Low-Dimensional Quantum Magnets: Single Crystal Growth and Heat Transport Studies

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Chapter 1

Introduction

In condensed matter, much of the interesting physics is a result of the quantum nature of particles. One of the most fundamental property of particles, the spin, has its origin in the principles of quantum mechanics, and understanding its behaviour is essential to explain the phenomenon of magnetism. In materials, unpaired spins of atoms of a lattice can interact and behave as a collective spin system. At zero temperature, the spin system is in its lowest energy state, the so-called ground state. At higher temperatures, so-called spin excitations are produced in the system that are of a dispersive nature, and are capable of transporting energy.

The reduction of dimensionality of the spin system from three dimensions (3D), leads to the emergence of observable quantum effects. It results in strong quantum fluctuations which increasingly dictate the ground state behavior [1–5]. As opposed to classical ferromagnetic or antiferromagnetic ground states in 3D, in lower dimensions disorder mostly prevails even at $T = 0$ and novel ground states arise, where spins lying far away from each other are able to couple with each other. If spins have a strong coupling in one direction via, say, an intrachain interaction $J$ and a very weak coupling in the other directions via an interchain interaction $J'$, the ratio $J/J'$ determines how well the system displays low-dimensional behavior. A large $J/J'$, like that present in the systems dealt with in this work, allows one to probe the effects of low-dimensionality over a wide range of experimentally accessible temperatures. Analytical and numerical treatment of systems in order to obtain thermodynamic quantities is simplified when the number of spatial dimensions is reduced. Such calculations then can be compared and validated with experiments on materials that closely realize simplified model Hamiltonians. Thus, this field provides for a fruitful interplay of theory and experiment.
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potentially giving scope for an insightful understanding of correlated systems in general.

One particularly interesting property of such low-dimensional systems is heat transport. Heat transfer processes in the solid state have always proved to be of fundamental and applied importance. An insight into the behaviour and interaction of quasiparticles, ground states, and associated excitations in the nonequilibrium state can be obtained from transport phenomena. Conventionally, electrons and phonons were known to be the carriers of heat in solids. However, recently, substantial experimental and theoretical evidence gathered towards establishing the idea that heat can be transported via excitations of the spin system. Large anisotropic heat transport properties have been observed in various low-dimensional cuprate systems like the 1D spin chain compounds, Sr$_2$CuO$_3$ and SrCuO$_2$ [6–10], the 2D Heisenberg antiferromagnet La$_2$CuO$_4$, [11–16], and spin-ladder compounds like (Sr,Ca,La)$_{14}$Cu$_{24}$O$_{41}$ [17, 18] and La$_2$Cu$_2$O$_5$ [19], which cannot be explained by conventional heat transfer processes, and which can arise only due to propagating spin excitations.

The nature of spin excitations is shown to be very different for spin systems with different spatial dimensions, and this makes it very interesting to investigate heat transport in a variety of spin structures. Much of the current interest is due to theoretical discoveries of anomalous transport properties in quantum integrable systems [20, 21]. Due to the integrability of the $S = \frac{1}{2}$ Heisenberg chain, the intrinsic spinon heat transport was predicted to be ‘ballistic’, causing the heat conductivity to diverge [22, 23]. But in real systems scattering mechanisms involving phonons and defects render the system non-integrable. However, experimental evidence of exceptionally large spinon heat conductivity and mean free path in 1D spin chains of the highly pure cuprate materials SrCuO$_2$ and Sr$_2$CuO$_3$, strongly supports the claim of ballistic transport [6–10].

Understanding heat transport in quantum systems has been an unsolved issue from the point of view of both theory and experiment [6–10, 12, 17, 20–40]. There is very little knowledge of the mechanisms and temperature dependence of scattering processes that involve the spin excitations, especially in lower dimensions where the quantum nature of the spin system plays an important role. There do exist some theoretical and experimental works in this regard, which indicate that scattering by impurities at very low temperatures and by phonons at higher temperatures are the processes that dictate the temperature and doping dependence of the mean free path of spin excitations in 1D systems [7–10, 26, 30, 34–37]. Quantitative descriptions in the framework of simplified semi-classical models that include scattering processes with impurities and phonons, in spite of being
empirical in nature, are able to model experimental observations with remarkable accuracy, and have been a valuable input to the theory of quasiparticle heat transport. In the direction of developing a fully quantum mechanical and microscopic theory of heat transport, systematic experimental heat transport experiments on clean and disordered $S = \frac{1}{2}$ low-dimensional systems of various kinds in different temperature regimes would thus be desirable.

Any experimental investigation to probe anisotropy in physical properties of materials requires high quality single crystals. Depending upon the experimental technique, different amount of sample is needed to perform a successful and unambiguous measurement. Measuring and analyzing physical quantities like thermal conductivity with a view to study the contribution from magnetic excitations, magnetic susceptibility, spin-lattice relaxation rates using NMR, and other anisotropic properties requires single crystals with dimensions of the order of a few millimeters. To study dynamic response of materials by probing magnetic excitations at low energies, inelastic neutron scattering is probably the best tool available. Due to low flux of available neutrons beams and weak interactions of neutrons with matter, large single crystals weighing a few grams are necessary for good resolution. It is well known that transport properties are very sensitive to the presence of imperfections and impurities in the crystal. Also, many physical properties, like the appearance of superconductivity in cuprates, depend crucially on factors like stoichiometry. Thus, a systematic study mandates high quality single crystals devoid of impurities. Therefore, a part of this thesis focuses on the growth of single crystals of the materials of interest. We have used the travelling solvent floating zone (TFSZ) method to synthesize large single crystals ranging from a few millimeters to a few centimeters in dimensions.

One interest of this work concerns spin chain compounds, SrCuO$_2$ and Sr$_2$CuO$_3$, where the effect of impurity-induced disorder on spin dynamics and thermal transport properties has been investigated. Theoretically, impurities or defects are known to have strong observable effects on the properties of $S = \frac{1}{2}$ chains [41–45]. Not many systematic experimental studies, apart from a few [32, 46–50], have focussed on this problem, thereby preventing the theoretical results from being verified. As sensitive probes for disorder, thermal transport measurements, nuclear magnetic resonance (NMR) and inelastic neutron scattering (INS) have been used to probe how the ground state, spin excitations and their dispersion are modified in the presence of impurities. With thermal transport studies on the doped versions of these compounds, we systematically address the scattering mechanisms involved and provide evidence for strong spin-phonon coupling in such systems.
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Very little is known about scattering and heat transport in antiferromagnetic 2D spin systems. Investigations on the heat transport properties of the 2D Heisenberg antiferromagnet, La$_2$CuO$_4$, are restricted to low temperatures of 300 K, where the magnetic contribution is still large \([11–16]\). With a view to understand the behaviour of heat conductivity at higher temperatures by shedding light on the scattering mechanisms, heat transport up to very high temperatures has been investigated for the first time. This is aimed at motivating theoretical work on the long-standing problem of magnon transport in 2D. Also, to study the effects of small impurity concentrations on the heat conductivity, single crystals of Ni- and Zn-doped La$_2$CuO$_4$ have been grown.

Among low-dimensional magnets, the class of spin-ladder compounds is of special interest as they are invaluable in understanding the physics of the crossover from 1D to the 2D nature of spin systems. Quantum effects lead to drastic dependencies of their properties on the number of legs in the spin-ladder. For example, gapped and ungapped spin excitation spectra have been predicted and experimentally verified for spin ladders with even and odd number of ladder-legs, respectively, arising from differences in ground states \([51]\). However, experimental realizations of ladder systems are few, especially spin ladders with number of legs greater than two \([52, 53]\). This calls for exploratory and systematic studies for synthesizing new materials that realize such spin-ladders, and motivates a part of the work in this thesis which concerns the crystal growth of a five-leg ladder compound, La$_8$Cu$_7$O$_{19}$. In addition, the single crystal growth of a diamagnetic delafossite, LaCuO$_2$, has been discussed in detail, as single crystals of this compound have been synthesized for the first time.

The thesis is structured as follows. In chapter 2, theoretical concepts of low-dimensional quantum magnets are briefly introduced to illustrate fundamental differences that arise in material properties as a function of dimensionality. In chapter 3, heat transport is discussed in the context of different quasi-particles that carry heat, with an emphasis on magnetic excitations, followed by a short introduction to the different experimental techniques that were used in this work in chapter 4. Chapter 5 introduces structural, magnetic, transport properties of the materials that are investigated with a view to motivate the work carried out in this thesis. Then, in chapter 6, the basics of crystallization processes and the TFSZ method, and the details of the crystal growth experiments are dealt with. Finally, chapters 7, 8, 9, 10 discuss the experimental results for different materials, with an emphasis on their heat transport properties. At the end, a short appendix discusses some inconclusive results of heat transport experiments on Co- and Zn-doped SrCuO$_2$ compounds.
Chapter 2

Low-dimensional systems

The matter below is based on literature available in textbooks, PhD theses and review articles referenced as [2, 3, 51, 54–61].

2.1 Magnetic interactions: Heisenberg model

A two-electron system, like a H₂ molecule, can be considered to understand the origins of magnetic interactions, and the Heisenberg model. The Hamiltonian (\( \hat{H} \)) for this system consists of only terms that describe Coulomb interactions in the system. If we consider the H₂ molecule with two atoms centered at \( \vec{R}_a \) and \( \vec{R}_b \), the Hamiltonian can be written as,

\[
H = H_{at}(\vec{r}_1 - \vec{R}_a) + H_{at}(\vec{r}_2 - \vec{R}_b) - \frac{e^2}{|\vec{r}_1 - \vec{R}_b|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_a|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{R}_a - \vec{R}_b|} \tag{2.1}
\]

The first two terms (\( H_{at} \)) arise from energies of isolated atoms, the next two terms describe the electron-proton attraction, and the last two terms describe the electron-electron and proton-proton repulsion respectively. For a neutral H₂ molecule one expects one electron in each atomic orbital, thus resulting in four
spin configurations: $|↑↑⟩$, $|↑↓⟩$, $|↓↑⟩$, $|↓↓⟩$. These can be chosen as the basis for constructing the eigenstates. For the spin part, if $H$ is isotropic in spin-space then, $s$, the total spin, and $m_s$, the $z$-component of the total spin are good quantum numbers because the corresponding operators commute with the Hamiltonian.

If $\hat{S}^{tot}$ is the total spin operator then,

$$\hat{S}^{tot}^2 = (\hat{S}^a)^2 + (\hat{S}^b)^2 + 2 \hat{S}^a \cdot \hat{S}^b$$  \hspace{1cm} (2.2)

where, $\hat{S}^a$ and $\hat{S}^b$ are the spin operators. The eigenvalue of $(\hat{S}^{tot})^2$ is $s(s+1)$, where $s$ is the total spin quantum number for the two spins combined, which can be 0 or 1. The eigenvalues for $(\hat{S}^a)^2$ and $(\hat{S}^b)^2$ are $\frac{3}{4}$, and that for $\hat{S}^{tot}$ can be 0 or 2. Thus, for the singlet state, $s = 0$, $\hat{S}^a \cdot \hat{S}^b$ takes the value $-\frac{3}{4}$, and for the triplet state, $s = 1$, $\hat{S}^a \cdot \hat{S}^b$ takes the value $\frac{1}{4}$. The system therefore has two energies for $s = 0$ and 1. Each state is $2s+1$ times degenerate. The $z$-component of the spin, $m_s$, is 0 for the singlet state, and either -1, 0 or 1 for the triplet state.

The total wavefunction of the system is a combination of the orbital and spin wavefunctions, and has to be antisymmetric for electrons. Thus, either the spin part has to be symmetric and the orbital part antisymmetric, or the other way round. Thus, the symmetry of the orbital wave-function depends on the value of $s$. In other words, the Coulomb interactions depend on the value of the spin quantum number, and the flipping of spins, and changing the value of the total spin will change the distribution of electrons and the Coulomb energy of the system.

If $\psi_a(r)$ and $\psi_b(r)$ are the orbital wavefunctions of each of the electrons, and $\psi_{AS}$ and $\psi_{S}$ are corresponding antisymmetric and symmetric total orbital wave functions for the two-electron system, one has,

$$\psi_{AS} = \frac{1}{\sqrt{2(1 - \Omega)}} (\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1))$$ \hspace{1cm} (2.3)

$$\psi_{S} = \frac{1}{\sqrt{2(1 + \Omega)}} (\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1))$$ \hspace{1cm} (2.4)

where, $\Omega = \int \psi^*_a(r)\psi_b(r)dr^4$ is the overlap integral. If $\chi(\sigma_1, \sigma_2)$ is the total spin wavefunction, we can write the total wave function for the two-electron system as,
2.1. Magnetic interactions: Heisenberg model

Ferromagnetic order

\[ J > 0 \]

Antiferromagnetic order

\[ J < 0 \]

Figure 2.1: A schematic of a square lattice with spins coupled to each other either ferromagnetically \((J > 0)\) or antiferromagnetically \((J < 0)\).

\[ \Psi_{1,0,-1}^1(\vec{r}_1, \vec{r}_2) = \chi_{1,0,-1}^1(\sigma_1, \sigma_2)\psi_{AS}(\vec{r}_1, \vec{r}_2) \] (2.5)

\[ \Psi_0^0(\vec{r}_1, \vec{r}_2) = \chi_0^0(\sigma_1, \sigma_2)\psi_S(\vec{r}_1, \vec{r}_2) \] (2.6)

where, subscript denotes \(m_s\) and superscript denotes \(s\).

From equations 2.1, 2.3, 2.4, 2.5 and 2.6, with some basic algebra, it is straightforward to derive the energy splitting between the \(s = 0\) and \(s = 1\) states (see [56]), and this can be given as,

\[ E_T - E_S = 2 \left( \frac{\Omega^2 C_{ab} - I_{ab}}{1 - \Omega^4} \right) \] (2.7)

where, \(C_{ab}\) and \(I_{ab}\) are terms that describe Coulomb and exchange energies, respectively.

Knowing the singlet-triplet splitting and the electron wavefunctions, using equation 2.2, one can write an effective Hamiltonian instead of the full interaction Hamiltonian in eq. 2.1 for the system as,
\[ H^{\text{eff}} = \frac{1}{4} (E_S + 3E_T) - (E_S - E_T) \hat{S}^a \cdot \hat{S}^b \]

(2.8)

Here, the orbital and spin degrees of freedom are mapped onto only spin-flips and spin degrees of freedom. The constant term \( \frac{1}{4} (E_S + 3E_T) \) can be neglected as it only marks the absolute position of ground state energy level. And, one can replace the energy difference between the singlet and triplet states with \( J \), the so-called exchange interaction constant and write equation 2.8 as an effective spin Hamiltonian,

\[ H^{\text{spin}} = -J \hat{S}^a \cdot \hat{S}^b \]

(2.9)

From eq. 2.7 and eq. 2.8, depending on the value of \( C_{ab} \), \( I_{ab} \) and \( \Omega \), \( J \) can be positive or negative. For \( J > 0 \), \( E_S > E_T \), and the triplet state is preferred. For \( J < 0 \), \( E_S < E_T \), and the singlet state is preferred. Thus, for \( \Omega > 0 \) and \( \Omega^2 C_{ab} > I_{ab} \), i.e for sufficiently large overlap of orbitals, the coupling is antiferromagnetic. Such a description can be applied to interactions between spin degrees of freedom at sites on a lattice, as illustrated for a square planar lattice in two dimensions in Fig. 2.1. Thus, one can generalize this for many body systems, and we get the so-called Heisenberg model,

\[ \hat{H} = -J \sum_{i,j} \hat{S}_i \cdot \hat{S}_j \]

(2.10)

with \( J_{ij} \) being the exchange constant between the \( i^{th} \) and \( j^{th} \) spins.

### 2.2 Magnetic interactions: Hubbard model

The single band Hubbard model \cite{62} can be used to describe electronic correlations in a many-body system. As we shall see below, it maps a complex system of hybridized states, like the \( O_{2p} \) and \( Cu_{3d} \) states on a simple single-orbital model. The corresponding Hamiltonian can be written as,

\[ \hat{H} = -t \sum_{i,j,\sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + c_{i,\sigma}^\dagger c_{j,\sigma}^\dagger) + U \sum_j n_{j,\uparrow} n_{j,\downarrow} \]

(2.11)
It has two competing terms, $t$: the kinetic energy or the hopping term that favours delocalized charge, and $U$: the on-site electron-electron Coulomb energy.

For the case where $t = 0$ and $U \neq 0$, we have a situation where the atomic sites are decoupled, and two sharp energy levels exist at $E = 0$ and $E = U$, where the addition of each electron costs an energy equal to $U$. If a small $t$ is present ($t < U$, $t \neq 0$), the sharp energy levels turn into bands, namely the lower Hubbard band (LHB) and the upper Hubbard band (UHB). When $t \ll U$, as is the case for the cuprates which are dealt with in this work, the electrons are localized due to strong correlation and a so-called Mott-insulator results. With increasing $t$, the LHB and UHB become broader, and for $t \gg U$, a weakly correlated metal results where electron mobility is high due to band-overlap.

Now, consider two spins on neighbouring sites in a half-filled Hubbard model with $t < U$. For, $t = 0$, the ground state of the system is degenerate with respect to the spin orientation. Antiferromagnetic (AFM) and ferromagnetic (FM) configurations are equally preferred. Whereas, when $t$ is small and $\neq 0$, the AFM state has a lower energy due to the possibility of slight delocalization of charge. For small $t$ compared to $U$, the second-order perturbation theory can be used to find this energy difference due to which an AFM state is energetically preferred. This difference, $\Delta E_{\text{AFM}}$, is found to be equal to $(-4t^2/U)$. Thus, the Hamiltonian for a Mott-insulator at half-filling can be expressed as a Heisenberg Hamiltonian with $J = (-4t^2/U)$ \[61\], i.e. the Hubbard system at half-filling in the limit $t \ll U$ corresponds to an insulator with a system of interacting spins on a lattice. So, we have,

$$\hat{H} = -\sum_{i,j} J \hat{S}_i \cdot \hat{S}_j, \quad J = -4t^2/U. \quad (2.12)$$

Such is the case for insulating cuprates where $t \ll U$. In cuprates, the geometry of the lattice and the valency of the Cu and O atoms provides for an arrangement where two $S = \frac{1}{2}$ electrons can interact via a $180^\circ$ Cu-O-Cu exchange path. A mechanism called the superexchange is facilitated here, resulting in antiferromagnetic interaction \[63\]: There is an exchange interaction between the two Cu spins that is mediated by the non-magnetic O atom lying between them. Single unpaired $d$-electrons sit on each metal atom and two $p$-electrons sit in the outermost O orbitals. An antiferromagnetic coupling between the Cu spins lowers the energy of the system by delocalizing these electrons over the structural unit Cu-O-Cu. The single band Hubbard model describes well the electronic properties in such cuprates, although the three band Hubbard model that incorporates the
Chapter 2. Low-dimensional systems

Figure 2.2: Left: The CuO$_6$ octahedron, that is an integral part of many two-dimensional cuprates like La$_2$CuO$_4$. Right: The energetically split orbitals of Cu due to the crystal field experienced by it in the center of the octahedron.

Cu and O orbitals and their hybridizations achieves a more realistic description. As an example we can look at the parent high $T_c$ superconductor La$_2$CuO$_4$, that realizes the antiferromagnetic $S = \frac{1}{2}$ Heisenberg model on a square lattice [64]. La$_2$CuO$_4$ has an empty shell of La$^{3+}$, a full 2$p$ shell of O$^{2-}$ and Cu$^{2+}$ in the configuration 3$d^9$. These 3$d$ levels of Cu are split due to octahedral crystal field into $t_{2g}$ and $e_g$ orbitals. The Cu-O$_{apical}$ distance is larger than the Cu-O$_{in-plane}$ distance. Thus, the orbitals of Cu pointing out of plane, towards the apical oxygen (3$d^{x^2-y^2}$) have lower energy. The last 3$d^9$ unpaired electron therefore sits here. The octahedral CuO$_6$ unit along with the energetically split orbitals are shown in Fig. 2.2. The hybridized O$_{2p}$ and Cu$_{3d}$ states can be described by a single-orbital Hubbard model as shown schematically in Fig. 2.3. Here, $t \gg t'$, where $t$ and $t'$ are the in-layer and the out-of-layer hopping terms. Thus, the antiferromagnetic coupling is restricted to the CuO$_2$ layers. For this compound, $t \simeq 0.4\text{eV}$ and $U \simeq 8\text{eV}$ [2], and from this one can estimate $J$ to be $\sim 1000\text{K}$. The situation in such a compound with large $U$ is schematically shown in Fig. 2.3. Such an insulator is called a charge-transfer insulator. The two bands separated by the charge-transfer gap $\Delta$, half-filled 3$d$ and the filled 2$p$ band are shown. Upon switching on the Coulomb interaction $U$, the 3$d$ band splits into the UHB and the LHB, the difference between these bands equalling $U$. If $U$ is larger than $t$, then the LHB shifts to energies even lower than that of the O$_{2p}$ band, and the charge-transfer gap becomes the significant one which has to be overcome.
2.3 Quantum magnetism: 1D to 2D

2.3.1 1D

For spins arranged on a 1D chain, consider the Heisenberg Hamiltonian with nearest neighbour interaction,

\[ \hat{H} = J \sum_i \hat{S}_i \cdot \hat{S}_{i+1} \quad (2.13) \]

\[ \hat{H} = J \sum_i (\hat{S}_i^x \hat{S}_{i+1}^x + \hat{S}_i^y \hat{S}_{i+1}^y + \hat{S}_i^z \hat{S}_{i+1}^z) \quad (2.14) \]
Introducing raising and lowering operators, \( \hat{S}^+ = S_x + iS_y \) and \( \hat{S}^- = S_x - iS_y \) we can write the above Hamiltonian as,

\[
\hat{H} = J \sum_i (\hat{S}_i^z \hat{S}_{i+1}^z + \frac{1}{2}(\hat{S}_i^+ \hat{S}_{i+1}^+ + \hat{S}_i^- \hat{S}_{i+1}^-)) \tag{2.15}
\]

The second term will cause flipping of spins in the ground state. For a classical system, the ground state is an antiferromagnetic Néel state, where spins are treated in the molecular field approximation as classical vectors \([54]\). It can be easily shown that the energy of such a state will be \( E_{\text{Néel}} = -\frac{NJ}{4} \), where \( N \) is the number of sites. Another ground state is the ‘resonating valence bond’ (RVB) state which is a superposition of singlet states comprising of pairs of spins similar to the schematic for 2D, shown Fig. 2.6. It is also straightforward to prove that such a singlet state gives an energy of \( E_{\text{RVB}} = -\frac{3NJ}{8} \), when the above Hamiltonian is applied to it. Thus, the RVB state has a lower energy than the Néel state, and is a more probable candidate to describe the ground state properties.

Equation 2.15 represents the antiferromagnetic Heisenberg chain. Hans Bethe proposed an ansatz to exactly solve this model and calculate the ground state \([65]\). The ground state turns out to be a singlet state. The excitations of the ground state of a Heisenberg chain are known as spinons. They have \( S = \frac{1}{2} \), and are fermions. They follow a dispersion relation given by,

\[
\hbar \omega = \pi |J \sin(ka)| \tag{2.16}
\]
Figure 2.5: Left: $\chi(T)$ as calculated by EAT (black dots) [68] and as calculated by Bonner and Fisher (blue line) [69]. Right: the electronic specific heat co-efficient $c/T$ for a Heisenberg chain; inset: the specific heat versus the temperature.

where, $a$ and $k$ are the lattice parameter and the wave vector respectively. This was first obtained by Cloizeaux and Pearson [66], and its interpretation as being the spinon dispersion was given by Fadeev and Takhtajan [67]. The excitations are gapless as $\omega \rightarrow 0$ when $k \rightarrow 0$. These spin excitations can be visualized as spin flips and eventual movement of domain walls in opposite directions along an Ising chain (Fig. 2.4). A neutron scattering experiment, where $\Delta S = 1$, implies a creation or annihilation of two spinons. Thus, momentum $(k_1 + k_2)$ and energy $(h\omega_1 + h\omega_2)$ is measured for the spinon pairs that are created or annihilated, giving the two spinon continuum between equation 2.16 and $h\omega = 2\pi | J \sin(ka/2) |$.

Bonner and Fisher [69] numerically calculated the susceptibility of a Heisenberg spin chain for $T \geq 0.4J/k_B$ in 1964. The Bonner-Fisher susceptibility value for a large number of spins can be extrapolated to an expression that is generally used to fit experimental data [70],

$$
\chi(x) = \frac{n_s g^2 \mu_B^2}{J} \frac{0.5x + 0.2999x^2 + 0.60188x^3}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3}
$$

(2.17)

where, $x = J/2k_BT$. Further, exact calculations based on the Bethe ansatz were used to calculate the susceptibility at $T = 0$ by Griffith et. al [71] and Yang et.al [72] which can be given as,
where, \( n_s \) is the number of spin chains per unit area, and \( g \) is the \( g \)-factor. The extrapolation of this Bonner-Fisher susceptibility curve matches very well with this zero temperature value. Later, Eggert, Affleck and Takahashi (EAT) [68] used field theoretical methods and the Bethe ansatz to exactly obtain \( \chi(T) \). However, at very low temperatures of \( k_B T/J \lesssim 0.25 \), \( \chi(T) \) obtained by EAT deviates from the Bonner-Fisher susceptibility due to logarithmic corrections that become important in this temperature regime. Fig. 2.5 shows these susceptibilities. The expression for \( \chi(T) \) obtained by EAT can be written as,

\[
\chi(T) = \frac{n_s g^2 \mu_B^2}{J \pi^2} \left( 1 + \frac{1}{2 \ln(7.7 J/k_B T)} \right) \quad (2.19)
\]

Later, Klümper and Johnston et.al [73–75] accurately calculated, using a numerical Bethe ansatz method, the susceptibility and specific heat of a Heisenberg chain, which reproduced the result of EAT, and also agreed with the exact theory using the effective Hamiltonian approach [76–78] that was proposed by Lukyanov [79]. The calculated specific heat as a function of temperature and the coefficient of the specific heat \( c/T \) vs \( T \) is plotted in Fig. 2.5.

### 2.3.2 2D

According to the Mermin-Wagner-Berezinskii theorem [80] for an isotropic Heisenberg model in dimensions less than 2, thermal fluctuations (Goldstone modes that cost very small energy) destroy long range order at non-zero temperature. At \( T = 0 \) K, however, long range order is expected in 2D. Although no theorem exists to rigourously prove this, the evidence is substantial. Anderson [81] conjectured that the ground state of the 2D \( S = \frac{1}{2} \) Heisenberg antiferromagnet (2D-HAF) might be disordered and postulated the RVB state as a possible low energy state, a spin-liquid like state composed of singlets as shown in a schematic in Fig. 2.6. Although the ground state is not exactly solved, many theoretical methods like the spin-wave theory, mean-field theory and quantum Monte Carlo calculations have given a good deal of understanding [82–84]. In the framework of the spin-wave theory developed by Anderson and Kubo [85, 86], the bosonic quasiparticles for the 2D Heisenberg system at low \( T \) are well-defined spin wave
2.3. Quantum magnetism: 1D to 2D

Figure 2.6: A pictorial depiction of the resonance valence bond state proposed by Anderson, as being a linear combination of singlet states in 2D.

excitations called magnons. Similar excitations are also obtained by considering an itinerant picture in a mean field approximation [87].

As $T \to 0$, the system develops correlated regions of short range order which increase in size with decreasing temperature. This spin-spin correlation length, $\xi$, diverges as $T \to 0 K$. The Heisenberg Hamiltonian in equation 2.10 can be used to describe the 2D-HAFM and the spin fluctuations therein. Chakravarty et al. [88, 89] calculated using perturbative renormalization group theory and the non-linear sigma model, the correlation length at low-$T$. At $T > 0$ order disappears and the spin-spin correlation length exponentially decays as $\xi(T) = C \exp(\frac{cT}{k_B T})$. This exponential temperature dependence of the correlation length was also predicted by some other groups [83, 84, 90]. Later, Hasenfratz and Niedermeyer calculated the exact temperature dependence of the correlation length [91]. This can be given as,

$$\xi/a = \frac{c}{8} \frac{c/a}{2\pi \rho_s} \exp(2\pi \rho_s/T) \left[ 1 - \frac{1}{2} \left( \frac{T}{2\pi \rho_s} \right) + \mathcal{O} \left( \frac{T}{2\pi \rho_s} \right)^2 \right]$$  \hspace{1cm} (2.20)

where is $\rho_s$ the spin stiffness, and $c$ is the spin wave velocity. For the $S = \frac{1}{2}$ nearest neighbor 2D square lattice Heisenberg antiferromagnet $c/a = 1.18 \sqrt{J}$ and $2\pi \rho_s = 1.15 J$ [88, 91, 92].

Spin excitations and pair-magnon excitations in the prototype 2D Heisenberg antiferromagnet, La$_2$CuO$_4$, have been measured by neutron scattering [93–95] and
Chapter 2. Low-dimensional systems

Raman scattering [96]. These experiments show that the 2D antiferromagnetic correlations are \( \gtrsim 200 \text{ \AA} \) for \( T \sim 400 \text{ K} \). The energy scale of the spin fluctuations is very large, an idea of which is given by the value of \( J \approx 1500 \text{ K} \). The calculations of the correlation length match well with the results of neutron and Raman scattering experiments [95–97]. 3D ordering in real systems like \( \text{La}_2\text{CuO}_4 \) has been found, and is attributed to the finite interlayer coupling \( J' \). \( \text{La}_2\text{CuO}_4 \) show an anomaly in the susceptibility (\( \chi \)) at \( T_N \) [98–100]. The zero temperature properties however, theoretically, are found to be only weakly affected by small values of \( J' \). Thio et. al. [98] found that the role of Ising like anisotropies are weak in 2D. However, a small canting of spins out of the layered plane is necessary to explain the ferromagnetism exhibited below the ordering temperature. This canting of spins (the weak ferromagnetism) can be understood by adding the Dzyaloshinskii-Moriya term [101, 102] to the Hamiltonian. Thus we have,

\[
\hat{H} = \hat{H}_{\text{Heisenberg}} + \hat{H}_{\text{DM}}
\]

\[ 2.21 \]

\[
\hat{H} = -\sum_{i,j} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_{i,j} D_{ij} \cdot (\hat{S}_i \times \hat{S}_j)
\]

\[ 2.22 \]

2.3.3 Ladders

Spin ladders stand at the crossover between the one dimensional Heisenberg chain and the two-dimensional Heisenberg square lattice. \( n \)-leg ladders comprise of parallel chains of ions, connected to each other by an interchain coupling through the rungs, that is comparable in strength to the couplings along the chains. Among low dimensional magnets, the class of spin ladder compounds is of special interest as they are invaluable in understanding the physics of the crossover from one-dimensional to the two-dimensional nature of spin systems. They are known to show interesting magnetic ground states and even superconductivity upon charge carrier doping [51]. The dimensionality of the spin system plays an important role in deciding magnetic ground states. Reduction in dimensional degrees of freedom enhances effects due the quantum nature of the spin at experimentally accessible temperatures. Interestingly, these very quantum effects lead to drastic dependencies of magnetic properties on the number of legs of the spin ladder [103]. For example, gapped and ungapped spin excitation spectra have been predicted for spin ladders with even and odd number of ladder-legs respectively, arising from differences in ground states [51]. Even-leg ladders have spin-liquid/RVB
2.3. Quantum magnetism: 1D to 2D

Figure 2.7: (a) \(\chi(T)\) calculated by quantum Monte Carlo method for ladders of different number of legs, (b) shows an enlarged plot of the low temperature regime of \(\chi(T)\); taken from [57]

The Heisenberg Hamiltonian for ladders with \(n\) legs and length \(L\) can be written as,

\[
H = J_{\text{leg}} \sum_{i,j} \vec{S}_i \cdot \vec{S}_j + J_{\text{rung}} \sum_{i,j} \vec{S}_i \cdot \vec{S}_j
\]  

(2.23)

where, \(J_{\text{leg}}\) and \(J_{\text{rung}}\) are the exchange coupling constants along the legs and rungs of the ladder respectively. In a two leg ladder, if the coupling along the rungs is much stronger than the coupling along the legs in equation 2.23 \((J_{\text{rung}} \gg J_{\text{leg}})\), then a configuration with spins on each rung forming a singlet pair is preferred. This singlet ground state has zero total spin, and a finite amount of energy is required to create a triplet. This creates excitations due to the coupling along the legs and causes a magnon branch with dispersion \(\omega(k) = J_{\text{rung}} + J_{\text{leg}}(\cos k)\) [104]. The resulting spin gap between the ground and excited states can be given as, \(\Delta_{\text{spin}} = \omega(\pi) \approx J_{\text{rung}} - J_{\text{leg}}\). Along the legs of the ladder the spin-spin correlations decrease exponentially as a function of distance along the leg. For the case of \(J_{\text{rung}}/J_{\text{leg}} = 0\), the legs decouple and behave as two independent \(S = \frac{1}{2}\) Heisenberg chains. For the case of ladders with number ground state and spin correlations are short range, decaying exponentially. For odd-leg ladders, the behavior is akin to a single chain, with power-law decay of spin correlations.
of legs $n > 2$, for any $J_{rung} \gg J_{leg} \neq 0$, the ground state is again a $S = 0$ singlet with a finite gap, when $n$ is even. There have been theoretical studies using mean field approach and Renormalization Group (RG) theory that estimate the value of the gap for a four-leg ladder and it is found to be roughly half that of the two-leg ladder \[105–107\].

