Magnon heat transport 
and magnon-hole scattering in one 
and two dimensions spin systems

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Vorgelegt von

M.Sc.
Hanan Gouda Abd Elwahab Ahmed 
ElHaes 
aus Elkalyoubia - Ägypten

Berichter: Universitätsprofessor Dr. Bernd Büchner 
Universitätsprofessor Dr. Gernot Güntherodt

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Chapter 1

Introduction

The magnetic heat conductivity $\kappa_{\text{mag}}$ of quasi low-dimensional spin systems such as antiferromagnetic $S = 1/2$ chains, two-leg ladders and two dimensional antiferromagnets is currently attracting the interest of many researchers, since they possess intriguing properties. For example, the theoretical thermal Drude weight of the integrable $XXZ$ chain with $S = 1/2$ is finite, i.e. there is no spinon-spinon interaction which degrades the thermal current and hence $\kappa_{\text{mag}}$ is infinite [1, 2, 3, 4, 5]. For non-integrable systems like the two-leg $S = 1/2$ spin ladder the situation is less clear. On one hand it is currently under debate whether the thermal Drude weight is finite as in spin chains [6, 7, 8, 9]. After the initial suggestion of a finite Drude weight [6] more recent theoretical works indicate a vanishing Drude weight [7, 9]. In real systems, however, $\kappa_{\text{mag}}$ is always finite due to interactions of the magnetic excitations with other quasiparticles and defects. Prominent experimental examples for magnetic heat transport are the spin-ladder system (Sr, Ca, La)$_{14}$Cu$_{24}$O$_{41}$ and the two-dimensional antiferromagnetic La$_2$CuO$_4$, where pronounced magnetic peaks are observed in the total thermal conductivity $\kappa = \kappa_{\text{ph}} + \kappa_{\text{mag}}$ (with $\kappa_{\text{ph}}$ the phonon thermal conductivity) at high $T$ [10, 11, 12, 13, 14]. These high-$T$ anomalies reflect the dimensionality of the underlying magnetic structure, i.e., they are only observed when $\kappa$ is measured along the direction of ladders or, in the case of La$_2$CuO$_4$, parallel to the magnetic planes. In both cases the temperature dependence of $\kappa_{\text{mag}}$ at low temperatures is quite well understood. Here temperature independent scattering on static defects is dominating and the temperature dependence of $\kappa_{\text{mag}}$ is governed by the respective temperature dependent thermal occupation of magnons. At higher temperatures much less is known about the origin of the observed temperature dependence of $\kappa_{\text{mag}}$. Several temperature dependent scattering processes with other quasiparticles like charge carriers, magnons and phonons can play a role here.

At least since the discovery of high temperature superconductivity
the magnetism of low dimensional spin systems is also of more general interest. Magnetic excitations are considered as being responsible for the hole pairing mechanism in the high temperature superconductors and model calculations of holes doped into an antiferromagnetic background yield ground states which are in competition with superconductivity like the also experimentally observed stripe order. In two-leg $S = 1/2$ spinladders, which often are considered as toy systems allowing a better understanding of high temperature superconductivity, the role of magnetism for the charge dynamics is particularly demonstrative. Hole pairing, the prerequisite for superconductivity results from simple energetic arguments such as to lower the magnetic energy. Apart from superconductivity also a hole pair-ordered ground state has been predicted [16]. Superconductivity is indeed experimentally observed in $(\text{Sr, Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ which contains hole doped two-leg ladders [17]. Evidence for charge order in this material has been reported from optical experiments [18, 19, 20]. It is, however, unclear whether this charge order is located in the ladders or rather in the spin chains, which are also present in this material and where charge ordering is well known [21, 22, 23].

In this work the interaction of magnetic excitations and charge carriers in the low dimensional spin systems $(\text{Sr, Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ and slightly Sr-doped $\text{La}_2\text{CuO}_4$ is investigated experimentally using the magnetic thermal conductivity as a probe. Thereby not only interesting information about the nature of magnon hole scattering and the consequences for $\kappa_{\text{mag}}$ is obtained. Also information about the charge ordering in $(\text{Sr, Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ can be achieved.

The thesis is organized as follows. Chapter 2 gives basic information about transport properties in solids with a focus on the different relevant contributions to the thermal conductivity, i.e., phononic and magnetic heat conduction. An overview of the experimental techniques is provided by chapter 3. The relevant properties of the materials under investigation are discussed in chapter 4, followed by chapter 5, which summarizes the starting points for the questions addressed in this work. The experimental results are presented and discussed in chapter 6.
Chapter 2

Transport properties in solid state physics

2.1 Transport coefficients

The transport of electric charge and heat in a solid state is examined. For that purpose we consider a system of entropy carrying particles, which is initially in equilibrium. The particles can interact with each other (for example phonons, magnons) and also carry electric charge (for example electrons). The system is not supposed to be isolated, therefore particle currents and/or entropy currents can enter or emerge. On this system, little disturbance (electric field, temperature gradient) are imposed causing flow of heat (and charge). If the external disturbances remain constant, then the system will approach a stationary state (steady state) in which the current is a function linearly in the disturbance (linear response). In systems of free charge carriers, the entropy transport goes with the transport of the charge. In the presence of a temperature gradient and an electric field, the linear response of the electric current density \( j \) and the thermal current density \( j_q \) are obtained in the form [24, 25]

\[
\begin{align*}
  j &= L_{11}E + L_{12}T \\
  j_q &= L_{21}E + L_{22}T
\end{align*}
\]  

where \( \nabla T \) is the temperature gradient and \( E \) is the electrochemical potential. If the temperature gradient is equal to zero the flow of the electric current in the sample is proportional with the electrical field,

\[
  j = \sigma E.
\]

Linear responses means here that the Ohm’s law should hold, so that \( \sigma \) is independent on both \( j \) and \( E \). Comparison of this equation with equation
Chapter 2: Transport properties in solid state physics

2.1 gives,

\[ \sigma = L_{11}. \quad (2.4) \]

Under the condition \( j = 0 \), a temperature gradient \( \nabla T \) causes an electric field

\[ \mathbf{E} = S \nabla T. \quad (2.5) \]

This is called Seabek-effect. Comparing the above equation with equation 2.1 gives,

\[ S = -\frac{L_{12}}{L_{11}}. \quad (2.6) \]

An electric current under the condition \( \nabla T = 0 \) causes also a thermal current and is proportional to the electric current:

\[ j_q = \Pi j. \quad (2.7) \]

The proportional constant \( \Pi \) is called Peltier-coefficient. Comparison of the above equation with both 2.1 and 2.2 gives

\[ \Pi = \frac{L_{21}}{L_{11}}. \quad (2.8) \]

Following the Kelvin-Onsager relation, the Peltier coefficient is equal to the thermopower multiplied by the absolute temperature:

\[ \Pi = ST. \quad (2.9) \]

### 2.1.1 Thermal conductivity

For small temperature gradients the thermal current is observed to be proportional to the temperature gradient \( \nabla T \)

\[ j_q = -\kappa \nabla T. \quad (2.10) \]

Putting \( j = 0 \) in equation 2.1 we obtain

\[ \mathbf{E} = -\frac{L_{12}}{L_{11}} \nabla T. \quad (2.11) \]

Substituting the above equation in 2.2 we got the thermal current in the form

\[ j_q = L_{22} \nabla T - \frac{L_{21} L_{12}}{L_{11}} \nabla T \quad (2.12) \]

hence

\[ \kappa = \frac{L_{21} L_{12}}{L_{11}} - L_{22}. \quad (2.13) \]
2.2 Kinetic theory of the thermal conductivity

The kinetic theory deals with non-equilibrium phenomena in dilute gases. A dilute gases is one in which the range of interaction between the atoms or the molecules of the gas is much less than their average separation. The interaction of the particles may then be considered to be essentially instantaneous. The motion of the particles is described by straight paths.
that change direction by each instantaneous scattering process. In the
presence of external fields the straight paths may become curved, but
this does not change the fundamental separation of free-particle motion
and collision. In a dense liquid this separation may be lost and the use
of kinetic theory invalidated [24].

2.2.1 Simple kinetic model

The simple model allows a universal description of the thermal conduc-
tivity, independent on the kind of [28, 26] the heat carrying particles. The
description is based on the Drude model [29]. Suppose a small temper-

ature gradient is imposed along the x-direction in an insulating crystal
as shown in figure 2.1. From Drude model, we assume that a particle
experiences a collision with a probability per unit time equal to $1/\tau$. The
time $\tau$ is known as the relaxation time, the collision time or the mean
free time. The collision time $\tau$ is taken to be independent of the particle
position and velocity. The local density of the internal energy at the place
$x, u(x)$, would be given by the density of the internal energy of the system
in the equilibrium with the temperature $T(x)$. Each particle at a given
point will contribute to the thermal current density in the $x$-direction an
amount equal to the product of the $x$-component of its velocity with its
contribution to the energy density. To estimate this thermal current we
average the product of the energy density and the $x$-velocity over all the
places where the particles last collision might have occurred. We assume
that the collision which occurred a distance $\ell = v \tau$ from the point $x_o$ in
a direction making an angle $\Theta$ to the $x$-axis as in figure 2.1. This particle
collided last at point $P$ a distance $\ell \cos \Theta$ up the temperature gradient
and therefore carrying an energy $u(x_o - \ell \cos \Theta)$ with $x$-velocity $v \cos \Theta$.
The net thermal current is proportional to the product of these quantities
averaged over all solid angles, so the thermal current is given by:

$$ j_q = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} v \cos(\Theta) u(x_o - \ell \cos(\Theta)) \sin(\Theta) d\phi d\Theta. \quad (2.16) $$

From the development of the energy density around the point $x_o$, the
first order gives:

$$ j_q = -\frac{1}{3} c_v v \ell \frac{\partial T}{\partial x} \quad (2.17) $$

where $c_v$ is the specific heat of the particles and one of the quantities
that determines the temperature dependence of $\kappa$. If one compares this
to the definition of the thermal conductivity in equation 2.10 one finds
that:
2.3 Different contributions to the thermal conductivity

\[ \kappa = \frac{1}{3} c_v v \ell = \frac{1}{3} c_v v^2 \tau. \]  
(2.18)

In lower dimensions, the prefactor in equation 2.18 must be adapted as:

\[ \kappa = \frac{1}{d} c_v v \ell, \]  
(2.19)

where \( d \) is the number of the identified dimensions. A more accurate approach to the thermal conductivity using the Boltzmann-equation is obtained

\[ \kappa = \frac{1}{d} \frac{1}{(2\pi)^d} \int c_k v_k l_k dk \]  
(2.20)

where \( c_k, v_k, \) and \( l_k \) are the specific heat, velocity and the mean free path for phonon with wave vector \( k \).

2.3 Different contributions to the thermal conductivity

2.3.1 Phonon thermal conduction

In insulators, heat is easily transmitted by phonons. The phonons are the quanta of energy in each mode of vibration and the mean free path is a measure of the rate at which energy is exchanged between different phonon modes. We can again use the expression

\[ \kappa = \frac{1}{3} c_v v \ell \]  
(2.21)

to represent the heat conductivity, where \( v \) is now the mean phonon velocity, approximately equal to the velocity of sound in the crystal and \( c_v \) is the specific heat of the lattice. At normal and high temperature \( \ell \) is limited by the direct interactions among the phonons themselves, and at sufficiently high temperatures \( \ell \) is inversely proportional to \( T \). As the temperature decreases, interaction among the phonons become rapidly less effective in restricting \( \ell \), which thus increases more rapidly than \( 1/T \). For sufficiently perfect crystals this increase can be represented by an exponential of the form \( \ell \propto \exp(T^*/T) \), where \( T^* \) is a characteristic temperature for the particular crystal and is a fraction of the Debye temperature. At low temperature (\( \sim 0.1 \) to \( \sim 10 \) K) \( \ell \) may reach a constant value in the order of the size of the sample. In order to deduce the behavior of the thermal conductivity from that of the mean free path, the temperature variation of the heat capacity must be considered, but the mean velocity can be regarded as independent of the temperature.
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Figure 2.2: Typical variation of phonon mean free path and the thermal conductivity with temperature. From [30]

At temperatures which are high enough for the relation $\ell \propto 1/T$ to hold, $c_v$ is nearly constant so that $\kappa \propto 1/T$. As the temperature decreases, $c_v$ also decreases, eventually varying as $T^3$, but the exponential variation in $\ell$ is then so dominant that the conductivity too is essentially represented by the exponential variation. When the mean free path become constant, the temperature dependence of the conductivity reflects the $T^3$ behavior of the specific heat. The general form of temperature dependence for $\ell$ and the consequent variation of $\kappa$ are shown in figure 2.2 [31, 30].

