(6)	2.875(6)	2.87765(0)	2.878 (0)	2.87925(3)	2.8802 (3)
	Cu-O1	1.902(12)	1.927(17)	1.917(15)	1.976(16)	1.988(15)	1.946(13)	1.93(2)	1.959(15)
	Cu-O2	2.008(13)	1.986(18)	1.993(15)	2.01(3)	1.996(14)	1.978(14)	1.959(18)	1.988(14)
	Cu-O3	2.081(13)	2.035(14)	2.058(14)	1.985(14)	1.980(12)	2.052(12)	2.064(17)	2.056(13)
	Cu-O4	2.476(14)	2.39(2)	2.378(17)	2.29(2)	2.295(19)	2.369(16)	2.392(17)	2.325(19)
	Cu-O5	2.000(12)	1.994(15)	1.983(14)	1.997(14)	1.985(12)	1.987(13)	1.98(4)	2.010(14)
	Cu-O6	2.385(13)	2.462(19)	2.442(14)	2.591(14)	2.450(14)	2.397(13)	2.429(18)	2.402(14)
angles	Cu-O1-Cu	98.2(4)	96.4(4)	97.5(4)	92.1(4)	92.7(4)	95.4(4)	96.2(4)	94.7(4)
	Cu-O2-Cu	91.4(3)	92.7(4)	91.9(4)	92.5(4)	92.2(4)	93.4(4)	94.7(4)	92.9(4)
	Cu-O3-Cu	87.3(3)	89.9(4)	88.3(4)	94.1(4)	93.2(3)	89.1(3)	88.5(4)	89.0(3)
	Cu-O5-Cu	91.9(3)	92.2(4)	93.3(4)	90.9(4)	92.9(4)	92.9(4)	93.1(5)	91.6(4)

Appendix 28 bond lengths of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of x .

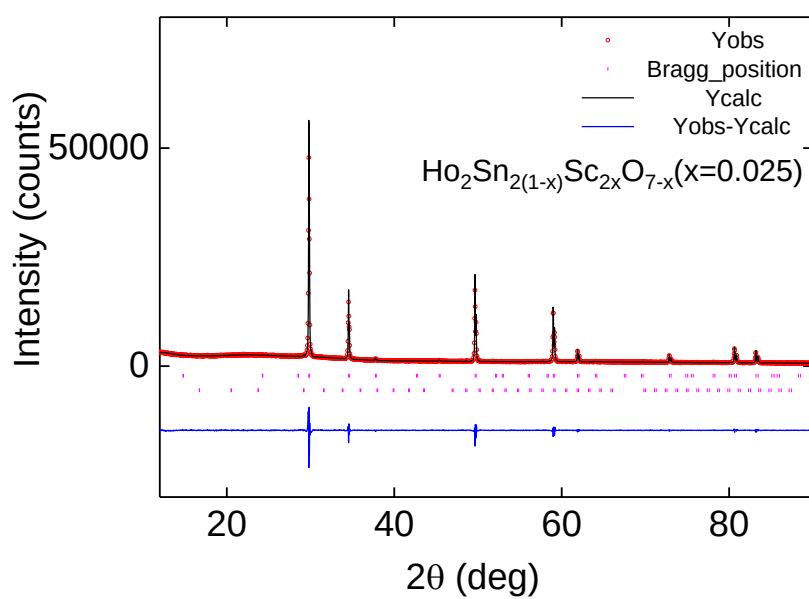
x	0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
Cu-Cu	2.87453(0)	2.873(9)	2.87893(2)	2.87564(0)	2.87720(0)	2.87385(0)	2.88090(0)	2.88299(0)
Cu-O1	1.902(12)	1.92(2)	1.901(19)	1.940(14)	1.972(15)	1.933(14)	1.928(14)	1.926(11)
Cu-O2	2.008(13)	2.01(3)	2.05(2)	2.025(14)	1.977(14)	1.978(14)	2.005(14)	1.994(12)
Cu-O3	2.081(13)	2.07(3)	2.157(17)	2.054(13)	2.020(13)	2.032(13)	2.070(13)	2.085(11)
Cu-O4	2.476(14)	2.40(3)	2.51(2)	2.442(16)	2.318(17)	2.336(17)	2.406(16)	2.429(12)
Cu-O5	2.000(12)	1.995(18)	1.987(17)	2.046(13)	1.979(12)	1.998(12)	2.002(13)	2.010(10)
Cu-O6	2.385(13)	2.448(18)	2.380(17)	2.435(14)	2.505(13)	2.559(13)	2.387(14)	2.384(11)

Appendix 29 Bond angles of $\text{LiCu}_{1-x}\text{Co}_x\text{SbO}_4$ as a function of x .