For odd $n$, say a three-leg ladder, each rung forms a doublet ground state with $S = \frac{1}{2}$ and doublet and quadruplet excited states. The doublets with $S = \frac{1}{2}$ states in each rung will now interact with each other via an effective interaction generated by the inter-rung coupling, $J_{rung}$. This interaction, $J_{eff}$ is rotationally invariant and thus has the Heisenberg form. The ground state eigenfunction is thus a product of doublets. A finite $J$ lifts the degeneracy of this $2^n$-fold degenerate ground state. Thus, the effective Hamiltonian can be written up to first order as,

$$H^{(1)}_{\text{eff}} = J_{\text{eff}} \sum_j \vec{S}_{i,tot} \cdot \vec{S}_{i+1,tot}$$  \tag{2.24}$$

$\vec{S}_{i+1,tot}$ is the total spin of the $i^{th}$ rung. Thus, one can map the low-energy states of an odd-leg ladder onto those of a spin chain. Therefore, we have, essentially, $S = \frac{1}{2}$ spins on a chain interacting via $J_{\text{eff}}$. As we know from earlier, such an arrangement has gapless excitations. This scenario is valid for all odd leg ladders and RG calculations have verified this picture \[110\]. The susceptibility $\chi$ as a function of temperature was calculated by quantum Monte Carlo method for ladders of different number of legs ($n$) by Frischmuth et al. \[57\] (Fig. 2.7). The
inset of Fig. 2.7 shows an enlarged plot of the low-temperature regime of \( \chi(T) \), where one can see that the susceptibility for even-leg ladders exponentially drops to zero as \( T \to 0 \). For larger \( n \), the drop sets in at smaller \( T \) and is steeper, i.e., the gap decreases substantially with increasing \( n \). Whereas the susceptibility approaches a finite value for odd-leg ladders, as is the case of a single chain.

Some of these theoretical predictions have been verified experimentally, in materials such as (VO)\(_2\)P\(_2\)O\(_7\) \([109]\) and the homologous series of cuprates \( \text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n} \) \([111]\), which contain weakly coupled arrays of ladders. Magnetic susceptibility measurements for two- and three-leg ladders is shown in Fig. 2.8. A sharp drop of \( \chi(T) \) at low-\( T \) indicates the presence of a spin gap in the two leg ladder, (VO)\(_2\)P\(_2\)O\(_7\), whereas \( \chi(T) \) approaches a constant value as \( T \to 0 \) for the three-leg ladder, \( \text{Sr}_2\text{Cu}_3\text{O}_5 \), as is expected for the case of spin chains. \( \chi(T) \) calculations using the quantum Monte Carlo method for \( n = 1 \) to 6 by Frischmuth et. al. \([57]\) agree qualitatively with these experimental results.
Chapter 3

Thermal conductivity in solids

Heat conduction in solids can occur due to propagating charge carriers like electrons and holes, excitations of the lattice called phonons, and excitations of the spin system, magnetic excitations. In metals, charge carries dominate heat transfer and in insulators phonons are the major heat carriers. The magnitude and temperature dependence of thermal conduction depends on various factors like concentration of carriers, interaction and scattering between them, lattice imperfections and defects, grain size, etc. However, there is no complete microscopic theory that describes thermal transport in details in a variety of systems. Here, we define and introduce the basic formulation for thermal conductivity and describe briefly the different modes of thermal transport in insulators. The discussions below are in the lines of previous works and textbooks [54, 56, 58, 59, 112–115].

3.1 Definition

Thermal conductivity is defined in the form of a rate equation that determines the conduction heat flux from the temperature distribution in the medium, also called as the Fourier’s law [116]. In the framework of the linear response theory this can be written as,

\[ \vec{j}_{th} = -\kappa(T) \nabla T \]  

(3.1)

where, \( \vec{j}_{th} \) is the current density. Here, thermal conductivity is defined as
the proportionality constant in the relation between temperature gradient and thermal current density in a solid. In general, thermal conductivity is a tensor, but it can be treated as a scalar for most lattice types by diagonalizing the tensor matrix.

### 3.2 Kinetic theory

Although there is no rigorous theory for understanding thermal transport, the kinetic theory, similar to that applied for gas molecules, works surprisingly well for all practical purposes. Here, excitations are treated as particles. Consider a temperature gradient $\nabla T$ in a gas of excitations where each particle of the gas has an atomic heat $c$. Thus, to change temperature by $\delta T$ each particle has to gain energy $c\delta T$. If the particle velocity of $v$ then for a moving particle,

$$\frac{\partial \varepsilon}{\partial T} = -cv \nabla T$$  \hspace{1cm} (3.2)

must be valid for local thermal equilibrium. The thermal current due to this moving particle per unit area will depend on the average distance travelled by it before scattering, i.e $vT$. Thus, the total thermal current will be,

$$j = -\frac{1}{3}nc\tau v^2 \nabla T$$  \hspace{1cm} (3.3)

where, $\tau v$ is the average mean free path and the $1/3$ factor comes from averaging over all directions. Combining this with the Fourier’s law of thermal conduction we get,

$$\kappa = \frac{1}{3}Cv\ell$$  \hspace{1cm} (3.4)

This applicability of this formula is limited though as $\tau$ is assumed to be independent of energy or position, which might not entirely hold for real systems. A somewhat more sophisticated approach to treating thermal transport is as follows. Instead of tracing each particle and its collisions, one looks at the system as a whole at time $t$ and characterizes it using a so-called distribution function $f_k(r, k, t)$ that signifies the probability of a state `$k$' being occupied. This statistical method of calculating the transport co-efficients is due to Boltzmann [117].
Chapter 3. Thermal conductivity in solids

$f_k(r,k,t)$ measures the number of heat carriers in the state ‘$\vec{k}$’ in a small region surrounding $\vec{r}$. This distribution function around $\vec{r}$ can be modified by the diffusion of carriers by scattering from one state to another. The total rate of change of the distribution function can thus be given as a sum of these changes which must be equal to zero when the system is in a steady state. Thus we have,

$$- \vec{v}_k \cdot \frac{\partial f_k}{\partial \vec{r}} - e \frac{1}{\hbar} (E + \frac{1}{c} v_k l H) \frac{\partial f_k}{\partial k} = - \frac{\partial f_k}{\partial t}$$  \hspace{1cm} (3.5)

If deviations of $f_k$ from equilibrium are small one can approximate the above equation into a linearized Boltzmann equation, which is the form used in practice, as,

$$- \vec{v}_k \cdot \frac{\partial f^0_k}{\partial T} \nabla T - \vec{v}_k \cdot e \frac{\partial f^0_k}{\partial \epsilon_k} \vec{E} = \int (f_k - f^0_k) - (f_{k'} - f^0_{k'}) \gamma^k_{k'} dk'$$ \hspace{1cm} (3.6)

This is a linear integral for the function $f_k - f^0$, i.e the difference in the nonequilibrium and equilibrium carrier distributions. The solution of such an equation must be linear in $E$ and $\nabla T$. Thus, the transport currents are linear functions of gradient of temperature and electric field, i.e,

$$j_{el} = (L_{EE})E + (L_{ET})\nabla T$$  \hspace{1cm} (3.7)

$$j_{th} = (L_{TE})E + (L_{TT})\nabla T$$  \hspace{1cm} (3.8)

where, $L_{EE}$, $L_{EE}$, $L_{ET}$, $L_{TE}$, $L_{TT}$ are the transport coefficients. In experiments, we do not measure these coefficients but we measure quantities like the thermal/electric conductivity that is related to the temperature gradient/electric field and the thermal/electric current by the Fourier’s/Ohm’s laws. Therefore putting $\nabla T = 0$ in equation 3.7 gives,

$$j_{el} = (L_{EE})E$$ \hspace{1cm} (3.9)

$$j_{th} = (L_{TE})E$$ \hspace{1cm} (3.10)

We thus have from the Ohm’s law ($i_{el} = \sigma E$), $L_{EE} = \sigma$. Similarly, by putting $i_{el} = 0$ and using the Fourier’s law we get for the thermal conductivity,
3.3. Phonons

\[ \kappa = -(L_{TT} - \frac{L_{ET}L_{TE}}{L_{EE}}) \]  

(3.11)

The second term is usually small, and we use \( \kappa = -L_{TT} \).

Using these relations and solving the linearized Boltzmann equation one can derive an expression for \( \kappa \) with \( k \)-dependent quantities similar to equation 3.4 as,

\[ \kappa = \int_{BZ} c_k v_k l_k dk \]  

(3.12)

where the integration runs over the entire Brillouin Zone (BZ). If we consider \( \tau_k \) as the scattering rate, and \( v_k \) as the velocity of excitations corresponding to the mean free path \( l_k \) (= \( \tau_k v_k \)), one can rewrite the above expression as,

\[ \kappa = \int_{BZ} c_k v_k^2 \tau_k dk \]  

(3.13)

We shall use this expression for analyzing our experimental quantities in this work. Also, expressions based on equation 3.12 for one- and two-dimensional Heisenberg systems will be discussed in the following sections which we use to extract the mean free path of magnetic excitations that transport heat.

3.3 Phonons

The Einstein model [118], based on Planck’s quantum conjecture, assumed a solid containing \( N \) ions to be composed of \( 3N \) one-dimensional oscillators considering independently vibrating atoms with frequency \( \omega \). The energy of these oscillators were quantized as,

\[ E = (n + \frac{1}{2})\hbar \omega \]  

(3.14)

Later the Debye model [119] revised this idea by describing the lattice vibrations as a system of coupled oscillators and the solid to be vibrating as a whole in the
form of normal modes. These semi-classical models were introduced mainly to explain the behavior of specific heat in solids as a function of temperature.

Upon solving the classical equations of motion for vibrations on a lattice one sees that the general motion of $N$ ions can be represented as a superposition of $3N$ normal modes of vibration with different characteristic frequencies that are quantized for each mode. Each mode is a travelling wave and can be expressed as,

$$u_s = u \exp \left( i(kna - \omega t) \right) \quad (3.15)$$

Each normal mode can have only a discrete set of energies and the total energy is given as,

$$E = \sum_{ks} \left( n_{ks} + \frac{1}{2} \right) \hbar \omega_s(k) \quad (3.16)$$

where, one can either say that $n_s^k$ is the excitation number of the normal mode of branch ‘$s$’ with wave vector $\vec{k}$, or that there are $n_s^k$ phonons of type ‘$s$’ having wave vector $\vec{k}$.

For a three dimensional lattice with a basis, for each value of the wave vector $\vec{k}$ there are $3p$ normal modes, $p$ being the number of ions in the basis. The frequencies $\omega_s(k)$ are functions of $\vec{k}$, with the periodicity of the reciprocal lattice. We thus get a dispersion relation that relates every point in $k$-space to a particular frequency $\omega(k)$. Here, three of the $3p$ branches are called acoustic branches, and the $3(p-1)$ branches are called optical branches. Acoustic modes have vanishing frequency in the long wavelength limit. Experimentally, one can map the dispersion relation in detail using neutrons, by measuring energy lost/gained by neutrons reflected off a sample as a function of angle due to interaction with phonons within the sample.

Lattice vibrations when approached classically using the harmonic approximation are unable to explain many experimentally observed properties like finite thermal conductivity. Thermal conductivity, in the harmonic approximation, must be infinite as there is no way to relax the heat current. However, in real systems the thermal conductivity is rendered finite due to:

1. Most importantly, scattering between phonons due to anharmonicity of the
3.3. Phonons

![Figure 3.1: Scattering of phonons represented by addition of their $k$ vectors in reciprocal space.](image)

- Hamiltonian of the phonon states will cause decay of thermal current with time.
- Lattice imperfections or impurities act as scattering centers for phonons.
- Even in a perfectly pure crystal boundary scattering at the sample surface will limit conduction.

To realize thermal energy transport, one can consider localized wavepackets. As a single normal mode with wave vector $\vec{k}$ involves the motion of ions throughout the crystal, by superposing states of a crystal, in each of which a normal mode with wavevector in an interval $\Delta k$ is excited. One can thus construct localized phonon-like disturbances/wavepackets travelling with a group velocity $v_s = \partial \omega_s(k)/\partial k$.

Anharmonic terms can be treated perturbatively. Cubic terms that are responsible for anharmonicity cause transitions wherein a phonon from branch $'s'$ with $\vec{k}_s$ decays into two phonons with $\vec{k}_{s'}^1$ and $\vec{k}_{s''}^2$, or two phonons merge to form one phonon. The probability of higher order transitions involving more than three phonons exponentially decreases with decreasing temperature. For transitions/collisions to occur, energy and momentum must be conserved, i.e,

$$\Sigma \hbar \omega_s(k)n_{k,s} = \Sigma \hbar \omega_{s'}(k')n_{k',s'}$$  \hspace{1cm} (3.17)

$$\Sigma \vec{k} n_{k,s} = \Sigma \vec{k}' n_{k',s'} + \vec{G}$$  \hspace{1cm} (3.18)

Phonon scattering processes are of two types: Normal processes and Umklapp processes. In normal processes before and after the collisions the crystal momentum remains the same, but in umklapp processes [120] it differs by a reciprocal
lattice vector $\vec{G}$. Two phonons with wave vector $\vec{k}_1$ and $\vec{k}_2$ can interact to give phonon $\vec{k}_3$, but this is only valid if $\vec{k}_3$ remains inside the first Brillouin-zone (BZ). Such a process is called a normal process. As the momentum of phonons is conserved in such a process, it does not affect heat conduction, thereby is not a resistive process \[115\]. But, if $\vec{k}_1$ and $\vec{k}_2$ are both greater than one fourth of the reciprocal lattice vector $\vec{G}$ then $\vec{k}_3$ will lie outside the first BZ. The periodicity of the reciprocal lattice now results in $\vec{k}_3$ being represented in the first BZ reversed as $\vec{k}_3 - \vec{G}$. This reversal of momentum results in lowering of thermal conduction and thereby such umklapp processes are resistive scattering processes. The scattering processes described above are illustrated schematically in Fig. 3.1.

Fig. 3.2(a) shows an typical example curve for a purely phononic system. The $T$-dependence of such a phononic thermal conductivity can be described qualitatively by considering the expression for $\kappa$ in equation 3.12. At low temperatures few phonons are excited and they interact via normal processes as they have small $\vec{k}$ near the center of the BZ. Here, we expect the $T$-dependence of $\kappa$ to be dominated by the $T^3$-like increase of the specific heat $c_k$. At higher temperatures this increase saturates into a peak. The magnitude of the peak in the heat conductivity curve is decided by the $T$-independent scattering of phonons with defects/impurities and sample boundaries. At higher $T$, we expect phonons with large $\vec{k}$ to interact via umklapp processes and eventually lead to a decrease of $\kappa$. If $n$ is the average density of phonons then,

$$\langle n \rangle \approx \frac{1}{\exp (\hbar \omega / k_B T) - 1} \quad (3.19)$$

The mean free path $l$ is inversely proportional to the phonon density $n$. Umklapp processes require that the interacting phonons have a wavevector of at least $\vec{G}/4$, which means that their energies are $\approx k_B \Theta_D/2$, $\Theta_D$ is associated with the maximum value of $\vec{k}$, i.e $\vec{G}/2$. In equation 3.19, for small $T$ we have,

$$\langle n \rangle \approx \exp (\hbar \omega / k_B T) - 1 \quad (3.20)$$

Considering $\omega = k_B \Theta_D/2$ we get,

$$\langle n \rangle \approx \exp (-\Theta_D/2T) - 1 \quad (3.21)$$

Thus we have,
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Figure 3.2: (a) Thermal conductivity of $\text{Al}_2\text{O}_3$ showing typical temperature dependencies, the red solid line is a Callaway fit to the measured conductivity (taken from [121]) (b) Thermal conductivity of different quartz samples that vary in purity from each other due to different irradiation times; curves 1, 2 and 3 are of samples in the decreasing order of purity between the purest quartz crystal curve, and the least pure quartz glass curve (taken from [122]).

$$\kappa \propto T^{-1}$$

$$\kappa \propto T^3 \exp \Theta_D/2T$$

(3.22)

i.e., $\kappa$ drops strongly with increasing $T$ in this regime. For larger $T$, above $\Theta_D$, we can approximate $n \approx T$, and we also see the specific heat becoming constant. Thus, in this temperature regime one expects, $\kappa \propto 1/T$. 


3.3.1 Callaway model

Callaway [123–125] devised a phenomenological model based on the Boltzmann equation that takes into account the different resistive processes involved in determining the thermal conduction of a solid. In the Debye approximation with $k$-independent particle velocity $v$, the expression is,

$$\kappa = \frac{k_B}{2\pi^2} \frac{(k_BT)^3}{\hbar^3} \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$  \hspace{1cm} (3.23)

$\tau_c$ is the combined scattering rate of individual contributions summed up using the Matthiessen’s rule [126] as,

$$\tau_c^{-1} = \tau_B^{-1} + \tau_D^{-1} + \tau_N^{-1} + \tau_U^{-1}$$  \hspace{1cm} (3.24)

This rule assumes that the functional independence of each scattering rate from another, which might be true in general, but can be considered so if each scattering process has a different temperature regime of dominance, where other processes are inactive. Scattering rates could be frequency dependent and thus can effect the frequency dependent distribution function of phonons. The term $\tau_B^{-1}$ that accounts for scattering at sample boundaries is dominant at low temperatures and is given as,

$$\tau_B^{-1} = \frac{v}{L}$$  \hspace{1cm} (3.25)

where $L$ is the sample length. The second term, $\tau_D^{-1}$ is a frequency dependent term that describes scattering of phonons off point defects and is given as,

$$\tau_D^{-1} = A\omega^4$$  \hspace{1cm} (3.26)

$A$ being a free parameter. The third and fourth terms signify the phonons scattering amongst themselves via normal and umklapp processes respectively. Although, normal processes are not thermally resistive, but can be responsible for generating umklapp processes indirectly. However, as their relevance is restricted to a small temperature range near the peak of thermal conductivity and as their effect is small we neglect this term. For umklapp process we have,
3.3. Phonons

![Figure 3.3: Thermal conductivity of a series of LiF compounds, (a) with varying concentrations of the Li\(^{6}\) isotope. (b) having different sample radii (taken from [128]).](image)

\[
\tau_U^{-1} = B \omega^\alpha T^\beta e^{-\Theta_D/k_B T}
\]  

(3.27)

Empirically, \(\beta\) may be fixed to 2, \(\alpha\) may vary from 1 to 5 depending upon the type of phonons and the crystal symmetry. This is discussed in detail in [125, 127].

At low \(T\), the Callaway model is known to describe experimental data for purely phononic systems very well. As this is a phenomenological model, physical interpretations of the parameters involved are not rigorous. Moreover, the model lies in the Debye approximation regime where phonon density and phonon velocity are not accurately described for high frequency, phonon polarization is ignored, Matthiessen’s rule might not be strictly applicable, and is an approximation for
low temperatures. Thus, the interpretation of the description of experimental results by the model must not be forced.

### 3.3.2 Experimental examples

Fig. 3.2(a) shows the thermal conductivity of Al$_2$O$_3$, a typical phononic conductor [121]. The low temperature rise follows a $T^3$ law corresponding to the temperature dependence of the specific heat. A peak with a magnitude decided by boundary and impurity scattering is followed by a $1/T$ decrease induced by umklapp like collisions among phonons.

In order to see how increasing concentration of defects/impurities affects the conduction by phonons, thermal conductivity of LiF crystals having different concentrations of the isotope Li$^6$ is shown in Fig. 3.3(a) [128]. With increasing concentrations of this isotope one sees a monotonic decrease in the thermal conductivity. Isotope Li$^6$ acts as structural defects in the array of Li$^7$ ions and thereby enhances the scattering of phonons. As the concentration of Li$^6$ is very small in the crystals, the only change seen in the conductivity curves is the reduction in the values of thermal conductivity in the temperature regime where the peak occurs, indicating that this is the regime where the thermal conductivity is most sensitive to defect/impurities. Fig. 3.2(b) plots the thermal conductivity of quartz and its impure versions having high defect density due to irradiation [122]. The impure versions show a drastic decrease in conductivity owing to very strong phonon-defect scattering.

To see the effect of sample boundary scattering, thermal conductivity of cylindrical LiF samples with increasing radii are plotted in Fig. 3.3(b) [128]. Increasing the radius of the sample gradually enhances the thermal conductivity at low temperatures and the peak itself. This indicates the importance of phonon-boundary scattering in deciding the magnitude of conduction in solids.

### 3.4 Magnetic excitations

Heat transport in solids can also occur via dispersive magnetic excitations. First evidence of such heat transport was found in the ordered two and three dimensional ferromagnets like CuCl$_2$(CH$_3$NH$_3$Cl)$_2$ [129] and Yttrium Iron Garnet (YIG) [130–133] respectively, and was described to be due to classical spin waves using
the spin wave theory \cite{129, 134, 135}. Later on, many other compounds including a vast number of cuprates like the 1D antiferromagnet KCuF$_3$ \cite{136, 137}, the ladder compound (Sr,Ca,La)$_{14}$Cu$_{24}$O$_{41}$ \cite{17}, other quasi 1D antiferromagnets SrCuO$_2$ and Sr$_2$CuO$_3$ \cite{6, 8, 9}, 2D Heisenberg antiferromagnet La$_2$CuO$_4$ \cite{12, 15}, etc. have shown large contribution to the heat conduction due to excitations of the corresponding spin system, much greater than the contribution from the phonons in these compounds. In spite of no long range order in such low-dimensional quantum magnets the nature of excitations is such that it allows for efficient heat transport even in the disordered state, as opposed to classical ordered ferromagnets like YIG. In the following section we shall briefly discuss the theoretical background of models that are used to quantitatively analyze the experimentally obtained magnetic thermal conductivity.

### 3.4.1 1D

**Boltzmann-type approach**

As a semi-classical treatment of heat transport due to magnetic excitations one could use the Boltzmann approach, introduced in section 3.2, to relate the thermal conductivity to the mean free path of the excitations. One can use equation 3.12. The specific heat $c_{\text{mag}}$ depends on the energy and the occupation function $n_k$ of the quasiparticles depending on the statistics that applies. Due to high values of the Debye temperature for magnetic excitations in compounds like La$_2$CuO$_4$, SrCuO$_2$ and Sr$_2$CuO$_3$, only small $\vec{k}$ modes are excited at temperatures $\lesssim 300K$, thus being in the linear regime of the spin excitation spectrum. Thus, as an approximation at these temperatures, one can treat the mean free path of excitations as momentum independent.

In one dimension, excitations are gapless for $S = \frac{1}{2}$ Heisenberg spin systems. Thus, the $\vec{k}$-states can be integrated over the entire Brillouin zone continuously. Also, the fundamental excitations can be described in terms of $S = \frac{1}{2}$ spinons, thus, one can apply the Fermi-Dirac statistics and write the specific heat as,

$$c_{\text{mag}} = \frac{2n_s}{\pi} \int_0^{\pi/2a} \frac{d}{dT} \frac{1}{\exp(\varepsilon_k/k_B T + 1)} \varepsilon_k dk. \quad (3.28)$$

where, $n_s$ is the number of spin chains per unit area. The group velocity $v_k$ can be given as the slope of the dispersion relation as, $v_k = (1/h)(d\varepsilon_k/dk)$.  

31
Thus, we get an expression for $\kappa_{\text{mag}}$ as,

$$
\kappa_{\text{mag}} = \frac{2n_s k_B^2 T}{\pi \hbar} l_{\text{mag}} \int_0^{J_\pi/2k_B T} \frac{x^2 \exp(x)}{(\exp(x) + 1)^2} dx.
$$

(3.29)

where, $x = \varepsilon_k/k_B T$, and $l_{\text{mag}}$ is approximated to be independent of energy.

The value of this integral is temperature independent at low $T$, and equal to $\pi^2/6$. Thus, for low $T$ we get an approximate expression for $\kappa_{\text{mag}}$ that matches exactly with the low-$T$ approximation obtained by the Drude weight approach that is described in the following section,

$$
\kappa_{\text{mag}} = \frac{\pi n_s k_B^2 T}{3 \hbar} l_{\text{mag}}(T)
$$

(3.30)

$l_{\text{mag}}$ can be now extracted from the experimentally obtained $\kappa_{\text{mag}}$.

**Drude weight approach**

Spinon heat conductivity and mean free path can also be approached via the definition of Drude weight. The brief discussion made below is based on detailed

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**Figure 3.4:** Left: the real part of conductivity $L_{ij}(\omega)$ as a function of frequency is sketched. Right: This shows current $j$ as a function of time for the case when transport is ballistic (taken from [138]).
derivations and theory that can be found in [22, 23, 33, 138, 139]. The transport coefficients are related to experimentally measured quantities like the heat conductivity according to the relations discussed in section 3.2. These coefficients are complex functions of the frequency $\omega$ and depend on the current-current correlation functions as,

$$L_{ij}(\omega) \equiv f(\omega, <j_i, j_j(t)>)$$  \hspace{1cm} (3.31)

where, $<j_i, j_j(t)>)$ is the current-current correlation function. The real part of $L_{ij}(\omega)$ can be decomposed into a $\delta$-function at $\omega = 0$ with a weight $D_{ij}$ and a regular part $L_{ij}^{\text{reg}}(\omega)$ as,

$$\text{Re}(L_{ij}(\omega)) = D_{ij}\delta(\omega) + L_{ij}^{\text{reg}}(\omega)$$  \hspace{1cm} (3.32)

The coefficients $D_{ij}$ are linear combinations of spin and thermal Drude weights, $D_s$ and $D_{th}$ respectively. For thermal conductivity in zero magnetic field, the coefficient $D_{22}$ corresponding to the transport coefficient $L_{22}$ (which in turn is equal to the thermal conductivity $\kappa_{\text{mag}}$), equals $D_{th}$, and $\kappa_{\text{mag}}$ can be written as,

$$\text{Re}[\kappa_{\text{mag}}(\omega)] = D_{th}\delta(\omega) + \kappa_{\text{mag}}^{\text{reg}}(\omega, T)$$  \hspace{1cm} (3.33)

This is how the Drude weight is defined [27, 28, 33, 38, 139]. The real part of conductivity $L_{ij}(\omega)$ as a function of frequency and the current as a function of time are plotted in Fig. 3.4.

Transport in 1D systems is called ballistic if the respective Drude weight is finite. The Drude weight measures the part of the current that does not decay with time. For integrable models like the $S = \frac{1}{2}$ $XXZ$ chain (see section 3.4.1), the Hamiltonian ($\hat{H}$) commutes with the current operator, i.e the energy-current operator is exactly conserved [23, 140], i.e,

$$[\hat{H}, j_{th}] = 0$$  \hspace{1cm} (3.34)

Therefore, theory predicts anomalous heat transport properties, like its divergence [139]. Integrability of a model may be defined as the model being solvable
Chapter 3. Thermal conductivity in solids

by the Bethe ansatz [138]. Other models like the spin-ladder, $S = 1$ chain, frustrated chain or the 2D Heisenberg antiferromagnet are not integrable, and hence an infinite conductivity is not expected from theory [138].

The Drude weight ($D_{th}$) of an $XXZ$-model (see section 3.4.1) was calculated by Klümper and Sakai [33], and is plotted in Fig. 3.5. At low temperature ($k_B T \approx 0.15$ J) approximation $D_{th}$ can be approximated as a linear function of temperature,

$$D_{th} = \frac{(\pi k_B)^2}{3 \hbar} v T$$

(3.35)

where $v$ is the spinon velocity and $k_B$ is the Boltzmann constant.

For real materials with Heisenberg chains, the thermal conductivity broadens to a Lorentzian of width $1/\tau$ due to extrinsic scattering. Thus we get,

$$\kappa_{\text{mag}}(T) \approx D_{th} \frac{\tau(T)}{\pi}$$

(3.36)

As the Drude weight is linear, $\kappa_{\text{mag}}$ is expected to have a $T$-dependence governed

Figure 3.5: Thermal Drude weight ($D_{th}$) of the $S = \frac{1}{2}$ $XXZ$ chain model to illustrate the linearity at low temperatures (taken from [33]).
by that of the scattering rate $\tau^{-1}(T)$. Here, the energy dependence of $\tau(T)$ is neglected. As the low-$T$ approximation for $D_{th}$ is known, it can be utilized to estimate the extrinsic scattering rate ($\tau^{-1}$) and hence the mean free path (assuming the relation $l_{mag} = \tau v$). Thus, as a relation between the thermal conductivity and the mean free path we have,

$$l_{mag} = \frac{3h}{\pi N_s k_B^2 T \kappa_{mag}}$$ (3.37)

where $N_s$ is the number of spin chains per unit area. However, as the scattering rates and the mean free paths are not modelled rigourously up till now, such an approach is still considered to be phenomenological. For higher temperatures ($k_B T > 0.15$ J), however, the $T$-dependence of the Drude weight needs to be considered explicitly.

**Mean free path analysis**

In 1D, although no rigorous model exists for describing the scattering processes involving magnetic excitations and phonons, one can gain some information by trying to describe the magnitude and temperature dependence of the mean free paths of these magnetic excitations by phenomenologically modelling the scattering processes. Such a model has been used and discussed earlier in the literature and seems to work surprisingly well when in comes to describing the temperature dependence of the mean free path of magnetic excitations below 300 K [8–10, 141]. However, this model treats the mean free path empirically, and physical interpretation of the modelling must not be forced.

The temperature dependence of $l_{mag}$ can be attempted to be modelled as a combination of two scattering processes. Phonons and boundaries are the main scatterers that dictate the behavior of $l_{mag}$ at low temperatures. At low-$T$, boundary scattering is the dominant process and at higher temperatures where phonon density is significant, spinon-phonon scattering dominates. Matthiessen’s rule can be used to sum the scattering rates of these two processes and we can write,

$$l_{mag}^{-1} = l_{s-b}^{-1} + l_{s-p}^{-1}$$ (3.38)

$l_{s-b}$ is a constant and determines the low-$T$ limit of $l_{mag}$ due to boundary scattering, and $l_{s-p}$ depends on exponential activation of phonon density and can
be described as a general umklapp process with a characteristic energy scale \( k_B T_u^* \) of the order of the Debye energy. Thus we have,

\[
l_{\text{mag}}^{-1} = l_0^{-1} + \frac{A_s T}{\exp (T_u^*/T)}
\]  

(3.39)

where, \( l_0 \), \( A_s \) and \( T_u^* \) are free parameters.

### 3.4.2 2D

#### Low temperature

A Boltzmann-like semi-classical approach based on the equation 3.12, as in the above section, leads to an expression for \( \kappa_{\text{mag}} \) in 2D. Here, the excitations are described by bosonic quasiparticles called magnons. Also, in the 2D Heisenberg antiferromagnet \( \text{La}_2\text{CuO}_4 \), the spin dispersion relation consists of two magnon branches with gaps \( \Delta_i \) as the energy to excite the singlet state (\( \Delta_1/k_B = 26K \) and \( \Delta_2/k_B = 58K \)). For a three dimensional ensemble of planes one has \( \kappa_{\text{mag}} = \frac{2}{3} \sum_i \kappa_i \), where \( \kappa_i \) is the thermal conductivity of a single magnon branch.

The specific heat \( c_{\text{mag}} \) for such excitations can analytically be given as,

\[
c_{\text{mag}} = \frac{d}{dT} \frac{\varepsilon_k}{\exp (\varepsilon_k/k_B T) - 1}
\]  

(3.40)

and at low temperatures, the magnon dispersion relation in the Debye approximation is,

\[
\varepsilon_k = \sqrt{\Delta_i^2 + (h v_0 k)^2}
\]  

(3.41)

where \( v_0 \) is the spin wave velocity, \( v_0 = 1.287 \times 10^5 \) m/s.

From these equations, one can write an expression for the thermal conductivity for the two magnon branches together as,
3.4. Magnetic excitations

Figure 3.6: Magnetic specific heat $c_{\text{mag}}/k_B$ of a $S = \frac{1}{2}$ Heisenberg antiferromagnet calculated using a high temperature series expansion, reproduced from [13].

\[ \kappa_{\text{mag}} = \frac{v_0 k_B l_{\text{mag}}}{2 a^2 c} \frac{T^2}{\Theta_M^2} \sum_{i=1,2} \int_{x_{0,i}}^{x_{\text{max}}} x^2 \sqrt{x^2 - x_{0,i}^2} \frac{e^x}{(e^x - 1)^2} dx, \tag{3.42} \]

Here, the integral is dimensionless, and $x_{0,i} = \Delta_i/(k_B T)$ and $x_{\text{max}} = \Theta_M/T$. $Z_c = 1.18$ is the quantum renormalization factor for $s=1/2$ spins. $\Theta_M = \sqrt{2\pi Z_c J}$ is the Debye temperature for magnons. The temperature dependence of the integral arises from $x_{0,i} = \Delta_i/(k_B T)$ and $x_{\text{max}}$. The $T$-dependence of $\kappa_{\text{mag}}$ for temperatures $T \gtrsim \Delta_i$ should roughly be $\kappa_{\text{mag}} \propto T^2$, as the integral is only weakly $T$-dependent in this $T$ range.
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High temperature

The specific heat $c_k$ can be calculated using a Debye-like approach, assuming a linear dependence of energy ($\varepsilon$) on momentum ($k$) for low temperatures, as described by equation 3.41 in the previous section. However, for higher temperatures such an approach is questionable because the $\varepsilon(k)$ curve deviates from linearity for higher energies. Therefore, for higher temperatures the theoretically calculated specific heat using the high-$T$ series expansion for a 2D Heisenberg square lattice can been used [13]. The result of these calculations is shown in fig. 3.6. However, we assume that the velocity of the excitations is momentum independent.

Thus, equation 3.13 can be written as,

$$\kappa_{\text{mag}} = \frac{1}{2} l_{\text{mag}} v_{\text{mag}} c_{\text{mag}}$$  \hspace{1cm} (3.43)

where, $c_{\text{mag}}$ is the magnetic specific heat, $v_{\text{mag}} = 1.163 \times 10^5$ m/s, is the spin wave velocity [142], and $l_{\text{mag}} (= v_{\text{mag}} \tau)$ is the magnon mean free path. Here, $\tau$ is assumed to be $\omega$-independent. Using the theoretical result shown in fig. 3.6 for $c_{\text{mag}}$, and the experimentally obtained $\kappa_{\text{mag}}$, one can easily extract $l_{\text{mag}}$ from equation 7.4.
Chapter 4

Experimental techniques

4.1 Thermal Conductivity: The Steady State Method

Thermal conductivity has been measured using the conventional steady state method at temperatures from 7 K to 350 K. Aspects regarding the principle and the experimental setup are dealt with in brief here, and details regarding the functionality and construction of the measurement probe can be found in [112].