Phonon-phonon interaction

For low temperatures, an explanation of what happens to $\ell$ must take into account two different types of phonon-phonon interaction, one of which is effective and the other is ineffective in keeping $\ell$ finite as defined in equation 2.21 [31]. This phonon mean free path is determined by two processes namely, geometrical scattering and scattering by other phonons. If the forces between the atoms were purely harmonic, there would be no mechanism for collision between different phonons, and $\ell$ would be limited by collisions of a phonon with the crystal boundary and by lattice imperfections. With anharmonic lattice interactions, there is a coupling between different phonons which limits the value of $\ell$. The most important scatter-
Different contributions to the thermal conductivity

ing mechanisms are those involving three phonons; they are of two kinds. In the first, two phonons combine to form a single phonon, while in the second, one phonon breaks up to give two phonons. Assuming that interaction between the phonons is possible, one will expect that there will be energy and momentum conservation in the three-phonon processes. Energy conservation and the momentum conservation will mean for the first process

\[ \omega + \omega' = \omega'' \]  
\[ k + k' = k'' + G \]

where \((\omega, k), (\omega', k')\) and \((\omega'', k'')\) are the frequencies and the wave vectors of the first, second, and third phonon respectively. For the second process

\[ \omega = \omega' + \omega'' \]  
\[ k = k' + k'' + G \]

where, \(G\) is the reciprocal lattice. The energy and momentum have been divided by \(\hbar\). If \(G = 0\), the three-phonon scattering is called a normal process or N-processes, if \(G \neq 0\), it is called an umklapp process or U-process. For N-process the phonon momentum

\[ J = \sum_K n_K \hbar K \]

is conserved because on collision the change in \(J\) is \(k'' - k' - k = 0\), where \(n_k\) is the number of phonons having wave vector \(k\). U-processes destroy momentum and changes the direction of energy flow. The difference between N-and U-processes is shown in the figure 2.3 [29, 31, 32]. U-process can not occur unless \((k + k')\) extends beyond the zone boundary. This requires that each of \(k\) and \(k'\) should be comparable with \((G/4)\). The probability of U-process would fall off as \(\exp(-\theta_u/T)\) at low temperatures, where the parameter \(\theta_u\) was expected to be comparable to \((\theta_D/2)\) [30].

High temperature \((T > \theta_D)\)

At these high temperatures the number of phonons is proportional with temperature \((n_k \propto T)\), so that the specific heat is almost temperatures independent. From three-Phonons-processes, the mean free path set by U-process varies as \(l \propto 1/n_k \propto 1/T\), since the excitation of all modes is proportional to \(T\) for temperatures larger than \(\theta_D\). Using equation 2.21 in order to estimate the thermal conductivity, gives:

\[ \kappa \propto \frac{1}{T}. \]
Experimentally this temperature dependence is confirmed in some cases, however, often one finds $\kappa \propto \frac{1}{T^x}$ with $1 \leq x \leq 2$ [28, 31]. Different reasons have been suggested for such deviations. On one hand $1/T$ behavior is to be expected only with constant volume. Through thermal expansion of the examined crystals, it comes however frequently to variations of the phonon spectrum, that could explain this deviations. This acceptance is confirmed through experiments on crystallized Argon with constant sample volume [31, 25]. On the other hand, the behavior divergent from $1/T$ can be explained in some cases not only by this effect; then four phonons processes must be also taken into consideration. These lead to a contribution to the thermal conductivity which varies proportionally to $T^{-\frac{3}{2}}$.

**Low temperature** ($T < \theta_D$)

At low temperature, the number of the phonons, which can take part in an Umklapp process is given by:

$$n_{ku} = \left( e^{\frac{\hbar \omega(k_u)}{k_B T}} - 1 \right)^{-1} \approx e^{-\frac{\hbar \omega(k_u)}{k_B T}}$$ (2.28)

With Debye frequency $\omega_D = k_B \Theta_D / \hbar$ and the parameter $\alpha \equiv \omega_D / \omega(k_U) \approx 2$ then

$$n_{ku} = e^{-\frac{\Theta_D}{k_B T}}.$$ (2.29)

The specific heat is in this temperature region proportional to $T^3$, while the mean free path $\ell$ is proportional to $1/n_{ku}$. Hence, from equation 2.21 the thermal conductivity is

$$\kappa \propto \left( \frac{T}{\Theta_D} \right)^{\frac{3}{2}} e^{\frac{\Theta_D}{k_B T}}.$$ (2.30)
2.3 Different contributions to the thermal conductivity

The thermal conductivity increases strongly with decreasing temperature in this temperature range, because the number of Umklapp processes responsible for the scattering of phonons and consequently the mean free path of the phonons increases exponentially [28]. Different theoretical work [31, 26] give a more general expression:

$$\kappa \propto T^\xi e^{\frac{\alpha D}{T}}$$

where $\xi$ and $\alpha$ are parameters of the order of unity. Such increasing of the thermal conductivity is only observed in a quite narrow temperature range, approximately $\frac{1}{30} < \frac{T}{\Theta_D} < \frac{1}{10}$ and requires almost perfect isotropically pure crystals.

At more lower temperatures ($T \to 0$), the mean free path of the phonons increases so strongly that it reaches finally the order of magnitude of the crystal dimensions and scattering of the phonons appears only at the boundary of the crystal. In this temperature range, the conductivity by the phonons becomes ballistic. Then by the limiting of the mean free path, the thermal conductivity does not increase any more, but it reaches a maximum and decreases again, and now proportional to the specific heat, how one observes easily from equation 2.18. The thermal conductivity is therefore in this temperature range proportional to $T^3$.

Phonon-defect-scattering

There are different kinds of defects which can disturb the perfection of an ideal crystal in addition to the scattering of phonons by each other (for example, transfer lines, impurities). In comparison with a sample without defects, the thermal conductivity of a sample with defects is always reduced and the strength of the suppression depends on the defect density as well as on the kind of defects [30, 28, 24]. The thermal conductivity as a function of temperature, which is measured for various isotopic compositions are displayed as log-log plots in figure 2.4 [33]. From the figure, the thermal conductivity of isotopically pure germanium $^{70}$Ge (99.99 %) is higher than the thermal conductivity of germanium with the natural isotopic composition for example $^{70}$Ge (96.3 %). At low temperatures, the thermal conductivity of isotopically pure $^{70}$Ge (99.99 %) follows the $T^3$ law characteristic for heat transfer under diffuse boundary scattering conditions. This indicates that the mean free path of the thermal phonon is comparable to the transverse dimensions of the sample. In isotopically disordered samples the temperature dependence of $\kappa$ is weaker than $T^3$.

This is due to the large contribution of isotopic scattering right down to lowest temperatures. At temperatures above the maximum the role of isotopic scattering decreases against the background of increasing three-phonon processes which give a temperature dependence of the form $\kappa \propto$
Figure 2.4: Temperature dependence of the thermal conductivity of Ge samples with different isotopic compositions [33].

$T^{-1}$ as the temperature approaches $\theta_D$. At room temperature the thermal conductivity of 99.99% $^{70}\text{Ge}$ is 20% higher than that of natural germanium [34].

**Phonon-magnon interaction**

Phonons and spin wave (magnons) can produce and destroy themselves in three-particle-processes. This type of scattering processes has been sparsely studied concerning its meaning for the thermal transport. Some work come to the result, that the relaxation time of the Phonon-Magnon-scattering for both phonon system and magnon system is longer than that of other relaxation times, therefore both systems can be considered as independent from each other. Consequently, phonon-magnon-scattering should have in general effects on the Phonons thermal conduction. Experimentally phonon-magnon-scattering is observed near the Néel temperature in some antiferromagnetic ordering substances in the form of an anomaly in the thermal conductivity [25, 35, 36].
2.3.2 Callaway model

A simple phenomenological model was proposed and applied for the calculation of lattice thermal conductivity at low temperature [37, 38]. It was assumed in this theory that, first, all phonon-phonon scattering processes can be represented by relaxation times which are functions of the wave vector of one mode only. Second, the phonon distribution is characterized by a Debye spectrum. Effects due to anisotropy and dispersion are neglected. Finally, the additivity of reciprocal relaxation times for independent scattering processes is assumed. On the basis of these considerations, the following expression was obtained for the thermal conductivity, $\kappa$:

$$\kappa = \kappa_1 + \kappa_2,$$  (2.32)

where

$$\kappa_1 = \frac{k_B}{2\pi^2 \nu} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^\Theta_D/T \frac{\tau_c x^4 e^x}{(e^x - 1)^2} dx$$  (2.33)

$$\kappa_2 = \frac{k_B}{2\pi^2 \nu} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^\Theta_D/T \left[ \frac{\tau_c x^4 e^x}{\tau_N (e^x - 1)^2} dx \right]^2 \int_0^\Theta_D/T \left( \frac{1}{\tau_N} \frac{x^4 e^x}{(e^x - 1)^2} dx \right).$$  (2.34)

In this equation, $k_B$ is Boltzmann’s constant, $\nu$ is the velocity of sound, $\Theta$ is the Debye temperature and $x$ is the usual dimensionless variable $\hbar \omega/k_B T$. $\tau_N$ is the relaxation time for the normal three-phonon scattering processes and $\tau_c$ is a combined relaxation time, whose reciprocal is the sum of the reciprocal relaxation time for all the scattering processes. If, for instance, in addition to the normal three-phonon scattering, one considers Umklapp processes, scattering by point defects and boundary scattering (relaxation times $\tau_U$, $\tau_D$ and $\tau_B$, respectively), then

$$\tau_c^{-1} = \tau_N^{-1} + \tau_U^{-1} + \tau_D^{-1} + \tau_B^{-1}.$$  (2.35)

The thermal conductivity as given by equation 2.33 becomes infinite in the limit in which $\tau_c$ approaches $\tau_N$. Normally, only the left part of equation 6.2 is used. The right part becomes significant in very pure materials.

2.3.3 Electronic heat transport

Electronic heat transport does not play a significant role in the present work. The Wiedemann-Franz law $\frac{\sigma}{T} = LT$ relates the electronic thermal conductivity $\kappa_{el}$ to the electronic conductivity and gives an upper bound for the electronic-contribution.
Figure 2.5: On the left: temperature dependence of the thermal conductivity of two samples of yttrium-iron-garnet in double logarithmic scale. The dotted line indicated the expected $T^2$ behavior. From [39]. On the right: the relative decrease of the thermal conductivity of yttrium iron garnet in an external magnetic field. The drawn lines correspond to different theoretical calculations. From [40].

### 2.3.4 Magnon thermal conduction

**Experimental results**

Heat transport in solids at low temperature is usually described by a theory of the motion and the scattering of the phonons and, in metals or semiconductors, electrons and holes. In a magnetically ordercrystal the propagating excitation of the spin system, known as magnons, can transport heat in the same manner as the more familiar lattice excitations or phonons. It was suggested early that, at a few hundreds of a degree kelvin, the heat transport by collective excitations of coupled paramagnetic ions might exceed that transported by phonons. In a ferrimagnetic dielectric, where spins are strongly coupled to their neighbours, the spin-wave heat transport might be important in the liquid helium range of 1 to 4 K. In this range the magnon system can have a specific heat equal to or greater than that of the phonons. The velocities of the excitations are comparable, and at sufficiently low temperatures their mean free paths are equal, since both are limited only by boundaries of the sample. There-
2.3 Different contributions to the thermal conductivity

Figure 2.6: Dispersion relation for coupled magnon-phonon mode in yttrium-iron-garnet for different magnetic fields $B$: a) in zero field ($B = 0$), b) $B = 0.5$ T and c) $B = 4$ T. From [40].

Therefore, at low temperatures a large fraction of the thermal conductivity of the crystal may be due to the magnons. Magnon conductivity has been recognized by a deviation of the thermal conductivity from $T^3$ behavior expected for boundary-limited phonons [41, 42, 36]. The heat conduction by magnon has been observed in ferrimagnetic yttrium iron garnet (YIG) [43, 39, 44]. Thermal conductivity of YIG exhibited the expected dependence on the temperature and magnetic field as shown in figure 2.5. The left part of the figure 2.5 shows the thermal conductivity of this substance in zero field which have been studied by Douglass et al [39]. The two samples have a different temperature dependence. Sample 1 has a low temperature conductivity which is nearly proportional to $T^2$. Sample 2, which has a lower conductivity at helium temperature, has a higher conductivity peak. The field dependence of the magnon thermal conductivity is shown in the right part of figure 2.5 [40]. By measuring the conductivity in fields that are large enough to remove the magnon contribution completely, it was estimated that about two-thirds of the zero-field conductivity was due to the magnons [45]. From the figure, not only the thermal conductivity decreases with increasing the field, but also it is saturated in high fields. The thermal conductivity decreases in the field can be also due to phonons, because an external field changes the energy of magnons and phonons. This is illustrated in figure 2.6. It is shown that the magnetic field dependence of the thermal conductivity of yttrium iron garnet can be accounted for, if the coupled magnon-phonon modes are employed in calculating the conductivity. On the other hand, the use of independent magnon and phonon modes does not leads to
Figure 2.7: Thermal conductivity of \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) parallel to the ferromagnetic levels (a) Temperature dependence in the zero field and in an external field \(B = 6.5T\) in double logarithmic scale. From [49]. (b) Dependence of the thermal conductivity on the external magnetic field at \(T = 2.9\) K (position of the maximum at \(B = 0\)). From [50].

satisfactory agreement between the theory and the experiment.

Experimental evidence for magnon conductivity has also been reported for ferromagnets EuS, CuCl\(_2\)(CH\(_3\)NH\(_3\)Cl); the ferrimagnet Li ferrite and the antiferromagnets CoCl\(_2\).6H\(_2\)O [45, 46, 47, 48]. However, comparing to yttrium iron garnet, the evidence for these materials is not as conclusive. In some cases it is based only on the temperature dependence of the conductivity, and in others cases depend only on the magnetic field. Also, in most cases there has been no attempt to compare the results qualitatively with the theoretical predictions. A further example for thermal conductivity has been found in \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4\), two-dimensional (2D) \(S = 1/2\) Heisenberg-ferromagnet [50]. Figure 2.7 shows the temperature and field dependence of the thermal conductivity of this compound. Figure 2.7 (a) shows the thermal conductivity as a function of temperature for \(n = 2\) in zero field and in an external field \(B = 6.5\) T measured by Coenen et al. [49]. In zero field, one can see at temperatures \(T < 3\) K that the increase of the thermal conductivity is proportional with \(T^2\) as it is expected for a two-dimensional ferromagnet. The external magnetic field suppressed the thermal conductivity in the range of
2.3 Different contributions to the thermal conductivity

Figure 2.8: Thermal conductivity in low dimension system. Left: Thermal conductivity of La$_2$CuO$_4$ parallel ($\kappa_{ab}$) and perpendicular ($\kappa_c$) to the CuO$_2$ plane as a function of temperature. Right: Thermal conductivity of Sr$_{14}$Cu$_{24}$O$_{41}$ along $a$- ($\kappa_a$), $b$- ($\kappa_b$) and $c$-axis ($\kappa_c$) as a function of temperature. From [25].