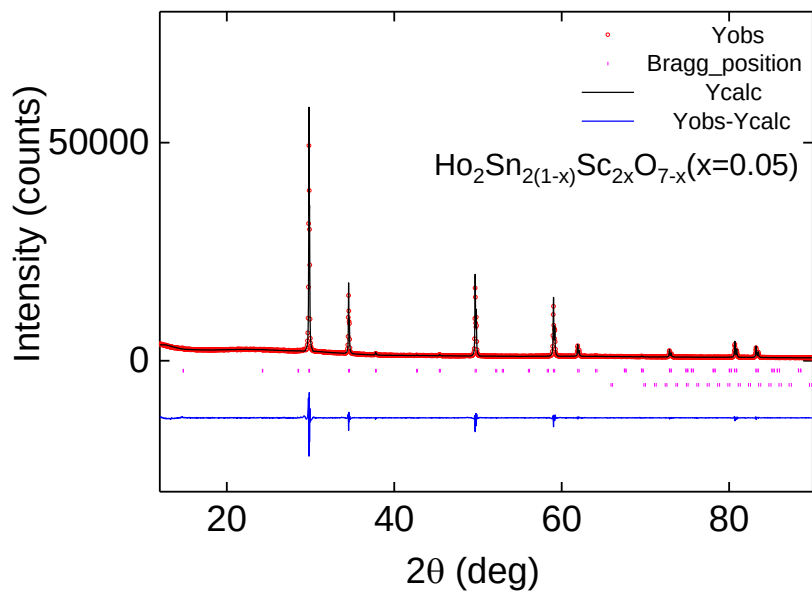
x	0	0.005	0.01	0.02	0.04	0.06	0.08	0.1
Cu-O1-Cu	98.2(4)	97.2(4)	98.4(4)	95.6(4)	93.7(4)	96.0(4)	96.7(4)	96.9(4)
Cu-O2-Cu	91.4(3)	91.4(4)	89.5(4)	90.5(4)	93.4(4)	93.2(4)	91.9(4)	92.6(3)
Cu-O3-Cu	87.3(3)	88.0(5)	83.7(3)	88.9(3)	90.8(4)	90.0(4)	88.2(3)	87.5(3)
Cu-O5-Cu	91.9(3)	92.1(4)	92.8(4)	89.3(3)	93.3(3)	92.0(3)	92.0(4)	91.6(3)



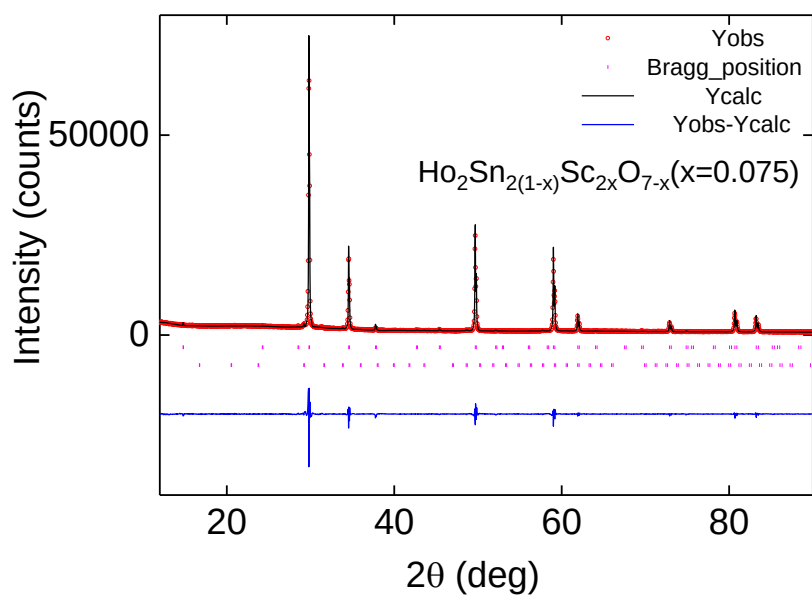
Appendix 30 X-ray diffraction pattern for $\text{Ho}_2\text{Sn}_2\text{O}_7$. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