4.1.1 Principle and technique

The measurement of thermal conductivity is based on the empirical relationship between the heat conduction in a material and the temperature gradient in the direction of heat flow as postulated by Fourier [116]. It states that the heat flux in a material is proportional to the temperature gradient (see section 3.1), i.e,

\[ j_q = -\kappa(\nabla T)_x. \]  \hspace{1cm} (4.1)

In the actual experiment, a schematic and a real image of which are shown in Fig. 4.1, the sample whose thermal conductivity is to be measured is fixed on a sample holder. The sample holder acts as a heat bath at constant temperature \( T_1 \). Then a temperature gradient is established along the length of the sample.
by means of a heater on top of the sample. The heater acts as another heat bath at a constant temperature $T_2$. Thus, a constant gradient of $T_1 - T_2$ exists in the sample once a steady state is reached. If we assume that all the heat produced in the heater is dissipated only through the sample, the power produced in the heater will be equal to the heat flowing through the sample. By measuring the current\(^1\) through the heater ($I_h$) and the voltage\(^2\) across it ($U_h$), one can calculate the heat current density ($j_q$) as,

$$j_q = \frac{P_h}{A} = \frac{U_h I_h}{A}. \quad (4.2)$$

The temperature gradient in the sample ($\nabla T$) that allows for the heat flow in the sample is measured by means of a thermocouple in terms of a voltage. Two ends of the thermocouple are glued to the sample at a distance of $l$ from each other. First the background thermal voltage ($U_{th}^{off}$) is determined with the heater switched off, and later the thermal voltage with the heater switched on is measured\(^3\) ($U_{th}^{on}$). The difference between these signals gives the pure thermal voltage. The thermal gradient can now be calculated from calibrated thermopower values ($S_{th}$) as,

$$(\nabla T)_x = \frac{\Delta T_x}{l} = \frac{U_{th}}{S_{th}l}. \quad (4.3)$$

By combining equation 4.1 and equation 4.2 we get the thermal conductivity $\kappa$ at a particular temperature $T$ as,

$$\kappa = \left| \frac{j_q}{(\nabla T)_x} \right| = \frac{U_h I_h S_{th}L}{A U_{th}}. \quad (4.4)$$

The temperature $T$ at which $\kappa$ is calculated is taken as the temperature approximately at the center of the sample and is given as,

$$T = T_0 + (d + \frac{L}{2})(\nabla T)_x, \quad (4.5)$$

where $d$ is the distance from the nearest thermocouple contact to the heat bath.

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\(^1\)Established using Keithley 2400/224/238 multimeter

\(^2\)measured using Keithley 2000 multimeter

\(^3\)measured using Keithley 2182/182 nanovoltmeter
4.1. Thermal Conductivity: The Steady State Method

4.1.2 Experimental setup

The thermal conductivity can be measured from room temperature down to liquid helium temperature using a setup that is illustrated in Fig. 4.2. Detailed descriptions of the setup can be found elsewhere [112]. The probe has a structure made of four stainless steel capillaries though which wire connections pass, at the bottom of which the sample holder is fixed. The sample is fixed by means of Ge varnish$^4$ or Super glue$^5$ onto the base of the holder. Other than providing good thermal contact, the insulating super glue tends to provide a firm mechanical hold of the sample onto the base, which is crucial for a successful measurement. Also, it dries faster, reaching its maximum rigidity in few minutes, thus being beneficial for samples that are air sensitive. A brass stage which is directly in contact with liquid helium provides the main thermal link. To avoid radiation losses of the heat that is supplied to the sample during measurement, the probe is first evacuated down to pressures of around $10^{-6}$ mbar and then is inserted into liquid helium. The sample holder is enclosed by a resistive heater cup made of copper$^6$ that is used to heat it up. The temperature of the sample holder is

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$^4$General Electric IMI 7031 Insulating Varnish

$^5$Uhu Sekundenkleber

$^6 R \approx 50\Omega$
measured and controlled using a temperature controller\textsuperscript{7} and a sensor\textsuperscript{8} fixed at the base of it. This allows to achieve temperature stability of around $\pm 30\text{ mK}$ at high temperatures near 300 K and around $\pm 1\text{ mK}$ at lowest temperatures. After inserting the probe in He, cryogenic vacuum is maintained inside the probe and no external pumping is required. In order to supply heat to the sample a cuboidal chip heater with resistance of around $3\text{ K}\Omega$ is glued on the sample and connected to the pins on the sample holder using Manganin\textsuperscript{9} wires. Manganin, with its high thermal resistance thermally isolates the heater from the sample holder. The thermocouples are made of $\text{Au}_{0.93}\text{Fe}_{0.07}$ and Chromel-P(FN) wires, that possess significant thermopower down to the lowest temperatures.

\textsuperscript{7}Lakeshore340

\textsuperscript{8}Lakeshore-Cernox\textsuperscript{TM}

\textsuperscript{9}Alloy: 86\% Cu, 12\% Mn, 2\% Ni
4.1.3 Errors

The primary source of error in these experiments mainly stems from errors in measurement of geometry of the setup, and errors due to heat losses. These errors have been taken into account while analyzing and interpreting the measurements. The determination of $\kappa$ necessitates the estimation of the dimensions of the sample and the distance between the thermocouple contacts. These are measured using an optical microscope$^{10}$, a digital camera$^{11}$ attached to it, and a software$^{12}$ that helps to digitally measure distances on an image. These temperature independent errors amount to a total of around 10%. Our assumption that the entire heat produced by the heater passes through the sample gives rise to an error as conductive, convective and radiative losses are inevitable. As the setup consists of the leads of the heater and the thermocouple connecting the sample to the heat bath, conductive heat losses are present. Convective heat losses, via gas molecules, in case of poor vacuum and radiative losses at higher temperatures have to be taken into account. Long, thin wires are used and a good vacuum is ensured to minimize errors due to convective and conductive heat losses. Corrections for radiative heat losses to the measured thermal conductivity have been discussed in detail elsewhere$^{112}$, although these errors can be minimized by using samples of smaller length and larger cross-sections. Another source of error, which is less than 5%, comes from the uncertainty in calibration of the thermocouple. Other errors due to electrical measurements ($<$1%) made by rather accurate instruments like nano-voltmeters and current sources can be considered as negligible.

4.2 Thermal Conductivity: The Dynamic Flash Method

Dynamic flash method is used for measuring thermal conductivity at high temperatures up to $\sim 800$ K, but is limited to temperatures above $\sim 160$ K due to the limit of the detector sensitivity. These measurements have been done on the LFA 457 MicroFlash setup by NETZSCH. In the Dynamic Flash Method the front face of a cylindrically shaped sample is uniformly heated using an unfocused laser pulse. The temperature increase on the rear surface as a function of

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$^{10}$Leica – MZ8
$^{11}$Leica Microsystems Inc. DFC280
$^{12}$Leica Image Manager IM50
Chapter 4. Experimental techniques

Figure 4.3: A schematic illustrating the measurement principle of the dynamic flash method, and a plot of a typical signal (temperature as a function of time) measured by the detector for La$_2$CuO$_4$ at 300 K.

time is measured (see Fig. 4.3 as an example). The mathematical analysis of this temperature/time function allows the determination of the thermal diffusivity $\alpha$, from which the $\kappa$ can be calculated by knowing specific heat $C_p$ as a function of temperature and density $\rho$, using the equation,

$$\kappa(T) = \rho \cdot C_p(T) \cdot \alpha(T).$$ (4.6)

The specific heat data was taken from [143], and the density was $\rho = 7.05$ g/cm$^3$. The primary errors in the LFA 457 MicroFlash setup arise from the determination of thickness of the sample, this being $\sim 3\%$, and due the detector sensitivity, which is $\sim 5\%$. A detailed account of the measurement principle and the setup can be found in [144].

4.3 Magnetic susceptibility

Magnetic susceptibility measurements were done using a 7T VSM-SQUID and a 5T MPMS-SQUID from Quantum Design. These devices employ the superconducting quantum interference device (SQUID) which is an extremely sensitive detector of magnetic flux. The SQUID sensor is inductively connected to the
sample via detection coils and it measures the magnetic moment of the sample when the sample is moved through these coils. A superconducting magnet is used to generate large magnetic fields up to 9T. The sensitivity of the SQUID is linked to the measurement of changes in magnetic field related to one flux quantum. On applying a constant biasing current in the SQUID, the measured voltage oscillates with change in the magnetic flux. Counting the oscillations allows evaluating the flux change which has occurred. For details about the measurement setup and the method one can refer [145].

4.4 Diffraction experiments and analysis

Powder x-ray diffraction was carried out using a STOE diffractometer (transmission geometry) with Molybdenum ($K_\alpha$ 0.709 Å) and Copper ($K_\alpha$ 1.5406 Å) x-ray sources. The diffractometer is equipped with a curved Ge(111) monochromator and 6o-linear position sensitive detector. Rietveld [146] refinement was carried out using FullProf in the WinPlotR program package [147]. For refinements a Thompson-Cox-Hastings pseudo-voigt peak profile function [148] was chosen. The parameters refined were the background, scale factor, zero position, lattice parameters, asymmetries and the atomic positions. Single crystal x-ray diffraction at room temperature was performed using the Bruker AXS Kappa APEX II CCD four-circle single crystal diffractometer with a Mo $K_\alpha$ source to probe crystallinity and to determine important parameters regarding the crystal structure. The Bragg reflections were integrated by EVAL-1437 [149]. Multi-scan and numerical absorption corrections with SADABS 3.8 [150] have led to similar results. Each time the spacegroup was determined by Xprep [151] and checked by PLATON 4.0 [152]. Preliminary structural analysis using the method mentioned in [153] (SIR2004), and the structure was then refined in detail using SHELX97 algorithm [151] in the APEX II or WinGX program.
Chapter 5

Materials and motivation

5.1 \( \text{La}_2\text{CuO}_4 \)

5.1.1 Crystal structure and magnetism

\( \text{La}_2\text{CuO}_4 \) is a prototype material that realizes the two dimensional \( S = \frac{1}{2} \) Heisenberg antiferromagnet on a square lattice [64], a very interesting and simplified object from the physical point of view. It is a parent compound for a whole range of high \( T_c \) superconductors that are obtained upon doping the pure material with charge carriers [64].

Fig. 5.1 shows the unit cell of \( \text{La}_2\text{CuO}_4 \), where Cu and O atoms form layers along the crystallographic \( ab \)-plane. In between two such CuO\(_2\) layers, two LaO sheets are located. The O atoms belonging to the LaO planes that are placed either directly above or below a copper atom result in the formation of a CuO\(_6\)-octahedron. \( \text{La}_2\text{CuO}_4 \) can exist as two different structural phases. Above \( T = 530 \) K, the tetragonal structural phase in the space group \( I4/mmm \) exists (HTT phase: High Temperature Tetragonal). The lattice parameters for this phase are \( a = b = 3.8 \) Å, \( c = 13.2 \) Å [154]. Below 530 K the lattice undergoes a transition into an orthorhombic structural phase in the space group \( Bmab \) (LTO phase: Low Temperature Orthorhombic). This phase has lattice parameters \( a = 5.36 \) Å, \( b = 5.41 \) Å and \( c = 13.14 \) Å [154]. In this phase crystallographic twinning is present, i.e., the crystal is composed of domains with the \( a \) and \( b \) axes interchanged.

Within the CuO\(_2\) planes a strong in-plane exchange coupling, characterized by
$J$ (1550 K) [95, 96], exists between the Cu spins. This coupling, antiferromagnetic in nature, operates according to the superexchange mechanism (see section 2.2). Between these planes there exists an inter-plane exchange coupling, $J'$, that is weak and around $10^{-5}$ times $J$ [98, 155]. In the LTO phase the CuO$_6$-octahedrons slightly tilt away from the $ab$-plane. This small distortion alters the electronic environment of the Cu spins, which can be captured by an additional term called the Dzyaloshinskii-Moriya interaction term in the spin Hamiltonian [98, 101, 102, 155, 156]. This alteration causes the spins to cant out of the $ab$-plane, and results in a net spin-moment in the planes that antiferromagnetically couple to moments in other parallel planes via $J'$. As has been discussed earlier (see section 2.2) La$_2$CuO$_4$ is a charge-transfer insulator, and for all practical purposes, can be described well by considering spins interacting on a square-planar lattice within the framework of the Heisenberg model.

Figure 5.1: Unit cell of La$_2$CuO$_4$. 
Chapter 5. Materials and motivation

5.1.2 Heat transport

La$_2$CuO$_4$ is one of the first compounds where heat conductivity has been observed to consist of large contribution from magnetic excitations at room temperature, in addition to contribution from phonons [12–16]. In spite of experimental observation of heat transport due to magnetic excitations, the microscopic origin of this transport channel and the scattering mechanisms responsible for it, is not understood.

The heat conductivity of La$_2$CuO$_4$ measured parallel ($\kappa_{ab}$) and perpendicular ($\kappa_c$) to the CuO$_2$ planes is shown in Fig. 5.2. $\kappa_{ab}$ shows a two-peak structure, a sharp phononic low-temperature peak at $\sim 25$ K and a much broader high temperature peak at $\sim 280$ K. $\kappa_c$, on the other hand, exhibits a low temperature peak similar to that observed in $\kappa_{ab}$, and a fall-off at higher temperatures like that of a typical phonon-only conductor. This large anisotropy in the in-plane and out-of-plane thermal conductivity, characterized by the high-$T$ peak in $\kappa_{ab}$, is a result of heat conduction due to magnetic excitations propagating in the $ab$-plane [12–16]. In the temperature range from 70 K - 158 K, where $\kappa_{mag}$ increases, Hess et. al. proposed that the low temperature increase of the magnetic heat conductivity can be modelled in the framework of a Boltzmann-like approach.
with a constant mean-free path due to magnon-defect scattering, where $\kappa_{\text{mag}}$ is proportional to the square of the temperature (see 3.4.2). However, the presence of a peak in $\kappa_{\text{mag}}$ indicates that at higher temperatures, other $T$-dependent dissipative scattering mechanisms set in that cause a decrease in the heat conductivity. These mechanisms are poorly understood though, and experimental and theoretical work is necessary for revealing them.

A qualitative comparison of the experimental data in the literature with theory gives us some more information regarding the involved scattering processes. Magnetic heat conductivity of La$_2$CuO$_4$ compound was recently calculated by Bayrakci et al., by taking scattering of magnons with boundaries and other magnons and using lifetimes of magnons extracted from linewidths that were experimentally obtained for the iso-structural Rb$_2$MnF$_4$ compound [157, 158]. The mean free path of magnons (580 Å) used in the calculation was taken from [12]. In Fig. 5.2, this calculation is compared with $\kappa_{\text{mag}}$ obtained from experiments by Hess et al. We see that the experimental data is limited to temperatures below 350 K. For a comparison with theory at higher temperatures, to validate whether magnon-magnon scattering processes are indeed solely responsible for the fall-off of $\kappa_{\text{mag}}$ or is it that other scattering mechanisms like magnon-phonon scattering are also relevant, experimental data for higher temperatures is needed.

Previous investigations of the heat conductivity for La$_2$CuO$_4$, had some limitations however. The single crystals which were used for the measurements were not of very high quality with regard to their purity, as will be evident from the experimental results presented in this work. Also, the steady-state technique used to measure heat conductivity in the literature is restricted to temperatures up to about 300 K, which just allows the peak in $\kappa_{\text{ab}}$ to be seen. Access to the behaviour of heat conductivity at higher temperatures would be necessary to have information about the $T$-dependence of the $\kappa_{\text{ab}}$ fall-off. This information about the high-$T$ regime, would be of high value when it comes to the understanding of the scattering mechanisms relevant for magnon heat transport.

5.2 Spin chains: Sr$_2$CuO$_3$ and SrCuO$_2$

Impurities are not always to be seen as undesirable defects that deteriorate physical properties of materials. On a fundamental level, they can often act as a valuable probe for understanding physical phenomena. The effect of impurities included in systems like 1D Heisenberg spin chain has been that of creating disorder. Disorder can be responsible for generating randomness in quantities like
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exchange coupling and bond strength. Such randomness has been always interesting from a theoretical point of view and has led to many fascinating results, thereby revealing interesting physics. Such results have especially been worked out for strongly correlated $S = \frac{1}{2}$ chains owing to the relative ease of calculating in one dimension. Strong quantum effects that are prominent in lower dimensions. Randomness leads to an interplay between quantum effects, strong correlations and the disorder that can be probed using theory and validated using experiment.

Impurities or defects are known to have strong observable effects on the properties of $S = \frac{1}{2}$ chains, some of them being mentioned below. Disorder in spin chains has theoretically been predicted to have drastic influence on magnetic ground states and excitations associated with it, and affect transport and thermodynamic properties as well [41–45]. They can destroy or create long range order in spin systems depending upon the nature of the ground state, or even drive the system into exotic phases [159–162]. Doping of low-dimensional systems can give rise to unconventional superconductivity or suppress superconductivity by localizing charges as well [163]. Also, extra spin degrees of freedom have been experimentally observed to emerge upon doping impurities into chains, these results being in consistency with field-theoretical calculations [46, 47]. Theoretical treatment of disordered $S = \frac{1}{2}$ chains using renormalization group (RG) analysis has led to the observation of exotic phases, where the interplay of disorder and quantum effects cause each spin to be paired with an other that could be located arbitrarily far away in the chain [42, 44, 164, 165]. Low-energy dynamical and transport properties of these chains have also been theoretically studied using RG, and have shown that such low-$T$ phase leads to diverging low-energy density of states. However, recent experiments observe depletion of low-energy states, upon creating impurity-induced disorder in the system. Also, this phase has been confirmed by low-$T$ experiments on materials that realize a random Heisenberg chain [48, 49]. Thus, an area that can be termed as quantum impurity physics is evidently enough an engaging field. Substantial work has been done on disordered spin systems with a view to understanding the effect of randomizing coupling strengths and signs between spins. However, there are few experimental studies that investigate how different kinds of disorder affect properties of a variety of spin systems. Dearth of experimental data has prevented validation of theoretical results obtained for varying amounts of disorder in spin systems. This motivates the need for more experiments that probe such disorder-related effects on low dimensional spin systems.

Disorder can be introduced in spin chains by doping atoms of similar ionic size as the original atoms into the crystal lattice. In this work, two kinds of disorders are realized. Ni has chemically substituted into the lattice of Sr$_2$CuO$_3$ at the
5.2. Spin chains: \( \text{Sr}_2\text{CuO}_3 \) and \( \text{SrCuO}_2 \)

Site of Cu, thereby introducing a spin \( S = 1 \) impurity in the chain. Ca has been substituted at the Sr site in \( \text{Sr}_2\text{CuO}_3 \), thereby introducing a spin \( S = 0 \) impurity outside the chain. The systems that have been investigated in this work are the following. Single crystals of \( \text{SrCuO}_2 \) doped with 1% Ni grown using the TFSZ method have been studied with NMR and INS to probe the effect of Ni on the low energy spin excitations. The single chain analog \( \text{Sr}_2\text{CuO}_3 \), doped with Ni and Ca, has been studied with regard to heat transport.

5.2.1 Crystal structure

Both \( \text{SrCuO}_2 \) and \( \text{Sr}_2\text{CuO}_3 \) are considered to be good realizations of \( S = \frac{1}{2} \) Heisenberg spin chain systems because of the arrangement of spins in the crystal structure. Cu sites with \( S = \frac{1}{2} \) spins are arranged so as to form quasi one-dimensional chains. In the case of \( \text{SrCuO}_2 \) there are two such spin chains running parallel to each other, and in \( \text{Sr}_2\text{CuO}_3 \) there is only one such chain. The most interesting unit from the point of view of magnetism are these chain units that exhibit unique and interesting quantum behavior.

In \( \text{SrCuO}_2 \), Cu and O atoms form zig-zag chain structures running parallel to the \( c \)-axis. It crystallizes in the \( Cmcm \) space group with lattice constants \( a = 3.56 \) Å, \( b = 16.32 \) Å and \( c = 3.92 \) Å [166]. The crystal structure facilitates a 180° overlap between the O and Cu orbitals, thereby, according to the Goodenough-Kanamori rules [63, 167], gives rise to a strong antiferromagnetic coupling between neighboring Cu spins via the so-called superexchange mechanism. The coupling constant \( J/k_B = 2100-2600 \) K along these chains [168, 169]. The interchain coupling being much smaller, \( J/k_B = 200-500 \) K [60, 168]. Three dimensional ordering is seen at \( T \approx 2 \) K, above which temperature strong quantum fluctuations inhibit long range ordering [170, 171].

\( \text{Sr}_2\text{CuO}_3 \) crystallizes in the \( Immm \) space group with lattice constants \( a = 12.68 \) Å, \( b = 3.91 \) Å and \( c = 3.48 \) Å. The structure consists of edge sharing single chains separated by Sr atoms running parallel to the \( b \)-axis [172]. The magnetic coupling along the chains is \( J/k_B = 2150 \) K - 3000 K, of similar magnitude as in \( \text{SrCuO}_2 \) [168, 173, 174]. But the interchain coupling of the well separated chains is negligibly small, \( J_\perp/k_B \approx 0.02 \) K. Three dimensional ordering is seen at \( T_N \approx 5.4 \) K [175, 176]. These independent spin chains make this material as the best candidate that realizes the \( S = \frac{1}{2} \) Heisenberg chain model.
Figure 5.3: (a) Crystallographic unit cell of SrCuO$_2$ showing the copper-oxygen double chain structure. (b) Crystallographic unit cell of Sr$_2$CuO$_3$ showing the copper-oxygen single chain structure.
5.2. Spin chains: \( \text{Sr}_2\text{CuO}_3 \) and \( \text{SrCuO}_2 \)

\begin{align*}
\text{SrCuO}_2 & \quad \text{Sr}_2\text{CuO}_3 \\
\end{align*}

**Figure 5.4:** Spin dispersion relation: The structure factor and the energy transfer are plotted as a function of the momentum \( Q \) for the spin chain compounds \( \text{SrCuO}_2 \) and \( \text{Sr}_2\text{CuO}_3 \)

### 5.2.2 Spin excitations

As has been discussed in section 3.4.1, the dispersion of spinons in compounds like \( \text{Sr}_2\text{CuO}_3 \) and \( \text{SrCuO}_2 \) is the two-spinon continuum as has been predicted for \( S = \frac{1}{2} \) Heisenberg chains. Fig. 5.4 shows the observed dispersion relation for spin excitations as measured by inelastic neutron scattering for these two compounds \cite{169, 177}. The observation shows that these spinons are gapless, showing a continuum of states down to the lowest measured energy.

Another microscopic probe that measures spin dynamics is nuclear magnetic resonance (NMR). Although this technique measures the dynamics only at frequencies very close to zero one can get valuable information on the low energy excitations. The plots of the inverse of the spin-lattice relaxation time \( (1/T_1) \) versus the temperature for the spin chain compounds \( \text{Sr}_2\text{CuO}_3 \) \cite{178} and \( \text{SrCuO}_2 \) \cite{179} are shown in Fig. 5.5. \( 1/T_1 \) is found to be almost constant in the entire temperature range from 4 K to 300 K. This is consistent with theoretical calculations for the \( S = \frac{1}{2} \) antiferromagnetic spin chain \cite{180}. This indicates that the excitations related to the spin systems are gapless in nature, a result that agrees
with the neutron measurements and what theory predicts.

5.2.3 Heat transport

Fig. 5.6 shows the heat conductivity measured parallel ($\kappa_\parallel$: filled circles) and perpendicular ($\kappa_\perp$: open circles) to the spin chains of the undoped compounds SrCuO$_2$ and Sr$_2$CuO$_3$. A large anisotropy in the measured heat conductivity is immediately obvious, with $\kappa_\parallel$ along the chains being much larger than $\kappa_\perp$ perpendicular to the chains over the entire temperature range. $\kappa_\perp (T)$ shows a sharp peak at low temperatures and falls off rather quickly at higher temperatures, a $T$-dependence characteristic of a purely phononic system. The heat conductivity perpendicular to the spin chains must be purely phononic because spinons possess dispersion only parallel to the chains. $\kappa_\perp (T)$ shows a much broader peak at low $T$ and falls off much slower than $\kappa_c (T)$ at higher temperatures, untypical of phonon-only systems. Although the observed anisotropy in SrCuO$_2$ is much larger than that in Sr$_2$CuO$_3$, it is significant in both cases. Large anisotropy in the magnitude and temperature dependence of $\kappa_\parallel$ and $\kappa_\perp$, anisotropic dependence of heat conductivity on the purity of the compound, and unconventional temperature dependence of $\kappa_\parallel$ have led to the well established conclusion that there is an additional contribution to the heat conduction parallel to the spin chains due to propagating magnetic excitations [6, 8, 9, 9]. Also, the difference between
5.2. Spin chains: $\text{Sr}_2\text{CuO}_3$ and $\text{SrCuO}_2$

![Thermal conductivity graphs](image)

**Figure 5.6:** Thermal conductivity measured parallel and perpendicular to the spin chains of undoped (a) $\text{SrCuO}_2$ and (b) $\text{Sr}_2\text{CuO}_3$.

The two heat conductivities $\kappa_\parallel$ and $\kappa_\perp$ gives the spinon heat conduction in the system. This novel channel of heat conduction in these compounds exists in addition to the conventional channel of heat transport via phonons. It has also been suggested that to describe the temperature dependence of the mean free path of these spinons one has to only take into account two scattering mechanisms, namely a temperature independent spinon-defect scattering and an umklapp-like temperature dependent spinon-phonon scattering [7, 9]. The temperature range in which this description seems to be valid for $\text{SrCuO}_2$ is rather wide and extends from lowest temperatures (7 K) to very high temperature (800 K) [144].

$\text{Sr}_x\text{Ca}_{1-x}\text{CuO}_2$

It is interesting to probe the effect of different kinds of disorder realized by different kinds of dopants and their position in the crystal lattice. In earlier works, it has been seen that an off-chain doping can lead to a more subtle effect of bond disorder than that caused by in-chain dopants. $\text{SrCuO}_2$ has been studied with regard to the effect of substituting Ca for Sr in small amounts [32, 50]. As Ca occupies sites outside but near the Cu-O-Cu spin chains, bond disorder, i.e. a spatial variation of the exchange interaction $J$, is realized in these chains. This study resulted in the following observations. Firstly, an off-chain impurity like Ca causing bond disorder in the spin chains, strongly suppresses spinon-heat
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**Figure 5.7:** (a) Heat conductivity of Sr$_x$Ca$_{1-x}$CuO$_2$ for $x = 0.0125$, 0.025, 0.05 and 0.01, measured parallel to the chains ($\kappa_c$), inset: perpendicular to the chains ($\kappa_a$). Data taken from [32]. (b) Spin-lattice relaxation rates in Sr$_x$Ca$_{1-x}$CuO$_2$ for $x = 0.05$, data taken from [50].

transport. Fig. 5.7(a), shows the heat conductivity measured parallel ($\kappa_c$) and perpendicular ($\kappa_a$) to the chains. A gradual and monotonic suppression of $\kappa_c$ and $\kappa_a$ is seen with increasing amounts of Ca doping. Also, the effect of Ca, viz. a strong suppression of $\kappa_{\text{mag}}$, decreases upon increasing its concentration and seems to saturate at around 10% Ca. This saturation was proposed to be related with the disorder-induced long distance decay of the spin-spin correlation [32].

From NMR studies on the Ca-doped SrCuO$_2$, it is seen that Ca-doping opens a gap in the spin excitation spectrum at low energies. Fig. 5.7(b) shows the spin-lattice relaxation as a function of temperature. The spin-lattice relaxation rate is seen to exponentially decrease below $\sim 90$ K, which marks the onset of a spin-gap with magnitude $\Delta \sim 50$ K [50].

In the present work, the single chain compound, Sr$_2$CuO$_3$, is chosen mainly because it contains a single spin chain as opposed to the two weakly interacting spin chains realized in SrCuO$_2$. Thereby the effect of bond disorder on spinon transport in a more simplified chain structure that is different from the double chain CuO$_2$ network in SrCuO$_2$ is being probed.
5.2. Spin chains: $\text{Sr}_2\text{CuO}_3$ and $\text{SrCuO}_2$

The effect of Ni on the heat transport of $\text{SrCuO}_2$ has been studied and discussed in [32]. The observations and conclusions are summarized below. Heat conductivity of $\text{SrCu}_{1-x}\text{Ni}_x\text{O}_2$ for $x = 0.0025$, 0.05 and 0.01 measured parallel to the chains ($\kappa_c$) and perpendicular to the chains ($\kappa_a$) is shown in Fig. 5.8.

Even the smallest Ni doping ($x = 0.0025$) was seen to have a drastic effect on the thermal conductivity. The broad peak in $\kappa_c$ at low temperatures for the undoped compound is strongly suppressed and the maximum is shifted towards lower temperatures. This is indicative of the suppression of the spinon heat conduction. An increase of the Ni doping to $x = 0.005$ and $x = 0.01$ leads to a further reduction of the maximum at low temperatures consistent with a higher impurity concentration and a small overall reduction of the thermal conductivity without a change in the shape of the curve with respect to the $x = 0.0025$. For the higher doping levels the position of the maximum at low temperatures remains unchanged. This is consistent with the previous analysis which explained the peak of the undoped compound as consisting of two contributions, the usual phononic peak and an additional peak attributed to the magnetic thermal transport [6]. It is mostly this latter contribution which is suppressed by the Ni doping. A quantitative analysis of the heat conductivity in the framework of the kinetic model
suggested that the temperature and doping dependence of the mean free path can be described by two scattering processes alone, viz. spinon-defect scattering and spinon-phonon scattering, and that Ni acts as a strong defect-like scatterer for spinons [58].

However, perpendicular to the chains a counter-intuitive effect is observed. For $x = 0.0025$, an enhancement of the peak in $\kappa_a$ is seen to a value almost double that of the undoped compound. $\kappa_a$ increases even more to a value of $\sim 450$ Wm$^{-1}$K$^{-1}$. for $x = 0.05$. Finally, for $x = 0.01$, peak value of the heat conductivity drops to a value below that for the $x = 0.0025$ case, but remains higher than that of the undoped compound. This nonintuitive enhancement of the phononic heat conductivity, $\kappa_a$, upon making the system dirty indicates that there is an additional scattering mechanism for spinons that is being lifted upon doping the system (refer [6]). In the current work we investigate the heat transport properties of SrCuO$_2$ doped with Ni, and also discuss the results of neutron scattering experiments on Ni-doped Sr$_2$CuO$_3$ in order to throw light on the effect of Ni on the low energy magnetic excitations in these spin-chain compounds.

5.3 $\text{La}_8\text{Cu}_7\text{O}_{19}$

Among low dimensional magnets, the class of spin ladder compounds is of special interest as they are invaluable in understanding the physics of the crossover from one-dimensional to the two-dimensional nature of spin systems. They are known to show interesting magnetic ground states and even superconductivity upon charge carrier doping [51]. The dimensionality of the spin system plays an important role in deciding magnetic ground states. Reduction in dimensional degrees of freedom enhances effects due the quantum nature of the spin at experimentally accessible temperatures. Interestingly, these quantum effects lead to drastic dependencies of magnetic properties on the number of legs of the spin ladder. For example, gapped and ungapped spin excitation spectra have been predicted and experimentally verified for spin ladders with even and odd number of ladder-legs respectively, arising from differences in ground states [51]. Owing to their reduced dimensionality, ladder compounds stand as valuable candidates in verifying theoretical models with experimentally obtained results [3, 182]. However, experimental realizations of ladder systems are few, especially spin ladders with number of legs greater than two [52, 53].

About two decades ago, Cava et. al [52] reported the existence of the homologous series $\text{La}_{4+4n}\text{Cu}_{8+2n}\text{O}_{14+8n}$, whose $n = 2$ ($\text{La}_2\text{Cu}_2\text{O}_5$) and $n = 3$ ($\text{La}_8\text{Cu}_7\text{O}_{19}$)
5.3. \textit{La}_8\textit{Cu}_7\textit{O}_{19}

Figure 5.9: (a) Susceptibility as a function of temperature for \textit{La}_8\textit{Cu}_7\textit{O}_{19} compound, as measured on polycrystals (taken from [52]); (b) Temperature dependencies of reduced intensity of magnetic scattering for \textit{La}_8\textit{Cu}_7\textit{O}_{19} (\(T_N = 103\) K) and its comparison with that of \textit{La}_2\textit{CuO}_4 (taken from [183]).

members, respectively, comprises of 4- and 5-legged \(S = \frac{1}{2}\) spin ladders. It is worth mentioning here that the member \(n = \infty\) of this series is the mother compound \textit{La}_2\textit{CuO}_4 of the high-temperature superconductors [64]. There has not been much progress towards understanding the magnetism of these spin ladder compounds as it is challenging to grow them as a single crystal for reasons explained below. Hence, attempts to synthesize such materials are very much needed. This work deals with the synthesis of the five-leg ladder material \textit{La}_8\textit{Cu}_5\textit{O}_{19} using the TFSZ method, and further describes in detail the crystal and magnetic structure of this compound that are indispensable to understand its properties. Also, magnetic and physical properties of this compound have been measured and are discussed in some detail.

\textit{La}_8\textit{Cu}_7\textit{O}_{19} is known to have a monoclinic structure with a space group \(C2/c\), and lattice parameters \(a \approx 13.84\)\AA, \(b \approx 3.756\)\AA, \(c \approx 34.64\)\AA, and \(\beta \approx 98.99^\circ\). As per literature, \textit{La}_8\textit{Cu}_7\textit{O}_{19} crystallizes in a very narrow temperature range in both oxygen and ambient atmospheres [52, 184–186]. There have been reports of single crystal growth of this compound using flux growth techniques [184, 186], but none using the travelling-solvent floating zone method (TSFZ). The susceptibility measured on polycrystalline \textit{La}_8\textit{Cu}_7\textit{O}_{19} is plotted in Fig. 5.9(a). A broad peak at around 200 K and a smooth decrease at high temperatures is seen. Cava et al. speculated the broad peak to arise from the magnetic behavior of the complex Cu-O planes and highly distorted copper-oxygen geometry that is present in this compound.
Zobkalo et al. [183] performed polarized neutron scattering in La$_8$Cu$_7$O$_{19}$. The temperature dependence of magnetic scattering for La$_8$Cu$_7$O$_{19}$ and La$_2$CuO$_4$ is plotted in Fig. 5.9(b). A Neel temperature of 103 K was observed for La$_8$Cu$_7$O$_{19}$. Also, the shape of the transition to the ordered state is very different from that of the 2D Heisenberg antiferromagnet La$_2$CuO$_4$. It was claimed that Cu moments in octahedral sites are oriented along the $b$-axis and coupled antiferromagnetically along the $c$-axis, whereas Cu moments within ribbons are oriented along the $a$-axis forming ferromagnetic pairs and coupled antiferromagnetically as one moves along the $a$-axis. However, such a description seems ambiguous even if it is assumed that authors describe the Cu moment coupling within one chemical unit cell. Due to a large number of atoms in the unit cell, there are several different possibilities that agree with the above mentioned description. Moreover, it does not give any information regarding the propagation along the $a$-axis for the former type of moments, and similarly, no information on the $c$-axis coupling for the latter one. Also, no information on the coupling along the $b$-axis is given. It suggests even
the interpretation that both sub-systems propagate with different propagation vectors. Therefore, the single crystals of La₈Cu₇O₁₉ grown in this work have also been used for reinvestigating the magnetic structure of La₈Cu₇O₁₉ in more detail to provide more information and verify the above claim.