$T < 6$ K by a factor of three as shown in figure 2.7 (b), and the thermal conductivity is now proportional to $T^2$ as it is expect for a quasi-two-dimensional phononic lattice [51]. However, it is to be marked, that the change of the temperature dependence in the magnetic field of $T^{-2}$ to $T^2$ is relatively small.

Figure 2.8 presents the best examples for one- and two-dimensional magnetic heat transport observed up to now. The left panel shows the in-plane ($\kappa_{ab}$) and out-of-plane ($\kappa_c$) thermal conductivity of the layered $S = 1/2$ antiferromagnet La$_2$CuO$_4$ which has a strong magnetic in-plane coupling and only a very weak out-of-plane coupling. The right panel presents the thermal conductivities along all crystal directions of the spin ladder material Sr$_{14}$Cu$_{24}$O$_{41}$ which contains $S = 1/2$ two leg spin ladders with the legs of the ladders along the $c$-direction. Due to the steep magnon dispersion in this two materials the magnetic thermal conductivity $\kappa_{\text{mag}}$ becomes significant at much higher temperatures than in the previously discussed cases. In each case $\kappa_{\text{mag}}$ causes a high temperature peak in the
thermal conductivity along the directions which is parallel the direction of propagating magnons. Hence, the anisotropy of $\kappa$ reflects the anisotropy of the underlying magnetic structure. In particular the large $\kappa_{\text{mag}}$ in the spin ladder compound is currently attracting a lot of attention, where the possibility of ballistic heat transport - as theoretically predicted for spin chains - is discussed [52, 3, 2, 4]. The properties and analysis of $\kappa_{\text{mag}}$ of these materials will be discussed in detail in chapters 5 and 6 after introducing the basic material properties in chapter 4.
Chapter 3

Experimental techniques

3.1 Transport measurements

3.1.1 Measurement apparatus

Figure 3.1 shows a schematic diagram of the probe which is used for the transport measurements. The sample holder is surrounded by two copper-cup (inner and heating cup) located in the bottom part of the stick. Four stainless steel capillary tubes and a thermal switch are connected to the sample holder. Through these capillary tubes, 50 $\mu$m of Cu-wires are installed for the measurements. The thermal switch is used to improve the heat flow between the sample holder and the reservoir. The sample room and the connected capillary tubes are surrounded by a stainless steel tube, which is used as a very tightly closed space to allow evacuation down to $10^{-5}$ mbar. The sample room is surrounded by a liquid helium, which is used as a cold reservoir, to cool down the sample from room temperature to nearly the temperature of the liquid helium (5 K). Temperatures above 5 K are reached by electric current flows through a wire heater, which is turned around the outer copper-cup (Heating-cup) surrounding the sample room. Two cernox temperature sensors are used to measure the exact sample temperature. The first sensor is glued on the base of the sample holder (Heating cup sensor) and the second is glued near the sample (Sample sensor). A temperature controller of type LakeShore 340 or LakeShore DRC-93CA is used to read the sensors and regulate the temperature. The temperature can be stabilized ($\pm 2$ mK) at any setpoint between 5 K-350 K.

3.1.2 Samples and sample contact

The single crystal samples, which have been investigated in this work, have been prepared by U. Ammerahl, M. Hücke and P. Ribeiro
Figure 3.1: Schematic diagram of the stick and the sample holder. From [25].
3.1 Transport measurements

[53, 54, 55] by using the travelling solvent floating zone method. Before starting the measurements, the samples have been oriented using Laue x-ray diffraction camera and catted into a rectangular shape of typical dimensions of 1-3 mm length, 0.2-0.5 mm thickness and 0.4-1.0 mm width. For the electronic contacts, a thin wire of copper (50 µm) with a two component of silver epoxy glue (Eupo-Tek H20E from Polytec, Waldbromm) were used. With this glue, the contact should be heated for a few minutes at a temperature from 350 °C to 400 °C to obtain a low contact resistances (nearly 1Ω). During this procedure the physical properties of the sample does not change. The installation of the sample in the measuring stick takes place by using an electrically insulating glue (GE-Kitt). There are two different methods to make a contact on the sample for both the electrical resistivity and the thermal conductivity measurements. These methods are two probe method and four probe method. In this work, all the thermal conductivity and electrical resistivity have been performed by the four probe methods.

3.1.3 Electrical resistivity measurement

The electrical resistivity $\rho$ of a sample of uniform cross-section area $A$ and length $l$ is obtained from the equation

$$\frac{V}{I} = \frac{\rho l}{A} \quad (3.1)$$

where $\frac{\rho l}{A}$ is called $R$, the electrical resistance of the sample. $V$ and $I$ are the applied voltage and the applied current, respectively.

3.1.4 Thermal conductivity measurement

According to equation 2.10 the definition of the thermal conductivity can be rewritten in the isotropic case with a thermal current density flow in $x$-direction in the form

$$\dot{j}_q = -\kappa (\nabla T)_x \quad (3.2)$$

where $T$ is the temperature, $\kappa$ is the thermal conductivity and the negative sign indicates that heat flows down a temperature gradient from the hotter ($T_1$) to the colder ($T_o$) regions. In the simplest steady-state method, which is shown in figure 3.2 heat is applied at one end of the sample of a uniform cross-section area $A$ and flow through the sample to the other end. From that point one can calculate the power $P$, which is produced by the heater and consequently produce a thermal current $\dot{j}_q$ flow through the sample

$$\dot{j}_q = \frac{P}{A} \quad (3.3)$$
Figure 3.2: Schematic diagram of the sample holder and the measurements principle. From [25].

A thermocouple is attached at two places along the sample separated by a distance \( l \) and the temperature difference \( \Delta T \) between them is measured. Then the temperature gradient is calculated from

\[
|\langle \nabla T \rangle_x| = \frac{\Delta T}{l}, \quad \Delta T > 0 \tag{3.4}
\]

So, the thermal conductivity is given by

\[
\kappa = \left| \frac{j_q}{\langle \nabla T \rangle_x} \right| = \frac{Pl}{A\Delta T}. \tag{3.5}
\]

Figure 3.2 represents the schematic diagram of the measurement principle. The sample holder is a platform inside the sample room. A handmade heater is used and glowed on the top of the sample to heat it. This heater is made by taking a manganin wire with cross section area of 15 \( \mu \text{m} \) and turn it around a copper rod (0.50 mm). Its resistance is in the range from 300 \( \Omega \) to 1 k\( \Omega \). The heater should have the same size as the sample cross section area. If the current flow through the sample heater and by connecting the thermocouple, so we can measure the temperature beside the sample holder \( T_o \) and beside the sample heater \( T_1 \). The temperature difference \( \Delta T \) between the two contact points can be measured by the thermocouple which made of two different material (Au-0.07 at \% Fe/Cromel -Leico Industries Inc., the wire cross section is 76 \( \mu \text{m} \)). The electrical power \( P \) of the sample heater and the temperature difference \( \Delta T \) proportional to the thermal voltage. The power \( P \) can be calculated from the current flow throw the sample heater \( I_h \) and the voltage drop \( V_h \) at the heater determines. The heater current is supplied by using a constant current source (Keithly 2400) and \( V_h \) is measured.
3.1 Transport measurements

by using multimeter (Keithly 2000 or hp 34401A). The thermal voltage $V_{th}$ of the thermocouple measured by using a nanovoltmeter (Keithly 182 or Keithly 2182). To calculate the temperature difference between the thermocouple contact, the thermopower $S_{th}$ of the thermocouple is need. Finally, to calculate the thermal conductivity, we need to measure the cross-section area of the sample $A$ and the distance between the two contact points of the thermocouple $l$. The cross-section area $A$ and the length $l$ are measured under an optical microscope (Leica MZ8). Then the thermal conductivity $\kappa$ can be calculated from the relation

$$\kappa = \frac{V_h I_h l S_{th}}{A \Delta V_{th}}, \quad (3.6)$$

where $\Delta V_{th}$ is the difference between both the hot and the cold ends of the sample. The temperature from 5 K up to room temperature is measured by a calibrated Cernox-sensor which is fixed on the sample holder near to the sample. The determined thermal conductivity is related to the sample temperature which caused between the two thermocouple contacts $T$, which is depend on the temperature of the sample room $T_o$ as follows

$$T = T_o + (d + \frac{l}{2})(\nabla T)_x. \quad (3.7)$$

Here $d$ is the distance between the sample holder and the thermocouple contact nearest to the sample holder. $T_o$ measured by a cernox temperature sensor, which is glued on the sample holder near the sample.

3.1.5 Experimental errors

Geometry

It is difficult to cut the samples exactly in a rectangular shape. This consequently leads to an uncertainty in the sample geometry. The error to determine the cross-section area $A$ and the distance between the thermocouple contact $l$ of the sample usually amounts to about 10 % of the ratio $l/A$. In bad defined of sample geometry, the uncertainty can become larger up to about 30 % of the absolute value.

Measuring instruments

It is to be mention that, the instruments which used in this work are highly precision. Due to this high precision instruments, experimental errors due to instrumentation are negligible.
Calibration of the thermocouple

The uncertainties in the calibration of the thermocouple give rise to an error less than about 5 percent of the absolute value of the thermal conductivity.

Thermal flow and radiation losses

The produced heat in the sample heater flows in the ideal case exclusively through the sample. Through parasitical effects, the total thermal current through the sample is always lower than that produced by the heater. According to that, the following effects can appear:

- Heat can be transported by molecules in the sample room.
- Heat can be lost through the Thermocouple. This can happen on one hand by direct flow of heat to the colder heat reserve because the thermocouple is also contacted to it. On the other hand the possibility of a thermal short circuit in the sample which leads to flow of heat from one end of the thermocouple to the other.
- The heat can also be lost through the heater supply lines which are confected with the colder heat reserved at temperature $T_o$.
- Both of heater and sample are possessing a higher temperature than the colder heat reservoir and therefore heat is lost by the thermal radiation.

Some of the thermal losses can be minimized. Convection is prevented by maintenance of a high vacuum. The loss of heat through the heater supply and thermocouple can be avoided by using very thin and long wires. Figure 3.3 illustrated the observed geometry. The error in the thermal conductivity due to the radiation losses can be given by

$$\kappa_R = C T_o^4 \frac{l}{A} = 4\sigma_{SB} T_o^4 [(a + b)L\varepsilon_S + F_H \varepsilon_H] \frac{L}{A},$$

(3.8)

where $\sigma_{SB}$, $\varepsilon_S$, $\varepsilon_H$, $F_H$, $A$ and $l$ are Stefan-Boltzmann-constant, the absorption coefficient of the sample, the absorption coefficient of the heater, the heater surface, the area of the sample and the distance between the two thermocouple contacts, respectively. $\kappa_R$ can be minimized by a choice of the appearing parameters

- The absorption coefficients for both of the heater and the sample can be reduced by polishing the sample surface.
The heater surface $F_H$ should be held as small as possible. It can be made however not smaller than the cross-section area $A$ because the heater must cover this area.

The ratio of sample $L/A$ should be selected as small as possible, but $L$ cannot be made smaller than about 0.5 mm. Here one has to calculate with large geometry uncertainties. Also the enlargement of the sample cross-section area is limited because the sample installation will be complicated. Increasing the cross-section area $A$ leads to increasing the surface of the heater. Hence, because of

$$\lim_{A \to \infty} \kappa_R > 4\sigma_{SB}\varepsilon_H T_o^3 L.$$  \hspace{1cm} (3.9)

$k_R$ can be minimized only up to a constant value.
Chapter 4

Material properties

4.1 Doped La$_2$CuO$_4$

4.1.1 Crystal structure

High Temperature Tetragonal phase

At high temperature ($T > 530$ K), La$_2$CuO$_4$ is a tetragonal structure (space group $I4/mmm$), which is called High-Temperature-Tetragonal-phase (HTT). This compound crystallizes in a body-center structure, which first was identified on K$_2$NiF$_4$. The lattice constants of this compound are $a = b \approx 3.8$ Å and $c \approx 13.2$ Å [25]. The crystal structure of La$_2$CuO$_4$ in the HTT-phase is shown in figure 4.1. The copper atoms are surrounded by octahedra of oxygen. Each copper atom has an oxygen above and below in the $c$-direction. The distance Cu-O in $c$-direction is 2.4 Å, which is considerably larger than the Cu-O in the plane (1.9 Å) [54, 56, 57]. In La$_{2-x}$Sr$_x$CuO$_4$ the CuO$_2$ planes are $= 6.6$ Å part, separated by two LaO planes, which form the charge reservoir that captures electrons from the conducting planes upon doping [58].

Low temperature orthorhombic phase

When the temperature is lowered below 500 K, La$_2$CuO$_4$ transforms to a single-face-centered orthorhombic structure (Low Temperature Orthorhombic, LTO) with the space group Abma. In the transition into the LTO-phase, the CuO$_6$-octahedra rotate around an axis within the CuO$_4$-plane in the [110]$_{HTT}$-direction. With this rotation, each two oxygen atoms are displaced above and below in the CuO$_2$-plane.