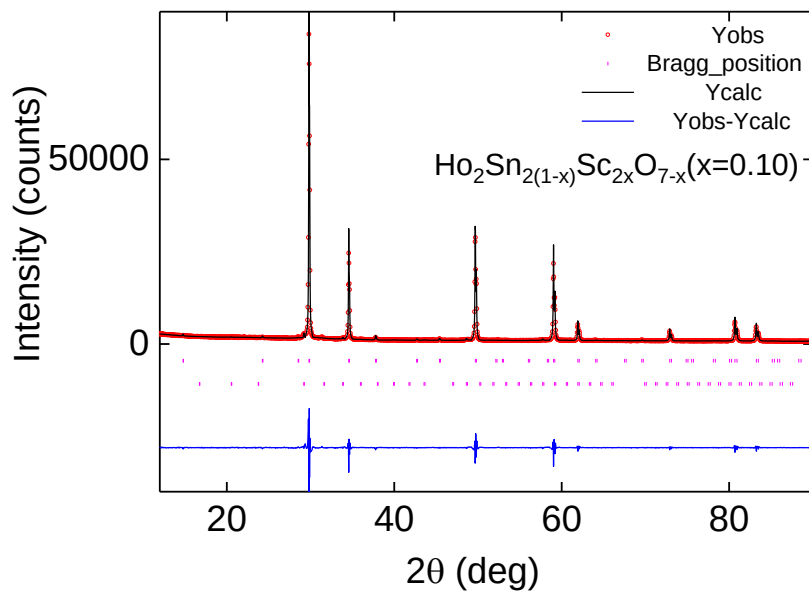
Appendix 31 X-ray diffraction pattern for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.025$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



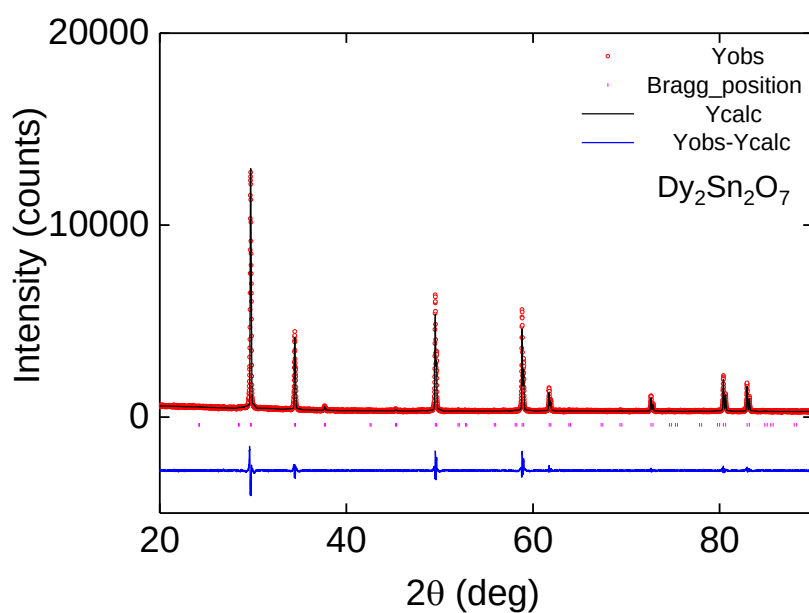
Appendix 32 X-ray diffraction pattern for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.05$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



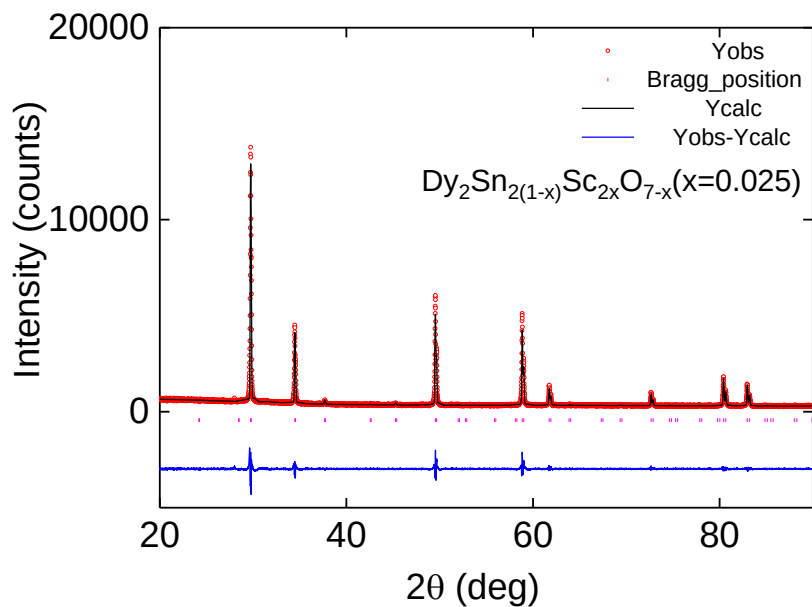
Appendix 33 X-ray diffraction pattern for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.075$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