5.4 LaCuO₂

The structure of delafossites with general formula A³⁺B¹⁺O₂ consists of edge sharing A³⁺O₆ octahedra that form triangular oxygen planes. Between two oxygen planes lies a plane of B¹⁺ cations that are linearly coordinated with oxygen atoms [187, 188]. Thus, LaCuO₂ has a layered structure, with triangular lattice planes consisting of O-Cu-O sticks and LaO₆ octahedra [188]. An illustration of the crystal structure is given in Fig. 5.10. Delafossites like LaCuO₂ and YCuO₂ have been studied with regard to intercalation of oxygen, thereby introducing holes, with a view towards understanding magnetism and superconductivity in cuprates [187]. They have also been studied from the photoelectrochemistry perspective as they show interesting luminescence properties [189, 190]. In the delafossite LaCuO₂, Cu¹⁺ is in the 3d¹⁰ configuration, and hence is diamagnetic. Doping oxygen in these systems reduces resistivity but does not give rise to metallicity even at the highest possible oxygen contents [187]. However, the valency of Cu increases upon doping oxygen and thereby introduces a magnetic character in the material. Not many studies have been undertaken on this material in this regard, as single crystals are required for accurate studies of magnetism and most of the physical properties. Earlier, only polycrystals of LaCuO₂ have been synthesized starting with stoichiometric mixtures of La₂O₃ and Cu₂O and firing at high temperatures in a N₂ or Ar atmosphere, or under vacuum at high pressures [187–190]. In this work LaCuO₂ has been synthesized as single crystals for the first time using a method involving the reduction of La₂Cu₂O₅, and its details have been discussed in section 6.3.4.
High quality single crystals are indispensable when it comes to studying the anisotropic properties of materials. Measuring physical properties and studying the effect of external perturbations like electric or magnetic fields, temperature gradients on single crystalline materials can yield a great deal of information on intrinsic response of condensed matter systems in general. When it comes to growing such single crystals, one has to carefully choose a suitable technique depending upon the constituents of the desired material and upon what application is the material needed for.

In our work we deal with compounds that melt incongruently, i.e compounds that, above a certain temperature, called the peritectic temperature, decompose into a mixture of a new solid and a liquid. Thus, we would prefer a method that makes this class of compounds easy to grow. Being particularly interested in the effects of chemical disorder, we intend to make chemical substitutions in very small amounts, which would require a crystal growth technique that results in a homogeneous distribution of a dopant in the grown crystal. Physical properties like heat transport of these materials that we are interested in, are known to be very sensitive to impurities, hence we would need a method that possibly minimizes contamination. Also, we require single crystals of large dimensions for experiments like neutron spectroscopy that can help us to understand important aspects about physical properties of such materials. The above conditions therefore narrow down our best possible choice to the travelling solvent floating zone method owing to its advantages that will be explained below.

At first we describe solidification processes in incongruently melting compounds, and then discuss how the floating zone method realizes this. Later, we describe
6.1 Phase diagrams

Figure 6.1: A schematic of a pseudo-binary phase diagram for phases A and B, showing the different regions of compositions along with how the corresponding microstructure is expected to look like. The green and red arrows along the liquidus lines indicates the movement of the composition of the melt.

the results of growth experiments that were performed to grow pure and doped versions of single crystals of some La- and Sr-based cuprates. For more detailed discussions on the floating zone method and its application for synthesizing low-dimensional cuprate materials and other oxides one may refer to [59, 191–193].

6.1 Phase diagrams

In order to understand the crystallization of partially miscible solids from completely miscible melts one has to refer to corresponding phase diagrams. In such a phase diagram, the volume fraction (in atomic % or weight%) of two immiscible or partially miscible solids are plotted on the horizontal axis, and a variable like temperature is plotted on the vertical axis. In the hypothetical schematic of a phase diagram shown in Fig. 6.1 we have two elements A and B, and a compound $A_xB_y$ on the $x$-axis. $\alpha$, $\beta$ and $\gamma$ are the regions of solubility of $A_xB_y$ and B in
A, A and B in $A_xB_y$ and $A_xB_y$ in B respectively. Hence, $\alpha$ means the region where one crystallizes a solid A with small amounts of $A_xB_y$ and B as inclusions. Apart from these narrow solubility regions one find regions where a mixture of two phases $\alpha$ and $\beta$ ($\alpha + \beta$) and $\beta$ and $\gamma$ ($\beta + \gamma$) exist. Points marked P and E correspond to the peritectic and eutectic compositions respectively. The peritectic composition/temperature is the one where $A_xB_y$ when heated up to $T_P$ decomposes into two phases, $\alpha$ and a liquid of composition $C_P$. The eutectic composition/temperature is the one where all three phases, the complete melt, the complete solid ($\alpha + \beta$) and solid + liquid ($\alpha$+liquid/$\beta$+liquid) can exist simultaneously. Here, a melt of composition $C_E$ is solidified at a fixed temperature into a two-phase mixture ($\alpha + \beta$), resulting in columnar/lamellar growth.

Let us now turn to Fig. 6.2. Here, we consider the cooling (solidification) process of a melt with composition $C_S$ as shown by the blue dashed line. Upon slowly cooling this melt we first reach the liquidus line where phase $\alpha$ begins to crystallize from the melt. This crystallizing $\alpha$ phase therefore shifts the composition of the remaining liquid to the right along the liquidus. The images on the right hand side of Fig. 6.2 shows a schematic of the expected microstructure. We see that small islands of solid $\alpha$ have crystallized in a melt of composition $C_L$. This continues to happen till the temperature reaches $T_P$. At this point the liquid has reached a composition $C_P$, which happens to be the so called peritectic composition of the compound $A_xB_y$, where now $A_xB_y$ starts crystallizing out of this melt as an additional phase in the already present $\alpha$ phase. This is seen in the microstructure schematic as red islands (green islands of $\alpha$ phase are already present) developing in the melt which now has the composition $C_P$. As the temperature is further decreased, this crystallization of $A_xB_y$ pushes the composition of the liquid further down the liquidus until it reaches the eutectic composition $C_E$. At this point, the entire liquid immediately solidifies in lamellar structures of alternating $A_xB_y$ and gamma phases, this being a property of the eutectic solidification process. The microstructure is expected to have a background of eutectically solidified liquid with alternate stripes of $\alpha$ and $\beta$ phases.

Such a process also occurs in a typical floating zone experiment concerning the growth of an incongruently growing compound like $A_xB_y$. Let us now see in the context of this method how one can grow single crystals of $A_xB_y$. 

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Travelling solvent floating zone method

In the TFSZ method, one tries to grow single crystals of a compound like \( A_x B_y \) by feeding its polycrystalline version and peritectically crystallizing single grain material out of it. In the phase diagram we start with a feed rod composed of the compound \( A_x B_y \) synthesized in the solid state.

6.2.1 Principle

The travelling solvent floating zone method involves the crystallization of a compound from a so-called molten floating zone that is formed by bringing together and melting two cylindrical rods made of the phase that is to be grown as a single crystal. This molten zone is translated along the length of the polycrystalline
rod to eventually obtain single crystalline material. In the hypothetical phase diagram in Fig. 6.2, the melt having the same composition as that of the starting material, lies at point A. Upon cooling, this melt will first crystallize into the $\alpha$ phase until the remaining melt is enriched in B and eventually reaches point P. At this point, the liquid will then crystallize to form the $A_xB_y$ phase via a peritectic reaction. The FZ then reaches a steady state, where a finite amount of material of composition $A_xB_y$ is fed into the zone forming a melt of composition $C_P$ which then crystallizes into $A_xB_y$ again. At this steady state, grain selection occurs and finally one single grain dominates the entire cross section of the growing crystal.

**Figure 6.3:** A photograph of the image furnace (CSI FZ-T-10000-H-II-VP)) by Crystal System Inc. that was used in this work.
6.2.2 Setup

This method uses the focussing of light to achieve high temperatures in small regions of space. In the used image furnace (CSI FZ-T-10000-H-II-VP)) by Crystal System Inc., four filament lamps are placed at the nearer focus of four ellipsoidal mirrors. When these lamps are switched on, the mirrors reflect the light from these lamps focus it onto the second focal point of these mirrors. The mirrors are aligned so as to have the second focal point merging at the same point in space. This results in the light from all mirrors being focussed at a single point where a ‘hot-zone’ is created in order to form the molten FZ. This is illustrated schematically in Fig. 6.4. The upper and lower shafts are positioned such that one has the focal point exactly on the axis of the feed and seed rods, thereby allowing to form and sustain the FZ. A photograph of the image furnace is shown in Fig. 6.3.

6.2.3 Feed and seed rods

Feed and seed rods of the same phase whose single crystals are desired are synthesized by reactions in the solid state. This involves sintering of appropriate amounts of powders of the constituents that form the compound at appropriate temperatures according to the respective phase diagrams. This solid state reaction occurs by the process of diffusion of atoms into their lowest energy sites, thereby forming the crystal lattice suited to that temperature. After the compound is formed and its phase purity is checked by x-ray diffraction, the powder is pressed in the form of rods. For this, latex tubes with inner diameter $\sim 5$ mm were used, in which the powder is carefully filled ensuring that the filling density along the length of the tube is uniform. One has to make sure that the feed is homogeneous along its length with respect to packing density, and composition. Also, the diameter of the rod must not be too large compared to the width of the lamp filaments in the furnace, which otherwise can lead to improper melting of the feed and the radial temperature gradients inside the floating zone. Then the tube is closed and any air from it is removed using a vacuum pump. This is done in order prevent the air from being trapped in the volume of the rod when the rod is pressed. The tube with the powder is then inserted into a cold isostatic press and is pressed at pressures of around 3000 bar. This results in cylindrical rods of length 8-10 mm that have to be sintered at high temperatures before using in the experiment. One has to take care that the rod does not develop a curvature during the filling, pressing or sintering process as this can result in precessing of the rod during the growth and thus affect the FZ stability and grain selection. An
appropriately high sintering temperature is necessary to make the rods dense, as not so dense rods will lead to suction of the melt in the floating zone by capillary effects of the pores in the feed rod. This step of preparing the feed and seed rods is a crucial one and often decides the outcome of the growth experiment.

Now with the feeding and seeding material of the composition $A_xB_y$, the growth experiment can be started. Fig. 6.4 shows the arrangement of the seed and feed rods with respect to the focus of the mirrors before the beginning of the experiment.

### 6.2.4 Atmosphere

In the four mirror furnace one can use oxygen or argon atmospheres in the growth chamber during the growth experiment. It is possible to maintain a constant
flow or a constant pressure of the gas in the chamber. A maximum pressure of 10 bar can be reached in the chamber. Thick protective quartz tubes having a wall-thickness of around 4 mm, are used to enclose the chamber at high pressures. Oxygen atmospheres can be useful for growing oxides where it is important to have a good oxygen stoichiometry in the compound. Argon atmospheres are useful for materials that are better grown in inert or reducing atmospheres. During growths in an oxygen atmosphere, in case of formation of oxygen bubbles, which occasionally occurred in our growth experiments due to the decomposition of CuO into Cu$_2$O, one had to introduce small amounts of Argon into the chamber. This would help the bubbles to diffuse out owing to the difference in partial pressures of O and Ar, which would otherwise result in accumulation of bubbles and eventual collapse of the FZ.

### 6.2.5 Solvent pellet and zone formation

In order to reach the steady state faster one starts with a solvent-pellet of composition around the peritectic point of the phase that is desired. If we start the growth directly by decomposing the feed into a solid of different composition and a liquid of the peritectic composition, very little of this liquid is initially available to establish the molten zone. Moreover, we need to go to high temperatures to
Chapter 6. Single crystal growth

completely melt the feed rod and then return back to lower temperatures near the peritectic point where the reaction takes place. Therefore, we start directly with a composition of the peritectic point that results in a liquid entirely of a composition which we would like our molten zone to be in stable state while crystallizing the desired phase. The choice of the solvent composition depends on the phase diagram of the system concerned and will be discussed later.

During the start of the experiment we first melt the solvent-pellet completely by sticking it to the bottom of the feed. The seed rod is positioned at the edge of the lower filaments’ image. This arrangement is shown in Fig. 6.4. A good visual indicator of the proximity to the peritectic temperature is when the seed starts showing the first signs of decomposition which is generally seen as the tips of the seed start turning paler/whitish. At this point the melt resulting from the solvent pellet is generally at the composition of the peritectic, and at this point the feed and seed rod can be joined to form the floating zone.

6.2.6 Rotation and translation of shafts

Almost immediately after forming the floating zone, the rotation of the feed and seed rods is started to facilitate convective mixing of the melt in the zone. This helps homogenizing the zone with respect to composition and temperature. After a completely molten FZ is formed the mirror stage is translated upwards at very slow speed of around 1 mm/h, this being the rate at which material is being crystallized on the seed. Such slow growth rates are necessary for incongruently melting materials in which case the composition of the FZ is very different from that of the feed and the growing crystal. One therefore needs to give sufficient time for decomposition of the feed and the shift in composition to stabilize by adequate mixing and homogenization of the melt. It can take up to 24 hrs or more for the floating zone to reach a stable condition where no more major adjustments of parameters are required. This depends upon the composition of the solvent, and the proximity of the composition of the desired phase to the peritectic composition. Eventually, factors such as convexity of the melt-crystal interface influence grain selection, and typically after 2-3 cm single crystalline material solidifies on the seed. One can also use a single crystalline seed which then results in much quicker grain selection.
6.2.7 Stability of the FZ

There are some indicators of a FZ tending towards or away from stability. Depending upon what is seen, the parameters of the growth have to be adjusted so as to steer the FZ to the right composition. Below, some indicators of a too high temperature of the zone are described.

Consider a situation where the melting of the feed rod is uniform and a sharp feed-zone interface exists. If gradually the zone becomes thinner and the diameter of the growing crystal increases, one can guess that the temperature of the FZ is too high. This generally happens because a high enough temperature can decrease the viscosity of the melt in the FZ, thus resulting in it flowing down the surface of the growing crystal just below the melt-crystal interface and forming a coating on the crystal. Also, the angle that the melt in the FZ makes with the growing crystal ($\theta$), or the shape of the zone is determined by the viscosity of the melt and thus the surface tension of the FZ. This angle might vary though depending on the material. However, in general, a higher the temperature leads to a less viscous melt, and as the surface tension reduces it causes the melt to form a highly acute angle with the crystal interface. For most materials, the angle $\theta$ is seen to be close to a right angle. An ideal zone shape for the case of many cuprates is shown in Fig. 6.5. However, in some materials one might encounter a FZ that makes an acute angle with the crystal interface without affecting the stability of the zone. Even in a stable FZ, if the temperature of the FZ is a little high means that the composition is above the peritectic point, and there are chances of having inclusions of the phase $\alpha$ in the growing crystal.

If the feed rod shows sign of improper melting, the temperature is possibly much lower than $T_P$. But this scenario could also occur due to improper alignment of the lamps of the furnace, or due to inhomogeneities in the feed. Although, the compound $A_xB_y$ can crystallize from anywhere on the liquidus line corresponding to this phase, it is advisable to grow the material close to the peritectic temperature. This is because, below the peritectic composition the phase may have a finite solubility region which allows for modifications in the stoichiometry of the compound, as is depicted by the region $\beta$ in the hypothetical phase diagram (Fig. 6.1). Another manoeuvre used to stabilize the molten zone is to have a relatively small upward translation of the feed, thereby reducing the effective growth rate by feeding material at a slower rate. If the FZ is at an appropriate temperature, this often helps in stabilizing the FZ.
Figure 6.6: X-ray diffraction spectra of 1% Ni doped SrCuO$_2$ used for the growth experiment; the peaks marked with a star arise due to small inclusions of the Sr$_{14}$Cu$_{24}$O$_{41}$ (x-ray source: Copper K$^\alpha = 1.5406$ Å).

Figure 6.7: The experimentally measured and calculated x-ray diffraction spectra of the as grown 1% Ni doped SrCuO$_2$ (x-ray source: Molybdenum K$^\alpha = 0.7093$ Å).

6.3 Crystal growth

6.3.1 Ni doped SrCuO$_2$

The TFSZ method was used to grown large single crystals of SrCu$_{1-x}$Ni$_x$O$_2$ for $x = 0.01$ and 0.02. Starting with highly pure powders of SrCO$_3$ (99.995% pure),
CuO (99.99% pure) and NiO (99.99% pure) polycrystalline SrCu$_{1-x}$Ni$_x$O$_2$ was obtained by performing multiple solid state reactions. The powders in stoichiometric amounts were mixed thoroughly using a mortar and a pestle. The mixture, in an alumina crucible, was then introduced in a furnace for the sintering process at high temperatures. This process was repeated five to six times starting from 920°C to 990°C, grinding and mixing the sintered powder after every step. After the final sintering, the obtained powder was checked for phase purity using x-ray diffraction. The x-ray diffraction pattern of the final powder is shown in Fig. 6.6. Once it was known that the powder is almost single phase SrCu$_{1-x}$Ni$_x$O$_2$ (with a small amount of Sr$_{14}$Cu$_{24}$O$_{41}$ as a secondary phase), feed rods were pressed for the growth experiment. As for most incongruently melting compounds one must choose the composition of the solvent pellet to be used for the growth. Fig. 6.8 shows the pseudo-binary phase diagram of the SrO-CuO system taken from [195]. From this experimentally obtained diagram we can see that the peritectic point for SrCuO$_2$ is at around 1084°C, and at the composition 71.5% CuO and 28.5% SrO. This is the point around which SrCuO$_2$ decomposes into a liquid rich in CuO upon heating. Also, this is the point at which SrCuO$_2$ can crystallize from a melt in a steady state condition. Hence, the composition of the solvent was chosen to be same as that of the peritectic composition.

The growth experiment was started with this solvent. Other experiments using a solvent pellet composed entirely of CuO were also performed, but were unsuccessful as it was difficult to stabilize the molten zone. A flow of O$_2$ through the growth chamber was used during the experiment. The growth chamber was evacuated and flushed with O$_2$ several times to ensure a pure atmosphere. The most important parameters for the successful growth are given in table 6.1.

The grown crystal showed the presence of facets and readily cleaved perpendicular to the longest crystallographic axis (b-axis). There was no relation between the growth axis and the axis along which the crystal cleaved. Fig. 6.9 shows a picture of the as grown crystal with a shiny surface, and the mirror-like cleavage planes (which is the crystallographic ac plane). It also shows an image of the cross-section of the lower part of the grown crystal taken under polarized light, to show the grain selection process that occurs with time during the growth experiment. From a polycrystalline seed having multiple crystallites, a single orientation is selected out in a length of around 2 cm. Fig. 6.7 shows the experimentally measured x-ray spectra of the 1% Ni doped SrCuO$_2$, along with the pattern obtained by Rietveld refinement method. With a space group Cmcm, the resultant lattice parameters obtained were $a = 3.5702$ Å, $b = 16.3278$ Å, $c = 3.9086$ Å.
Figure 6.8: A pseudo-binary phase diagram of the SrO-CuO system reproduced from [195]. The red line shows the desired phase and the red circle shows the corresponding peritectic point.

Table 6.1: Growth parameters for Ni doped SrCuO$_2$

<table>
<thead>
<tr>
<th>Feed/seed rods</th>
<th>SrCuO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamps</td>
<td>300 W</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Pure O$_2$</td>
</tr>
<tr>
<td>Solvent</td>
<td>71.5% CuO : 28.5% SrO pellet (with 1 % Ni)</td>
</tr>
<tr>
<td>Growth rate</td>
<td>1 mm/hr</td>
</tr>
<tr>
<td>Upward feed translation</td>
<td>0.15 mm/hr</td>
</tr>
<tr>
<td>Shafts’ rotation speed</td>
<td>18-20 rpm</td>
</tr>
</tbody>
</table>
6.3. Crystal growth

6.3.2 La$_2$CuO$_4$: Ni and Zn doped

High quality single crystalline La$_2$CuO$_4$ and its doped versions were grown using the TFSZ method. 99.99% pure La$_2$O$_3$, CuO, NiO and ZnO were used as starting chemicals for preparation of the polycrystalline feed/seed rods and the solvent pellet. La$_2$O$_3$ was dried at 950°C for 12 hours before mixing appropriate quantities of the starting powders. The starting powder weighing were initially mixed using a mortar and pestle and then mixed for 20 minutes using a ball mill. The powder was then subjected to a series of sintering and grinding steps from 900°C going up to 1000°C. The powders were held for 20 hours at each temperature, furnace cooled, ground and mixed thoroughly using the ball mill before proceeding to the next sintering temperature. The well sintered powders were then checked for phase purity using powder x-ray diffraction. The sintering was continued if the powders were not yet single phase. Pressed feed rods were then subjected to one final sintering process at 1200°C to make the rods highly dense and compact, the importance of which has be discussed earlier. A similar method was used to prepare the solvent pellet that was used in the growth experiments, except that the highest temperature used for sintering was 1000°C. The phase diagram of the La$_2$O$_3$-CuO system taken from [196] is shown in Fig. 6.10. From this we see that the peritectic composition for this phase is nearly 71 mol% CuO : 29 mol% La$_2$O$_3$. A composition of 80 mol% CuO : 20 mol% La$_2$O$_3$, close to the peritectic, was chosen for the solvent pellet for the growth of the pure as well as doped compounds. An oxygen pressure of 2 bar was needed to stabilize the growth and to have a good stoichiometry of oxygen in the grown phase. In spite of this, the as-grown crystals have a small excess of oxygen in them.
The parameters that were vital to bring the growth process into the steady state condition are mentioned in table 6.2. These parameters, of course differed a bit for the different compounds in this series, so a range is mentioned for the values of the parameters. As the solvent pellet was CuO rich, often CuO decomposed into Cu$_2$O during the beginning of the growth thereby releasing O$_2$ in the form of bubbles in the molten zone. With an O$_2$ pressure in the chamber these bubbles are unable to diffuse out and grow in size in the zone thereby increasing the volume of the zone and causing the zone to collapse ultimately. To avoid this, Ar was introduced into the chamber in small amounts to help the small bubbles of O$_2$ to diffuse out of the zone.

To gain some more understanding about the growth process, the floating zone was frozen at the end of the growth and analyzed using EDX. Fig. 6.11 shows...
6.3. Crystal growth

Table 6.2: Growth parameters for La$_2$CuO$_4$ and its doped versions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed/seed rods</td>
<td>La$_2$CuO$_4$</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>2 bar O$_2$ pressure</td>
</tr>
<tr>
<td>Solvent</td>
<td>80% CuO : 20% La$_2$O$_3$ pellet</td>
</tr>
<tr>
<td>Growth rate</td>
<td>1 mm/hr</td>
</tr>
<tr>
<td>Shafts’ rotation speed</td>
<td>20-25 rpm</td>
</tr>
<tr>
<td>Lamp power</td>
<td>around 65% @ 300 W</td>
</tr>
</tbody>
</table>

an SEM image of the quenched floating zone. The average composition of the zone as measured on several points all over the zone area was found to be 78 mol% CuO : 22 mol% La$_2$O$_3$ which is close to the composition of the peritectic point corresponding to the La$_2$CuO$_4$ phase. Such proximity of the FZ melt composition to the peritectic of the growing phase has also been observed for other compounds [194, 195, 197]. Such information adds to our understanding of growth mechanisms and their relation to phase diagrams in case of incongruently melting compounds like La$_2$CuO$_4$.

The grown crystal was then characterized using several methods and this is discussed in the following paragraphs. The set of pictures below in Fig. 6.12 show images of the grown crystals. From these images one can see that the surface of the grown crystals are shiny and have luster. Merely by visual inspection this is the first indication of goodness of the crystal quality, but by all means could be deceiving. The cross-sections of the crystal were characterized for single orientation by taking Laue images on multiple points of the section. Laue images were also used to orient the crystals for measurements. Fig. 6.13(a) shows a representative Laue image of the undoped crystal. This image remains the same for multiple points of the section, thus indicating the presence of a single orientation.

Fig. 6.13(b) shows, as a representative example, images of the cross-sections of the 0.3% Ni doped compound taken using the polarized light microscope. The uniform shade over the entire cross section confirms the presence of a single grain everywhere. The image on the left is from a section taken approximately 2 cm after the beginning of the growth which already shows single crystallinity, thus implying good grain selection for this crystal. The image on the right is taken from a section just before the growth was ended. Fig. 6.13(c) shows SEM images of the same cross-sections. No phase contrast is seen in the image indicating the presence of a single phase throughout the cross section. Other compounds in the series were also similarly characterized using polarized light microscopy and SEM to ascertain the presence of single grain and single phase, respectively. Similar good grain selection was seen in other compounds of the series too.
Chapter 6. Single crystal growth

Figure 6.11: SEM image of the quenched zone from the growth of pure La$_2$CuO$_4$.

Fig. 6.13(c) shows SEM images of the grown crystal taken using the BSE detector. No visible phase contrast could be seen even at highest magnification levels. EDX was then performed of multiple spots on cross-sections of crystal which were to be used for measurement. The results confirmed that the ratio of La to Cu was indeed 2:1 and the material is phase pure La$_2$CuO$_4$. Fig. 6.14 and Fig. 6.15 show the observed and calculated x-ray diffraction patterns for the pure, Ni-doped and Zn-doped La$_2$CuO$_4$ samples respectively. Rietveld refinement resulted in a good match between the calculated and the experimental spectra with an $R_{Bragg}$ of less than 4 for all the compounds. The pure and the doped compounds are found to have the $Cmce$ space group, and the corresponding lattice parameters obtained by the refinement are given in table 6.3. The parameters of the doped and undoped compound do not vary appreciably, which is expected owing to the very small doping concentrations. The atomic positions used in the model for refining the data were taken from [198].

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As mentioned earlier, the as-grown crystals have excess oxygen atoms in the CuO layers, and can bring about changes in the observed magnetic properties, like decreasing the ordering temperature. This extra oxygen can be removed by subjecting the samples to 2 to 3 hours of annealing in a continuously evacuated atmosphere of around $10^{-4}$ mbar. For samples with stoichiometric oxygen content, the Neél temperature is observed to be 325 K.

The effect of doping on heat transport is being studied on the grown single crystals of doped versions of La$_2$CuO$_4$ with dopant as Ni (magnetic impurity) and Zn (non-magnetic impurity). The undoped single crystals have also been used for a visible pump x-ray absorption probe experiment to investigate "photo-doping", where holes and electrons will be excited optically across the charge transfer gap. This aims to analyze the ultrafast relaxation back to the Mott-Hubbard insulator ground state and thereby determine the lifetime of the holon-doublon excitation, an exciting current problem in non-equilibrium theory. However, the results of these experiments are not conclusive yet and will not be discussed as a part of this work.
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Figure 6.13: (a) Laue diffraction image, (b) polarized light image of cross section, and (c) SEM image of cross sections of the grown crystal taken from the beginning part and end part.

Table 6.3: Lattice parameters of pure and doped La$_2$CuO$_4$ obtained by Rietveld refinement.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$a$(Å)</th>
<th>$b$(Å)</th>
<th>$c$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group: $Cmce$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>undoped</td>
<td>5.3536</td>
<td>13.1436</td>
<td>5.4021</td>
</tr>
<tr>
<td>0.1 % Ni</td>
<td>5.3537</td>
<td>13.1416</td>
<td>5.4014</td>
</tr>
<tr>
<td>0.3 % Ni</td>
<td>5.3543</td>
<td>13.1415</td>
<td>5.4031</td>
</tr>
<tr>
<td>0.1 % Zn</td>
<td>5.3532</td>
<td>13.1315</td>
<td>5.4050</td>
</tr>
<tr>
<td>0.3 % Zn</td>
<td>5.3524</td>
<td>13.1389</td>
<td>5.4013</td>
</tr>
</tbody>
</table>
6.3. Crystal growth

![Diagram of x-ray diffraction spectra](image)

**Figure 6.14:** Experimentally measured and calculated x-ray diffraction spectra of the pure and Ni doped La$_2$CuO$_4$ samples, (a) Undoped (b) 0.1 % Ni (c) 0.3 % Ni (x-ray source: Copper K$_\alpha$ = 1.5406 Å).

### 6.3.3 La$_8$Cu$_7$O$_{19}$

Cava et. al. were the first to report the existence and synthesis of the homologous series of compounds La$_{4+4n}$Cu$_{8+2n}$O$_{14+8n}$, of lanthanum cuprates to which the two compounds La$_2$Cu$_2$O$_5$ and La$_8$Cu$_7$O$_{19}$ compounds belong [52]. Using the information provided there, single crystals of La$_8$Cu$_7$O$_{19}$ have been grown using flux growth techniques and has been shown to have a narrow region of crystallization of $\sim$ 1035°C [184, 186]. Phase diagrams therein show that La$_2$Cu$_2$O$_5$ and La$_8$Cu$_7$O$_{19}$ crystallize very close to each other with regards to composition, near to that of the eutectic (92 mol % CuO). The atmospheres in which one can grow these phases is unclear, though. Sekhar et. al [186] and Barillo et. al [184] were
successful in growing single crystals of La$_8$Cu$_7$O$_{19}$ only under ambient conditions. They did not use any oxygen partial pressure for the synthesis experiments. On the other hand, in the solid state, polycrystalline La$_8$Cu$_7$O$_{19}$ could be synthesized as a single phase only in an O$_2$ flow as observed by Cava et. al [52].

Solid state synthesis

In order to verify the formation of the two phases in different atmospheres and temperatures, we performed synthesis experiments using a solid state reaction route (see table 6.4). First, with a view to investigate the formation of La$_8$Cu$_7$O$_{19}$

Figure 6.15: Experimentally measured and calculated x-ray diffraction spectra of the pure and Zn doped La$_2$CuO$_4$ samples, (a) Undoped (b) 0.1 % Zn (c) 0.3 % Zn (x-ray source: Copper K$^{\alpha} = 1.5406$ Å).
Table 6.4: Summary of solid state synthesis showing the products obtained under different atmospheres, m.s.p means minor secondary phase

<table>
<thead>
<tr>
<th>Temperature (La₂O₃: CuO)</th>
<th>Ambient atmosphere</th>
<th>O₂ atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020-1035°C (4 : 7)</td>
<td>La₂CuO₄ &amp;</td>
<td>La₈Cu₇O₁₉</td>
</tr>
<tr>
<td></td>
<td>La₂Cu₂O₅ (m.s.p) &amp;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>La₈Cu₇O₁₉ (m.s.p)</td>
<td></td>
</tr>
<tr>
<td>998-1020°C (1 : 2)</td>
<td>La₂Cu₂O₅</td>
<td>La₈Cu₇O₁₉ &amp;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>La₂Cu₂O₅ (m.s.p) &amp;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>La₂CuO₄ (m.s.p)</td>
</tr>
</tbody>
</table>

in air, we fired a mixture containing La₂O₃ and CuO in the molar ratio 4:7, at temperatures between 1020 - 1035°C for 24 hr in ambient atmosphere, and quenched it by pulling out of the furnace at these temperatures. As a result, we obtained mixtures of La₂CuO₄ with La₂Cu₂O₅ and La₈Cu₇O₁₉ as minor phases. However, when the same solid state synthesis experiment as above was performed in flowing O₂, single phase La₈Cu₇O₁₉ was formed upon quenching the fired mixture, in accordance to the results of Cava et al. [52].

Then, to check the formation of La₂Cu₂O₅ in ambient atmosphere, a mixture of La₂O₃ and CuO in a molar ratio of 1:2 was fired at temperatures between 998°C and 1020°C, in air. This resulted in the formation of single phase La₂Cu₂O₅, which agrees with the result from Cava et al. [52]. Finally, to check the formation of La₂Cu₂O₅ in O₂ atmosphere, the above experiment was repeated in an O₂ flow. The resultant powder had La₈Cu₇O₁₉ as the major phase, indicating the favorability of formation of the latter phase only in an O₂ environment in spite of a slightly off-stoichiometric starting mixture.

Crystal growth

From these experiments we could conclude that in order to crystallize phase pure La₈Cu₇O₁₉ we needed to perform growth experiments in an oxygen atmosphere. We, thus, attempted to grow the phase La₈Cu₇O₁₉ using a feed rod of the same composition under 9 bar of static O₂ pressure, as well as under O₂ and Ar flow at atmospheric pressure. However, in repeated trials of this experiment the molten zone could not be stabilized. We faced problems like insufficient melt in the floating zone and inappropriate feed melting.
Chapter 6. Single crystal growth

Table 6.5: Summary of crystal growth from melt showing the products obtained under different atmospheres.

<table>
<thead>
<tr>
<th>Feed Rod</th>
<th>Ambient atmosphere</th>
<th>Argon atmosphere</th>
<th>O₂ atmosphere</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂Cu₂O₅</td>
<td>Unsuccessful</td>
<td>LaCuO₂</td>
<td>La₈Cu₇O₁₉</td>
<td></td>
</tr>
<tr>
<td>La₈Cu₇O₁₉</td>
<td>Unsuccessful</td>
<td>-</td>
<td>Unsuccessful</td>
<td></td>
</tr>
</tbody>
</table>

As we had observed from the solid state synthesis experiments that La₈Cu₇O₁₉ is formed as a major phase in an O₂ atmosphere even if one starts with a slightly off-stoichiometric starting mixture, in our subsequent experiment we used polycrystalline, phase pure La₂Cu₂O₅ as a feed rod to attempt to grow La₈Cu₇O₁₉ from a melt, in an O₂ atmosphere, using the TSFZ method. In this way we were able to grow phase pure single crystalline La₈Cu₇O₁₉.