By doping with Sr instead of La, a few changes occur in the structural composition in comparing with the undoped La$_2$CuO$_4$: The holes brought with the doping posses a strong O-2$p$-Character in the oxygen plane.
(see section 4.1.2). This leads actually to shortening Cu-O-distances and therefore a reduction of the bond lengths do not match with rising Sr content at a steady temperature [56]. This result is a stabilization of the HTT phase, which appears as a reduction of the phase-transition-temperature $T_{HT}$ from HTT to LTO phase. The structural instability in LTO phase in La$_{2-x}$Sr$_x$CuO$_4$ dose not lead also to an additional low-temperature phase transition.

**Low temperature tetragonal phase**

In La$_{2-x}$Sr$_x$CuO$_4$, the partial substitution of small rare earth like Nd or Eu for La induces a further phase transition from the LTO phase into the so called Low-Temperature-Tetragonal phase (LTT). In this phase the CuO$_6$ octahedra tilt along the [100]$_{HTT}$-direction. The transition temperature depends mostly on the Sr and the amount of the rare earth ion. For example, in La$_{1.8-x}$Eu$_{0.2}$Sr$_x$CuO$_4$ $T_{LT} \approx 130$ K. The LTT phase has a space group $P4_2/nmc$.
Chapter 4: Material properties

4.1.2 Electronic properties of La$_{2-x}$Sr$_x$CuO$_4$

The basic electronic, magnetic and structural characteristics of the a$_{2-x}$Sr$_x$CuO$_4$ are explained in the following (see figure 4.2). The undoped La$_2$CuO$_4$ is a three-dimensional antiferromagnetic order ($T_N \approx 325$ K [54]) insulator with an energy gap of $\Delta = 2$eV [59]. In an ionic formula the valences (La$^{3+}$)$_2$Cu$^{2+}$(O$^{2-}$)$_4$ are present. La$^{3+}$ and O$^{2-}$ therefore are in [Xe] - and [Ne] - noble gas configurations, the Cu$^{2+}$ is in a [Ar]$3d^9$ configuration. On each Cu-place, there is a hole in the 3d shell. More exactly this hole is in the 3$d_{x^2-y^2}$ orbital, because the Cu$^{2+}$ ion is induced in a Jahn-Teller tetragonal field. This leads to a local magnetic moment of the Cu$^{2+}$-ions with a Spin $S = 1/2$. The insulating characteristics can be understood in the frame work of a three band model [60]. The 3$d_{x^2-y^2}$ orbital of the Cu ions are viewed to be hybridized with the 2$p_x$ and 2$p_y$ orbital of the neighbors oxygen ion. A further Coulomb repulsion $U$ between the electrons on the same Cu-place leads to a splitting of the

Figure 4.2: Phase diagram of La$_{2-x}$Sr$_x$CuO$_4$, the diagram represented electronic, magnetic and structural characteristics. From [25].
4.1 Doped La$_2$CuO$_4$

Figure 4.3: A schematic representation of the states in La$_{2-x}$Sr$_x$CuO$_4$:
(a) without local Coulomb-repulsion, (b) situation in the charge transfer-insulator with finite Coulomb-repulsion and transfer-energy, (c) hole doped charge transfer-insulator. From [25].

Cu-3d-conduction band, which for $U = 0$ would be half filled and therefore metallic (see figure 4.3(a)). This splitting forms a full and an empty Cu-3d-conduction band (so called Hubbard-bands), which have an energy $U$ between them and consequently they are insulating. In La$_2$CuO$_4$, the Coulomb-energy $U = 8$ eV is clearly larger than the energy gap $\Delta = 2$ eV [61]. The lowest activation energy of electrons in the upper Hubbard band happens below the expended energy $\Delta$ of the O 2$p$-band, which lies between both Hubbard-bands [61, 60]. This situation is illustrated in figure 4.3(b).

The antiferromagnetic correlations between the Cu-spins can be understood by considerations concerning the ground state energy: Proceeding from an insulating state, which correspond to a strict localization of the electrons on the respective Cu-places, its energy can be decreased by slight delocalizations, which means increase of the kinetic energy. Considering now two neighboring Cu-places, hopping of an electron from one place to the next under the assumption of the retention of the spin direction is only possible if the spins of both electrons are antiparallel; due to the Pauli-exclusion, jumping of electrons with parallel spins is impossible [62]. Charge carrier doping in La$_2$CuO$_4$ can be achieved on one side by replacement of the La by Sr or Ba, on the other side by excess of oxygen.
Chapter 4: Material properties

(La$_2$CuO$_{4+\delta}$, $\delta > 0$). The phase diagram of the oxygen doped La$_2$CuO$_4$ is very complicated; especially because from a certain oxygen content there happens a phase separation with ranges of different oxygen concentration and therefore different hole doping. Hence, a detailed discussion of the qualities of the oxygen-doped La$_2$CuO$_4$ may not be abdicate [63, 64]

Spectroscopic analysis [64, 65] prove that concerning the situation of the insulating La$_2$CuO$_4$ described above, Sr-doping generates hole states in the O-2$p$-Band (see figure 4.3(c)). Through hybridization of the four O-2$p$-Orbital surrounding a Cu-ion with the 3$d_{x^2-y^2}$-orbital of the Cu-ion, a hole is distributed among this four O-2$p$-Orbital and generates a local singlet (Zhang-Rice-Singlet [66]). The holes in the CuO$_2$-plane disturb the long range order of the spins, so that with increasing hole content the Ne\'el-temperature decreases very quickly. For a Sr content $x > 0.02$ no more long range order is observed. Instead of this, a spin glass phase with static magnetic order appears at low temperatures ($T < 15K$). It is controversial, if the spin glass phase coexists with the superconductivity phase ($x > 0.06$) [67, 68, 69, 70].

Due to the anisotropic crystal structure the electrical resistivity also is strongly anisotropic: The electrical resistivity measured along the CuO$_2$-plane $\rho_{ab}$ is several orders smaller than the resistivity measured perpendicular $\rho_c$ [71]. As the Sr-doping increases the state density of the Fermi surface, the electrical resistivity also changes significantly: With increasing Sr-content the absolute value of the electrical resistivity $\rho_{ab}$ decreases in the total temperature range - an insulator-metal-transition takes place. At low Sr-content ($\sim 0.01$), the resistivity already shows a metallic behavior at high temperature and a localization behavior is found at low temperature [54, 72, 71]. In the Sr-doping range between 0.06 and 0.25, superconductivity is observed at low temperature. The highest jump temperature to the superconductivity phase is observed for $x = 0.15$ ($T_c = 38K$). Furthermore a local minimum in the temperature dependence of $T_c$ exists near to Sr = 1/8 [73, 74]. At $x > 0.25$, fermi-liquid behavior is observed [59, 71].

The mechanism of the superconductivity is not fully understood yet. The key for an understanding of this phenomenon is assumed to be related to the unusual carrier characteristics of the normal conduction phase. Furthermore, the relevance of antiferromagnetic fluctuations, which are observed in experiments of the inelastic neutron scattering is discussed [75].
4.1 Doped La$_2$CuO$_4$

La$_2$CuO$_4$ is considered as a model system for a 2-dimensional Heisenberg-antiferromagnet (2D-HAF) with spin = 1/2 on a square lattice. Among the CuO$_2$ plane the Cu-spins are coupled with the next neighbours by 180°-Cu-O-Cu super-exchange by a very high exchange constant \( J \approx 1550 \text{ K} \) [76, 77, 78, 79]. Mermin and Wagner theorem excludes a spontaneous magnetic order of one- and two-dimensional isotropic Heisenberg magnets of finite temperatures [81], hence also for the 2D-HAF. However, in the stoichiometric La$_2$CuO$_4$ for \( T_N < 325 \text{K} \) three dimensional antiferromagnetic order is observed [54]. The reason is a finite interplanar coupling, so that the magnetism is not perfectly two dimensional.

4.1.3 Magnetic properties of La$_{2-x}$Sr$_x$CuO$_4$

La$_2$CuO$_4$ is considered as a model system for a 2-dimensional Heisenberg-antiferromagnet (2D-HAF) with spin = 1/2 on a square lattice. Among the CuO$_2$ plane the Cu-spins are coupled with the next neighbours by 180°-Cu-O-Cu super-exchange by a very high exchange constant \( J \approx 1550 \text{ K} \) [76, 77, 78, 79]. Mermin and Wagner theorem excludes a spontaneous magnetic order of one- and two-dimensional isotropic Heisenberg magnets of finite temperatures [81], hence also for the 2D-HAF. However, in the stoichiometric La$_2$CuO$_4$ for \( T_N < 325 \text{K} \) three dimensional antiferromagnetic order is observed [54]. The reason is a finite interplanar coupling, so that the magnetism is not perfectly two dimensional.
However, the interplanar coupling constant $J_\perp$ compared to $J$ is much weaker: $J_\perp/J \approx 10^{-5}$ [82]. One reason for the weak interplanar coupling is due to the special geometric arrangement of the spins - each spin is located centered above or below its four next neighbours-spins in the adjacent planes. This causes a strong frustration of the interplanar exchange, which promotes a magnetic decoupling of the individual planes. Therefore the magnetism in La$_2$CuO$_4$ is quasi-two dimensional. This becomes apparent by the fact, that the spin-spin correlations for $T > T_N$ behave as it is expected for an ideal 2D-HAF: In the figure 4.4 the inverse correlation lengths of the Cu-spins are shown as a function of temperature according to Birgeneau [80]. It is clearly shown, that the spins are still correlated above $T_N$ over a relatively large range. So the correlation length $\xi$ slightly above $T_N$ has a value 400 Å ($\sim$ 100 lattice constants) and at 800 K it is around 15 Å ($\sim$ 4 lattice constants) [54]. The solid line drawn in the figure is the theoretically expected correlation length of the 2D-HAF according to Chakravarty, Halperin and Nelson, respectively Hasenfratz and Niedermayer [83, 84], which correlates almost perfectly with the experimental data (see references [54, 85]). Moreover it is seen, that the structural phase transition from the HTT- to the LTO-phase has no significant effect on the correlation length.

Although till today no exact solution for the ground state $T = 0$ of an ideal 2D-HAF on a square lattice is found, there exists a common consensus about the fact, that the ground state is a long range ordered with finite sublattice magnetization, which respective to the sublattice magnetization of the classical Néel state are reduced up to 40 % due to quantum fluctuations [86]. For the effective magnetic basic state normally it is assumed, that the weak interplanar coupling only insignificantly effects the ground state properties [86]. Spin excitations in La$_2$CuO$_4$ therefore are modelled within the spin wave theory [86, 85, 87] and are in a very good agreement with the measurements of the magnon-dispersion-relation of La$_2$CuO$_4$ by inelastic neutron scattering [79, 88]. Coldea et al. found a perfect correlation between the spin wave fits and the experiment [88]. According to the authors this is only verified, if for the modelling not only the interaction of the next, but also of the next-next neighbours and a ring exchange within a placket of 4 Cu- and O-ions is taken into consideration. Despite of this agreement, the nature of the spin excitations in La$_2$CuO$_4$ is the subject of actual controversy discussions; on one hand the relevance of a higher energetic multi-magnon-continuum is discussed for the interpretation of the experimental data [87, 89], on the other hand alternative approaches than the spin wave theory are taken into consideration. Instead of a Néel ground state, for example Ho et al. assume a so called Resonating Valence Bond state (RVB-state) as ground
4.2 \((\text{Sr, Ca, La})_{14}\text{Cu}_{24}\text{O}_{41}\)

state [90] and refer to the magnetic excitation low dimensional spinons [89].

4.1.4 Zn-doped \(\text{La}_{2-x}\text{Sr}_x\text{Cu}_4\)

In general the influence of a Zn-doping on the structural phases occurring in a \(\text{La}_{2-x}\text{Sr}_x\text{Cu}_4\) is only small[91, 92, 93, 94, 95]: \(\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4\) has a HTT and LTO-modification as well as \(\text{La}_{2-x}\text{Sr}_x\text{Cu}_4\). \(T_{HT}\) increases with increasing Zn-content. The reason for this increase is found in an increasing bond length mismatch [54]. This increase probably depends on the fact that \(\text{Zn}^{2+}\) deforms its surrounding much less than \(\text{Cu}^{2+}\); in contrast to \(\text{Cu}^{2+}\), \(\text{Zn}^{2+}\) is not a Jahn-Teller-Ion.

The magnetic properties for \(\text{Cu}\) of \(\text{La}_{2}\text{Cu}_4\) are also effected by Zn-doping. By partial substitution of the \(\text{Cu}\) with \(\text{Zn}\), instead of \(\text{Cu}^{2+}\)-ions with spin \(S = 1/2\) non-magnetic \(\text{Zn}^{2+}\)-ions ([\(\text{Ar}\)3d10]-configuration) are found. For the magnetism this means a static dilution of the spin lattice, because spins are removed from the lattice. Comparing with the decrease of the Néel temperature \((T_N)\) due to the charge carrier doping in \(\text{La}_{2-x}\text{Sr}_x\text{Cu}_4\), \(T_N\) is decreased significantly slower in \(\text{La}_{2}\text{Cu}_{1-y}\text{Zn}_y\text{O}_4\) with increasing Zn-content. \(T_N\) decreases almost linearly with Zn-content \(y\) [54, 96], where

\[
T_N(z) = T^0_N(1 - z/z_c). \quad (4.1)
\]

Here, \(T^0_N\) is the Néel-temperature of the undoped \(\text{La}_{2}\text{Cu}_4\) and \(z_c \approx 0.33\) is from \(T_N(z)\) with \(z < z_c\) linearly extrapolated for critical Zn-content, which disappears at \(T_N(z)\) [54].