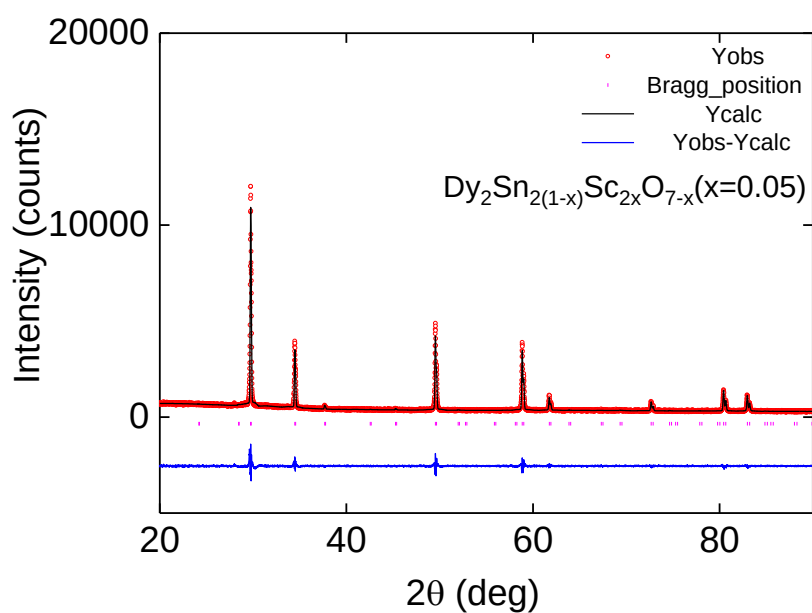
Appendix 34 X-ray diffraction pattern for $\text{Ho}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.10$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



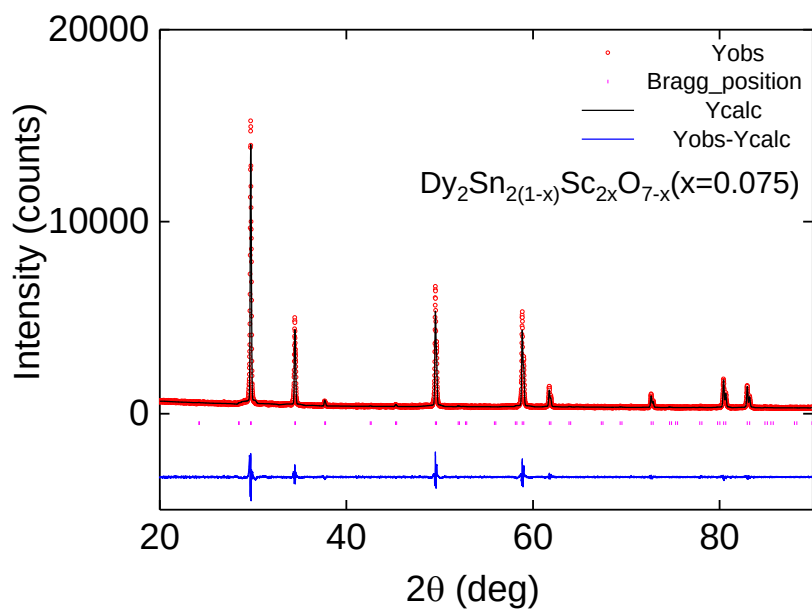
Appendix 35 X-ray diffraction pattern for $\text{Dy}_2\text{Sn}_2\text{O}_7$. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