Feed rod preparation

La₂Cu₂O₅ has been synthesized in single crystalline form earlier by various groups, both under oxygen [19, 199] and ambient atmospheres [52, 184, 200]. However, we observed that, in the solid state, it is difficult to synthesize it as a single phase in large quantities when an oxygen atmosphere is used (see table 6.4). Therefore, to synthesize La₂Cu₂O₅ the thoroughly mixed starting powders were introduced in a pre-heated furnace at 1002°C and kept for 24 hours in an ambient atmosphere. Then, the crucible was rapidly pulled out of the furnace at the same temperature in order to quench the phase. This step was repeated four times to ensure a homogeneous single phase. Powder X-ray diffraction was used to confirm the formation of La₂Cu₂O₅ as a single phase. The above used method is similar to the one mentioned by Cava et al. [52]. Cylindrical feed rods of length ~ 8 cm and diameter ~ 5 mm were then pressed from the powder. The pressed rods of La₂Cu₂O₅ were sintered at 800°C for 24 hours in a muffle furnace in air, where cooling and heating rates were set to 200°C/h. The powder x-ray diffraction pattern of the sintered feed rod confirmed that the La₂Cu₂O₅ remained stable after sintering at 800°C.

A solvent disk of pure CuO weighing ~ 70 mg was used. The growth was carried out in an oxygen pressure of 9 bar, and a very slow growth speed of around 0.5 mm/h was chosen. The feeding speed (i.e., the speed at which the feed rod was allowed to move with respect to the floating zone) was kept around...
0.42 mm/hr. The feed and seed rods were rotated in opposite sense with speeds of ∼20 rpm. The grown crystal had a diameter of ∼4 mm, due to lower feeding speed compared to the growth speed.

We were successful in growing phase pure La$_8$Cu$_7$O$_{19}$ as single crystals only by using the above conditions. The high O$_2$ pressure that was used helped facilitate the formation of the molten zone and stabilize the growth of La$_8$Cu$_7$O$_{19}$. It also helped to suppress bubble formation during decomposition of the CuO solvent. Similar experiments of trying to grow La$_8$Cu$_7$O$_{19}$ starting with a La$_2$Cu$_2$O$_5$ feed in ambient atmosphere and argon atmosphere did not work. In ambient atmosphere, the molten zone could not be stabilized. However, in argon atmosphere we could stabilize the molten zone, but the resultant phase that was grown turned out to be phase pure LaCuO$_2$, which must have resulted from the reduction of La$_2$Cu$_2$O$_5$ [201]. The results regarding the solid state stability and the results of growth trials from melt are summarized in table 6.5.

Fig. 6.16(a) shows a photograph of the as-grown sample. The seed rod, with a relatively larger diameter than that of the crystal, is seen on the far left hand side of the image. The crystal is seen growing on the seed from the area where a bulge
Chapter 6. Single crystal growth

Figure 6.17: Experimental powder diffraction pattern for the as-grown crystal (red) along with the Rietveld refined pattern (black) (x-ray source: Molybdenum K$\alpha$ = 0.7093 Å).

is seen. The surface of the crystal looks rough and without luster because of a polycrystalline peripheral ring, described below, that runs all along its length. Fig. 6.16(b) shows the Scanning Electron Microscope (SEM) image of the cross section of the crystal taken in the Backscattered Electron Detection mode (BSE), and the inset zooms into the periphery. Apart from two main cracks running along the cross section (which might have developed due to thermal stress during the process of decreasing the lamp power to freeze the molten zone) and the periphery of the crystal, we can see that the cross-section contains a peripheral ring of inclusions, which by WDXA was found to be a mixture of the eutectic composition and an excess of CuO. A similar composition of this peripheral ring was found to occur throughout the length of the grown crystal. Also, in some parts of the crystal towards the end of the growth, inclusions of La$_2$Cu$_2$O$_5$ were found in the central regions of the cross section of the crystal. Fig. 6.16(c) shows the Laue diffraction image of the cross section taken from the mid-region of the as-grown sample (Fig. 6.16(a)), indicating single crystallinity. This image remains the same for multiple points on the section, thus indicating the presence of a single orientation throughout.

Fig. 6.17 shows the experimentally obtained powder diffraction pattern for the as-grown crystal. This was first compared with literature [52, 185], and found to agree very well as all the peaks of the reported patterns matched with our experimental pattern, confirming that the grown phase is indeed La$_8$Cu$_7$O$_{19}$. Refining the experimental pattern starting with a model as per [185], we find that the structure has monoclinic symmetry with a $C2/c$ space group, and with lattice parameters $a = 13.829$ Å, $b = 3.758$ Å, $c = 34.595$ Å, $\beta = 99.32^\circ$. The
simulated pattern for $\text{La}_8\text{Cu}_7\text{O}_{19}$, after refinement, matches the experimental powder diffraction pattern well thus confirming phase purity. A Bragg R-factor of 6.91 was obtained. No peaks from impurity phases were identified. Effect of texture and stress were not refined as the main motive of refinement was to confirm phase purity, and these possibly account for difference in observed and simulated intensities.

In order to gain some insight into the growth process the floating zone was frozen at the end of the growth experiment and analyzed using WDXA. Fig. 6.18 shows an SEM image of the vertical cross-section of the frozen floating zone (FZ). The feed rod, the solid-liquid interfaces, the actual zone and the growing crystal are marked. The FZ broke into two pieces during the cutting procedure, hence the image shows two separate pictures of the upper and lower half of the FZ. WDXA revealed that the average composition of the central and upper part of the molten zone, taken at points marked by red in Fig. 6.18, is 88% CuO and 12% $\text{La}_2\text{O}_3$. For a molten zone in steady state the composition of the frozen zone generally corresponds to peritectic composition of the phase under consideration [194, 195, 197]. From this we can say that the average composition in these parts of the zone corresponds to that of the peritectic point associated with the decomposition of phase $\text{La}_2\text{Cu}_2\text{O}_5$, labelled as 1 in Fig. 6.19. Interestingly, we
find that the average composition of the lower part of the zone (marked by blue points in Fig. 6.18), near the zone-crystal interface is 86% CuO and 14% La2O3 slightly different than that of the central and upper part of the zone. The observed small composition shift of the floating zone under the steady state condition may indicate the existence of a small temperature gradient along the length of the zone, such that the lower section of the zone which is about 2% CuO deficient should be slightly higher in temperature compared to the upper section. Judging from the narrowness and close proximity of the temperature/composition regions over which these two phases exist, the observed composition variation can easily arise from a temperature gradient as small as 1 K. Since the phases La2Cu2O5 and La8Cu7O19 exist as two distinct phases only excluding a narrow temperature interval, of the order of about 10°C, the rate of change of composition with respect to temperature around the point labelled as 1 in Fig. 6.19 is estimated to be about 1.25%.

In a scenario where the diameter of the growing crystal is smaller than that of the feed rod, a slightly higher temperature at the melt-crystal interface can be expected. The reason for this can be understood from the fact that for a given material the power required to establish a stable FZ scales roughly with the diameter of the feed rod which should be melted to form a molten zone. In
6.3. Crystal growth

Figure 6.20: (a) Susceptibility as a function of temperature \((\chi(T))\) measured for the three times sintered single phase powder \(\text{La}_8\text{Cu}_7\text{O}_{19}\) sample. (b) Two representative peaks (A and B) from the X-ray diffraction spectra of the once (blue data), twice (green data) and thrice (black data) sintered powders, along with that for the powdered single crystal (red data).

Typical growth experiments such small temperature differences at the upper and the lower interfaces are inconsequential, however, in the present case due to a sheer proximity of the two phases, a very unusual situation has been witnessed where the crystals of phase \(\text{La}_8\text{Cu}_7\text{O}_{19}\) are grown by melting a feed rod of phase \(\text{La}_2\text{Cu}_2\text{O}_5\). The process self-sustains itself by rejecting excess CuO from the feed rod along the peripheral regions of the growing crystal. This is further assisted by a convex shape of the melt-crystal interface which is typically observed in a FZ experiment due to a small radial temperature gradient along the melt crystal interface [202–205].

The repeatability of the growth experiments confirms that it is indeed possible to grow \(\text{La}_8\text{Cu}_7\text{O}_{19}\) by adopting this method. WDXA was done on several points on the cross-section surface and from the average compositional ratio, \(\text{La} : \text{Cu} : \text{O}\), the formula of the compound was deduced to be \(\text{La}_{8.03\pm0.5}\text{Cu}_{6.98\pm0.5}\text{O}_{19.01\pm1.1}\). This ratio was also checked for different pieces of the crystal using ICP-AES, and the resultant formula was found to be \(\text{La}_{7.95\pm0.11}\text{Cu}_{7.02\pm0.22}\text{O}_{19.02\pm0.15}\). These analyses were important, in combination with others, to ascertain that the ratio of La:Cu is indeed 8:7 to distinguish this phase from the close neighbor \(\text{La}_2\text{Cu}_2\text{O}_5\), where the La:Cu ratio is 1:1.
To further validate the appearance of this anisotropy, we synthesized single phase La$_8$Cu$_7$O$_{19}$ powder and measured its susceptibility as a function of temperature. To obtain single-phase La$_8$Cu$_7$O$_{19}$ by the method described above in this section, multiple sintering steps were required to achieve single phase powders. To illustrate the importance of multiple sintering processes in obtaining phase pure powder further, Fig. 6.20(b) shows two reflections from the powder XRD pattern of powders subjected to one, two and three sintering steps along with that of the grown single crystal. Peak A and B belong to the phase La$_8$Cu$_7$O$_{19}$. With increasing number of sintering steps one sees a shift of peak A and B towards the position corresponding to the single crystal, thus indicating that the three times sintered powder has a structural homogeneity close to that of the single crystal sample. Fig. 6.20(a) shows the magnetic susceptibility of the single phase La$_8$Cu$_7$O$_{19}$ polycrystalline powder obtained in our study. No anomaly is seen around 103 K in the powder sample’s susceptibility (Fig. 6.20(a)). This is explained because the anomalies seen in $\chi(T)$ along the different directions of the single crystal additively cancel out due to their anisotropy, and we see a smooth averaged-out curve for the powder sample.

### 6.3.4 LaCuO$_2$

Earlier, only polycrystals of LaCuO$_2$ have been synthesized starting with stoichiometric mixtures of La$_2$O$_3$ and Cu$_2$O and firing at high temperatures in a N$_2$ or Ar atmosphere, or under vacuum at high pressures [187–190]. Up to now, the reduction method has not been employed successfully to synthesize single crystalline LaCuO$_2$ from La$_2$Cu$_2$O$_5$, although other delafossites like YCuO$_2$ have been synthesized using Y$_2$Cu$_2$O$_5$ as the starting material [187, 206]. Therefore, using a similar approach, we have synthesized LaCuO$_2$ as a single crystal. The phase diagram of the La$_2$O$_3$-CuO binary system in air [200], suggests that the phase La$_2$Cu$_2$O$_5$ melts incongruently, and there exists a considerable difference between the composition of solid La$_2$Cu$_2$O$_5$ and the melt from which it crystallizes. However, the temperature regimes and atmospheres in which LaCuO$_2$ exists in the phase diagram has not been investigated in detail, although this compound and its crystal structure are well-known in the literature. The TFSZ method is proven to be effective for the crystal growth of incongruently melting compounds [191, 193]. We therefore employed this method to grow single crystals of LaCuO$_2$ by a reduction of La$_2$Cu$_2$O$_5$ from a melt.

La$_2$O$_3$ and CuO of 99.99% were used as starting chemicals for preparation of the polycrystalline La$_2$Cu$_2$O$_5$ feed and seed rods. La$_2$O$_3$ was dried at 950°C for 12
6.3. Crystal growth

Figure 6.21: (a,b): Photographs of the as grown crystal ingot. The polycrystalline peripheral ring and the crystal in the central part is seen in (b). (c): A Laue image of the diffraction pattern of the crystal surface.

hours before mixing the starting powders. La$_2$Cu$_2$O$_5$ was synthesized in the solid state by following a sintering method similar to the one in the reference [52]. The thoroughly mixed powders were introduced in a pre-heated furnace at 1000°C and held for 24 hours in an Alumina crucible. Then, the crucible was carefully pulled out of the hot furnace directly in order to air-quench the phase. Cylindrical feed rods of length $\sim$ 6 cm and diameter $\sim$ 5 mm, were pressed at 3000 bar using a cold isostatic press. A small solvent disk of pure CuO weighing $\sim$ 80 mg was used to initiate the growth. The growth chamber was evacuated and flushed multiple number of times, and then a steady Ar flow ($\sim$ 100 cc/min) at 2 atm was maintained throughout the experiment in order to have a reducing atmosphere in the growth chamber. A slow growth speed of around 1 mm/hr was used. The upper and lower shafts were rotated opposite to each other at 25 rpm. Lamps with 300 W power were used in the mirror furnace that produce a temperature gradient of $\sim$ 20°C/mm in the region around the growth interface. The most important parameters of the growth experiment are mentioned in table 6.6.

In the growth of incongruently melting compounds, due to a significant difference between the composition of solid and the melt from which it crystallizes, a
Table 6.6: Growth parameters for LaCuO$_2$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed/seed rods</td>
<td>La$_2$Cu$_2$O$_5$</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ar</td>
</tr>
<tr>
<td>Solvent</td>
<td>CuO pellet ($\sim$ 80 mg)</td>
</tr>
<tr>
<td>Growth rate</td>
<td>1 mm/hr</td>
</tr>
<tr>
<td>Shafts rotation speed</td>
<td>25 rpm (opposite direction)</td>
</tr>
<tr>
<td>Lamps</td>
<td>300 W</td>
</tr>
<tr>
<td>Temperature gradient at growth interface</td>
<td>$\sim$ 20°C/mm</td>
</tr>
</tbody>
</table>

Figure 6.22: A Scanning Electron Microscope (SEM) picture of the quenched floating zone to illustrate the convexity of the growth interface. The inset shows a zoomed image of the area marked by a red square, showing the microstructure of the zone.

A solvent of a composition close to the liquidus region of the compound is generally used in order to have sufficient amount of melt of this composition [191, 193] when forming the FZ. However, as no information is available about the crystallization regimes of LaCuO$_2$, a CuO-pellet was used as a solvent to begin the growth because its composition, and the temperature at which it decomposes are not so far away from that of the liquidus region of La$_2$Cu$_2$O$_5$, which was used as the feeding material [200]. At the beginning of the growth the melt produced by decomposing CuO helped in establishing the FZ with ease, which was not possible otherwise. Upon starting the growth without a solvent, directly by decomposing the feed material, very little liquid was initially available to establish the molten zone and the FZ kept breaking due to insufficient melt. It was difficult to stabilize the molten zone for more than a few hours in the growth experiments that
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Figure 6.23: Experimental powder diffraction pattern for the as-grown crystal (red) along with the Rietveld refined pattern (black) (x-ray source: Molybdenum $K_\alpha = 0.7093$ Å).

were tried in O$_2$ atmospheres, and resulted in the formation of La$_2$Cu$_2$O$_5$ and La$_8$Cu$_7$O$_{19}$. An Ar atmosphere was used to prevent the formation of La$_2$Cu$_2$O$_5$ or La$_8$Cu$_7$O$_{19}$, and facilitate the reduction of La$_2$Cu$_2$O$_5$ to LaCuO$_2$.

The quality of the grown crystal was analyzed with regard to crystallinity and phase purity using different methods. Powder x-ray diffraction at using a STOE diffractometer (transmission geometry) with Molybdenum ($K_\alpha = 0.709$ Å) x-ray source was carried out at room temperature on several powdered pieces of the grown crystal to confirm phase purity. The diffractometer is equipped with a curved Ge(111) monochromator and 6°-linear position sensitive detector. The sample was measured in transmission geometry, using a thin layer of powder glued onto a polyacetate film. Electron backscattered diffraction images using the Scanning electron microscope (SEM) were used to check for possible secondary phase inclusions. The elemental composition was ascertained using Energy Dispersive X-ray Analysis (EDX) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The Laue diffractometer equipped with a Seifert ID3003 generator, a Tungsten anode and a MWL 120 detector from Multiwire Laboratories, Ltd. was used to make diffraction images at different spots on cross-sections of the grown crystal to check for single crystallinity and grain size.

Upon analyzing cross sections of the crystal at different parts of the grown rod (Fig. 6.21(a)), a thin polycrystalline peripheral ring containing a mixture of CuO and La$_2$Cu$_2$O$_5$ was found all along the length of the rod. However, the central part of the rod was single crystalline LaCuO$_2$ (Fig. 6.21(b)) that readily cleaved
Chapter 6. Single crystal growth

Table 6.7: The refined atomic positions obtained from single crystal diffraction. The obtained lattice parameters are, \(a = 3.832(16) \text{ Å}, b = 3.832(4) \text{ Å}, \) and \(c = 17.098 \text{ Å}; \) for the refinement Bragg R-factor = 4.395, RF-factor = 2.987.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>La1</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>O1</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.1079</td>
</tr>
</tbody>
</table>

into flake-like pieces, a feature typical of layered delafossite structures [187, 206], and yielded yellow colored powder when crushed. Fig. 6.21(c) shows the Laue diffraction image of a cleavage plane of the crystal, shows single crystallinity.

A slow growth rate of around 1 mm/h and counter-rotation of upper and lower shafts (25 rpm) was used to facilitate diffusion during crystallization at the growth interface and for homogeneity of the melt-composition in the FZ respectively. The growth interface, as seen in the SEM image of the quenched FZ in fig. 6.22, under steady state conditions, possesses a convex shape. Studies in the literature indicate that a slightly convex interface toward the liquid is desirable as it improves the quality of the grown crystal [207]. A concave interface is unfavorable because it tends to favour the concentration of defects along the core of the growing crystal [208]. Although a high rotation speed facilitates homogeneity of the FZ composition, it reduces the convexity of the growth interface [209] and thereby effects stability of the FZ and the quality of the grown crystal. Thus, a rotation speed of around 25 rpm which resulted in a convex growth interface is possibly an important parameter for the successful growth. In previous unsuccessful experiments, in spite of using a CuO solvent and similar values of feed/seed rotation, growth rate and lamp power as that of the successful experiment, it was difficult to stabilize the FZ because the improper melting of the feed rod caused changes in the volume of melt in the FZ. The improper melting of the feed rod suggested the presence of inhomogeneities in the feed rod with regard to either density or phase purity. Also, suction of melt into the feed rod was observed, which reduced the amount of melt in the FZ. This indicated that the density of the rod is low and that the rod is porous. With a view to overcome these possible problems, the sintering process used to form \(\text{La}_2\text{Cu}_2\text{O}_5\) was repeated four times in order to ensure phase purity. Later, the pressed feed rods were then sintered at slightly higher temperature of 900°C than previously used 800°C, in order to improve density. Powder x-ray diffraction confirmed the formation of \(\text{La}_2\text{Cu}_2\text{O}_5\) as a single phase. In the successful growth experiment, the homogeneity and density of the feed rod was reflected in the observation of uniform melting of the feed rod
6.3. Crystal growth

and a sharp feed-zone boundary with very little suction of melt from the FZ into the feed rod. Thus, in addition to the use of a solvent-pellet and an Ar atmosphere, a homogeneous and dense feed rod consisting of single phase $\text{La}_2\text{Cu}_2\text{O}_5$ seemed to be an important factor for the success of the growth experiment. From our experiments, one sees that it is possible to grow single crystals of $\text{LaCuO}_2$ from a melt formed by decomposing $\text{La}_2\text{Cu}_2\text{O}_5$. However, detailed studies, in different atmospheres, regarding the temperature regimes where $\text{LaCuO}_2$ exists in the $\text{La}_2\text{O}_3$-$\text{CuO}$ phase diagram are needed however to throw light on the precise mechanism of the growth.

Fig. 6.23, shows the experimentally obtained powder diffraction pattern for the as-grown crystal along with the simulated pattern. An initial comparison with literature on polycrystalline $\text{LaCuO}_2$ [188] shows that all the peaks of the reported pattern matched with our experimental pattern, indicating we have grown the desired $\text{LaCuO}_2$ phase. Refining the experimental pattern, we see that the refined pattern matches well with the experimental one. We obtain rhombohedral symmetry with a $\text{R}3\text{m}$ space group with lattice parameters $a \approx 3.832\text{Å}$, $b \approx 3.832\text{Å}$ and $c \approx 17.098\text{Å}$, in agreement with literature [188]. The atomic positions, lattice parameters and quality of refinement are given in Table. 6.7. All the peaks were indexed and were found to match with the simulated pattern, with no peaks arising from impurities. Effect of texture and stress were not refined as the main motive of refinement was to identify confirm phase purity, and these possibly account for small difference in observed and simulated intensities which remain unrefined.
Figure 6.25: Resistivity($\rho$) as a function of temperature. Inset: ln ($\rho$) is plotted against $1/T$ and the red line shows a linear fit to it.

SEM images at different magnifications are shown in Fig. 6.24, the inset showing a higher magnification image of the area marked in red. These images are taken in the Backscattered Electron (BSE) mode with an electron beam acceleration voltage of 15 kV. There is no trace of any inclusions as secondary phase which would otherwise be visible as phase contrast. One can see sharp and well defined cleavage planes in the images, characteristic of a delafossite crystal. Small broken pieces of the crystal and dirt due to sample handling are visible on the surface. EDX was done on several pieces of the crystal and the average compositional ratio, La : Cu, was deduced to be 1.00 : 0.99. This ratio was also checked for different pieces of the crystal using ICP-AES, and from this the resultant formula was found to be La$_{0.98\pm0.15}$Cu$_{0.99\pm0.19}$O$_{2.05\pm0.15}$. From the above analyses we can say that the synthesized crystal is a good quality single crystal of LaCuO$_2$.

To gain insight into the relation between the growing crystal and the phase diagram we analyzed the composition of the floating zone using SEM. One can clearly see the lamellar structure in the zoomed-in image of the FZ corresponding to a eutectic solidification (Fig. 6.22). The average composition of the zone was found to be 85% CuO : 15% La$_2$O$_3$. As we expect the melt in the floating zone to be of a composition near the peritectic region corresponding to La$_2$Cu$_2$O$_5$ (as our feed rod was La$_2$Cu$_2$O$_5$), it is likely that in the phase diagram of the CuO-La$_2$O$_3$
system in an Ar atmosphere, the liquidus region of La$_2$Cu$_2$O$_5$ extends from the eutectic point (92% CuO) to up to compositions of 85 % CuO : 15% La$_2$O$_3$.

Electrical resistivity ($\rho$) from 180-300 K was measured using the four probe method. The resistivity at 295 K was measured to be $\sim 0.85\text{M}\Omega\text{-cm}$, and was found to increase exponentially with decreasing temperature indicating an insulator-like behavior. We fit the data by an exponential $\rho(T) \propto \exp(-E_g/k_B T)$, where $E_g$ is the insulating gap energy. From the fit, the value of the insulating gap was found to be 0.14 eV. Fig. 6.25 shows $\rho(T)$, and the inset shows a plot of $\ln(\rho)$ versus $1/T$ along with a linear fit to determine the gap energy.
Chapter 7

La$_2$CuO$_4$: Heat Transport

7.1 Heat transport

The heat conductivity of La$_2$CuO$_4$ measured earlier in the literature using the steady state method was discussed in section 5.1, where the emergence of a peak in $\kappa_\parallel$ due to magnons at around 280 K indicated temperature-dependent scattering mechanisms setting in. However, very little is known about these scattering mechanisms involving magnons, and moreover these investigations are restricted to low temperatures of 300 K, where the magnetic contribution is still large. With a view to explore the behaviour of heat conductivity of at higher temperatures, and to shed light on the scattering mechanisms, heat transport up to very high temperatures (813 K) has been investigated for the first time. These high temperature measurements were carried out by Oleg Mityashkin using the dynamic flash method, and more discussions can be also found in his PhD thesis [144]. These investigations aim at gaining insight into the scattering processes relevant in different temperature regimes, and motivating theoretical work on the long-standing problem of magnon transport in 2D.

Fig. 7.1 shows the heat conductivity of undoped La$_2$CuO$_4$ measured parallel ($\kappa_\parallel$) and perpendicular ($\kappa_\perp$) to the $ab$-plane in a wide temperature regime from 7 K at 813 K using two methods. The blue curves denote the measurements done using the steady state method and the red curves denote the measurements done using the dynamic flash method (see chapter 4 for descriptions of methods). $\kappa_\perp$ and $\kappa_\parallel$ measured using both methods are in good agreement in the temperature range around 300 K, where there is an overlap is the measured temperature range.
7.1. Heat transport

Figure 7.1: Thermal conductivity of La$_2$CuO$_4$ as a function of temperature as measured parallel ($\kappa_\parallel$) to the $ab$-plane and perpendicular ($\kappa_\perp$) to it. The red colour symbols indicate the measurement points obtained by the dynamic flash method and the blue symbols correspond to steady state measurements. The gray region indicates a possible anisotropy of 30% in the phononic heat conductivity, that contributes to the uncertainty in $\kappa_{\text{mag}}$, the magnon heat conductivity.

To analyze the data we regard the data obtained from both these techniques as one data-set from 7 K to 813 K. At temperatures higher than 300 K, $\kappa_\perp$ keeps decreasing steadily to a value of 2 Wm$^{-1}$K$^{-1}$ at 813 K, as expected, considering the fact that it stems purely from phonons. $\kappa_\parallel$ on the other hand, after showing a broad peak at around 280 K, decreases sharply at high temperatures and reaches a value of around 3.75 Wm$^{-1}$K$^{-1}$ at 813 K. Thus, even at the highest temperature of measurement there still exists an anisotropy in the heat conductivity along and perpendicular to the plane, signifying the presence of conduction via magnetic excitations.

We now extract $\kappa_{\text{mag}}$, and analyze it using the approach introduced in section 3.4. Assuming that the phononic heat conductivity is isotropic, we extract


Figure 7.2: (a) Magnetic thermal conductivity as a function of temperature ($\kappa_{\text{mag}}(T)$, red symbols) compared with data in literature [11, 12, 14–16]. (b) The low-$T$ fit (the black solid line) to the experimental data using equation 7.1. The gray region shows the uncertainty in the estimation of $\kappa_{\text{mag}}$ due to possible anisotropy of the phononic heat conductivity, and the red open symbols show the data that has not been considered for further analysis due to significant errors.

the magnetic heat conductivity $\kappa_{\text{mag}}$ by subtracting $\kappa_\perp$ from $\kappa_\parallel$, a method that has been frequently used in the literature [141].

7.1.1 Magnetic heat conductivity

$\kappa_{\text{mag}}$ as a function of temperature is plotted in Fig. 7.2(a). In the low-temperature regime from 50 K - 200 K, $\kappa_{\text{mag}}$ increases sharply. Around 230 K it exhibits a maximum reaching the value of approximately 35.4 Wm$^{-1}$K$^{-1}$, and then decreases strongly up to the highest temperature of 813 K to a value of 1.72 Wm$^{-1}$K$^{-1}$. If we compare this $\kappa_{\text{mag}}$ to that obtained previously in references [12–16] by other research groups, we see that the $\kappa_{\text{mag}}$ obtained in this work is much higher. Except for the data by Yan et al. all other curves are well below our $\kappa_{\text{mag}}$ at all temperatures. From the comparison with $\kappa_{\text{mag}}$ from the literature it is evident that the single crystals grown in this work are of very high crystalline quality, and high purity. Scattering of magnons off both boundaries and defects is reduced to a large extent, thereby enhancing conductivity.
7.1. Heat transport

In the low-temperature regime, $\kappa_{\text{mag}}$ can be modelled in the framework of the Boltzmann-like approach with a constant mean-free path due to magnon-boundary scattering, as has been discussed in section 3.4.2. Such an approach has been used for analyzing $\kappa_{\text{mag}}$ in earlier work [12]. Recalling from section 3.4.2, the heat conductivity can be written as,

$$
\kappa_{\text{mag}} = \frac{v_0 k_B l_{\text{mag}}}{2a^2c} \frac{T^2}{\Theta_M^2} \sum_{i=1,2} \int_{x_{0,i}}^{x_{\text{max}}} x^2 \sqrt{x^2 - x_{0,i}^2} \frac{e^x}{(e^x - 1)^2} dx,
$$

(7.1)

where the integral is dimensionless, and $x_{0,i} = \Delta_i/(k_B T)$ and $x_{\text{max}} = \Theta_M/T$. $Z_c = 1.18$ is the quantum renormalization factor for $s = \frac{1}{2}$ spins. $\Theta_M = \sqrt{2\pi Z_c J}$ is the Debye temperature for magnons.

While fitting equation 7.1 to the experimental data, an additive shift of the $\kappa_{\text{mag}}$ curve which gives a further free parameter other than $l_{\text{mag}}$. This shift accounts for the uncertainties in the magnitude of $\kappa_{\text{mag}}$ that arise during its extraction from the measured heat conductivities parallel and perpendicular to the $ab$-plane. The fit to the experimental data is shown in fig. 7.2(b). A good fit is obtained for temperatures in the range 50 K - 150 K. At temperatures lower than 50 K, the error in $\kappa_{\text{mag}}$ becomes significant, as shown by the gray region in fig. 7.2(b), and the fitting procedure is restricted up to this temperature. At temperatures higher than 150 K, the experimental $\kappa_{\text{mag}}$ deviates from the extrapolated fit. This can be understood in terms of the $T$-dependence of $l_{\text{mag}}$ due to $T$-dependent scattering processes. The fit results in a constant and very large mean free-path value of around 3500±250 Å\(^1\), which is equal to almost 1000 lattice spacings, and an additive shift of -0.23 Wm\(^{-1}\)K\(^{-1}\).

A good fit in this low-temperature regime indicates that $T$-dependent scattering processes may not be important at these temperatures, and that a temperature-independent scattering process dominates. The most likely process might be the $T$-independent scattering mechanism of magnons off boundaries in the 2D square lattice, leading to a constant $l_{\text{mag}}$ over this $T$-range where other $T$-dependent scattering processes are still not effective enough. Such an interpretation is also found in [12], to explain a similar but much smaller constant mean free path of around 580 Å (see section 5.1 and 3.4.2). The very large mean free path found in this work translates into the conclusion that the crystals grown in this work are of remarkably higher quality, and that continuous 2D planes exist over

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\(^1\)The error in the mean free path was determined by fitting equation 7.1 to the $\kappa_{\text{mag}}$ obtained by adding and subtracting a maximum error of 30% stemming from possible phononic anisotropy.
larger distances. Note that the extracted $l_{\text{mag}}$, if interpreted as being limited by boundaries, is much smaller than the crystal diameter (which in the case of our measurements was around 3-4 mm). The crystal diameter is the limiting length in the case of phonon-boundary scattering because, for three-dimensional phonons the effect of a discontinuity in the 2D structure is not expected to be very strong. However, in a 2D square lattice like La$_2$CuO$_4$, the existence of discontinuities in the 2D planes where the magnons propagate is likely to act as a very strong boundary, akin to how the crystal peripheries act for the case of phonon propagation. This boundary is much smaller than the crystal diameter and becomes responsible for determining the mean free path due to magnon-boundary scattering. The presence of a peak and the strong decrease of $\kappa_{\text{mag}}$ clearly indicate that at higher temperatures, apart from $T$-independent scattering processes, other $T$-dependent dissipative scattering mechanisms set in, that cause a decrease in the heat conductivity. Scattering of magnons with phonons and other magnons are probable mechanisms responsible for heat conduction in this $T$-regime.

A qualitative comparison of this $\kappa_{\text{mag}}$ at higher temperature with results of theoretical calculations throws some light on the scattering mechanisms that could be involved. Fig. 7.3 compares the $\kappa_{\text{mag}}$ obtained in this work and that of Hess et al., with theoretical calculations by Bayrakci et al.. As discussed earlier in section 5.1, the boundary limited mean free path of magnons (580 Å) used in the calculations was taken from Hess et al. [12], and there exists a clear discrepancy between the experiment and theory as far as the magnitude and position of the peak with respect to temperature is concerned. There seems to be a reasonable agreement at low temperatures though where magnon-boundary scattering is evidently dominant. The main difference between $\kappa_{\text{mag}}$ from Hess et al. and that from the present work, is that the new crystals grown and measured here are of very high quality with regard to crystallinity and purity. This is evident from the large difference in the mean free path of magnons, which is obtained to be around six times greater than that of Hess et al.. Fig. 7.3 shows that the calculations and the data from Hess et al. differ from our experimental $\kappa_{\text{mag}}$ in the entire temperature range. The mean free path of magnons due to boundary scattering is an essential input in the calculations of Bayrakci et al. and has been taken from Hess et al. Thus, at least at low temperatures, the disagreement between the calculated $\kappa_{\text{mag}}$ and our experimental $\kappa_{\text{mag}}$ could arise due to the above difference. However, the agreement of the calculations by taking into account the new $T$-independent mean free path due to scattering at boundaries obtained from our experiments is not yet checked.

At higher temperatures the decrease in the experimental $\kappa_{\text{mag}}$ is much stronger
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Figure 7.3: Magnetic thermal conductivity as a function of temperature ($\kappa_{\text{mag}}(T)$, red symbols) compared with calculations by Bayrakci et al. (black solid line) [157, 158]. Red symbols are data from this work, blue symbols are $\kappa_{\text{mag}}$ taken from Hess et. al [12]. The gray region shows the uncertainty in the estimation of $\kappa_{\text{mag}}$ due to possible anisotropy of the phononic heat conductivity.

than the calculated $\kappa_{\text{mag}}$, despite the larger low-temperature boundary limited mean free path. This disagreement therefore could indicate that assuming only boundary and magnon-magnon scattering processes, as has been done in their calculations by Bayrakci et al., is not enough to describe experimental $\kappa_{\text{mag}}$, and that additional $T$-dependent scattering processes have to be taken into account in order to explain the experimental results.