4.2 \((\text{Sr, Ca, La})_{14}\text{Cu}_{24}\text{O}_{41}\)

4.2.1 Crystal structure

The crystal structure of \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) consists of two interpenetrating subcells. One is the \(\text{Sr}\) layer and the \(\text{Cu}_2\text{O}_3\)-layer, two leg Heisenberg-spin ladder with spin \(S = 1/2\). The other layer in this system is \(\text{CuO}_2\)- one dimensional chain. The \(\text{CuO}_2\) contains linear chain of \(\text{Cu}\)-ions, which are linked by a two nearly \(90^\circ\) Cu-O-Cu-bonds. On the other hand, the \(\text{Cu}\)-ions in the subcell \(\text{Cu}_2\text{O}_3\)-ladder are linked by \(180^\circ\) Cu-O-Cu bonds. The layers in both subcells are stacked along the b-axis, whereas the one dimensional chains and the two leg ladders are aligned incommensurably along the c-axis with an average cell of \(7 \times c\) (ladder) and \(10 \times c\) (chain), respectively [10, 18, 97]. Figure 4.5 shows a three dimension view of the
Chapter 4: Material properties

Figure 4.5: Three dimension crystal structure of Sr$_{14}$Cu$_{24}$O$_{41}$ with chains (ketten) and ladders (leitern) subcells along the $c$-axis. From [53].

crystallographic structure of Sr$_{14}$Cu$_{24}$O$_{41}$. The ladder and the Sr-ions together form a subcell with the lattice constants $a \approx 11.3 \, \text{Å}$, $b \approx 12.6 \, \text{Å}$ and $c \approx 3.9 \, \text{Å}$. The chain subcell has the same lattice constants $a$ and $b$, however the lattice constant $c$ is a little bit smaller $c \approx 2.75 \, \text{Å}$. The symmetry of the ladder-subcell is independent of the doping (space group $Fmmm$), while the chain subcell in Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ without La-ion connections, shows a symmetry dependent on temperature and doping (space group $Fmmm$ or $Amma$) [53, 22, 98]. The structure of the chain and the ladder subcells are represented in figure 4.6.

4.2.2 Electric and magnetic properties

In the chemically undoped substance Sr$_{14}$Cu$_{24}$O$_{41}$, the Cu-ions are not only present as Cu$^{2+}$. This can be recognized from the formal valance $(\text{Sr}^{2+})_{14}(\text{Cu}^{2.25+})_{24}(\text{O}^{2-})_{41}$. This means an intrinsic holes doping in Sr$_{14}$Cu$_{24}$O$_{41}$, e. g. the chains and the ladders. These holes are not distributed uniformly among the chains and the ladders: measurements of the optical conductivity [99] and the Near-Edge-X-ray Absorption Fine Structure (NEXAFS) [100] show a hole concentration of about
one hole per unit formula in the ladders at room temperature. At low temperatures, the results obtained from the neutron scattering experiment [21, 22] and thermodynamic studies [53, 101] are consistent with a charge ordered state in the chains. Therefore, the hole concentration in the chains is about 6 holes per formula unit (0.6 holes per Cu place), where the holes and spins in the chains do not form a dimers. The dimers have a singlet-ground state with a spin-gap of about 130 K.

Eccleston et al. have found an anisotropy of the rungs and leg couplings ($J_{\parallel} = 1508$ K, $J_{\perp} = 835$ K) from the neutron scattering data [102], while Matsuda et al. found $J_{\parallel} \approx J_{\perp} \approx 1280$ K in the undoped ladders [103]. This result is qualitative in a good agreement with the results that are obtained from the optical spectroscopy by Windt et al. [104]. However, the authors suggest a much higher coupling constant ($J_{\parallel} \approx J_{\perp} \approx 1550$ K). The Triplet-spin gap $\Delta_{spin}$ in the ladder has been determined by neutron scattering [102] and NMR measurements [23] which, is found to be about 400 K.
4.2.3 Influence of Ca doping

The Sr$^{2+}$-ions isovalent can be replaced by Ca$^{2+}$-ions. Upon partial substitution of Ca for the isovalent Sr, the holes are redistributed from the chains to the ladders. This self-doping leads to a decrease of the electrical resistivity and, eventually, a crossover from insulator behavior in Sr$_{14}$Cu$_{24}$O$_{41}$ to metallic behavior as the carrier concentration is increased [53, 99, 105]. Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ at a very high Ca-content ($x = 12$) becomes superconductive under an application of a high external pressure [17, 106]. The charge order dimer distance of the chains is destabilized and breaks down for $x > 5$ [53, 107, 21, 101, 108]. The charge transfer from the chains to the ladders as a function of the doping is confirmed by the spectroscopic methods at room temperature [99, 109]. However, different values of holes content in the ladders are reported. Nuecker et al. have been found at room temperature that, the ladders increase from 0.8 holes per formula just at $x = 0$ to only 1.1 holes per formula at $x = 12$ [109]. From the NMR investigations, the spin gap $\Delta_{\text{spin}}$ is found to decrease with increasing Ca-content [110, 111, 112]. Neutron scattering experiment however found, that the spin gap of the high Ca-content ($x = 11.5$) has the same value of $\Delta_{\text{spin}}$ as in the undoped compound ($x = 0$).

4.2.4 Influence La doping

The hole content in (Sr,Ca)$_{14-y}$La$_y$Cu$_{24}$O$_{41}$ is reduced by the partial substitution of the bivalent Sr- or Ca-ions by trivalent La. In (Sr,Ca)$_{14-y}$La$_y$Cu$_{24}$O$_{41}$, the ladders as well as the chains approach to a state with hole free spin ladders and chains by more increasing $y$. A completely hole free material would arise at $y = 6$. Already at low La-content ($y \approx 2$) the ladders are almost hole free [109]. The dimer-ground state of the chains, which is present in Sr$_{14}$Cu$_{24}$O$_{41}$ is quickly destroyed. Instead, the chains for $y > 4$ form an antiferromagnet order ground state at low temperature ($T < 12$ K). The spins within the chain are ordered ferromagnetic and neighboring chains are ordered antiferromagnetic [53, 112, 113, 101].

4.2.5 Influence of Zn-doping

In the two leg ladder material Sr(Cu$_{1-x}$ Zn$_x$)$_2$O$_3$, which is physically related to Sr$_{14}$Cu$_{24}$O$_{41}$, Zn-doping destroys the ground state with spin gap of an antiferromagnetic ground state, which possesses a spectrum without energy gap [114, 115, 116]. At low Zn concentrations, there is a transition situation: a (Pseudo-) energy gap of size like that it has been
found in the undoped system can be found. Thus, a very small amount of impurities affects severely the low-temperature properties of the ladder [117]. Therefore, Zn doping Sr$_{14}$Cu$_{24}$O$_{41}$ on the copper site, used to study the magnetic and nonmagnetic stoichiometry of the magnetism in the ladders and chains [53]. Furthermore, Zn atoms are believed to selective substitute the planar Cu without changing the charge doping [118].

### 4.2.6 Two-leg spin ladder

#### Undoped two-leg spin ladder

The Hamilton-operator of the two-leg Heisenberg-spin ladder with spin 1/2 and antiferromagnetic coupling [16] is

$$
\mathcal{H} = J_{\parallel} \sum_{\rightarrow} S_i \cdot S_j + J_{\perp} \sum_{\downarrow} S_i \cdot S_j,
$$

(4.2)

where the coupling constants are positive ($J_{\parallel}, J_{\perp} > 0$) and are separated by summed over from the next neighbours within the rungs ($\rightarrow$) and along the legs ($\downarrow$). The ratio between the leg- and rung-coupling $J_{\parallel}/J_{\perp}$ determines the physical characteristics of the leaders. For the case of $J_{\parallel} = 0$, the system possesses a spin gap. In this situation the spins on each rung form non interacting spin singlets ($S = 0$). In order to break one of this rung singlet and produce a local rung triplet ($S = 1$), the energy $J_{\parallel}$ must be paid. If now a small ladder coupling is switched on ($J_{\parallel} \ll J_{\perp}$, strong coupling), only slight changes occur. The triplets delocalize and an $S = 1$ magnon bond $\hbar \omega(k) \approx J_{\perp} + J_{\parallel}(\cos k)$ emerges. The spin gap is at $k = \pi$ and amounts to $\Delta_{\text{spin}} = \hbar \omega(\pi) \approx J_{\perp} - J_{\parallel}$.

The other extreme $J_{\parallel}/J_{\perp} = 0$ decouples the legs, so that two independent spin chain emerge and the energy spectrum shows no energy gap ($\Delta_{\text{spin}} = 0$). Now a finite rung coupling $J_{\perp} > 0$ is sufficient to generate a spin gap wide increases with increasing $J_{\perp}$ [16]. For any relations $J_{\perp}/J_{\parallel} > 0$, the singlet-ground state is a spin liquid since the spin-spin correlations decrease exponentially as a function of distance. The ground state can be viewed as a singlet-state of the rungs with weak antiferromagnetic correlations in leg direction, where the correlations grow with increasing $J_{\parallel}$. The energy gap and the whole dispersion are shifted to higher energies with rising $J_{\perp}$ (see figure 4.7).

#### Hole doped two-leg ladder

The basic features of a two-leg spin ladder with hole doping can be illustrated in the situation of strong coupling ($J_{\parallel} \ll J_{\perp}$). If one hole is added, equivalent to removing a spin $S = 1/2$, the other spin of the
original singlet becomes free and no longer reduces its energy by singlet formation. If two separated holes are added to the system, each one produces substantial energy damage to the spin background, since both break a singlet (see figure 4.8 a)). If the two holes form a pair on a rung (see figure 4.8 b)), the number damaged spin singlets reduced from two to one [122, 16, 121]. Hence, the magnetic energy of the system repulsion, leads to a natural tendency of hole paring, which certainly costs some energy due to coulomb repulsion. This has lead to the prediction of d-wave superconductivity in such hole doped ladders [16, 123, 122, 124, 125]. Superconductivity was indeed observed in highly Ca-doped Sr$_{14}$Cu$_{24}$O$_{41}$ under presser [17]. Alternatively, a charge order ground state consisting of hole pairs has been predicted. Optical experiments give evidence for a resulting charge density wave in the material [18]. However, it is unclear, whether the charge density wave is located in the chain or ladder substructures.
Figure 4.8: Schematic representation of hole added to the ladder. a) individual holes added to the ladders destroy spin singlets. b) The number of destroyed Singlets can be minimized by adding pairs of holes. From [121]
Chapter 5

Magnon thermal conductivity in low dimension spin system

5.1 La$_2$CuO$_4$- a two-dimensional antiferromagnet

The thermal conductivity of a La$_2$CuO$_4$ single crystal, which represents a model system for the two-dimensional spin-1/2 Heisenberg antiferromagnet on a square lattice recently has been measured by C. Hess et al. [14]. Figure 5.1 represents the thermal conductivity of La$_2$CuO$_4$ parallel to the $ab$-plane $\kappa_{ab}$ and perpendicular to it ($\kappa_c$) as a function of temperature. $\kappa_c$ exhibits a typical temperature dependence of pure phononic thermal conductivity $\kappa_{ph}$. In contrast to this, the low-temperature peak of $\kappa_{ab}$ is followed by a minimum around 80 K and a strong increase of $\kappa_{ab}$, which develops into a broad peak around 300 K, exceeding the low-temperature peak.

Since the material is electrically insulating, the high-temperature peak in $\kappa_{ab}$ can only originate from phononic or magnetic heat transport$^1$. An origin by acoustic phonons has been ruled out by the partial substitution of La by isovalent Eu: Such doping enhances the scattering of the phonons and therefore the phononic thermal conduction should be suppressed. While a suppression is indeed observed for $\kappa_c$, where no high-temperature peak is present, the high-temperature peak in $\kappa_{ab}$ is enhanced. It has been pointed out recently, that also optical phonons contribute to the heat transport in La$_2$CuO$_4$ [129]. However, Eu-doping should also enhance the scattering of the majority of optical phonons.

$^1$In principle, a high-temperature anisotropy of the $\kappa$-tensor could also arise to anisotropic radiative heat transport in the material [126, 127, 128]. However, the optical properties of La$_2$CuO$_4$ are almost isotropic in the relevant energy range $h\nu < 0.1$ eV [59] which rules out such a possibility.
modes, which makes an optical phonon origin unlikely as well. Nevertheless, such can not be ruled out completely, since there exist optical phonon modes which are confined to the CuO$_2$-planes and remain therefore unaffected by Eu-doping. An explanation of the high-temperature peak by heat transport by magnetic excitation is much more convincing. The magnetism is truly two dimensional with strong AF-exchange within the planes and it is not expected to be influenced by Eu-doping since the magnetism remains essentially unchanged. $\kappa_{ab}$ then is to be viewed to consist of a usual phonon background and a magnon contribution $\kappa_{mag}$ while $\kappa_c$ is purely phononic. In figure 5.1, $\kappa_{mag}$ of La$_2$CuO$_4$ was extracted by subtracting $\kappa_{ab,ph}$ (dashed line in figure 5.1) from $\kappa_{ab}$ and represented by the open squares. $\kappa_{ab,ph}$ was achieved by scaling the corresponding data for $\kappa_c$ such as to match its low-temperature peaks with that of $\kappa_{ab}$.