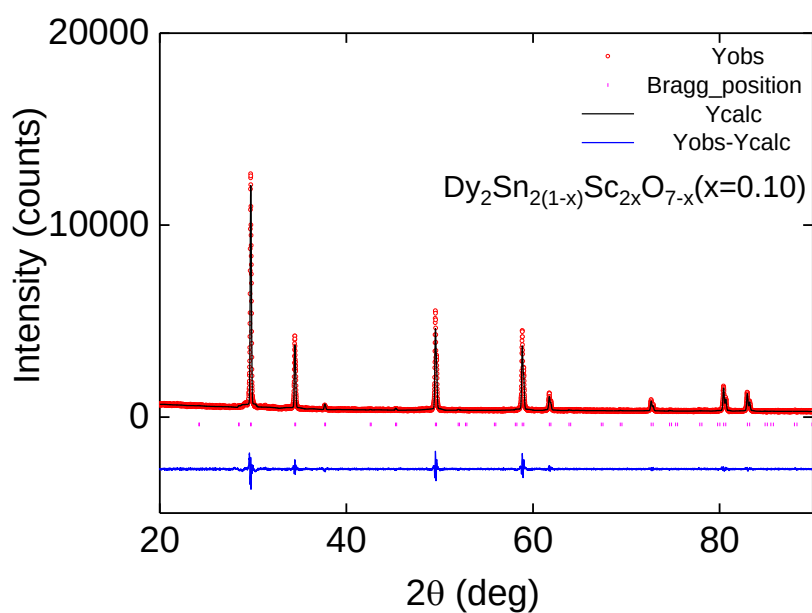
Appendix 36 X-ray diffraction pattern for $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.025$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



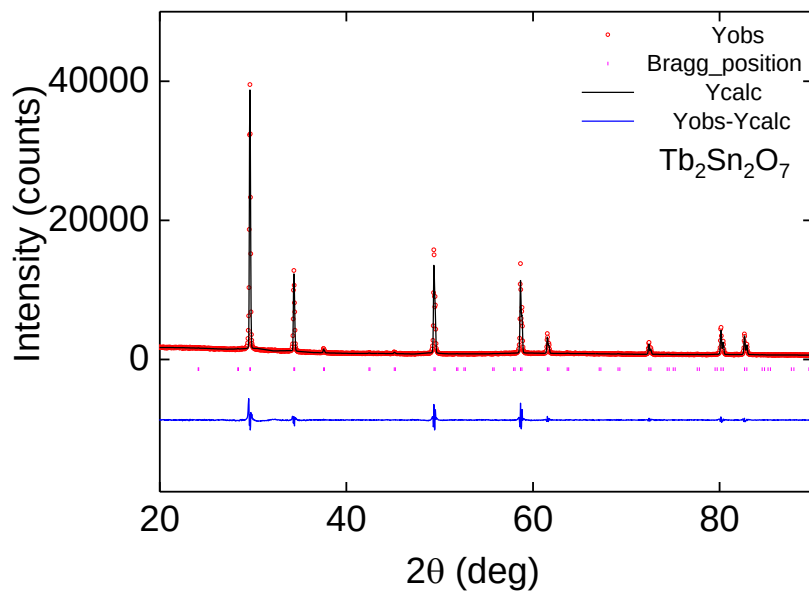
Appendix 37 X-ray diffraction pattern for $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.05$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



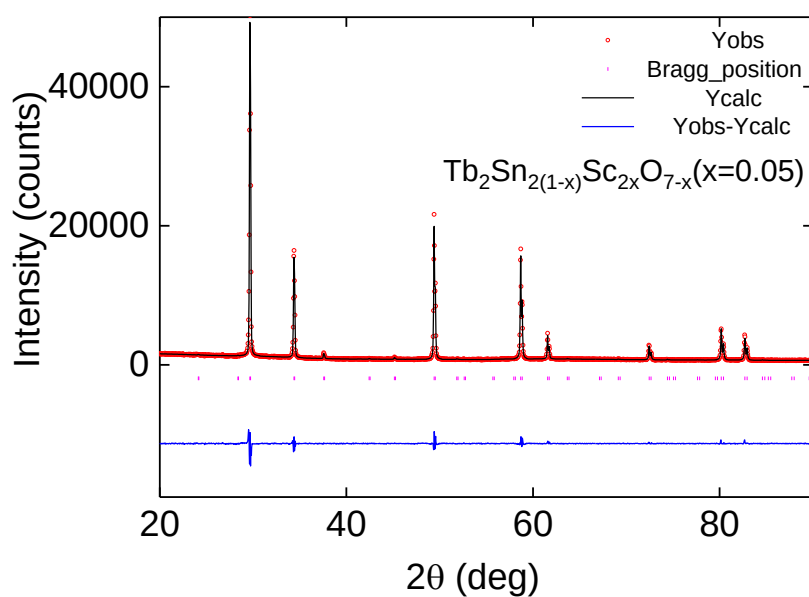
Appendix 38 X-ray diffraction pattern for $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.075$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