After having quantitatively analyzed the low-$T$ regime of $\kappa_{\text{mag}}$, using a constant $T$-independent mean free path, in the following section we include the high temperature regime of $\kappa_{\text{mag}}$ up to 813 K and attempt to empirically analyze the mean free path of magnons using $T$-dependent scattering processes.
7.1.2 Magnon mean free path

In order to extract the magnon mean free path \( l_{\text{mag}} \) from \( \kappa_{\text{mag}} \), we use the kinetic model discussed in section 3.2, which can be written for 2D as

\[
\kappa = \frac{1}{2} \int_{BZ} c_k v_k^2 \tau_k dk
\]  

(7.2)

When considering the scattering rate \( \tau^{-1} \), one might intend to apply an analogy of the Callaway model for phonons (refer 3.3), where \( \tau^{-1} \) is given as a sum of scattering rates for different processes like scattering off boundaries, point-defects, and other relevant excitations. Generally, \( \tau^{-1} \) is dependent on temperature and on frequency \( (\omega) \) for each process. For umklapp scattering processes that are temperature dependent one can write \([123, 124] \),

\[
\tau_1^{-1} = A^{(1)} \omega^\beta T^\gamma \exp\left(-\frac{T_{u}^{(1)}}{T}\right)
\]  

(7.3)

where, \( A^{(1)} \) is a constant signifying the coupling strength, and \( T_{u}^{(1)} \) is a characteristic temperature of the scattering process. However, the power laws for the \( \omega \)- and \( T \)-dependence are not known for the case of magnetic excitations in a 2D system. Thus, for a preliminary analysis we let \( \alpha = \beta = 0 \). We also set \( \gamma = \delta = 1 \) because these empirically selected \( T \)-dependencies very well describe the \( T \)-dependence of the mean free path due to magnetic excitations in the case of \( S = \frac{1}{2} \) spin chain cuprates. For the scattering off point defects, the \( \omega \)-dependence is neglected because at low temperatures \( \omega \)- and \( T \)-independent boundary scattering dominates, whereas at higher temperatures which are at focus here, the exponential umklapp terms dominate.

Recalling the approach based on the kinetic model that was discussed in section 3.4.2, the expression for the magnetic heat conductivity \( \kappa_{\text{mag}} \) can be written as,

\[
\kappa_{\text{mag}} = \frac{1}{2} l_{\text{mag}} v_{\text{mag}} c_{\text{mag}}
\]  

(7.4)

where, \( c_{\text{mag}} \) is the magnetic specific heat, obtained from theoretical calculations (see section 3.4.2). Using the above equation, and the experimentally obtained
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Figure 7.4: Mean free path of the magnetic excitations as a function of temperature ($l_{\text{mag}}$, black open symbols). Fits weighted at low, high and full temperature ranges are shown as blue, red and green curves respectively according to equation 3.39. The red open symbols are points that have been excluded in the analysis, and the grey region shows the errors.

The resulting magnon mean free path is plotted in Fig. 7.4 as open circles.

$l_{\text{mag}}$ is now quantitatively analyzed in order to provide some insight into the scattering mechanisms that might be present. As of now there is no rigorous theoretical model for scattering processes of magnetic excitations in 2D. However, in order to provide some preliminary quantitative insight into the scattering, we attempt to analyze $l_{\text{mag}}$ using an empirical approach that considers two scattering mechanisms, a $T$-independent scattering process and a $T$-dependent process. As discussed above, we use the expressions for the scattering rates with an empirically selected $T$-dependence and neglecting the $\omega$-dependence. Such a treatment has been used earlier in literature for $S = \frac{1}{2}$ spin chain compounds and has worked surprisingly well (refer 5). Thus for the mean free path we have,
Chapter 7. \( \text{La}_2\text{CuO}_4 \): Heat Transport

<table>
<thead>
<tr>
<th></th>
<th>( l_0 ) (Å)</th>
<th>( T_u^* ) (K)</th>
<th>( A_s ) ((10^3 \text{ m}^{-1}\text{K}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full T range</td>
<td>2992 ± 840</td>
<td>1745 ± 260</td>
<td>8.19 ± 2.5</td>
</tr>
<tr>
<td>Low T range</td>
<td>3936 ± 730</td>
<td>1083 ± 250</td>
<td>0.154 ± 0.3</td>
</tr>
<tr>
<td>High T range</td>
<td>1187 ± 490</td>
<td>2421 ± 290</td>
<td>1.6 ± 6.8</td>
</tr>
</tbody>
</table>

Table 7.1: Fit parameters for the magnetic mean free path by equation 3.39. The errors in the fit parameters were extracted by fitting \( l_{\text{mag}} \) that was calculated by adding and subtracting a maximum error of 30% in \( \kappa_{\text{mag}} \) that stems due to a possible anisotropy in phononic heat conduction.

\[
l_{\text{mag}}^{-1} = l_0^{-1} + \left( \frac{\exp(T_u^{*(1)}/T)}{A_s^{(1)}T} \right)^{-1}.
\]

To check the validity of such a description of \( l_{\text{mag}} \), three fits weighted at different temperature ranges were done (solid lines in Fig. 7.4). These weighted fits were performed by restricting the fitting routine to pre-defined temperature ranges. The fit-parameters are shown in the table 7.1. A fit equally weighted on the entire temperature range (green line), a fit weighted at high temperature (red line) and a low-T weighted fit (blue line) were performed. We see that the full-T range fit fails to describe the experimental \( l_{\text{mag}} \) well in the temperature range from 400 K to 813 K, and underestimates the data at \( T < 200 \) K. The low-T weighted fit describes the data very well in the temperature range 150 K - 300 K. However, this low-T fit strongly deviates from the experimental \( l_{\text{mag}} \) above 300 K. The experimental \( l_{\text{mag}} \) decreases with increasing temperature more strongly than the fit does. The high-T weighted fit also fails to model \( l_{\text{mag}} \) in the entire temperature range, fitting the data well only at temperatures above \( T \approx 300 \) K. \( T_u^{*(1)} \), which gives the characteristic energy scale of the excitations that are involved in magnon scattering processes, takes a value of more than 1000 K in the case of all three fits. This indicates, one the one hand, that modelling magnon scattering by just one exponentially \( T \)-dependent process and a \( T \)-independent process is not enough to capture the scattering processes in \( \text{La}_2\text{CuO}_4 \) in the whole temperature range, and that additional scattering mechanisms or a different functional form of it has to be taken into account.

Assuming the exponential \( T \)-dependence of one scattering process to be reasonable, we move a bit further with the treatment of the data. In order to check for the presence of further scattering mechanisms, we specifically include a second energy scale in the empirical approach used above. Another \( T \)-dependent umklapp-like scattering processes is introduced as,
7.1. Heat transport

\[ \tau_2^{-1} = A^{(2)} \omega \beta T^\delta \exp(-T_u^{(2)}/T) \] (7.6)

again with \( \alpha = \beta = 0, \) and \( \gamma = \delta = 1. \) So, apart from \( T \)-independent boundary scattering, we now have \( T \)-dependent scattering processes for two energy scales representative of two different modes. Thus we get,

\[ l_{mag}^{-1} = l_0^{-1} + \left( \frac{\exp(T_u^{(1)}/T)}{A_s^{(1)} T} \right)^{-1} + \left( \frac{\exp(T_u^{(2)}/T)}{A_s^{(2)} T} \right)^{-1}. \] (7.7)

Figure 7.5 shows the fit to \( l_{mag} \) according to equation 7.7, and the fit parameters are shown in the table 7.2. This fit describes the experimental \( l_{mag} \) well in the
Chapter 7. \(\text{La}_2\text{CuO}_4\): Heat Transport

temperature range from 150 K to 700 K. A mean free path of \(l_0 = 4204 \pm 710\) Å due to magnon-boundary scattering is obtained from this fit, which agrees within the error with the mean free path, \(l_0 = 3500 \pm 250\) Å, obtained by using the low-temperature Boltzmann-like approach with a constant magnon mean free path. The resulting characteristic temperatures \(T_u^{*(1)}\) and \(T_u^{*(2)}\), which give us an idea of the maximum energies of the modes that take part in the scattering, are found to be \(\approx 17\) THz and \(\approx 63\) THz respectively. On comparing these frequencies with frequencies of phonons experimentally obtained by L. Pintschovius et al. \[210, 211\] on the isostructural \(\text{La}_2\text{NiO}_4\) compound, we find that the lower phonon frequency (\(\approx 17\) THz) can be associated with the breathing-mode of frequency 14.7 THz. Coupling of this mode to the magnons is physically justified as this mode modulates the Cu-O-Cu coupling, thereby acting as a possible scatterer.

<table>
<thead>
<tr>
<th>Two energy fit</th>
<th>(l_0) (Å)</th>
<th>(T_u^{*(1)}) (K)</th>
<th>(T_u^{*(2)}) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy(THz)</td>
<td>4204 ± 710</td>
<td>847 ± 108</td>
<td>2759 ± 360</td>
</tr>
</tbody>
</table>

Table 7.2: Two-phonon energy fit parameters for the magnetic mean free path according to equation 7.7. The errors in the fit parameters were extracted by fitting \(l_{\text{mag}}\) that was calculated by adding and subtracting a maximum error of 30\% in \(\kappa_{\text{mag}}\) that stems due to a possible anisotropy in phononic heat conduction.

The higher frequency of 57 THz (\(\approx 2800\) K), however, is much larger than the maximum possible phonon frequency (\(\approx 20\) THz) that can be excited in this compound. Thus, the second umklapp term in equation 7.7 cannot describe scattering off phonons because of unphysical phonon frequencies. However, this high energy mode could be in some way linked to the magnetism of this compound because the energy scale is of the order of magnitude of the magnetic exchange coupling in these compounds, \(J\), which is around 1550 K. In phononic systems, the Debye temperature signifies the characteristic energy scale for scattering processes between phonons, and is supposed to be the maximum possible energy of a vibrational mode. An analogous Debye temperature for magnons can be thought of as the energy of the magnons at the zone boundary, i.e, the energy scale given by \(J\). Thus, presuming that very low-energy magnon-scattering processes are negligibly important, the energy scale obtained from the fit seems to capture scattering processes due to interaction between magnons present at high temperatures in this compound. However, such a deduction must be approached with some leniency due to its speculative nature. As there hardly exists any knowledge in the literature about interaction between magnons in two-dimensional antiferromagnets and about scattering processes between them with regard to magnon heat transport, these experimental investigations provide a valuable input towards understanding these issues.
Correlation length

It is intriguing to look at the spin-spin correlation length in this compound in order to check for its possible relevance to the scattering term involving the high-energy scale, that seems to exist as per the analysis. The mean free path \( (l_{\text{mag}}) \) and the spin-spin correlation length are compared in Fig. 7.6. The extraordinary purity of the crystal grown in this work apparently leads to an enhancement of \( l_{\text{mag}} \) to a value close to the correlation length. The correlation length was calculated according the expression that was introduced in section 3.4.2 [88, 91, 92] given as,

\[
\xi/a = \frac{e}{8} \frac{c/a}{2\pi \rho_s} \exp(2\pi \rho_s/T)[1 - \frac{1}{2} \left( \frac{T}{2\pi \rho_s} \right)]
\]  

(7.8)
where is $\rho_s$ the spin stiffness, and $c$ is the spin wave velocity. For the $S = \frac{1}{2}$ nearest neighbor 2D square lattice Heisenberg antiferromagnet, $2\pi \rho_s = 1.15 J$ [88, 91, 92]. The correlation length for the correlation length contains a Boltzmann factor $\exp(2\pi \rho_s/T)$, and a corresponding energy scale, which has a similar form as $l_{\text{mag}}(T)$, except for the factor $T$ (see equation 7.7). This energy scale ($\sim 1.5 J$) was in a range similar to that of the exchange coupling constant $J$. This similarity in the energy scales of the possible high energy scattering process responsible for reducing the mean free path, and that of the correlation length seems to suggest that the correlation length might play a role in limiting the mean free path of magnons. This raises the question of whether the spin-spin correlation length is a physically significant aspect in heat transport via magnons, and whether it is responsible for temperature dependent scattering. It is worthwhile to mention that the empirical model that has been used to try and describe $T$-dependent magnon scattering is very elementary, and hence an interpretation based on the fits should be not be forced.

However, more sophisticated theoretical calculations by Brenig and Chernyshev [212] suggest that in addition to scattering of magnons off phonons and other magnons, the magnon heat conductivity is strongly influenced by the spin-spin correlation length and the downturn seen in the experimental $\kappa_{\text{mag}}$ at high temperatures is reproduced well by considering the effect of the correlation length.

**Thermal Hall effect**

Also, experiments were performed on pure La$_2$CuO$_4$ in order to check for the presence of the thermal Hall effect/magnon Hall effect, that has been recently postulated and experimentally found to occur in magnetic insulators where there exists significant heat transport via magnons [213, 214]. However, in the limit of the device sensitivity$^1$ no visible thermal Hall voltage was detected in the measurements.

**7.1.3 Summary**

Heat transport in the pure compound has been measured and studied for the first time up to very high temperatures ($\sim 813$ K). A good agreement between the dynamic flash method used for measuring high temperature heat conductivity

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$^1$Keithley 2182/182 nanovoltmeter
and the conventional steady state method is obtained over a wide temperature regime. An unprecedentedly high magnetic heat conductivity has been measured indicating that the quality of the grown single crystal is extraordinarily high. At high temperatures $\kappa_{\text{mag}}$ strongly decreases compared to the phononic heat conductivity, suggesting that additional temperature dependent scattering mechanisms, other than the temperature independent boundary scattering, are present that limit conduction by magnons. Qualitative comparison of the experimental $\kappa_{\text{mag}}$ to recent calculations seems to suggest that only taking into account the scattering of magnons off boundaries and other magnons is apparently insufficient to fully describe the strong suppression of $\kappa_{\text{mag}}$. The scattering of magnons with other excitations like phonons could be in addition important to explain this strong decrease. From our preliminary analysis of the experimental data based on empirical models for scattering analogous to the phononic Callaway model, it is seen that along with a $T$-independent boundary scattering process, two umklapp-like $T$-dependent scattering terms seem to describe the temperature dependence of $\kappa_{\text{mag}}$ in the entire measured temperature range. One of these terms having a characteristic energy scale could correspond to phonon modes in the compound, thus indicating the relevance of phonons in the scattering processes that limit magnon heat conduction. The energy scale involved in the second term is of the order of magnitude of the magnetic exchange coupling $J$. There are indications that this high energy scale might be manifested through the correlation length that possibly limits the mean-free path of magnons. Finally, a theoretical model that treats $T$-independent and $T$-dependent magnon scattering processes with boundaries, and other quasiparticles together, taking into account a possible influence of the spin-spin correlation length is required to explain the experimental results and describe the physics of scattering in the $\text{La}_2\text{CuO}_4$ compound for the whole temperature range. Finally, in order to better understand the role of point-like defects and boundaries in magnon scattering processes, and the temperature regimes in which they are observably dominant, single crystals of $\text{La}_2\text{CuO}_4$ with small amounts of Ni and Zn doped at the Cu-site have been grown. Ongoing heat transport measurements on these crystals will possibly give insight into the role of substitutional impurities in limiting heat transport via magnons, i.e., whether such impurities act as point-like defects or whether they act as boundaries for the magnons, or whether their effect is just screened.
Chapter 8

Impurity effects I: Ni doped SrCuO$_2$ and Sr$_2$CuO$_3$

8.1 Heat transport

8.1.1 Sr$_{2}$Cu$_{1-x}$Ni$_x$O$_3$

Heat conductivities that were measured perpendicular to the spin chains ($\kappa_c$) of Sr$_2$Cu$_{1-x}$Ni$_x$O$_3$ for $x = 0$, 0.005, 0.01, 0.02 are shown in Fig. 8.1. $\kappa_c$ of the undoped compound ($x = 0$), was described earlier in section 5.2, and its behaviour as a function of temperature is similar to that of a purely phononic conductor. Upon doping small amounts of Ni, the heat conductivity exhibits drastic changes. For $x = 0.005$, contrary to conventional notion, $\kappa_c$ increases sharply to a very large peak value of $\sim 770$ Wm$^{-1}$K$^{-1}$, For $x = 0.01$, $\kappa_c$ increases further to an even larger peak value of $\sim 1260$ Wm$^{-1}$K$^{-1}$, more than three times the peak value for the pure compound. Finally, for $x = 0.02$, $\kappa_c$ decreases to a value of $\sim 420$ Wm$^{-1}$K$^{-1}$, but remains far above the peak value for the undoped compound. This variation in magnitude of the peak of $\kappa_c$, upon doping, is seen only in the temperature regime of 7 K to 100 K. The heat conductivities above 100 K hardly differ in the undoped and the doped compounds. The inset of Fig. 8.1 shows the non-monotonic behavior of $\kappa_c$ as a function of the dopant’s concentration. The enhancement of $\kappa_c$ is maximum for $x = 0.01$. From the above, the trend of change of the heat conductivity as a function of doping concentration seems to be qualitatively similar for Ni-doped SrCuO$_2$ and Sr$_2$CuO$_3$, though the magnitude of
8.1. Heat transport

Figure 8.1: Heat conductivity ($\kappa_c$) perpendicular to chain for different Ni concentrations are plotted as a function of temperature; inset: the magnitude of the peak in $\kappa_c$ is plotted as a function of the Ni concentration to illustrate the anomalous increase.

The enhancement of the phononic conductivity is much larger in the case of Ni-doped Sr$_2$CuO$_3$ (see section 5.2). This increase of the phononic heat conductivity upon introducing defects in the material by impurity-doping, is counter-intuitive. As discussed in section 3.3, typically a strong decrease in conductivity is observed for phononic systems when the smallest concentration of impurity is introduced.

The thermal conductivities measured parallel to the chains ($\kappa_b$) of Ni-doped Sr$_2$CuO$_3$ are plotted in Fig. 8.2. $\kappa_b$ for the pure compound was described earlier in section 5.2, where a significant contribution from magnetic excitations was responsible for a broad peak with a value of $\sim 500$ Wm$^{-1}$K$^{-1}$, and a slower high-$T$ decrease, relative to $\kappa_c$. Upon doping Ni the behaviour of $\kappa_b$ strongly changes. For $x = 0.005$, $\kappa_b$ is strongly enhanced at low temperatures ($\lesssim 80$ K), with a peak value of $\sim 820$ Wm$^{-1}$K$^{-1}$. The shape of the curve, though, is very different from that of the pure compound. A sharper and more phononic-like peak is now observed in the $x = 0.005$ compound. For $x = 0.01$, $\kappa_b$ is enhanced...
even more up to a peak value of $\sim 930 \text{ Wm}^{-1}\text{K}^{-1}$, the peak-shape remaining similar to the $x=0.005$ case. Finally, for $x=0.02$ the peak value is reduced to $\sim 660 \text{ Wm}^{-1}\text{K}^{-1}$, but the value remains still higher than that for the undoped case. The enhancement in $\kappa_b$ for the doped compounds is seen for temperatures $\lesssim 80 \text{ K}$, similar to that observed in the case of $\kappa_c$. Above 80 K, $\kappa_b$ for the pure compound remains larger than that for the doped compounds up to 300 K. Also, above this temperature there is almost no variation in $\kappa_b$ as a function of the doping concentration. The inset of Fig. 8.2 shows the non-monotonic behavior of $\kappa_b$ as a function of the dopant’s concentration. The enhancement of $\kappa_b$ is maximum for $x=0.01$, as in the case of $\kappa_c$. Such a trend in $\kappa_b$ is not observed for the Ni-doped SrCuO$_2$ compound.

Judging from the shape and magnitudes of the curves for $\kappa_b$, one can infer that the magnetic contribution to $\kappa_b$ in the pure compound is strongly suppressed as
soon as the smallest amount of Ni is introduced into the system. Most of the contribution to $\kappa_b$ in the doped compounds therefore arises due phonons. Thus, overall, one can say that there is a strong enhancement of the phononic heat conductivity in the system as a whole, both parallel and perpendicular to the chains. The increase of phononic thermal conductivity in Ni-doped SrCuO$_2$ is not seen parallel to the chains in spite of the strong suppression of the spinon heat conduction. The enhancement is observed only perpendicular to the chains where no contribution from spinons is present (refer to Fig. 5.8 in chapter 5). This is probably because in the ratio of spinon to phonon heat conductivities is much lower in Sr$_2$CuO$_3$ than that in SrCuO$_2$ (see section 5.2), and the relative magnitude of increase of phononic conduction in the case of Ni-doped SrCuO$_2$ is low compared to the magnitude of the total heat conductivity for the undoped compound parallel to the chains.

8.1.2 Spinon heat conductivity and mean free path

The spinon heat conductivity ($\kappa_{\text{mag}}$) of the Ni-doped Sr$_2$CuO$_3$ series is extracted by subtracting $\kappa_{\perp}$ from $\kappa_{\parallel}$ and is plotted in Fig. 8.6. Data only above 70 K are presented and analyzed, because the errors due to a possible anisotropy in phononic conductivity become fairly significant below these temperatures. While there is a large peak for the undoped compound, only a very small upturn is present towards low temperatures in the set of curves for the doped compounds, thereby indicating a strong suppression of spinon heat transport. There is a monotonic decrease of $\kappa_{\text{mag}}$ as a function of doping, indicating that the anomalous enhancement of $\kappa_c$ and $\kappa_b$ seen upon doping is due to the increase in phononic conductivity. We now extract and analyze the spinon mean free path, under the framework of the kinetic model (see section 3.4.1), to look at the scattering mechanisms that are responsible to limit conduction due to spinons.

The spinon mean free path ($l_{\text{mag}}$) for the pure and doped compounds is plotted in Fig. 8.3 as open symbols. As expected from the behaviour of the magnetic heat conductivity, the mean free path also gets smaller with increasing Ni-doping. Reading off the $y$-intercept from the plotted graphs for $l_{\text{mag}}$, at low temperatures of around 100 K, the pure compound shows a very large mean free path of $\sim$ 1200 Å, whereas upon doping the slightest amount of Ni ($x = 0.005$), the mean free path drops to $\sim$ 200 Å. For $x = 0.01$ and $x = 0.02$ it drops to $\sim$ 150 Å and $\sim$ 80 Å respectively. At room temperature the mean free path for $x = 0.005$ is around half that of the undoped compound. Qualitatively, this indicates that Ni acts as a strong scatterer of spinons propagating along the chains. We now try to
model the temperature dependence of $l_{\text{mag}}$ by taking into account two scattering processes, spinon-phonon scattering and spinon-defect scattering, as discussed in section 3.4.1. The fits for the doped and undoped compounds are shown as solid lines in Fig. 8.3.

**Table 8.1**: Fit parameters obtained by fitting $l_{\text{mag}}$ for the Ni-doped Sr$_2$CuO$_3$ series by equation 3.39. The errors in the fit parameters were extracted by fitting $l_{\text{mag}}$ that was calculated by adding and subtracting a maximum error of 30% in $\kappa_{\text{mag}}$ that stems due to a possible anisotropy in phononic heat conduction.

<table>
<thead>
<tr>
<th>Ni content</th>
<th>$l_0$ (Å)</th>
<th>$T_u^*$ (K)</th>
<th>$A_s$ ($10^6$ m/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>5093 ± 510</td>
<td>210</td>
<td>0.74 ± 0.3</td>
</tr>
<tr>
<td>x = 0.005</td>
<td>282 ± 45</td>
<td>210</td>
<td>1.12 ± 0.44</td>
</tr>
<tr>
<td>x = 0.01</td>
<td>145 ± 26</td>
<td>210</td>
<td>2.29 ± 0.69</td>
</tr>
<tr>
<td>x = 0.02</td>
<td>90 ± 10</td>
<td>210</td>
<td>2.83 ± 0.8</td>
</tr>
</tbody>
</table>

For the fitting procedure we have fixed $T_u^*$ for the doped compounds to the value obtained for the undoped compounds. The fits are quite good at temperatures above 100 K. As discussed in section 5.2 the mean free path for the undoped compound is explained by a general umklapp-like scattering process with phonons and a temperature independent spinon-defect scattering rate. While it is still possible to understand the high temperature part of $l_{\text{mag}}$ for the doped compounds by this model, for low temperatures (below 100 K) this is no longer feasible due to the significant error in $l_{\text{mag}}$ (gray region in Fig. 8.3). The parameters of the fit are listed in table 8.1. $A_s$ changes slightly as a function of doping but is of the same order of magnitude for all doping levels. The slight variation in this parameter accounts for uncertainties in determining $\kappa_{\text{mag}}$, and a small variation in the spin-phonon coupling strength in the pure and doped compounds. Second, the spinon-defect scattering length $l_0$, which represents a lower bound for the low-$T$ limit of $l_{\text{mag}}$ and which should significantly depend on the sample’s purity is very different for the pure and the doped compounds and decreases sharply upon doping. The doping dependence is most sensitive to the parameter $l_0$, and thus implies that Ni impurities mainly act as defect-like scattering centers for spinons. This behavior of Ni as a strong defect-like scatterer, and the doping dependence of $l_{\text{mag}}$ being modelled well by only two scattering processes is similar to that found in the case of Ni-doped SrCuO$_2$ (see section 5.2). We mention that at low temperatures (below 100 K), the extraction of $\kappa_{\text{mag}}$ is prone to large error due to anomalous increase of phononic heat conduction. As a result of large error, an analysis of the spinon mean free path at these temperatures using the above method would not be meaningful.
Figure 8.3: Spinon mean free path \((l_{\text{mag}})\) for different concentrations of Ni is plotted (open symbols) as a function of temperature for \(\text{Sr}_2\text{CuO}_3\) (the grey area gives the estimated error due to the procedure of extraction of \(\kappa_{\text{mag}}\)). The solid lines are fits according to \(l_{sp} = \exp\left(\frac{T_u}{T}/A_sT\right)\); inset: a semi-log plot of \(l_{\text{mag}}\) vs \(T\), to clearly illustrate the changes upon doping.

Fig. 8.4 shows the low temperature constant mean free path \((l_0)\) plotted against the inverse of Ni concentration \((1/x)\) and the mean Ni-Ni distance along the chains of \(\text{SrCuO}_2\) and \(\text{Sr}_2\text{CuO}_3\). There is a good scaling observed for \(l_0\) in both the series of compounds with the inverse of Ni concentration as \(l_0 = 2.65(1/x)\text{Å}\) for Ni-doped \(\text{SrCuO}_2\) and \(l_0 = 1.47(1/x)\text{Å}\) for Ni-doped \(\text{Sr}_2\text{CuO}_3\), implying that the effect of Ni is equally strong for all doping concentrations, and of a similar nature for both the compounds. Also, a qualitative difference between the mean free paths for \(\text{SrCuO}_2\) and \(\text{Sr}_2\text{CuO}_3\), with regard to the scaling is observed. For \(\text{SrCuO}_2\), the mean free path of the excitations close in magnitude to the distance between adjacent Ni atoms. However, for the case of \(\text{Sr}_2\text{CuO}_3\), the mean free path is much smaller than the average distance between neighbouring Ni atoms.
Figure 8.4: Spinon-defect scattering length, $l_0$, is plotted against the inverse of Ni concentration ($x$) (lower $x$-axis) and the mean distance between two Ni atoms (upper $x$-axis) for (a) Sr$_2$CuO$_3$ and (b) SrCuO$_2$; the solid lines are linear fits to the data. The $y$-axis on the right gives an idea of the mean free path in terms of the number of lattice spacings between two Cu sites ($d_0$).

8.1.3 Phonon mean free paths

We focus now in more detail on the unconventional enhancement of the phononic heat conduction upon doping. In Fig. 8.5, the mean free path of phonons, $l_{ph}$, in the single chain Sr$_2$Cu$_{1-x}$Ni$_x$O$_3$ and the double chain SrCu$_{1-x}$Ni$_x$O$_2$ compounds is plotted to illustrate its magnitude and doping dependence at low temperatures, where the peak in the phononic heat conductivity occurs. This was calculated in the framework of the kinetic model (see section 3.2) according to the equation

$$\kappa_{ph} = \frac{1}{3} c_{ph} v_{ph} l_{ph},$$

where, $c_{ph}$, $v_{ph}$, $l_{ph}$ are the specific heat of the phonon system, the velocity of sound, and the phonon mean free path. The experimentally measured specific heat ($c_p$) for the undoped compounds Sr$_2$CuO$_3$ and SrCuO$_2$ was used in the above equation, as an approximation for $c_{ph}$ for the doped compounds as well. The change in phononic specific heat with increasing amount of Ni was neglected as it is expected to be small for very low concentrations of Ni. The magnetic
8.1. Heat transport

Figure 8.5: Phonon mean free paths extracted using the kinetic model (3.2) for different doping levels of (a) the single chain Sr$_2$Cu$_{1-x}$Ni$_x$O$_3$, and (b) the double chain SrCu$_{1-x}$Ni$_x$O$_2$ compounds.

Specific heat was assumed to be negligibly small. The velocity of phonons ($v_{ph}$) was calculated according to [54],

$$v = \frac{k_B}{\hbar} (6\pi^2 n)^{1/3},\quad (8.2)$$

where, $n$ is the number density of atoms and $\Theta_D$ is the Debye temperature. From these values and eq. 8.1, $l_{ph}$ was calculated for each of the compounds. Debye temperatures for the pure compounds Sr$_2$CuO$_3$ and SrCuO$_2$ were taken from literature [7, 10], and was assumed to be the same for the doped compounds.

$l_{ph}$ has a large value at low temperatures in these compounds. $l_{ph}$ is clearly larger for the doped versions than for the pure compounds. As expected, $l_{ph}$ at low temperatures is the highest for the 1% doped SrCuO$_2$ ($\sim 5 \times 10^5$ Å), and for the SrCuO$_2$ doping series the 0.25 % compound has the highest $l_{ph}$ ($\sim 3.5 \times 10^4$ Å). At around 40 K, the mean free paths for the pure and doped compounds become small and very similar in magnitude.

In short, we have observed the following in heat transport experiments: In Sr$_2$CuO$_3$, there is a very strong enhancement of both $\kappa_c$ and $\kappa_b$ upon doping Ni...
Figure 8.6: Spinon heat conductivity ($\kappa_{\text{mag}}$) parallel to chain for different concentrations of Ni is plotted as a function of temperature for Sr$_2$CuO$_3$ (the gray area gives the estimated error due to the procedure of extraction of $\kappa_{\text{mag}}$).

into the system due to an increase of the phononic conductivity both parallel and perpendicular to the chains. Also, as discussed in section 5.2, the phononic heat conductivity perpendicular to the chains ($\kappa_a$) of Ni-doped SrCuO$_2$ is strongly enhanced upon doping, whereas heat conductivity parallel to the chains ($\kappa_c$) decreases as a function of doping.

It is well known that the peak at low temperatures in a purely phononic system is determined by phonon-defect scattering alone (see section 3.3). This is the reason why a decrease in the peak value is seen upon doping impurities into most phononic conductors. Therefore, an enhancement of the phononic conductivity seen upon doping Ni into Sr$_2$CuO$_3$ and SrCuO$_2$ can only be understood by the existence of an additional scattering mechanism that limits the heat conductivity in the undoped compound. Upon doping, this scattering mechanism is then
suppressed gradually. Spinons are the only other known propagating excitations within the spin chain in the undoped compound, giving rise to additional contribution to the heat conductivity. Therefore, strong phonon scattering by spin excitations (phonon-spinon scattering) present in the undoped compound is a reasonable assumption.

Below we therefore investigate the low energy magnetic spectrum in more detail in order to better understand the doping induced suppression of the conjectured phonon-spinon scattering. For this, Nuclear Magnetic Resonance (NMR) and Inelastic Neutron Scattering (INS) have been performed on Ni-doped SrCuO$_2$ and Sr$_2$CuO$_3$.

### 8.2 Inelastic Neutron Scattering (INS)

Inelastic neutron scattering experiments were performed on 4 g of single crystalline SrCu$_{0.99}$Ni$_{0.01}$O$_2$ to probe the spin excitation spectrum. Time of flight (TOF) experiments were performed on the MAPS spectrometer at ISIS and the SEQUOIA instrument at ORNL. Thermal 3-axis neutron experiments were done at the IN8 spectrometer at ILL. Finally, cold neutron data were taken at TASP 3-axis spectrometer at PSI. A detailed discussion on the experimental method and the findings can be found in [215]. Here, a brief summary of the results that are most relevant to this work is presented.

An indicative result of the neutron experiments is shown in Fig. 8.7(a), where it can be clearly seen that there is a sudden decrease of spectral weight in the low-energy region of the spin excitation spectrum, indicating the presence of a gap. One can see two vertical streaks of intensity at $q_\parallel = \pm \pi$, which correspond to very steeply dispersive magnetic excitations near the antiferromagnetic zone center. There is a drastic suppression of the intensity of these lines and they vanish completely at very low energies, indicating the presence of a spin-gap. $S(\omega) = \int S(\omega, q_\parallel) dq_\parallel$ is plotted for different temperatures in Fig. 8.7(b), to show how the spectral weight is suppressed strongly below $\sim 8$ meV, at all temperatures.

The spin-gap does not seem to be the result of a spin-Peierls-like phase, as no structural transitions were seen in calorimetric and Raman measurements. However, it can be understood as a generic feature of a single chain with random defects. Such a treatment has been theoretically done by Eggert and Affleck [43], where they conclude that an $S = 1$ impurity severs the chains and remains magnetically inactive. This points to the idea that the low energy dynamics
Chapter 8. Impurity effects I: Ni doped SrCuO$_2$ and Sr$_2$CuO$_3$

Figure 8.7: (a) Time of flight (TOF) spectrum taken at $T = 6$ K and projected on the plane of energy transfer ($\hbar \omega$) and momentum transfer along the chains ($q_\parallel = \hbar c$); (b) The experimentally obtained momentum integrated structure factor at different temperatures using TOF (solid symbols) and three-axis (open symbols) spectroscopy. The lines are calculated using 8.3 for 1.7% Ni concentration.

should be fully explained by effective chain fragmentation.

From the fragmented chains of different length, we must have finite-size gaps that depend on the chain length as $\Delta_L = \Delta_0/L$. This will result in a spin pseudogap, a situation where a distribution of gap energies is present. To quantify this effect, the momentum integrated structure factor $S(\omega)$ has been calculated using rather simple arguments as has been described in detail in [215]. The resultant expression is,

$$S(\omega) \approx S_\infty(\omega) \left( \frac{\Delta}{2\hbar \omega} \right)^2 \operatorname{arcsinh}^2 \left( \frac{\Delta}{2\hbar \omega} \right)$$

(8.3)

where, $S_\infty(\omega)$ is the structure factor for an infinitely long perfect chain, and the rest of the expression is a defect-induced gap ‘envelope’ function which introduces a typical gap $\Delta$.