A linearized Boltzmann approach has been used to calculate $\kappa_{mag}$ theoretically. From this theory, the two dimensional (2D) thermal conductivity $\kappa_i$ of a single magnon dispersion branch labelled by $i$ is given by

$$\kappa_i = \frac{1}{2} \left[\frac{1}{(2\pi)^2}\right] \int \nu_k l_k \epsilon_k (d/dT)n_k \, dk,$$  \hspace{1cm} (5.1)
where $v_k$, $l_k$, $\epsilon_k$ and $n_k$ are velocity, mean free path, energy and Bose function of a magnon. The magnetic thermal conductivity $\kappa_{\text{mag}}^i$ of a three-dimensional ensemble of planes as realized in La$_2$CuO$_4$ is given by

$$\kappa_{\text{mag}}^i = \frac{2}{c} \kappa^i,$$

(5.2)

where $c$ is the lattice constant of the La$_2$CuO$_4$ perpendicular to the plane. In order to calculate the $\kappa_{\text{mag}}^i$, the magnon dispersion relation $\epsilon_k$ of the two branches $i = 1, 2$ is approximated with the 2D-isotropic expression

$$\epsilon_k = \sqrt{\Delta_i^2 + (\hbar v_0 k)^2},$$

(5.3)

which describes the dispersion observed experimentally [88] for a small value of $k$. $v_0$ here is the spin wave velocity while the $\Delta_1$ and $\Delta_2$ are the spin gaps of each magnon branch. By defining the characteristic temperature $\Theta_M = (\hbar v_0 \sqrt{\pi})/(ak_B)$, where $a$ is the lattice constant of the CuO$_2$ planes and assuming that the momentum is independent of mean free path, i.e., $l_k \equiv l_{\text{mag}}$, then $\kappa_{\text{mag}}^i$ for each branch is given by

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

(5.4)

Here, the integral is dimensionless but temperature dependent via $x_{0,i} = \Delta_i/(k_B T)$ and $x_{\text{max}}$. The upper boundary $x_{\text{max}}$ can be set to infinity without affecting the fit at temperatures $T < 300$ K. Since from neutron scattering experiments $v_0 \approx 1.287 \times 10^5$ m/s [79] as well as $\Delta_1/k_B = 26$ K and $\Delta_2/k_B = 58$ K [130] are well-known quantities, $l_{\text{mag}}$ is the only unknown parameter in equation 5.4. The above equation (5.4) has been fitted to the experimental data and the fitting curve is represented by a solid line in figure 5.1. A slight deviations between the fitted and the experimental data towards low temperature has been found, which appear due to the uncertainties in $\kappa_{\text{ab,ph}}$. The deviations at high temperature are understood in terms of the temperature dependence of $l_{\text{mag}}$ due to enhanced magnon scattering. The data are consistent with a constant $l_{\text{mag}}$ for temperature within the fit interval and below. This indicates, that magnon-magnon scattering or magnon-phonon scattering in this range is unimportant. Therefore, relevant processes are sample-boundary scattering or scattering at static magnetic defects. The magnon mean free path $l_{\text{mag}}$ is found to be $l_{\text{mag}} \approx 560$ Å. This value is too small to be attributed to scaling on the crystal dimension. Hence, defect scattering is found to be dominant. This was qualitatively and quantitatively verified by comparing the distance of magnetic defects as determined from the defect concentration with the magnetic mean free path $l_{\text{mag}}$. Such defects can
be induced in La$_2$CuO$_4$ by substituting a small amount of Cu$^{2+}$ ions by nonmagnetic Zn$^{2+}$ ions.

As shown in figure 5.2, $\kappa_{mag}$ is decreasing systematically with increasing Zn content as it is expected for the static defects. The solid line in figure 5.2 represents fits according to equation 5.4. The determined $l_{mag}$ is plotted as a function of the reciprocal defect concentration (1/z) in the inset of figure 5.2. As is evidence from the figure, $l_{mag} \approx \frac{1}{z} \times a$. This not only strongly confirms that magnon defect scattering dominates at low temperature, it is also a quantitative corroboration that the high-temperature peak in $\kappa_{ab}$ is indeed of magnetic origin. Moreover, the applicability of the kinetic model is demonstrated by this result. Hence, the magnon thermal conduction in this material can in principle be used to study the interaction of magnetic excitations with other quasiparticles like phonons and holes in the case of La$_{2-x}$Sr$_x$CuO$_4$. 

Figure 5.2: Magnon thermal conductivity $\kappa_{mag}$ of La$_2$Cu$_{1-z}$Zn$_z$O$_4$ ($z = 0, 0.005, 0.008, 0.01, 0.02, 0.05$) as a function of temperature. From [25].
5.2 \((\text{Sr, Ca, La})_{14}\text{Cu}_{24}\text{O}_{41}\)- a S = 1/2 spin ladder material

The up to now best example for one-dimensional magnetic heat transport has been observed in the composite material \((\text{Sr, Ca, La})_{14}\text{Cu}_{24}\text{O}_{41}\). Figure 5.3 shows the thermal conductivity of \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) and \(\text{Ca}_{9}\text{La}_{5}\text{Cu}_{24}\text{O}_{41}\) as a function of temperature, which is measured parallel (\(\kappa_c\)) and perpendicular (\(\kappa_a\) and \(\kappa_b\)) to the chain/ladder direction [11]. \(\kappa_a\) and \(\kappa_b\) of \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) (left part of figure 5.3) exhibit the typical temperature dependence of phonon thermal conductivity, i.e. a pronounced low temperature peak is observed and the thermal conductivity monotonically decreases with further rising temperature (see section 2.3.1). A very clear low temperature peak is present in \(\kappa_c\) as well. However, \(\kappa_c\) increases strongly above \(\approx 40\) K and a second very pronounced maximum of the heat conductivity occurs at \(T \approx 140\) K followed by a sharp decrease. Above 250 K the heat conductivity seems to saturate. Both the very large values of \(\kappa_c\) at intermediate temperature and the strange temperature dependence with the pronounced second maximum differ drastically from the usual phonon heat conduction \(\kappa_{ph}\) [10, 11]. In fact, \(\kappa_c(T)\) re-

Figure 5.3: Thermal conductivity of \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) and \(\text{Ca}_{9}\text{La}_{5}\text{Cu}_{24}\text{O}_{41}\) as a function of temperature. Solid lines represent the estimated phononic background of \(\kappa_c\). From [11].
5.2 \((\text{Sr,Ca,La})_{14}\text{Cu}_{24}\text{O}_{41}\) - a \(S = \frac{1}{2}\) spin ladder material

![Diagram showing magnon thermal conductivities of \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) and \(\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}\) as a function of temperature.](image)

Figure 5.4: Magnon thermal conductivities of \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) and \(\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}\) as a function of temperature [11].

...sembles strongly the temperature dependence of the in-plane thermal conductivity found in \(\text{La}_2\text{CuO}_4\), indicating an also magnetic origin of the intriguing \(\kappa_c\) of the \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\). The right part of figure 5.3 represents the thermal conductivity of \(\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}\) as a function of temperature. At low temperature the thermal heat conductivity of this compound that contains undoped spin ladders and only slightly doped spin chains is much smaller than in stoichiometric \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) for both directions \((a \& c)\). Similar to \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\), \(\kappa_c\) strongly increases above 40 K and stays at a very large value at room temperature. In contrast, \(\kappa_a\) decreases monotonically as the temperature rises and stays very small in the whole temperature range indicative of a strongly suppressed phonon thermal conductivity. The suppression of the low temperature peak in \(\kappa_a\) and \(\kappa_c\) of \(\text{La}_5\text{Ca}_9\text{Cu}_{24}\text{O}_{41}\) upon the substitution of low different ions, i.e. Ca and La, for Sr confirms that \(\kappa_a\) and the low temperature peak in \(\kappa_c\) can indeed be regarded as purely respectively mostly phononic, since the two ions on one lattice site induce scattering of phonons and hence a suppression of \(\kappa_{ph}\). The enhancement of the high-temperature peak in \(\kappa_c\), despite of such doping, clearly shows that the high-temperature contribution is not
of phononic origin. Again, in both compounds electronic contribution can be excluded since the resistivity is too high [10]. Hence, the anomalous $\kappa_c$ is most naturally explained by magnetic heat conduction arising from the low-dimensional magnetic ladder and/or chain structures. In fact, a chain-related origin seems to be very unlikely since the La ions induce strong disorder in the chain subunit and moreover, drastically change the electronic and magnetic properties [113, 131, 132]. Furthermore, the magnetic energy spectrum of the chains is rather flat [22] which excludes significant heat transport from the chains. In contrast, the doping only weakly affects the ladder substructures while the dispersion relation for magnons in the ladders is very steep [102, 133]. It was hence concluded just from quantitative arguments that the high temperature peak in $\kappa_c$ of Sr$_{14}$Cu$_{24}$O$_{41}$ and Ca$_9$La$_5$Cu$_{24}$O$_{41}$ arises due to one-dimensional magnetic heat transport in the ladder subunits of the material [10, 11]. In order to calculate this magnon contribution to the thermal conductivity ($\kappa_{mag}$), the phonon background is estimated using a Debye model at low temperature and subtracted from the measured $\kappa_c$. Figure 5.4 shows the magnon thermal conductivity $\kappa_{mag}$ of both compounds Sr$_{14}$Cu$_{24}$O$_{41}$ and Ca$_9$La$_5$Cu$_{24}$O$_{41}$ as a function of temperature. At low temperature, $\kappa_{mag}$ of both compounds is similar, however, a pronounced differences occur at higher temperature. There $\kappa_{mag}$ of Sr$_{14}$Cu$_{24}$O$_{41}$ has a lower value than Ca$_9$La$_5$Cu$_{24}$O$_{41}$.

A kinetic approach to describe $\kappa_{mag}$ of the ladders starts with the simple expression

$$\kappa_{mag} = \frac{d}{dT} \sum_k v_k \epsilon_k n_k l_k,$$

(5.5)

where $v_k$, $\epsilon_k$ and $l_k$ are the velocity, energy and mean free path of the magnetic excitations. Assuming $l_k \equiv l_{mag}$ and using the distribution function

$$n_k = \frac{3}{3 + e^{\epsilon_k/k_BT}},$$

(5.6)

yields the expression for the magnon heat conductivity

$$\kappa_{mag} = \frac{3}{\pi} \frac{N}{h} \frac{l_{mag}}{k_B T^2} \int_{\Delta_{ladder}}^{\epsilon_{max}} \frac{\exp(\epsilon/k_BT)}{[\exp(\epsilon/k_BT) + 3]^2} \epsilon^2 d\epsilon.$$

(5.7)

where $N$ is the number of ladders and $\epsilon_{max}$ is the band maximum of the spin excitation. At temperature below 300 K, $\kappa_{mag}$ does not depend on $\epsilon_{max} \approx 200$ meV [102, 103]. The exponential increase of $\kappa_{mag}$ at low temperature, implies that this expression can be used to fit experimental data in the corresponding temperature range, with the spin gap $\Delta$ and the mean free path as fit parameters. The fit describes the data very well in the temperature ranges $\approx 40 - 100$ K (Ca$_9$La$_5$Cu$_{24}$O$_{41}$) and $\approx$
5.2 (Sr, Ca, La)$_{14}$Cu$_{24}$O$_{41}$ - a $S = 1/2$ spin ladder material

Figure 5.5: Temperature dependence of the magnon thermal conductivities of Sr$_{14}$Cu$_{24}$O$_{41}$ and Ca$_9$La$_5$Cu$_{24}$O$_{41}$ at low temperature (open circles) in comparison with fit the data using equation 5.7 (solid lines) and fit by a simple activation (dotted lines). From [25].

40 - 80 K (Sr$_{14}$Cu$_{24}$O$_{41}$), respectively (see figure 5.5) The fit yield spin gap values of 396 K (Sr$_{14}$Cu$_{24}$O$_{41}$) and 418 K (Ca$_9$La$_5$Cu$_{24}$O$_{41}$) which are in good agreement with neutron scattering results [102, 134]. In both cases a remarkably large low temperature value for the mean free path of $l_{mag} \approx 3000$ Å is found.

The deviation of the theoretical $\kappa_{mag}$-curve from the experimental data at temperature $T > 100$ K signals a more and more growing importance of scattering processes which reduce $l_{mag}$. The temperature dependence of $l_{mag}$ can be calculated with e.g. 5.7 from the experimental data if a temperature independent gap is assumed$^2$. The resulting $l_{mag}(T)$, calculated with $\Delta$ extracted in the previous step, shows in figure 5.6. At low temperature the plot reflects the high low temperature values of $l_{mag}$ extracted beforehand. In the case of Ca$_9$La$_5$Cu$_{24}$O$_{41}$ $l_{mag}$ shows a plateau at 3000Å for $T < 100$ K and then strongly decreases as temperature rises above 100 K and reduces at room temperature to a still quite

$^2$In principle such deviations could also arise from a temperature dependence of the spin gap. This is, however, rather unlikely and therefore not considered further.
Figure 5.6: Magnon mean free paths of Ca$_9$La$_5$Cu$_{24}$O$_{41}$ (open symbols) and Sr$_{14}$Cu$_{24}$O$_{41}$ (full symbols) as a function of temperature [11].