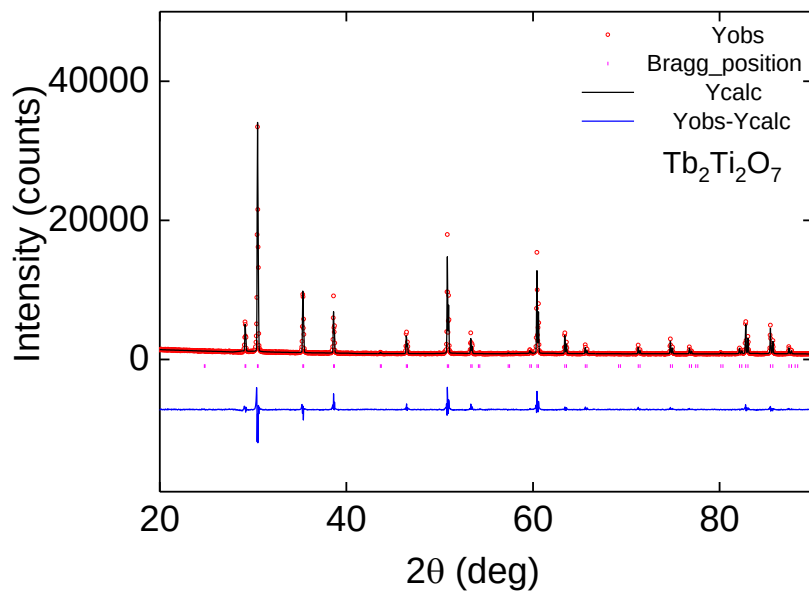
Appendix 39 X-ray diffraction pattern for $\text{Dy}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.10$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



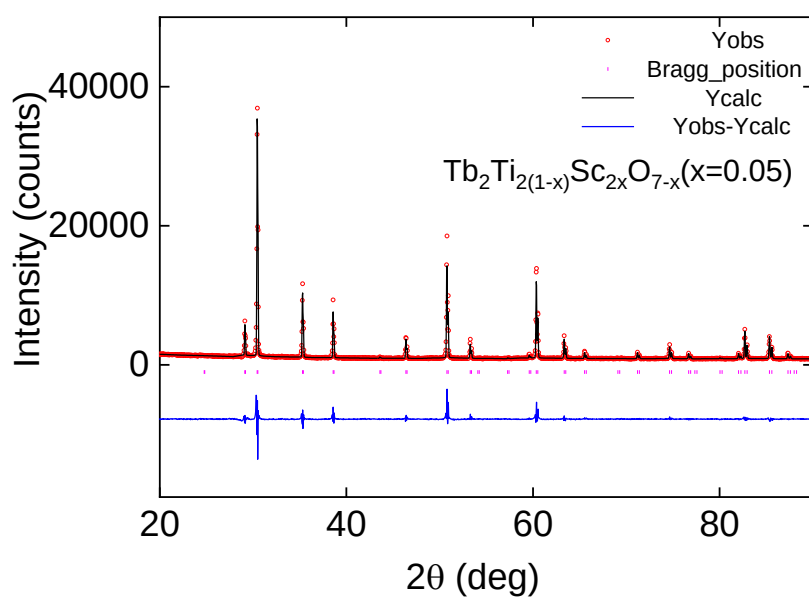
Appendix 40 X-ray diffraction pattern for $\text{Tb}_2\text{Sn}_2\text{O}_7$. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



Appendix 41 X-ray diffraction pattern for $\text{Tb}_2\text{Sn}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.05$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



Appendix 42 X-ray diffraction pattern for $\text{Tb}_2\text{Ti}_2\text{O}_7$. Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.



Appendix 43 X-ray diffraction pattern for $\text{Tb}_2\text{Ti}_{2(1-x)}\text{Sc}_{2x}\text{O}_{7-x}$ ($x=0.05$). Observed data are shown by the red dots and the solid black line is the modelled data. Pink tick marks indicate the position of Bragg reflections. The blue line is the difference plot.