This model quantitatively reproduces the observed data as seen in Fig. 8.8. The experimentally obtained $S(\omega)$ matches very well with $S(\omega)$ that has been calculated using the theoretical expression 8.3 for the case of 1.7% Ni concentration. However, the model calculations for 1% Ni, do not match well with the
8.2. Inelastic Neutron Scattering (INS)

Figure 8.8: The experimentally obtained (symbols) and theoretically calculated (solid and dotted lines) momentum integrated dynamic structure factor, $S(\omega)$, for Ni-doped SrCuO$_2$ at low temperatures of 2 K, 3 K and 6 K. Model calculations are according to equation 8.3 for the case of infinite and fragmented $S = \frac{1}{2}$ antiferromagnetic spin chains for different doping levels.

The experimental data for the 1% Ni-doped crystal. Two probable reasons for this apparent disagreement could be either the empirical nature of the model, or a possible deviation of the actual Ni content in the grown crystal. For SrCuO$_2$, the double chain structure can bring in uncertainty, as this can result in each Ni site acting as a boundary for spinons in both the chains thereby effectively doubling the Ni concentration and giving better agreement with theory. Interestingly, the mean free path, $l_0$, due to impurity scattering which was obtained from the analysis of the heat transport experiments on the 1% Ni-doped SrCuO$_2$ crystal, translates into an effective Ni concentration of $\sim 1.6\%$ in the spin chains. This result agrees very well with the concentration of Ni, 1.7%, for which the calculations based on chain fragmentation physics matches with the experimental data obtained from INS. However, the extreme depletion of spectral weight below 2 meV due to exponentially low probability of having very long chain segments in the diluted system, is a feature of experiment that is perfectly captured by the model. Recent neutron scattering measurements on Ni-doped Sr$_2$CuO$_3$ also point to the existence of a spin-gap at low-energies of the spin excitation spectra [216].

Thus, we see that Ni-doping opens a spin-gap of around 8 meV in the spin exci-
Chapter 8. Impurity effects I: Ni doped SrCuO$_2$ and Sr$_2$CuO$_3$

Figure 8.9: Spin-lattice relaxation rates ($T_1^{-1}$) for (a) 1% Ni and 2% Ni doped Sr$_2$CuO$_3$, and (b) 1% Ni doped SrCuO$_2$ compounds [179].

This spin-gap is explained as a finite-size gap arising due to fragmentation of chains.

8.3 Nuclear Magnetic Resonance (NMR)

The Cu$^{63}$ NMR spin-lattice relaxation rates $T_1^{-1}$ were measured in fields around 7 T, and are plotted in Fig. 8.9. As has been discussed in section 5.2, for pure SrCuO$_2$, $T_1^{-1}$ is constant over a wide temperature range with an upturn at low temperatures, in consistency with theoretical predictions (see Fig. 8.9(a)). The relaxation curve of $T_1^{-1}$ for SrCu$_{0.99}$Ni$_{0.01}$O$_2$ is constant at $T > 120$ K, but decreases exponentially below a crossover temperature of $\sim 120$ K. Such a behavior is typical of a system where a gap is present in the low energy regime of the spin excitation spectrum. From a fit to the activated temperature dependence of $T_1^{-1}$, using [50], $T_1^{-1} = \text{const} \times \exp (-\Delta/T)$ an average activation energy of around 200 K is obtained. Such an exponential decrease of $T_1^{-1}$ has also been observed in the case of Ca-doped SrCuO$_2$, where a spin-gap develops at low-$T$ [50]. Further, spin-lattice relaxation rates $T_1^{-1}$ measured for 1 % Ni-doped Sr$_2$CuO$_3$ (see Fig 8.9(b)) also exponentially decreases below $\sim 200$ K. However, for 2% Ni-doped Sr$_2$CuO$_3$ the exponential decrease of $T_1^{-1}$ begins at a higher temperature ($\sim 170$ K), and an average activation energy of around 400 K is
obtained compared to 200 K for the 1% doped sample. Because the activation
energy and the crossover temperature are approximately doubled by increasing
the doping level from 1% to 2%, it could be inferred that the average gap energy is
twice as large in the case of 2% Ni-doping than in the case of 1% Ni-doping. Thus,
NMR measurements on the Ni-doped Sr$_2$CuO$_3$ and SrCuO$_2$ indicate the presence
of a spin gap that roughly scales with the doping level. This is in good qualitative
agreement with INS measurements that observe a pseudogap behavior in the case
of 1% Ni-doped SrCuO$_2$. Thus, the results from microscopic probes like NMR
and INS are consistent with the idea that Ni essentially causes fragmentation of
the spin chains.

8.4 Physical picture

Ni-doping thus leads to the observation of two interesting effects. It causes a
strong enhancement in the phononic conduction due to reduction of phonon scat-
tering, and it induces the development of a spin gap of $\sim$ 8 meV at low energies
of the spin excitation spectrum. The properties of this spin gap as probed by
NMR and INS, point to the presence of Ni-induced fragmentation of the spin
chains; a picture that is further evident from the heat transport measurements
where perfect scaling is observed for the spinon mean free paths due to impurity
scattering.

The unconventional enhancement of phononic heat conductivity that is ob-
served is puzzling. However, an explanation based on the idea that the spin gap
depletes the low energy phonon-spinon scattering phase space seems promising.
By looking at the dispersion relations for phonons and spinons in Sr$_2$CuO$_3$ and
SrCuO$_2$, one sees that some of the low lying phonon branches lie in the same
energy regime of that of the low energy spinon branches $[169, 215, 217]$. The
phonons having small $\vec{k}$ lying close to the Brillouin-zone center lie in the energy
regime where the spin gap of $\sim$ 8 meV exists. Such an arrangement facilitates the
scattering between phonons and spinons in the undoped spin chain compounds.
Now, by creating a spin gap by doping Ni there arises a drastic depletion of the
density of low energy spinons that was partly responsible for scattering phonons
and lowering phononic heat conductivity. This dearth of scatterers now enables
phonons to much more efficiently conduct and hence leads to a dramatic increase
in phononic heat conductivity.

Both parallel and perpendicular to the chains, the dramatic enhancement of
$\kappa_{\text{phonon}}$ is significant only at low temperatures up to $\sim$ 80 K. At higher temper-
Chapter 8. Impurity effects I: Ni doped SrCuO$_2$ and Sr$_2$CuO$_3$

atures the phononic heat conductivity for the undoped and doped compounds merge. These observations are expected because of the following reasoning. It is known that the effect of phonon-defect scattering processes are significant only at low temperatures where the peak in the heat conductivity occurs. Also, the size of the gap in the Ni-doped samples is of the order of 100 K. This means that the doping dependence of phonon-spinon scattering must be weak at higher temperatures where the gap can be energetically overcome. The population of thermally excited phonons is large enough to have a high phonon-phonon scattering probability, that should be doping independent for small doping concentrations, and mask the effect of the other relevant scattering processes.

Thus, interestingly, through heat transport experiments, Ni doping allows us to see evidence for a strong phonon-spinon scattering channel present in both the compounds. However, theoretical investigations of this scattering channel by considering a spin-phonon coupling must be undertaken in order to the understand the mechanism more microscopically, and to explain quantitatively the above experimental observations. It is worth mentioning that, preliminary measurements of NMR and INS on SrCuO$_2$ doped with other impurities like Co and Zn, do not detect the presence of a gap in the spin excitation spectrum [218]. However, spinon heat transport is seen to be strongly suppressed in the doped compounds, and the phonon heat transport is seen to be strongly enhanced (see Fig. A.3 and Fig. A.1 in Appendix A). Analogous to the case of Ni-doped SrCuO$_2$, such an enhancement of the phononic heat conductivity indicates the presence of a spin gap in the Co- and Zn-doped compound. Thus, the preliminary results for Co- and Zn-doped compounds seem to be contradictory and hence inconclusive. However, these observations suggest that other than the fragmentation of chains by impurities, the local effects that emerge in the vicinity of the dopant and effect the physical properties of the compound, seems to depend on the kind of ion that has been substituted.

8.5 Summary

For Sr$_2$CuO$_3$, heat conductivity measurements show that Ni-doping causes a strong enhancement of the phononic conductivity at low doping levels, which is seen in the measurements both parallel and perpendicular to the spin chains. The spinon heat conductivity on the other hand is strongly suppressed. Upon analyzing the mean free path of spinons using an empirical scattering model, one sees that it is able to describe its temperature dependence at temperatures higher
than 100 K, but taking into account only $T$-independent spinon-defect and $T$-dependent spinon-phonon scattering. These observations for Ni-doped Sr$_2$CuO$_3$ are qualitatively similar to the case of Ni-doped SrCuO$_2$, where the magnitude of increase in the phononic conductivity upon doping Ni is smaller. This non-intuitive increase of phononic heat conduction on making the system dirty, points to the existence of a strong phonon scattering mechanism that limits the phononic heat conductivity in the undoped compound and which is gradually suppressed upon doping.

A spin gap is found to be present at low energies in the spin excitation spectrum of the Ni-doped Sr$_2$CuO$_3$ and SrCuO$_2$ from NMR and INS measurements. The emergence of this gap depletes low energy spinons that limited phononic heat conductivity in the undoped compounds due to spinon-phonon scattering processes. The unavailability of these spinons in the doped compounds that are gapped, reduces scattering of phonons and thereby enhances the phononic heat conductivity. Thus, we indirectly observe the opening of the spin gap in the heat conductivity measurements of Ni-doped SrCuO$_2$ and Sr$_2$CuO$_3$. Therefore, a magnetic impurity like Ni strongly affects the spin excitation spectrum and spinon transport in these materials which are very good approximations of $S = \frac{1}{2}$ Heisenberg chains. Such an impurity also reveals a very strong spin-phonon coupling and thus the importance of the scattering mechanism between phonons and spinons in limiting heat conduction at low temperatures. This clear evidence of a strong spin-phonon coupling in the two quasi 1D systems, Sr$_2$CuO$_3$ and SrCuO$_2$, encourage further studies on probing the nature of this coupling and its effects on scattering mechanisms.
Chapter 9

Impurity effects II: Ca doped Sr\(_2\)CuO\(_3\)

9.1 Heat transport

9.1.1 Heat conductivity parallel and perpendicular to spin chains

Fig. 9.1 shows the heat conductivity of the pure and doped compounds as a function of temperature, measured along the direction of the spin chains (\(\kappa_b(T)\)). Upon doping, the broad peak in \(\kappa_b(T)\) at \(\sim 20\) K is reduced from \(\sim 512\) W m\(^{-1}\)K\(^{-1}\) at \(x = 0\) to \(\sim 350\) W m\(^{-1}\)K\(^{-1}\) at \(x = 0.01\), and the shape of the curve changes. The broad peak in the undoped compound develops into a sharper phononic-like peak and a shoulder indicative of spinon contribution that has now reduced in magnitude. Increasing the Ca content to \(x = 0.05\) further suppresses the peak of \(\kappa_b\) to \(\sim 195\) W m\(^{-1}\)K\(^{-1}\), and this trend continues up to \(x = 0.5\). In the inset of Fig. 9.1, we see that for higher doping concentrations (\(x = 0.1\) and \(x = 0.5\)) the heat conductivity shows a positive slope above \(\sim 100\) K up to 300 K. Whereas, for lower concentrations (\(x = 0.01\) and \(x = 0.05\)) a negative slope exists up to 300 K, as in the case of the undoped compound.

Fig. 9.2 shows the heat conductivity measured perpendicular to the spin chains (\(\kappa_c(T)\)). Upon doping increasing amounts of Ca, the peak magnitude of \(\kappa_c(T)\) gradually decreases as is expected for a purely phononic system due to increased
9.1. Heat transport

scattering of phonons off Ca impurities. The black solid curves in Fig. 9.2 show fits for all Ca concentrations employing the Callaway model for phononic heat transport [123]. From Fig. 9.2 we see that the fits are good and the temperature dependence of the heat conductivity perpendicular to the spin chains is perfectly consistent with pure phononic heat transport. Decreasing magnitudes of $\kappa_c$ with increasing concentrations of dopant can be captured in the model mainly by changing the parameter related to the phonon-defect scattering probability, thereby indicating enhanced scattering.

It is worth mentioning that Ca-doping creates a spin-gap of a magnitude $\Delta \sim 50$ K in the spin excitation spectrum of Sr$_2$CuO$_3$ [219]. However, the size of this gap is almost half of that of the gap present in the case of Ni-doped Sr$_2$CuO$_3$, which is around 100 K. As the size of a gap is relatively small in the case of Ca-doping, its effect on the phonon heat conductivity is not as strong as in the case of Ni-doping, where a drastic enhancement of the phononic heat conductivity is seen (see chapter 8).

We model the phononic heat conductivity perpendicular to the chains using a phenomenological model devised by Callaway (see section 3.3.1). Fig. 9.2 shows $\kappa_c$.
Figure 9.2: Heat conductivity $\kappa_c$ as a function of temperature, measured perpendicular to the chains. Inset: A semi-log plot of $\kappa_c$ versus temperature to better illustrate the changes upon introducing disorder. The solid black curves are fits to the curves according to the Callaway model.

Table 9.1: Callaway fit parameters for the $\kappa_c(T)$ curves.

<table>
<thead>
<tr>
<th>Ca content ($x$)</th>
<th>$B$ $(10^{-31}$ K$^{-1}$ s$^2$)</th>
<th>$b$</th>
<th>$A$ $(10^{-44}$ s$^3$)</th>
<th>$L$ $(10^{-4}$ m)</th>
<th>$\Theta_D$ (K)</th>
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<td>3.55</td>
<td>2.41</td>
<td>0.31</td>
<td>2.98</td>
<td>261 K</td>
</tr>
<tr>
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<td>5.07</td>
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<td>1.42</td>
<td>7.82</td>
<td>265 K</td>
</tr>
<tr>
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<td>6.13</td>
<td>2.84</td>
<td>3.69</td>
<td>4.72</td>
<td>262 K</td>
</tr>
<tr>
<td>0.1</td>
<td>8.35</td>
<td>3.13</td>
<td>9.77</td>
<td>10.7</td>
<td>262 K</td>
</tr>
<tr>
<td>0.5</td>
<td>8.60</td>
<td>4.36</td>
<td>13.82</td>
<td>0.17</td>
<td>265 K</td>
</tr>
</tbody>
</table>

($T$) for all Ca concentrations and the corresponding Callaway fits. The obtained values of the free parameters from the best fit are given in Table 9.1. $\kappa_c(T)$ for the pure compound was fit first, and then $\kappa_c(T)$ for the doped compounds were tried to be fit by keeping all other parameters except A fixed, i.e. only varying the phonon-defect scattering strength. It was found that it is not possible to fit the $\kappa_c(T)$ curves just by changing this parameter. To obtain good fits, the intra-phonon scattering parameters and the boundary scattering length also had to be varied. One can see that the parameter $A$ steadily increases with increasing
concentration of Ca defects indicating the increasing strength of phonon-defect scattering, which is mainly responsible for the reduction of $\kappa_c(T)$ upon doping. The difference in boundary scattering parameters only indicates a difference in the sample geometries. Finally, a small variation in parameter $B$ could imply that the dopant possibly induces slight changes in the phononic dispersion branches, thereby affecting the scattering strength between phonons, in addition to playing the role of defects-like scatterers.

### 9.1.2 Spinon heat transport

It is well known that subtracting $\kappa_c$ from $\kappa_b$ provides a good estimate of the spinon heat conductivity ($\kappa_{\text{mag}}(T)$) \cite{6-10}. Fig. 9.3 shows $\kappa_{\text{mag}}(T)$ for different doping levels of Ca. Here, we can see that $\kappa_{\text{mag}}(T)$ drastically decreases for the Ca-doped samples. Strong suppression of $\kappa_{\text{mag}}$ indicates that in the doped compounds spinon transport is gradually impeded as a result of increasing scattering of spinons off defects induced by increasing amounts of Ca. For higher doping concentrations, $x = 0.1$ and 0.5, we can clearly see that $\kappa_{\text{mag}}$ increases at higher temperatures, with an almost linear increase for $x = 0.1$. This interesting observation reflects the intrinsic properties of spinon transport in a $S = \frac{1}{2}$ Heisenberg spin chain as will be explained in more detail further below. The grey regions around the curves of $x = 0.05$ and 0.5 doped Ca depict the uncertainty in $\kappa_{\text{mag}}$.

We now analyze $\kappa_{\text{mag}}$ by extracting the mean free path of spinons, $l_{\text{mag}}$. As discussed in section 3.4.1, it can be approached in two ways. One is by treating the low temperature spinon transport in the framework of a semi-classical kinetic model, and the other is to use the more microscopic Drude weight approach. The low temperature behaviour of the Drude weight of a Heisenberg chain is linear in temperature and is given as,

$$D_{\text{th}} = \frac{(\pi k_B)^2}{3\hbar} v T,$$

where $v$ is the spinon velocity and $k_B$ is the Boltzmann constant. The relation between the mean free path and the thermal conductivity can be given as,

\footnote{As the method for extraction of magnetic heat conductivity relies on the assumption of isotropic phononic heat conduction, there could always be an error in our estimation that stems from the anisotropy of phononic conduction parallel and perpendicular to the chains. This error is large at low temperatures as the magnitudes of $\kappa_b$ and $\kappa_c$ are large in this regime, thus creating significant uncertainty in the extracted $\kappa_{\text{mag}}$. The errors have been calculated by taking into account a 30% anisotropy in the phononic heat conductivity parallel and perpendicular to the chains.}
Figure 9.3: Magnetic heat conductivity $\kappa_{\text{mag}}$ as a function of temperatures for the undoped and the Ca-doped compounds. Inset: A semi-log plot of $\kappa_{\text{mag}}$ versus temperature to more clearly show the increase of $\kappa_{\text{mag}}$ with increasing temperature for higher concentrations of Ca. Solid black lines are $\kappa_{\text{mag}}$ recalculated using the fits for $l_{\text{mag}}$ and Eq. 9.2. The grey regions, shown exemplarily for $x=0.05$ and $x=0.5$, depict the uncertainties associated with the extraction of $\kappa_{\text{mag}}$.

\[ l_{\text{mag}} = \frac{3h}{\pi N_s k_B^2 T \kappa_{\text{mag}}}, \]  

where $N_s = 2/ab$ is the number of spin chains per unit area.

### 9.1.3 Spinon mean free path

Eq. 9.2 is used to extract and analyze the spinon mean free path. $l_{\text{mag}}$, as a function of temperature for the pure and doped Sr$_2$CuO$_3$ is plotted in Fig. 9.4, the inset showing a semi-log plot of the same. Upon doping, the magnitude of the mean free path at low temperatures strongly and monotonically decreases, the trend being similar to that observed in $\kappa_{\text{mag}}$. In all cases, $l_{\text{mag}}$ decreases with increasing $T$. Note that $l_{\text{mag}}$ for $x = 0.5$ is nearly constant at temperatures above 100 K, whereas for lower concentrations we see a temperature dependent decrease. As has been pointed out already for the pure compound [7, 8, 10],
9.1. Heat transport

Figure 9.4: Mean free path of spinons as a function of temperature $l_{\text{mag}}(T)$ and the fits according to Eq. 9.3. The grey regions around the curve for $x = 0.05$ and $x = 0.5$ depict the uncertainty associated with the calculation of $l_{\text{mag}}$. Inset: a semi-log plot of $l_{\text{mag}}$ versus temperature.

The $T$-dependent decrease can qualitatively be well explained by spinon-phonon scattering which becomes increasingly important with rising $T$. The doping-induced shortening of the mean free path can be qualitatively ascribed to strong spinon scattering due to Ca-induced disorder in the doped compounds. We now attempt to model $l_{\text{mag}}(T)$ using Matthiesen’s rule and taking into account two scattering processes for spinons, viz. spinon-defect scattering and spinon-phonon scattering (see section 3.4.1). Thus we have $l_{\text{mag}}^{-1} = l_0^{-1} + l_{sp}^{-1}$, where $l_0$ describes the $T$-independent spinon-defect scattering whereas $l_{sp}(T)$ accounts for the $T$-dependent spinon-phonon scattering. For the latter, we assume a general umklapp process with a characteristic energy scale $k_B T_u^*$ of the order of the relevant phonon energies, which is commonly used in literature [6, 8–10, 141]. Thus we get the expression,

$$l_{\text{mag}}^{-1} = l_0^{-1} + \left( \frac{\exp{(T_u^*/T)}}{A_s T} \right)^{-1},$$

which can be used to fit the data with $l_0$, $A_s$ and $T_u^*$ ($A_s$ is a measure of the coupling strength) as free parameters.
Chapter 9. Impurity effects II: Ca doped Sr$_2$CuO$_3$

Figure 9.5: Magnetic heat conductivity $\kappa_{\text{mag}}$ as a function of temperature for $x = 0.1$ and $x = 0.5$ compounds. Solid lines are $\kappa_{\text{mag}}$ recalculated using the fits for $l_{\text{mag}}$ and Eq. 9.2. Grey regions around the curve indicate the uncertainties in $\kappa_{\text{mag}}$.

The fits for the undoped and doped compounds are shown in Fig. 9.4 and the fit parameters in Table 9.2. We obtain good fits for the pure and $x = 0.01$ compounds in the temperature range from 50-300 K, and for the $x = 0.05$, 0.1, 0.5 compounds the fits are good in the temperature range from 150-300 K. It is apparently enough to take into account just spinon-defect scattering to describe the doping dependence of $l_{\text{mag}}$ and umklapp-like spinon-phonon scattering to explain the $T$-dependence of $l_{\text{mag}}$, where the latter remains essentially the same upon doping. In order to fit the data, we have fixed $T_u^*$ as 210 K (obtained by fitting $l_{\text{mag}}$ for the pure compound) for the whole doping series allowing $l_0$ and $A_s$ to vary. In the model, $T_u^*$ stems from the characteristic energy scale $k_B T_u^*$ of the umklapp process, which is of the order of the Debye energy [9, 10] suggestive of acoustic phonons being involved in the scattering process. Hence, it is physically justified to fix $T_u^*$ for the doped compounds, as the Debye energy is not expected to change substantially with doping. $A_s$ changes slightly as a function of doping but is of the same order of magnitude for all doping levels. The slight variation in this parameter accounts for uncertainties in determining $\kappa_{\text{mag}}$, and a small variation in the spin-phonon coupling strength in the pure and doped compounds.
9.1. Heat transport

The spinon-defect scattering length $l_0$, which represents a lower bound for the low-$T$ limit of $l_{mag}$ and which should significantly depend on the sample’s purity, decreases strongly upon doping and is very different for the pure and the doped compounds as can be seen in Table 9.2. This parameter is most sensitive to changes in the Ca concentration, indicating that Ca defects primarily act as efficient barriers for the propagating spinons, i.e. the disorder-induced scattering can be well described by intra-chain defects. We mention that the deviation of the experimentally extracted $l_{mag}$ from the fits at low temperatures ($\lesssim 150$ K) can be attributed to the large error inherent in $l_{mag}$ which is shown by the grey region surrounding the curves. As this error is large for the heavily doped compounds where the mean free paths are small, the fits are expected to be inaccurate at low temperatures.

**Table 9.2:** Fit parameters obtained by fitting $l_{mag}$ by Eq. 9.3. The errors in the fit parameters were extracted by fitting $l_{mag}$ that was calculated by adding and subtracting a maximum error of 30% in $\kappa_{mag}$ that stems due to a possible anisotropy in phononic heat conduction.

<table>
<thead>
<tr>
<th>Ca content ($x$)</th>
<th>$l_0$ (Å)</th>
<th>$T_u$ (K)</th>
<th>$A_s$ ($10^5$ m/K)</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>5093 ± 510</td>
<td>210</td>
<td>0.74 ± 0.3</td>
</tr>
<tr>
<td>0.01</td>
<td>1139 ± 140</td>
<td>210</td>
<td>8.19 ± 1.35</td>
</tr>
<tr>
<td>0.05</td>
<td>212 ± 38</td>
<td>210</td>
<td>4.85 ± 1.1</td>
</tr>
<tr>
<td>0.1</td>
<td>127 ± 19</td>
<td>210</td>
<td>4.2 ± 0.88</td>
</tr>
<tr>
<td>0.5</td>
<td>48 ± 13</td>
<td>210</td>
<td>1.19 ± 0.53</td>
</tr>
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</table>

Using the fits obtained for $l_{mag}$, we can recalculate $\kappa_{mag}$ using Eq. 9.2, and plot these curves (black solid curves in Fig. 9.3) over the experimental curves to have a further illustration of the analysis. These recalculated curves, within the kinetic model, give us a good idea of the evolution of $\kappa_{mag}$ in the entire temperature range, from the dilute doped compound, where it smoothly decreases with increasing temperatures, to the heavily doped compound where it increases almost linearly with increasing temperatures.

We now turn in more detail to $\kappa_{mag}$ for the $x = 0.1$ and $x = 0.5$ doped compounds for which a monotonic increase with rising $T$ is found (Fig. 9.5). Remarkably, an almost linear temperature dependence above $T \approx 150$ K is seen for $x = 0.5$. Such a linear temperature dependence of $\kappa_{mag}$ has been observed before in the highly disordered quasi one-dimensional compound CaCu$_2$O$_3$ and reveals the intrinsic temperature dependence of the heat transport of a $S = \frac{1}{2}$ Heisenberg chain [30]. It is well known that the temperature independent spinon-
Chapter 9. Impurity effects II: Ca doped Sr$_2$CuO$_3$

Figure 9.6: Spinon-defect scattering length, $l_0$, is plotted against the inverse of Ca concentration ($x$) (lower x-axis) and the mean distance between two Ca atoms (upper x-axis) for SrCuO$_2$ (open symbols) and Sr$_2$CuO$_3$ (filled symbols); the solid lines are linear fits to the data. The y-axis on the right gives an idea of the mean free path in terms of the number of lattice spacings between two Cu sites ($d_0$).

A defect scattering mechanism that leads to a temperature independent $l_{\text{mag}}$ is the dominant mechanism at low temperatures and at higher temperatures spinon-phonon scattering becomes dominant. Having a large number of defects in the chain, which is the case for the doped compounds, will enhance the probability of spinons scattering off defects rather than spinons scattering off phonons. If the defect concentration is sufficiently high, the temperature dependence of the spinon-phonon scattering mechanism can be completely masked by the temperature independent spinon-defect scattering mechanism and, in turn, lead to a temperature independent spinon mean free path, i.e. a temperature independent scattering time $\tau$. Thus, the $T$-dependence of the experimental $\kappa_{\text{mag}}$ represents directly that of the thermal Drude weight (Eq. 9.1).

Finally, in order to investigate the Ca-induced scattering process further, we plot the obtained values of the spinon-defect scattering length $l_0$ as a function of the mean distance between two Ca atoms and the inverse of Ca concentration in Fig. 9.6. Here, we see that $l_0$ scales perfectly with the inverse of Ca concentration as $l_0 = 2.93(1/x)$ Å $\sim 3d_0$, where $d_0 = 3.91$ is the lattice spacing between two Cu sites along the chain [166, 172]. This corroborates that the Ca-induced bond...
disorder can perfectly be captured in terms of effective defects in the chain, where the scattering probability per defect is equally strong at all concentrations. From this plot we also see that the Ca-Ca distance is smaller by a factor of 3 than the spinon-defect scattering length $l_0$.

We compare this finding with the results of a recent analogous study of the Ca-doped double spin chain compound, SrCuO$_2$ [58] (open symbols in Fig. 9.6). For this compound we see that $l_0$ can be described as $l_0 = 4.3(1/x)$ Å + $l_{lim}$, where $l_{lim}$ ($\approx 140$ Å) is an offset. Therefore, the spinon-defect scattering length, $l_0$, does not scale with the inverse of the Ca concentration, indicating that already at intermediate concentrations ($x = 0.1$) the effect of Ca saturates and the mean free path of spinons is not reduced any further upon increasing the Ca concentration. This is different from the perfect scaling that we observe for the single chain compound. The offset observed in Ca-doped SrCuO$_2$ was interpreted to be due to a limit set by the disorder-induced long distance decay of the spin-spin correlation ($\xi$), $\xi$ being calculated for a single $S = \frac{1}{2}$ Heisenberg chain [58]. However, this claim does not seem to be valid in our case as the effect of Ca is equally strong at all doping levels. Thus, the proposed connection between the two quantities ought to be just a coincidence. The physical origin of the difference in the effect of Ca-induced bond disorder for the two compounds SrCuO$_2$ and Sr$_2$CuO$_3$, that essentially differ only in the structure of the spin chains, remains unclear though.

9.2 Summary

The effect of introducing an off-chain impurity like Ca, thereby creating bond disorder, on the heat transport of the prototype single spin chain compound Sr$_2$CuO$_3$ has been studied. A drastic suppression of the magnetic heat conductivity parallel to the chains indicating that the propagation of spinons is very sensitive to even the slightest bond disorder is observed. The temperature dependence of the mean free path of spinons can be modelled by spinon-defect and spinon-phonon scattering processes, and the reduction of the mean free path upon doping is accounted for mainly by increased scattering of spinons off effective in-chain defects, where the scattering probability per defect is equally strong in the entire doping range. This result is very different from the case of Ca-doped double spin chain compound SrCuO$_2$.

Interestingly, large disorder present in the compounds doped with high concentrations of Ca leads to a linearly increasing intrinsic spinon heat transport of the spin chain due to prevailing spinon-defect scattering and thus a vanishing
temperature dependence of the spinon mean free path. Thus, Ca-doped Sr$_2$CuO$_3$ represents a unique case where the impact of impurities can be studied in a wide range of doping, covering very clean as well as very dirty limits.
Chapter 10

La₈Cu₇O₁₉: Properties

After having discussed the single crystal growth of the five-leg ladder compound, La₈Cu₇O₁₉, in section 6.3.3, here we first discuss details of its crystal and magnetic structures that were determined using single crystal x-ray diffraction and elastic neutron diffraction respectively. Then, as preliminary results, the measured physical properties of this compound, namely the magnetic susceptibility, specific heat, heat conductivity and thermal expansion are briefly discussed.

10.1 Crystal structure

Single crystal diffraction was performed at room temperature using a Bruker AXS Kappa APEX II CCD four-circle single crystal diffractometer with a Mo Kα source. A total of 13480 reflections (n_{int}) were measured in the recording range of θ = 27°. The obtained lattice parameters were, a = 13.8261(16) Å, b = 3.7532(4) Å, c = 34.585 Å, β = 99.331(5)°, and are in good agreement with that obtained from the powder data from this work (see section 6.3.3) and that from literature [52, 184–186]. The obtained space group C2/c led to 2023 unique reflections (n_{all}). The good quality of the fit is evident from R_{all} = 0.0362 and R_{int} = 0.0301. The atomic positions of different sites obtained from this measurement are summarized in Table 10.1, and were similar to that obtained from the powder diffraction pattern refinement. In addition, these refined atomic positions were very similar to that obtained using neutron diffraction on the same single crystal [220]. Also, chemical disorder as a factor being responsible for unrefinable residual intensities in the powder x-ray diffraction pattern (section 6.3.3) can be discarded.
Chapter 10. \textit{La}_8\textit{Cu}_7\textit{O}_{19}: Properties

Figure 10.1: The picture (a) shows the unit cell of \textit{La}_8\textit{Cu}_7\textit{O}_{19}; smallest spheres: O, largest spheres: La, filled black spheres: Cu. The crystallographically inequivalent Cu atoms are marked. Cu4 atoms are the tetrahedrally co-ordinated Cu4 sites between the ladder planes. The rungs of the ladder are indicated by bold lines; (b) depicts the joining of two five-leg ladder units, where one can see Cu3 and Cu4 atoms forming a complex ribbon-like structure. The distorted octahedra formed by the different Cu atoms are also indicated; (c) depicts the arrangement of Cu3 and Cu4 atoms on the puckered leg (bold lines), and of those between the ladder planes. The tetrahedra formed by Cu4 atoms and the strongly distorted octahedra formed by Cu3 atoms are also shown. In (b) and (c) only Cu and O atoms are shown for clarity.
Table 10.1: The quality of the refinement and the refined atomic positions and displacements obtained from single crystal diffraction

\[
\begin{align*}
a &= 13.8261(16) \text{Å} \\
b &= 3.7532(4) \text{Å} \\
c &= 34.585 \text{Å} \\
\beta &= 99.331(5) ^\circ
\end{align*}
\]

Data collection

\[
\begin{align*}
n_{\text{int}} &= 13480 \\
n_{\text{all}} &= 2023 \\
R_{\text{int}} &= 0.0486 \\
\theta_{\text{all}} &= 1.19 ^\circ - 27.48 ^\circ
\end{align*}
\]

Refinement

\[
R_{\text{all}} = 0.0362
\]

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<th>(y)</th>
<th>(z)</th>
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<td>La1</td>
<td>8f</td>
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<td>8f</td>
<td>0.29960</td>
<td>0.4658(2)</td>
<td>0.39370</td>
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<td>La3</td>
<td>8f</td>
<td>0.55190</td>
<td>0.0073(2)</td>
<td>0.42270</td>
</tr>
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<td>La4</td>
<td>8f</td>
<td>0.18130</td>
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<td>0.28850</td>
</tr>
<tr>
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<td>4e</td>
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<td>0.9805(4)</td>
<td>1/4</td>
</tr>
<tr>
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<td>8f</td>
<td>0.6199(1)</td>
<td>0.4845(3)</td>
<td>0.35790</td>
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<tr>
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<tr>
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<td>0.527(2)</td>
<td>0.4701(2)</td>
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<td>O9</td>
<td>8f</td>
<td>0.4547(5)</td>
<td>0.462(2)</td>
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<td>0.3384(6)</td>
<td>0.476(2)</td>
<td>0.2693(2)</td>
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as there was no such observable disorder in the single crystal x-ray diffraction measurements.

Fig. 10.1 shows the unit cell and the different copper sites. The legs of the rungs run along the \(b\)-axis ([010]). The rungs of the ladder (shown as bold lines in Fig. 10.1) run parallel to the [101] direction. Cu1 atoms lie at the center of
Table 10.2: Main Copper-Oxygen bond angles and bond distances, where superscripts denote the following positions: (i) -0.5+x, 0.5+y, z; (ii) x, 1+y, z; (iii) 0.5+x, 0.5+y, z; (iv) 0.5+x, -0.5+y, z; (v) 1-x, 1+y, 1-z; (vi) 1-x, -y, 1-z; (vii) -0.5+x, -0.5+y, z; (viii) x, -1+y, z; (ix) 0.5-x, 0.5+y, 0.5-z; (x) 0.5-x, -0.5+y, 0.5-z; (xi) -x, y, 0.5-z; (xii) 1.5-x, 1.5-y, 1-z; (xiii) 1.5-x, 0.5-y, 1-z; (xiv) 1-x, y, 0.5-z.