A large value of about 500Å. $l_{mag}$ of Sr$_{14}$Cu$_{24}$O$_{41}$ already shows a plateau since $l_{mag}$ a heady starts to decrease at temperature $T > 80$ K. The decrease is clearly stronger than in Ca$_9$La$_5$Cu$_{24}$O$_{41}$ since it starts at lower temperature and the reduction of $l_{mag}$ is more profound at room temperature, where $l_{mag} \approx 60$ Å. The different $l_{mag}$ of both compounds at room temperature can straightforwardly be related to the different material properties: while Ca$_9$La$_5$Cu$_{24}$O$_{41}$ contains practically undoped ladders, a considerable hole doping is observed in the ladders of Sr$_{14}$Cu$_{24}$O$_{41}$ [100]. Hence, the strong suppression of $l_{mag}$ in Sr$_{14}$Cu$_{24}$O$_{41}$, indicating much more scattering of magnons than in Ca$_9$La$_5$Cu$_{24}$O$_{41}$, is most naturally related to magnon-hole scattering. At low temperature, however, this is less clear, since $l_{mag}$ of Sr$_{14}$Cu$_{24}$O$_{41}$ increases strongly as the temperature is lowered and reaches exactly the same value as $l_{mag}$ of Ca$_9$La$_5$Cu$_{24}$O$_{41}$. Therefore, if indeed magnon-hole scattering is dominating at high temperatures it becomes completely unimportant at low temperature.

It is the main purpose of this work to further investigate this intriguing observation. One approach to this problem is to modify the hole concentration in the ladders and to observe the resulting changes in $\kappa_{mag}$ and $l_{mag}$. Further, since the quantitative and qualitative analysis of $l_{mag}$ strongly relies on the rather simple kinetic model described
above, a quantitative check of the extracted $l_{mag}$ in a similar way as it has been done in the case of La$_2$CuO$_4$ is essential. This is in particular necessary because Alvarez and Gros following exact diagonalization calculations suggested a mean free path in the Ca$_9$La$_5$Cu$_{24}$O$_{41}$, which is about a factor 17 smaller than found with the kinetic model [6].
Chapter 6

Results

6.1 Sr-doped La$_2$CuO$_4$

6.1.1 Experimental results

In this chapter, the measurement of the thermal conductivity of La$_{2-x}$Sr$_x$CuO$_4$ will be presented and discussed. In order to adjust the stoichiometry of oxygen content for the measurements, the single crystals are tempered before the measurement in argon atmosphere for one day at 900 °C. The stoichiometry of oxygen content was checked by determining the Néel-temperature from susceptibility measurements.

Measurement on polycrystals

Thermal conductivity of La$_{2-x}$Sr$_x$CuO$_4$ with low Sr-contents ($x = 0, 0.011, 0.017$) has been measured on polycrystalline samples [25]. The results are represented in figure 6.1. The thermal conductivity $\kappa$ of the undoped compound qualitatively has the same behavior as $\kappa_{\text{ab}}$ of the single crystal of this stoichiometry [14]. At low temperature, $\kappa$ of the all Sr-contents shows a pure phononic peak. This peak is followed by a minimum around 100 K. With further increasing the temperature, the thermal conductivity $\kappa$ increases and reaches a maximum value at room temperature. Comparison with the data of Sr-doped samples, reveals two features. First, the phononic peak is suppressed with increasing the Sr-content. Second, the high temperature maximum disappears completely with a very small Sr-content of $x = 0.011$. At high temperature still a slight increase can be seen. Since no anisotropic information is contained in these measurements, it is difficult to judge, however, if this increase arises from the magnon thermal conductivity or due to optical contributions to the phonon heat conductivity.
Measurements on single crystals

Therefore, the thermal conductivity has been measured for Sr-doped La$_{2-x}$Sr$_x$CuO$_4$ on a single crystal sample. Figure 6.2 represents the data for $x = 0.01$ measured in the $c$-direction ($\kappa_c$) as well as parallel to the CuO$_2$-plane ($\kappa_{ab}$) as a function of temperature. From the data, $\kappa_c$ has a pure phononic peak at low temperature. $\kappa_c$ decreases with further increasing temperature and then is nearly saturated at high temperature. The thermal conductivity, $\kappa_{ab}$, parallel to the CuO$_2$-plane also shows a pure phononic peak at low temperature. Additional to the mainly phononic heat transport, $\kappa_{ab}$ increases slightly with increasing temperature up to room temperature. The phononic peak value of $\kappa_{ab}$ ($\sim 15$ W/Km) is considerably larger than that of $\kappa_c$ ($\sim 12$ W/Km). It is also evident from this data that the magnetic high temperature peak of $\kappa_{ab}$ at $x = 0$ (inset of figure 6.2) is suppressed strongly with only 1% Sr-doping.
Figure 6.2: Thermal conductivity $\kappa$ of $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$ as a function of temperature with thermal current parallel ($\kappa_{ab}$, open circles) and perpendicular ($\kappa_c$, full circles) to the CuO$_2$-planes. Inset: $\kappa_{ab}$ of the undoped $\text{La}_2\text{CuO}_4$ which is measured by C.Hess [25].

6.1.2 Analysis and Discussion

Low temperatures

As can be seen from the data in figure 6.2, the low temperature phononic peak of $\kappa_c$ is lower than that of $\kappa_{ab}$ unlike $\kappa_c^{\text{max}} > \kappa_{ab}^{\text{max}}$ as normally observed in similar compounds. This suppression of $\kappa_c$ has been attributed to anomalous scattering of phonons on a liquid stripe phase [135]. However, since this is of minor importance for the magnetic heat transport at high temperature, this will not be discussed further.

High temperatures

At high temperatures, $\kappa_c$ shows no increase while $\kappa_{ab}$ increases slightly indicating an additional contribution in this direction. It is difficult to say whether the increase comes from magnon thermal conductivity or due to optical contributions to the phonon heat conduction. The magnon ther-
6.1 Sr-doped La$_2$CuO$_4$

Figure 6.3: Thermal conductivity $\kappa_{ab}$ of La$_{1.99}$Sr$_{0.01}$CuO$_4$ as a function of temperature. Solid line is $\kappa_{ph}$ obtained by $\kappa_c \times 1.31$. Dashed line: $\kappa_{ph}$ as described by the function $\kappa_{ph} = \alpha/T + \beta$, where $\alpha = 490$ and $\beta = 2.8$.

mal conductivity as extracted in the following analysis therefore should only be regarded as an upper bound of possible magnetic contributions to $\kappa_{ab}$

**Separation of the $\kappa_{ph}$ and $\kappa_{mag}$**

Two methods are used to estimate $\kappa_{ph}$ in order to extract the heat conduction due to magnons $\kappa_{mag}$ from $\kappa_{ab}$. Firstly, it is supposed that the temperature dependence of the phonon thermal conductivity can be described for temperatures above the phononic maximum by the function $\kappa_{ph} = \alpha/T + \beta$ where $\alpha$ and $\beta$ are fit parameters. This fit of $\kappa_{ph}$ is shown by the dashed line in figure 6.3. Secondly, it was tried to estimate the phononic part of $\kappa_{ab}$ from the temperature dependence of $\kappa_c$. $\kappa_c$ was multiplied by the factor 1.31 to match the phononic maxima of $\kappa_{ab}$ with the scaled curve of $\kappa_c$. This scaled curve is displayed by the solid line in figure 6.3.

The magnon thermal conductivity $\kappa_{mag}$ is calculated by subtracting $\kappa_{ab,ph}$ from $\kappa_{ab}$. Figure 6.4 shows the magnon thermal conductivity $\kappa_{mag}$. 

![Graph showing thermal conductivity of La$_{1.99}$Sr$_{0.01}$CuO$_4$ as a function of temperature. The graph includes a solid line representing $\kappa_{ph}$ obtained by $\kappa_c \times 1.31$, and a dashed line representing $\kappa_{ph}$ as described by the function $\kappa_{ph} = \alpha/T + \beta$, where $\alpha = 490$ and $\beta = 2.8$. The graph also shows a scaled curve of $\kappa_c$ multiplied by 1.31 to match the phononic maxima of $\kappa_{ab}$ with the phononic maxima of $\kappa_{ab}$.](image-url)
which is calculated by two different ways as a function of temperature. From the figure one can see that both $\kappa_{\text{mag}}$ increase with increasing temperature. $\kappa_{\text{mag}}$ calculated by scaling $\kappa_c$ exhibits a lower value than that calculated by using the function $\kappa_{ph} = \alpha/T + \beta$. Since the slight increase in $\kappa_{ab}$ may also be completely due to optical phonons, we use $\kappa_{\text{mag}} \equiv 0$ and the curve determined with the $1/T$ fit as possible errors of $\kappa_{\text{mag}}$ determined by scaling $\kappa_c$.

The resulting $\kappa_{\text{mag}}$ of La$_{1.99}$Sr$_{0.01}$CuO$_4$ is compared with that of the undoped La$_2$CuO$_4$ and La$_{1.8}$Eu$_{0.2}$CuO$_4$ [25] (see figure 6.5). All curves increase with increasing temperature. La$_2$CuO$_4$ and La$_{1.8}$Eu$_{0.2}$CuO$_4$ have a maximum at room temperature. In the doped compound the maximum of $\kappa_{\text{mag}}$ is apparently strongly suppressed. This suppression is most be explained by strong magnon hole scattering.

Magnon mean free path

Now the magnon mean free path can be calculated from this estimation of $\kappa_{\text{mag}}$ using equation 5.4. The calculated $l_{\text{mag}}$ is represented in figure 6.6.
6.1 Sr-doped La$_2$CuO$_4$

Figure 6.5: Magnon thermal conductivity $\kappa_{mag}$ of La$_{2-x}$Sr$_x$CuO$_4$ ($x = 0, 0.01$) and La$_{1.8}$Eu$_{0.2}$CuO$_4$ as a function of temperature. The undoped La$_2$CuO$_4$ and La$_{1.8}$Eu$_{0.2}$CuO$_4$ have been taken from [25].

Comparing with $l_{mag}$ of La$_2$CuO$_4$, La$_{1.8}$Eu$_{0.2}$CuO$_4$ and La$_{2}$Cu$_{0.99}$Zn$_{0.01}$O$_4$ [25]. It is evident from the figure that for hole free compounds $l_{mag}$ $\approx$ constant at low temperature and then decreases as temperature increases reflecting the $T$-regimes for magnon-defect scattering and scattering on other quasiparticles (magnons, phonons), respectively. $l_{mag}$ of La$_{2-x}$Sr$_x$CuO$_4$ ($x = 0.01$) is much smaller compared to all other cases. The presented cases are weakly decreasing with rising temperature. However, due to the large error in the phonon background the significance of this $T$-dependence is questionable and therefore not discussed further. Nevertheless, the overall magnitude of $l_{mag} \approx 100 - 150$ Å can safely be regarded as an upper bound. Particularly intriguing is the comparison with the $l_{mag} \approx 260$ Å of the Zn-doped material with 1% of static defects instead of mobile ones which are present in the Sr-doped material by the same amount. It has been found previously that $l_{mag} \approx d_{Zn-Zn}$ at low temperature, i.e. in the case of magnon-defect scattering the mean free path is a good measure for the defect distances. $l_{mag} \approx d_{Zn-Zn}$ is clearly not the case if magnon-hole scattering is dominating, since $l_{mag}$ is at least a factor $\sim 2$ smaller. This is consistent with the picture that hole delo-
Figure 6.6: Magnon mean free paths $l_{\text{mag}}$ of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0, 0.01$), $\text{La}_{1.8}\text{Eu}_{0.2}\text{CuO}_4$ and $\text{La}_2\text{Cu}_{0.99}\text{Zn}_{0.01}\text{O}_4$ as a function of temperature. The undoped $\text{La}_2\text{CuO}_4$, $\text{La}_{1.8}\text{Eu}_{0.2}\text{CuO}_4$ and $\text{La}_2\text{Cu}_{0.99}\text{Zn}_{0.01}\text{O}_4$ have been taken from [25].

calize and thereby create distorted areas of the Néel state which extend over several lattice sites, causing a strong scattering of magnons. This is in good qualitative agreement with the decreasing magnetic correlation length seen in neutron scattering experiment [136].

Conclusion

Qualitatively, the strong suppression of the high-$T$ peak in the in-plane thermal conductivity of $\text{La}_2\text{CuO}_4$ upon Sr-doping gives a further confirmation that this peak is indeed of magnetic origin. This doping quite effectively destroys the antiferromagnetic order which is consistent with the disappearance of the magnetic peak. However, in the sample investigated in this work with a doping level of 1% holes the Néel state is still quite robust since $T_N \approx 230$ K. The strong suppression of $\kappa_{\text{mag}}$ therefore indicates that each hole causes a strong distortion of the antiferromagnetic correlation in its vicinity which extends over several lattice
6.2 Spin ladders I – Zn doping

6.2.1 Experimental results

As in La$_2$CuO$_4$, static nonmagnetic defects can be generated by a partial substitution of the Cu-ions with Zn-ions. The influence of these defects on the thermal conductivity of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ has been measured for different Zn-contents ($x = 0, 0.125, 0.25, 0.5, 0.75$). Figure 6.7 represents $\kappa_c$ of the different Zn-doped samples in comparison with the undoped Sr$_{14}$Cu$_{24}$O$_{41}$ [11]. Upon doping Zn-content, the thermal conductivity $\kappa_c$ is gradually suppressed in the whole temperature range and exhibits less pronounced peaks. The magnetic peak broadens and apparatus shifts to higher temperatures.

The high temperature peak is observed only along the $c$-axis and does not exist in the thermal conductivities along the $a$-axis. Figure 6.8
**Chapter 6: Results**

**Figure 6.8:** Thermal conductivity of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ ($x=0.125, 0.25, 0.5, 0.75$) along $c$- and $a$-axes ($\kappa_c, \kappa_a$) represented by full and open circles, respectively, as a function of temperature.

presents the data of $\kappa_a$ and $\kappa_c$ for Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ ($x=0.125, 0.25, 0.5, 0.75$). In all cases, $\kappa_c$ increases after passing the low temperature maximum (the phononic peak) while $\kappa_a$ decreases monotonically with increasing temperature. Hence, magnetic contributions lead also in Zn-doped ladders to a strongly anisotropic $\kappa$-tensor.