<table>
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<th>Atoms</th>
<th>Bond distance (d) (Å)</th>
<th>Atoms</th>
<th>Bond angle (deg)</th>
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<td>Cu1-O1</td>
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<td>O1\textsuperscript{ii}-Cu1-O1</td>
<td>180.00(1)</td>
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<tr>
<td>Cu1-O1\textsuperscript{ii}</td>
<td>1.874(10)</td>
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<td>90.2(2)</td>
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<td>178.6(3)</td>
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<td>2.421(8)</td>
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<td>1.968(7)</td>
<td>O8-Cu4-O5</td>
<td>97.5(3)</td>
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the five-leg ladder and Cu3 atoms at the edge of the ladder. Cu2 atoms are the ones lying between Cu1 and Cu3 sites. Cu atoms at sites Cu1, Cu2 and Cu3 lie at the center of corner-sharing octahedra formed by oxygen atoms. These octahedra are slightly distorted with regard to the angles that the central Cu atom makes with the in-plane oxygen atoms (in-plane O-Cu-O bond angle) and with the apical oxygen atoms (apical O-Cu-O bond angle), i.e., the in-plane or apical O-Cu-O bond angle is not exactly 180°. The in-plane and apical oxygen atoms of the octahedra are shown in picture (b) of Fig. 10.1. The distortion of the octahedra increases as we move from the center of the ladder (Cu1) to the edge of the ladder (Cu3). The Cu1 octahedron has no apical distortion but has a small in-plane distortion of 0.494(6)° along the rungs. The Cu2 octahedron has an apical distortion of 0.501(3)° and an in-plane distortion of 1.371(1)° along the rungs. The Cu3 octahedron is highly distorted, apically by 24.254(3)° and in-plane by 22.287(9)°. The distortions of the Cu1 and Cu2 octahedra are too small to be illustrated, but the distortion of the Cu3 octahedron can be clearly seen in pictures (b) and (c) of Fig. 10.1. The Cu3 octahedral distortion is strong enough to pucker the leg structure formed out the Cu3 atoms. This can again be seen in pictures (b) and (c) of Fig. 10.1.

Importantly, there are also Cu atoms (Cu4) that occupy sites in the structure that lie in-between ladder planes, thereby providing magnetic exchange paths for interaction between two adjacent ladder-planes. The copper atoms at these sites do not lie at the centers of oxygen octahedra but at the center of distorted edge sharing tetrahedra. Adjacent ladder planes are bridged by these edge-sharing tetrahedra along the $a$-axis ([100]). In pictures (b) and (c) of Fig. 10.1 one can also see that apart from near 180° Cu-O-Cu bond angles, there are near 90° Cu-O-Cu bonds for Cu atoms at sites where two five leg ladders join. The arrangement of Cu4 and Cu3 atoms provides for more than one oxygen-mediated exchange path for interaction between them. As examples of such exchange paths along bonds between the Cu3 and Cu4 sites are marked as dotted lines in picture (b). Such strong variations in environment and bond angles as a function of crystallographic position could severely modify the type of exchange interactions and magnitude of ordered Cu moments. Some of the important bond angles and distances are listed in Table 10.2. Hence, apart from the five-leg ladder unit the unit cell has a complicated alternating ribbon-like structure formed by Cu4 and Cu3 atoms that runs along the $a$-axis, almost perpendicular to the ladder planes. The picture (c) in Fig. 10.1 illustrates the complex arrangement of Cu3 and Cu4 atoms that connect adjacent ladder planes. These ribbon-like structures, that comprise of tetrahedrally centered Cu4 and the strongly distorted octahedrally centered Cu3, together with the distortions of the Cu1 and Cu2 octahedra, could very well be crucial in determining the nature of magnetism that arises in this
Figure 10.2: Specific heat \( C_p \) (blue symbols) in the temperature range around 103 K, the black line is a guide to the eye. Inset: \( C_p \) in the entire temperature range from 0.6 K to 300 K to illustrate the \( T \)-dependence.

10.2 Specific heat

Specific heat of this compound was measured on this compound in the temperature range 0.6 K to 300 K (Fig. 10.2) using the Physical Property Measurement System (PPMS) by Quantum Design. A significant anomaly is seen at \( \sim 103 \) K, which indicates that there is a bulk transition in the material. In order to check whether this transition has a magnetic origin the bulk magnetic susceptibility...
10.3 Magnetic susceptibility

Figure 10.3: $M(T)$: Susceptibility as a function of temperature along all three axes with magnetic field (H) of 0.2 T.

was measured.

10.3 Magnetic susceptibility

Fig. 10.3 shows the susceptibility curve measured in a magnetic field of 0.2 T. The susceptibility along all three principal directions shows a broad maximum at temperature $\sim 180$ K, below which it smoothly decreases. At $\sim 103$ K, there is an anomaly seen in the $M(T)$ curve, which coincides with antiferromagnetic ordering reported in the literature [183]. This anomaly is anisotropic along the $b$ and $c$ axes, and does not appear along the $a$-axis. Susceptibility was also measured at higher magnetic fields up to 7 T, but there was no effect on the transition
temperature. As there is no structural transition occurring in the material at this temperature as has been verified by neutron diffraction, the anomaly at 103 K is attributed to magnetic ordering in the material.

Qualitatively, the broad maxima in the $M(T)$ curves resemble the Bonner-Fisher type susceptibility of a $S = \frac{1}{2}$ Heisenberg chain [69]. In fact, the magnetic susceptibility of an odd-leg ladder is expected to be very similar to that of a single chain [51, 163, 182]. It is therefore, tempting to interpret the data along these lines. The broad maxima in $M(T)$ typically appears at a temperature of around $0.64J$ in 1D $S = \frac{1}{2}$ Heisenberg chains, thereby indicating the strength of the magnetic interactions [68]. The value of $J$ in spin ladder and spin chain cuprates wherein octahedrally coordinated Cu spins are coupled via the oxygen mediated superexchange are typically in between 1000-2000 K [168, 173, 221].

This fact indicates that the peak of observed at $\sim 180$ K is not related to the five-leg ladder structure of the Cu-O-Cu network (see Fig. 10.1). However, a likely candidate which is responsible for this peak could be the complex ribbon-like structure formed by the Cu3 and Cu4 atoms shown in Fig. 10.1(b), i.e., the Cu-O-Cu network at the edges of the ladders and between the ladder planes, with Cu having highly distorted octahedral and tetrahedral environments, rather than a typical octahedrally centered Cu spin. Such a structure could alter the exchange coupling strengths between these Cu spins and give rise to a second energy scale that in turn becomes responsible for the maxima in the magnetization at lower temperature.

## 10.4 Muon spin resonance ($\mu$SR)

Muon spin resonance spectroscopy was performed on this compound at temperatures above and below 103 K (Fig. 10.4) in order to microscopically confirm the presence of ordering. At temperatures above 103 K, one does not see any oscillations in the $\mu$SR signal. However, at low temperatures, clear oscillations can be resolved at short time scales. These oscillations in any muon spin resonance experiment are indicative of magnetic ordering in the sample [222]. In order to fit the measured data, two oscillatory components along with damping terms have to be used, which points to two inequivalent sites where the muons stop in the sample, that is, the muons experience two different local magnetic fields inside the sample. Also, judging from the relative magnitudes of the signal in the magnetically ordered and disordered state, one finds that the magnetic volume fraction of the sample is close to 100 % [223].
10.5 Magnetic structure

In order to throw light on the magnetic structure, neutron diffraction experiments were performed on the D23 diffractometer at Institut Laue Langevin using a standard cryostat capable of reaching temperatures down to 1.7 K [220]. The sample, in a form of a semi-cylinder with diameter of about 3 mm and length of 5 mm, was attached by means of a dental glue to an aluminium holder with its $b$-axis along the rotational axis of the diffractometer. This geometry restricts the reachable number of reflections with respect to the $b$-axis, however, the accessible reflections are better resolved. Data were also recorded with a smaller sample in a form of a cuboid with dimensions 2x2x2 mm$^3$ that had an arbitrary orientation. Resulting data sets were combined. To generate all possible magnetic structures allowed by symmetry of the crystal structure and the experimental propagation vector, the symmetry analysis as developed by Bertaut [224] implemented in computer codes MODY [225] and BasisReps [147] has been used.
Chapter 10. La₆Cu₇O₁₉: Properties

Figure 10.5: Rocking curves of the (a) nuclear Bragg reflection (2 0 4) at 10 K and 115 K, with the difference between them, and the (b) Magnetic Bragg reflection (−3 2 1 2 6) measured on the larger sample at identical conditions.

Long reciprocal scans revealed that all the Bragg reflections due to magnetic order can be indexed with a unique propagation vector \( q = (\frac{1}{2} \frac{1}{2} 0) \). Fig. 10.5 shows rocking curves through a representative nuclear Bragg reflection (2 0 4) and a magnetic Bragg reflection, (−3 2 1 2 6), measured at 10 K and 115 K are shown. A single peak in these curves indicates the presence of a single orientation in the entire bulk of the measured sample. While at low temperatures a clear magnetic Bragg reflection is observed, no intensity can be discerned at high temperature. This difference in the scattered intensity is attributed to an antiferromagnetic ordering. Since magnetic reflections at low temperatures are resolution limited, the magnetic order is of a long-range character.

In the vicinity of second-order, continuous or critical order-disorder transitions, where the fluctuations in magnetization increase, there are anomalies in the scattering of neutron beams passing through the material. These anomalies reflect the fluctuations in the magnetization around the critical region, and can be characterized by so-called critical exponents that are specific to models. These exponents capture the behaviour of fundamental quantities like specific heat, susceptibility, magnetization, etc. close to the critical point. The critical exponents in a con-
10.5. Magnetic structure

Figure 10.6: Temperature dependence of the integrated intensity of the representative magnetic reflection \((-\frac{3}{2}, \frac{1}{2}, 6\)) measured on the larger sample in zero field. The inset shows the temperature dependence of the peak intensity of the same reflection measured in a small temperature range around the magnetic phase transition together with the best fit to the formula describing the decrease of the staggered magnetization in an antiferromagnet [226].

Continuous transition only depends on the dimensionality of the model system, the dimensionality of the order-parameter of the system, and whether the interaction is short or long range. The critical exponent of the system can be obtained from the variation in scattering intensity across the phase transition. The temperature dependence of the integrated intensity \(I\) (Fig. 10.6) shows that although the intensity decreases with increasing temperature only slowly, it suddenly drops above \(\approx 95\) K and disappears above the proposed magnetic phase transition temperature. A more detailed temperature dependence of the magnetic reflection and the best fit (obtained in the range above 100 K) to the empirical formula [226]

\[
I = I_0 \left(1 - \frac{T}{T_N}\right)^{2\beta},
\]  

(10.1)
Chapter 10. La$_8$Cu$_7$O$_{19}$: Properties

Figure 10.7: Schematic representation of the AF structure of La$_8$Cu$_7$O$_{19}$. For clarity, only the Cu magnetic moments are shown. The color indicates the paired moments. Colors with a red touch denote moments residing in octahedra environment, blue colors indicate moments situated in ribbons.

which describes the temperature dependence of the staggered magnetization in an antiferromagnet as seen by neutrons, given in the inset of Fig. 10.6, suggests that the magnetic phase transition equals to 102.5(3) K. The critical $\beta$ exponent that amounts to 0.23(4) is somewhat lower than the value expected for a 3D antiferromagnet, but still substantially larger than a value of 0.125 expected for an Ising system [226]. At the same time, this value is larger than that one of 0.13(2) found by Zobkalo et al. [183].

A detailed discussion of the results for the magnetic structure can be found it [220]. Here, we discuss briefly the essential findings related to the magnetic structure. Fig. 10.7 shows a schematic representation of the deduced AF structure of La$_8$Cu$_7$O$_{19}$, and table 10.3 shows the refined magnetic structure parameters and the couplings of each moment within the unit cell.

Possible ways in which the magnetic structure can be represented, that is, the ways in which pairs of moments are coupled with each other depends on the symmetry of the crystallographic unit cell. Among these so-called ‘irreducible representations’ of the magnetic structure, the moments within one unit cell are related by the inversion either ferromagnetically or antiferromagnetically and can have any spatial orientation. From the measurements, it is observed that one needs to combine two different irreducible representations, $\Gamma_1$ and $\Gamma_2$, in order to get good agreement with the measured data. In other words, some moments
Table 10.3: Refined magnetic structure parameters of La$_8$Cu$_7$O$_{19}$ determined from the best fit to model associated with half of the moments in the 4e position coupled according to $\Gamma_1$ and half according to $\Gamma_2$ and in the 8f site mostly according to the $\Gamma_2$ irreducible representations, respectively. $\phi$ denotes the angle between a Cu moment and the $a$-axis, $\theta$ is the angle which makes the Cu moment with the $c$-axis.

<table>
<thead>
<tr>
<th>Site (Wyckoff position)</th>
<th>Moment $(\mu_B)$</th>
<th>$\phi$ (deg)</th>
<th>$\theta$ (deg)</th>
<th>relation (ir.rep.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>e1</td>
<td>0.37 (5)</td>
<td>90 (0)</td>
<td>90 (0)</td>
<td>e3 ($\Gamma_1$)</td>
</tr>
<tr>
<td>e2</td>
<td>-0.37 (5)</td>
<td>90 (0)</td>
<td>90 (0)</td>
<td>e4 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f11</td>
<td>0.49 (3)</td>
<td>90 (0)</td>
<td>90 (0)</td>
<td>f15 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f12</td>
<td>-0.49 (3)</td>
<td>90 (0)</td>
<td>90 (0)</td>
<td>-f16 ($\Gamma_1$)</td>
</tr>
<tr>
<td>f13</td>
<td>0.49 (3)</td>
<td>90 (0)</td>
<td>90 (0)</td>
<td>f17 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f14</td>
<td>0.49 (3)</td>
<td>90 (0)</td>
<td>90 (0)</td>
<td>-f18 ($\Gamma_1$)</td>
</tr>
<tr>
<td>f21</td>
<td>0.45 (2)</td>
<td>259 (10)</td>
<td>90 (0)</td>
<td>f25 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f22</td>
<td>0.45 (2)</td>
<td>358 (11)</td>
<td>90 (0)</td>
<td>f26 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f23</td>
<td>0.45 (2)</td>
<td>282 (6)</td>
<td>90 (0)</td>
<td>f27 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f24</td>
<td>0.45 (2)</td>
<td>183 (11)</td>
<td>90 (0)</td>
<td>f28 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f31</td>
<td>0.44 (3)</td>
<td>233 (8)</td>
<td>90 (0)</td>
<td>f35 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f32</td>
<td>0.44 (3)</td>
<td>279 (7)</td>
<td>90 (0)</td>
<td>f36 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f33</td>
<td>0.44 (3)</td>
<td>315 (6)</td>
<td>90 (0)</td>
<td>f37 ($\Gamma_2$)</td>
</tr>
<tr>
<td>f34</td>
<td>0.44 (3)</td>
<td>266 (7)</td>
<td>90 (0)</td>
<td>f38 ($\Gamma_2$)</td>
</tr>
</tbody>
</table>

La$_8$Cu$_7$O$_{19}$ at $T = 10$ K, Space group: C 2/c, Observed refl. 179, $\chi^2$ 6.7, $R_f$ (%) 16.2

are coupled in accordance with $\Gamma_1$ and some according to $\Gamma_2$. In $\Gamma_2$, for the 4e Wyckoff position 4e, Cu moments at the e1 and e3 sites are coupled ferromagnetically and moments at the e2 and e4 sites couple antiferromagnetically within one crystallographic unit cell. For the 8f position, moments are ferromagnetically coupled as independent pairs. In $\Gamma_1$, the coupling between the pairs of moments is reversed. Also, moment directions in adjacent unit cells along the $a$-axis and the $b$-axis are reversed and they preserve their orientations along the $c$-axis.

It is seen that La$_8$Cu$_7$O$_{19}$ orders antiferromagnetically at low temperatures with two kinds of Cu moments divided into two subsystems coupled in a complicated non-collinear fashion. Moments in the 4e Wyckoff sites and 8f sites (atoms f11 to f18) with octahedral environment, that form linear chains running along approximately [101] direction (see fig. 10.1) are coupled antiferromagnetically within
the chains and are confined along the shortest crystallographic $b$-axis. Moments residing on the other 8f Wyckoff sites, (atoms f31 to f38) which form the rather complicated ribbons (see fig. 10.1) seem to be confined perpendicular to the $c$-axis, having larger component along the $b$-axis direction.

The remaining moments (atoms f21 to f24) that provide the connection between octahedral and ribbon sites and are situated at either end of a chain (see fig. 10.1) have directions that vary in space. The data does not seem to be very sensitive to changes in the directions of these moments. All moment magnitudes are close to 0.4 $\mu_B$. The deduced AF structure of La$_8$Cu$_7$O$_{19}$ is in disagreement with the structure described of Zobkalo et al. (see section 5.4). However, at least in the case of Cu moments in octahedral sites the two solutions agree well. For Cu moments situated in ribbons, orientations in some cases are rather different. The exact origin of the anisotropy in the long range magnetic ordering transition step itself at 103 K remains unclear though. Further high field experiments are planned in order or better understand this.

10.6 Heat conductivity

Finally, the heat transport in this compound was investigated with a view to check for any possible contribution of propagating magnetic excitations. Heat conductivity ($\kappa$) using the steady state method was measured along all three crystallographic axes in the temperature range 7-300 K (Fig. 10.8). There is a large anisotropy observed. $\kappa$ along the legs of the ladder ($b$-axis) has the highest value with a peak at $\sim$ 280 W m$^{-1}$K$^{-1}$. The peak values of $\kappa$ along the $c$ and $a$ directions are 145 W m$^{-1}$K$^{-1}$ and 50 W m$^{-1}$K$^{-1}$ respectively. The conductivity along all three directions resemble that of purely phononic systems.

<table>
<thead>
<tr>
<th>Axis</th>
<th>$B$ $(10^{-30})$</th>
<th>$b$ $(10^{-44})$</th>
<th>$A$ $(10^{-4})$</th>
<th>$L$ $(10^{-4})$</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.56</td>
<td>1.63</td>
<td>43.97</td>
<td>10.17</td>
<td>100 K</td>
</tr>
<tr>
<td>b</td>
<td>79.9</td>
<td>2.06</td>
<td>7.44</td>
<td>7.17</td>
<td>100 K</td>
</tr>
<tr>
<td>c</td>
<td>1.28</td>
<td>2.13</td>
<td>65.22</td>
<td>1.15</td>
<td>100 K</td>
</tr>
</tbody>
</table>

A fit to the measured curves was performed using the Callaway model for phononic heat conductivity (see section 3.3.1), and a good fit was obtained over
10.6. Heat conductivity

Figure 10.8: Heat conductivity as a function of temperature ($\kappa(T)$) measured along all three crystallographic directions. The black curves indicate fits to the data according to the Callaway model [123]. Inset: $\kappa(T)$ at temperatures below 75 K to clearly illustrate the low-$T$ peaks.

the entire temperature range. All the parameters of the model have to be varied without which it is difficult to obtain good fits. Such a large anisotropy in phononic heat conduction could be the result of a large anisotropy in the dispersion of phonons in the crystal. The parameters of the Callaway fit are given in Table 10.4. There is no discernable sign of heat transport due to magnetic excitations in this temperature range, although there might be some contribution from magnetic excitations which adds to the phononic background in such a way that the overall $T$-dependence still is phononic-like. Specific doping experiments of similar type as discussed in chapters 8 and 9 could clarify this point further, but are beyond the scope of the present work.
10.7 Conclusions

The crystal structure of La$_8$Cu$_7$O$_{19}$ has been discussed, pointing out quantitative details about the different Cu sites and the oxygen environments that they are located in. It is seen that the magnetic structure is complicated and non-collinear. The material orders antiferromagnetically with the propagation vector $q = (\frac{1}{2} \frac{1}{2} 0)$ below $T_N = 102.5 (3)$ K. Crystallographically, Cu magnetic moments divide into two sub-systems, depending on the environment. Moments situated at centers of oxygen octahedra orient along the $b$-axis and couple to neighboring moments antiferromagnetically, whereas those creating a complicated ribbon structure possess all three cartesian components. The $\mu$SR signal confirms that the materials undergoes a bulk 3D magnetic ordering at low temperatures. Further, measurements of the magnetic and physical properties confirm that this material exhibits a bulk, three dimensional, long range antiferromagnetic ordering at $\sim 103$ K. The microscopic origin of the anisotropy in the magnetic properties is unclear though, and further experiments like electron spin resonance (ESR) are planned in order to determine anisotropy associated with the $g$-factor. Due to a complicated crystal structure and a large unit cell, the situation is far from one that realizes an isotropic five-leg ladder Hamiltonian. Thus, comparisons between theory and experiment are limited by the details of the crystal structure that turns out to be crucial in deciding the character of the underlying spin system. Although, La$_8$Cu$_7$O$_{19}$ structurally realizes a five-leg ladder, its structural details that possibly bring in a second energy scale to the magnetism and which determine the $T$-dependence of the magnetic susceptibility, make it difficult to study the properties of a true five-leg ladder model. The heat conductivity of this compound along the three axes resembles that of pure phononic systems, and no sign of contributions due to magnetic excitations is seen.
Chapter 11

Summary

This experimental work focuses on the single crystal growth and heat transport properties of pure and doped versions of compounds that realize low-dimensional spin structures, with a view to gain insight into the different scattering mechanisms that are responsible for transport, and to motivate the need for theoretical work towards a complete understanding of heat transport in strongly quantum systems.

Single crystals of pure La$_2$CuO$_4$ were grown using the travelling floating zone method (TFSZ). Heat transport in the pure compound was experimentally measured for the first time up to very high temperatures of 813 K using two methods, namely the steady state method for low temperatures and the dynamic flash method for measuring high temperatures. An unprecedentedly high magnetic heat conductivity has been measured indicating that the quality of the grown single crystal is extraordinarily high. At high temperatures $\kappa_{\text{mag}}$ strongly decreases compared to the phononic heat conductivity, suggesting that additional temperature dependent scattering mechanisms, other than the temperature independent boundary scattering, are present that limit conduction by magnons. Qualitative comparison of the experimental $\kappa_{\text{mag}}$ to recent calculations seems to suggest that only taking into account the scattering of magnons off boundaries and other magnons is apparently insufficient to fully describe the strong suppression of $\kappa_{\text{mag}}$. The scattering of magnons with other excitations like phonons could be in addition important to explain this strong decrease. From our preliminary analysis of the experimental data based on empirical models for scattering analogous to the phononic Callaway model, it is seen that along with a $T$-independent boundary scattering process, two umklapp-like $T$-dependent scattering terms seem to describe the temperature dependence of $\kappa_{\text{mag}}$ in the entire...
measured temperature range. One of these terms having a characteristic energy scale could correspond to phonon modes in the compound, thus indicating the relevance of phonons in the scattering processes that limit magnon heat conduction. The energy scale involved in the second term is of the order of magnitude of the magnetic exchange coupling $J$. There are indications that this high energy scale might be manifested through the correlation length that possibly limits the mean-free path of magnons. A theoretical model that treats $T$-independent and $T$-dependent magnon scattering processes with boundaries, and other quasiparticles together, taking in to account a possible influence of the spin-spin correlation length seems to be required to explain the experimental results and describe the physics of scattering in the La$_2$CuO$_4$ compound for the whole temperature range. Finally, in order to better understand the role of point-like defects and boundaries in magnon scattering processes, and the temperature regimes in which they are observably dominant, single crystals of La$_2$CuO$_4$ with small amounts of Ni and Zn doped at the Cu-site, La$_2$Cu$_{x}$Ni$_{1-x}$O$_4$ and La$_2$Cu$_{x}$Zn$_{1-x}$O$_4$ for $x = 0.001$ and 0.003, have been grown. Ongoing heat transport measurements on these crystals will possibly give insight into the role substitutional impurities in limiting heat transport via magnons, i.e, whether such impurities act as point-like defects or whether they act as boundaries for the magnons, or whether their effect is just screened.

Heat conductivity measurements on single crystals of Sr$_2$Cu$_{1-x}$Ni$_x$O$_3$ for $x = 0.005, 0.01$ and $0.02$, grown by N. Sekhar Beesetty at the University of Paris-Sud, show that substituting small amounts of Ni for Cu in Sr$_2$CuO$_3$ causes a very strong enhancement of the phononic conductivity at low doping levels, which is seen in the measurements both parallel and perpendicular to the spin chains. The spinon heat conductivity on the other hand is strongly suppressed. The $T$-dependence of the mean-free path of spinons is described well at temperatures higher than 100 K taking into account only $T$-independent spinon-defect and $T$-dependent spinon-phonon scattering, using an empirical scattering model. These observations are qualitatively similar to the case of Ni-doped SrCuO$_2$, where the magnitude of increase in the phononic conductivity upon Ni-doping is smaller. Single crystals of SrCu$_{1-x}$Ni$_x$O$_2$ for $x = 0.01$ were grown in this work using the TFSZ method, in order to investigate the spin-excitation spectrum using inelastic neutron scattering experiments (INS) and nuclear magnetic resonance (NMR). These experiments clearly indicated the development of a spin gap of $\sim 8$ meV at low energies. Single crystals of Sr$_2$Cu$_{1-x}$Ni$_x$O$_3$ were also studied using INS and NMR, and a doping-dependent spin-gap was observed in these compounds too. The properties of this spin gap as probed by NMR and INS, point to the presence of Ni-induced fragmentation of the spin chains; a picture that is further evident from the heat transport measurements where perfect scaling is observed.
for the spinon mean free paths due to impurity scattering. The observed enhancement of phononic heat conductivity for these compounds could possibly be related to the appearance of the spin gap. The emergence of a gap depletes low energy spinons which, in the undoped compound, via a strong spin-phonon coupling, limited phonon heat conductivity due to spinon-phonon scattering processes. The unavailability of these spinons now reduces scattering of phonons and thereby enhances the phononic heat conductivity, which is what we observe in the heat conductivity experiments. Thus, we indirectly observe the opening of the spin gap in the heat conductivity measurements of Ni doped SrCuO$_2$ and Sr$_2$CuO$_3$. Therefore, a magnetic impurity like Ni strongly affects the spin excitation spectrum and spinon transport in these materials which are very good approximations of $S = \frac{1}{2}$ Heisenberg chains. Such an impurity also reveals a very strong spin-phonon coupling and thus the importance of the scattering mechanism between phonons and spinons in limiting heat conduction at low temperatures.

The evidence of strong spin-phonon coupling in these quasi 1D systems encourage further studies on probing the nature of this coupling and its effects on scattering mechanisms.

The effect of introducing an off-chain impurity like Ca, thereby creating bond disorder, on the heat transport in Sr$_2$CuO$_3$ has been studied. A drastic suppression of the magnetic heat conductivity parallel to the chains indicating that the propagation of spinons is very sensitive to even the slightest bond disorder is observed. The $T$-dependence of the mean-free path of spinons can be modelled by spinon-defect and spinon-phonon scattering processes, and the reduction of the mean free path upon doping is accounted for mainly by increased scattering of spinons off effective in-chain defects, where the scattering probability per defect is equally strong in the entire doping range. Interestingly, large disorder present in the compounds doped with high concentrations of Ca leads to a linearly increasing spinon heat conductivity, thus reflecting the intrinsic spinon heat transport in a $S = \frac{1}{2}$ Heisenberg spin chain. Although we observe that in the case of both 2D and 1D systems, a semi-classical kinetic model for heat transport along with empirical models of scattering processes describe the temperature dependence of the measured heat conductivity surprisingly well in the temperature regime up to 300 K, interpretations based on these analyses must be treated as preliminary, and as a step towards microscopically understanding heat transport in low-dimensional systems such as the ones discussed in this work.

Single crystals of La$_8$Cu$_7$O$_{19}$ were grown using the TFSZ method for the first time. The crystal structure of La$_8$Cu$_7$O$_{19}$ was investigated in detail by single crystal diffraction, to throw light on the quantitative details about the different Cu sites and the oxygen environments that they are located in. Using neutron
diffraction, it is seen that the magnetic structure is complicated and non-collinear. The material orders antiferromagnetically with the propagation vector \( q = (\frac{1}{2} \quad \frac{1}{2} \quad 0) \) below \( T_N \sim 103 \text{ K} \). This bulk magnetic ordering is also observed using other probes like \( \mu \text{SR} \) and specific heat, and magnetization measurements. The heat conductivity of this compound along the three axes resembles that of pure phononic systems, and no sign of contributions due to magnetic excitations is seen. The microscopic origin of the anisotropy in the magnetic properties is unclear though, and further experiments like electron spin resonance (ESR) are planned in order to determine anisotropy associated with the \( g \)-factor. Due to a complicated crystal structure and a large unit cell, the situation is far from one that realizes an isotropic five-leg ladder Hamiltonian. Thus, comparisons between theory and experiment are limited by the details of the crystal structure that turns out to be crucial in deciding the character of the underlying spin system. Although, \( \text{La}_{8}\text{Cu}_{7}\text{O}_{19} \) structurally realizes a five-leg ladder, its structural details that possibly bring in a second energy scale to the magnetism make it difficult to study the properties of a true five-leg ladder model.

Single crystals of \( \text{LaCuO}_2 \) have been grown for the first time using the travelling-solvent floating zone method. The crystal was grown in an Ar-atmosphere by reduction of \( \text{La}_2\text{Cu}_2\text{O}_5 \), which was used as the feed rod composition for the growth. The grown crystals have been characterized thoroughly with respect to phase purity and single crystallinity. Ar atmosphere helped in the reduction of the starting compound into the obtained phase. A CuO solvent and a slow growth rate were important for stabilizing the molten zone and hence the growth process. As we are now able to synthesize pure \( \text{LaCuO}_2 \) in single crystalline form, experiments on intercalating \( \text{O}_2 \) into it using high pressure, and measurement of its physical properties are planned.
Appendix A

A.1 Heat conductivity: Co- and Zn-doped SrCuO$_2$

A.1.1 SrCu$_{1-x}$Co$_x$O$_2$

The heat conductivity measured parallel ($\kappa_c$) to the spin chains of SrCu$_{1-x}$Co$_x$O$_2$ is shown in fig. A.1 for $x = 0, 0.0025, 0.005, 0.01$. For $x = 0$, as discussed in section 5.2, a broad peak consisting of contributions due to both phonons and spinons is observed. For $x = 0.0025$, this peak becomes less broad, and reduces in magnitude, indicating that the spinon contribution is suppressed. The spinon contribution is further suppressed for $x = 0.005$, as the peak becomes significantly sharper than that for $x = 0.0025$, and the peak position shifts to lower temperatures. For $x = 0.01$, the peak magnitude of $\kappa_c$ reduces even more. As can be seen in the log-log plot (inset of fig. A.1), the heat conductivity curves for $x = 0.0025$ and $x = 0.005$ show a shoulder which begins at $\sim 50$ K, instead of a $1/T$ phononic-like decrease. This shoulder must correspond to the still-present contributions due to spinons at high temperatures, which are not yet completely suppressed. The much broader peak in the case of $x = 0.0025$ indicates that a significant spinon contribution is still present even at low temperatures, around the peak in $\kappa_c$, which is observed to decrease for higher doping levels. Thus, a gradual but strong, monotonic decrease of the spinon heat conduction is observed with increasing Co concentration.
Fig. A.1 shows the heat conductivity ($\kappa_a$) of SrCu$_{1-x}$Co$_x$O$_2$, measured perpendicular to the spin chains. As discussed in section 5.2, the heat conductivity of undoped SrCuO$_2$ is purely phononic in this direction. On doping Co ($x = 0.0025$), the heat conductivity near the maximum shows an expected decrease upon doping. However, for $x = 0.0025$, there is a small increase of $\sim 50$ Wm$^{-1}$K$^{-1}$ above $\kappa_a$ for the undoped compound. Finally, for $x = 0.01$, $\kappa_a$ decreases and has a peak-value slightly lower than that for the $x = 0.0025$ compound. Thus, for the case of $x = 0.0025$, an unexpected increase of $\kappa_a$ is observed, that does not seem to be in agreement with the conventional idea of monotonic decrease of phononic conductivity as a function of increasing dopant concentration (see section 3.3).
A.1. Heat conductivity: Co- and Zn-doped SrCuO$_2$

Figure A.2: Heat conductivity ($\kappa_a$) perpendicular to chain for different concentrations of Co is plotted as a function of temperature for Co-doped SrCuO$_2$ compounds; inset: peak value of $\kappa_a$ plotted against the doping concentration.

A.1.2 SrCu$_{1-x}$Zn$_x$O$_2$

The heat conductivity measured parallel to ($\kappa_c$) and perpendicular ($\kappa_a$) to the spin chains of SrCu$_{1-x}$Zn$_x$O$_2$, for $x = 0$ and 0.01, is shown in fig. A.3 and the inset of fig. A.3 respectively. The broad peak in $\kappa_c$ for $x = 0$ reduces to a sharp phononic-like peak for $x = 0.01$. However, the heat conductivity perpendicular to the chains shows a strong increase upon doping.

The observed decrease of $\kappa_c$ for $x = 0.01$ in the case of Zn-doping is of a similar magnitude at all temperatures as that in the case of Co-doping. The difference between the effect of Zn and Co for the case of $x = 0.01$, is the strong increase of $\kappa_a$ for Zn-doping above the undoped case compared to the decrease observed for Co-doping.

As for the case of Ni-doped SrCuO$_2$, the unexpected increase observed in the
heat conductivity perpendicular to the chains ($\kappa_a$) of the Co- and Zn-doped SrCuO$_2$ compounds might be linked to the opening of a spin-gap at low energies in the spin excitation spectrum. However, measurements on crystals with other intermediate and higher doping concentrations are necessary in order to see a trend in the variation of $\kappa_a$ as a function of doping content, and to explain the observed behaviour of heat conductivity.

Figure A.3: Heat conductivity ($\kappa_a$) perpendicular to chain for different Zn concentrations ($x$) are plotted as a function of temperature; inset: the magnitude of the peak in $\kappa_a$ is plotted as a function of the Zn concentration to illustrate the trend of the change.
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Publications


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