### 6.2.2 Analysis and discussion

**First qualitative interpretation**

Qualitatively, the suppression of both phononic and magnetic transport channels of $\kappa_c$ upon doping is a natural consequence of the formed structural and magnetic defects: Different constituents on the same lattice site (Cu and Zn) must induce scattering of phonons. Similarly, the Zn$^{2+}$-ions create non magnetic sites in a $S = 1/2$ spin ladder built by predominantly Cu$^{2+}$-ions. Therefore, the magnetic excitations must scatter on these sites.
6.2 Spin ladders I – Zn doping

Figure 6.9: Estimations of the phonon background for the thermal conductivity of Sr\(_{14}\)Cu\(_{24-x}\)Zn\(_x\)O\(_{41}\) (\(x = 0.125, 0.25, 0.5, 0.75\)) along the c-axis \(\kappa_c\) (solid line represent the phonon background). The uncertainties of the phonon background are shown by dashed line on the representative example of \(x = 0.125\).

**Separation of phonon and magnon thermal conductivity**

The phonon and magnon contributions to the thermal conductivity can be separated by extrapolating the phononic thermal conductivity in the range of the low temperature maximum. The procedure of estimating \(\kappa_{ph}\) is to fit \(\kappa_c\) at temperature \(T < 45\) K with the Debye model [137] and extrapolate this fit towards higher temperatures. In the analysis of \(\kappa_{ph}\) of Sr\(_{14}\)Cu\(_{24-x}\)Zn\(_x\)O\(_{41}\), the further constraint is put that all fit parameters except phonon-defect scattering should be identical for all compounds. We use the expression 2.33 which is discussed in chapter 2

\[
\kappa_{ph} = \frac{k_B}{2\pi^2 \nu} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \frac{\tau_c x^4 e^x}{(e^x - 1)^2} dx
\]  

(6.1)

with the scattering rate

\[
\tau_c^{-1} = \frac{\nu}{L} + BT\omega^3 \exp\left(-\frac{\Theta_D}{\alpha T}\right) + C\omega^4,
\]  

(6.2)
Figure 6.10: $\kappa_{\text{mag}}$ of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ ($x = 0.125, 0.25, 0.5, 0.75$) as a function of temperature. The gray shaded area displays the experimental uncertainty resulting from the uncertainty of $\kappa_{\text{ph}}$ for the representative case $x = 0.125$.

where $\omega$, $\Theta_D$ and $v$ are the Debye frequency, Debye temperature and mean phonon velocity, respectively. $L$, $B$, $\alpha$ and $C$ are free fit parameters. The results of $\kappa_{\text{ph}}$ are shown in figure 6.9 as solid lines. Such an extrapolation of $\kappa_{\text{ph}}$ certainly comes along with some uncertainties. These uncertainties are taken into account by estimating positive and negative deviations from $\kappa_{\text{ph}}$. An example of these deviations is shown by dashed lines in figure 6.9 for $x = 0.125$.

Magnon thermal conductivity $\kappa_{\text{mag}}$

From the above analysis, $\kappa_{\text{mag}}$ can be calculated by subtracting $\kappa_{\text{ph}}$ from $\kappa_c$: $\kappa_{\text{mag}} = \kappa_c - \kappa_{\text{ph}}$. The obtained results for $\kappa_{\text{mag}}$ of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ ($x = 0.125, 0.25, 0.5, 0.75$) are displayed in figure 6.10. From the figure one can see that the magnon peak is systematically suppressed with increasing Zn-content. $\kappa_{\text{mag}}$ for $x = 0.125$ and $x = 0.25$ firstly increases with increasing temperature and then shows a maximum around $\sim 200$ K. With further heating $\kappa_{\text{mag}}$ decreases. For $x = 0.5$ and $x = 0.75$, $\kappa_{\text{mag}}$ increases monotonically with increasing temperature up to 300 K with-
out an obvious maximum. The magnon peak which is observed at high temperature is shifted to higher temperature upon increasing Zn-content and seems to disappear at $x = 0.5$ and $x = 0.75$.

The static non-magnetic defects, which are generated in $\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}$ by Zn-ions in the ladders cause a systematic reduction of the magnon thermal conductivity as illustrated in figure 6.10. The peak-like shape apparent in the curves at $x = 0.125$ and $x = 0.25$ is typical for temperature-dependence of the thermal conductivity of a system with a moderate number of impurities. At low temperature, where the scattering rates are only weakly temperature dependent, the strong increase of the quasiparticle number generates an increasing thermal conductivity. At high temperature the rate of scattering increases strongly with rising temperature and hence the thermal conductivity decreases. The relevant scattering processes for $\kappa_{\text{mag}}$ of the undoped compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ are scattering on defects at low temperatures and magnon-hole scattering at high temperatures [12, 25]. In the case of slightly doped samples with Zn-concentration $< 3\%$, it is reasonable to assume that this situation is in principle preserved, but with the particularity that the defects relevant for the magnon scattering are mainly defined by the Zn-dopants. $\kappa_{\text{mag}}$ evolves accordingly upon doping since the peak-like structure decreases and eventually vanishes at $x \geq 0.5$. The monotonic increase of $\kappa_{\text{mag}}$ in this doping range indicates that the scattering at the Zn-induced defects more and more dominates even at more elevated temperature.

**Magnon mean free path $l_{\text{mag}}$**

We will now analyse $\kappa_{\text{mag}}$ quantitatively (see section 5.2) to extract information about the mean free path $l_{\text{mag}}$. The analysis is based on the kinetic description of the heat transport in the spin ladders [11, 138],

$$
\kappa_{\text{mag}} = \frac{3Nl_{\text{mag}}}{\pi \hbar k_B T^2} \int_{\Delta_{\text{ladder}}}^{\epsilon_{\text{max}}} \frac{\exp(\epsilon/k_BT)}{(\exp(\epsilon/k_BT) + 3)^2} \epsilon^2 d\epsilon.
$$

(6.3)

Since the spin gap $\Delta_{\text{ladder}} = 396$ K of undoped $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ [11] is not likely to change upon the Zn-doping [139, 116] $^1$, $l_{\text{mag}}$ can directly be calculated from the $\kappa_{\text{mag}}$ data.

The data of the calculated $l_{\text{mag}}$ is presented in figure 6.11. From the figure, one can see that $l_{\text{mag}}$ decreases with rising temperature as $l_{\text{mag}}$ of the undoped compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ does [11]. This decrease becomes

$^1$It has been reported that in the spin ladder system $\text{SrCu}_2\text{O}_3$ Zn-impurities lead to magnetic order and low energetic magnetic excitations at low temperatures if the Zn-concentration with respect to Cu exceeds $\sim 1\%$. 


weaker with increasing the Zn-content. In particular, $l_{mag}$ at low temperature is strongly suppressed with increasing doping.

In order to analyse $l_{mag}$ in more detail it is necessary to anticipate the temperature dependence of magnon-hole scattering in pure Sr$_{14}$Cu$_{24}$O$_{41}$ (cf. section 6.3), which is closely related to a charge ordering transition at $T_{CO} \approx 240$ K. At temperature below about 100 K, i.e., deep in the charge ordered state, magnon hole scattering is not substantial. It becomes more and more dominating at higher temperatures and unfurls its full strength at temperature above about 240 K, i.e., above the charge ordering temperature. Thereby $l_{mag}$ in Sr$_{14}$Cu$_{24}$O$_{41}$ reduces from $l_0 \approx 3000$ Å at temperature $T < 100$ K down to about 60 Å at 300 K.

As will be shown in section 6.3, following Matthiesen’s rule it is possible in Sr$_{14}$Cu$_{24}$O$_{41}$ to separate

$$l_{mag}^{-1} = l_0^{-1} + l_h^{-1}$$

into contributions due to scattering on static defects, $l_0$, and on mobile holes, $l_h$. The observed reduction of magnon mean free path upon Zn-doping is indeed consistent with a more and more reduced scattering on
6.2 Spin ladders I – Zn doping

Figure 6.12: The estimated magnon mean free path $l_{\text{mag}}^*$ of $\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}$ ($x = 0.125, 0.25, 0.5, 0.75$) as a function of temperature. The dashed lines represent the mean distance of the Zn-ions in the ladders. The hole mean free path of $x = 0$ is shown in the inset (taken from [25]).

the static defects $l_0$ due to scattering of magnons on Zn-ions and only slight change of $l_h$. In order to illustrate this, the mean free path of the Zn-doped samples can be estimated under simplified conditions. We assume that the Zn-ions distribute equally between chains and ladders. $d_{\text{Zn-Zn}}$ is then the mean distance of the Zn ions within one ladder, i.e., we consider the probability of running into a Zn-ion when we go along the ladder from one rung to the next: This is just the Zn-concentration with respect to all Cu-sites times two since there are two Cu-sites on each rung: $P = x/12$. The mean distance is then simply the distance between the rungs $c = 3.9 \\text{Å}$ divided by the probability $P$, hence, $d_{\text{Zn-Zn}} = 3.9 \\text{Å}^* 12/x$. Also we assume that $l_o = d_{\text{Zn-Zn}}$ and $l_h$ is the same as in the undoped material $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (cf. inset of figure 6.12), hence

$$l_{\text{mag}}^{* - 1} = d_{\text{Zn-Zn}}^{-1} + l_h^{-1}. \quad (6.5)$$

From the above equation, the magnon mean free path can be estimated theoretically. The results of $l_{\text{mag}}^*$ are shown in figure 6.12.
Figure 6.13: $l_{\text{mag}}$ of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ as a function of $d_{\text{Zn-Zn}}$. Solid line: fit line through origin. The error bars arise due to uncertainties in the determining $\kappa_{\text{ph}}$ and have been obtained by using different estimation for $\kappa_{\text{ph}}$ (figure 6.9 and figure 6.11).

For temperature $T > 100$ K there is a similarity in both magnitude and temperature dependence between the results of the experimental $l_{\text{mag}}$ and the estimated $l_{\text{mag}}^*$. $l_{\text{mag}}$ which is shown in figure 6.11 is subject to unavoidable uncertainties at temperature less than about 100 K since the ratio $\kappa_{\text{mag}}/\kappa_{\text{ph}}$ is small and hence in this temperature range errors in the estimation of $\kappa_{\text{ph}}$ have large effects on the estimations of $\kappa_{\text{mag}}$ and $l_{\text{mag}}$.

A reliable determination of the experimental $l_{\text{mag}}$ can therefore only be expected at higher temperature. However, at $T \approx 100$ K such errors become reasonably small and $l_{\text{mag}} \approx d_{\text{Zn-Zn}}$ should hold. At temperature $T \approx 100$ K the $l_{\text{mag}}^*$ in figure 6.5 have almost reached their low temperature values $l_0 = d_{\text{Zn-Zn}}$, as is indicated by dotted lines. Therefore, the experimental $l_{\text{mag}}$ is tested for such a linear scaling at this temperature. Figure 6.13 shows $l_{\text{mag}}$ of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ as a function of $d_{\text{Zn-Zn}}$ at 100 K. As is evident from the figure, $l_{\text{mag}}$ scales almost perfectly with $d_{\text{Zn-Zn}}$ and a linear fit to the data points yields a slope 1.33, which is very close to unity. Hence, the kinetic model yields values for $l_{\text{mag}}$ which correspond well to the defect distances.
Figure 6.14: Electrical resistivity $\rho$ of $\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}$ ($x = 0, 0.125, 0.25, 0.5, 0.75$) as a function of temperature. Left: $\rho_c$ which is measured along $c$-axis. Right: $\rho_a$ which is measured along $a$-axis. Inset: The logarithmic derivative of $\rho_c$.

**Destruction of the charge ordering state**

The strict comparison of figure 6.11 and 6.12 reveals also some differences at high temperature. While $l_{\text{mag}}$ shows a very distinct change near the charge ordering temperature $T_{\text{CO}} \approx 240$ K, i.e. with rising temperature $l_{\text{mag}}$ strongly decreases and passes an inflection point, such is only very clear in $l_{\text{mag}}$ at $x = 0.125$. At the higher doping level $x = 0.25$ this signature of the charge ordering is already very weak and eventually disappears completely for $x = 0.5$ and $x = 0.75$, where $l_{\text{mag}}$ almost linearly decreases as the temperature is raised from 100 K to 300 K. In order to study the influence of Zn-doping on the charge order more directly, the electrical resistivity of the material has been measured along the $c$- and $a$-axes as shown in figure 6.14. Two unexpected observations are made in the temperature and doping dependence of $\rho_c$ (see left panel of figure 6.14). Firstly, $\rho_c$ decreases with increasing Zn-content, i.e. the electrical transport is enhanced. This is not only in stark contrast to the general expectation that impurities increase scattering and hence increase the resistivity. It is also just the opposite to the effect of Zn-doping of the closely related $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, where a strong increase of the resistivity is
found [91, 94, 140]. Secondly, the charge order anomalies in the resistivity are strongly suppressed upon Zn-doping. At \( x = 0 \) the pronounced increase of slope which occurs in \( \rho_c \) at \( T \approx 220 \text{K} \) clearly indicates the onset of charge ordering at lower temperature. This feature becomes gradually weaker as Zn is doped into the material. This is most clearly seen in the inset of figure 6.14, where the logarithmic derivatives \( \delta_{c,s} = \frac{d}{d(1/T)} \ln \rho_c \) of the Zn-doped material are shown. The pronounced peak at \( \sim 220 \text{K} \) found in \( \delta_c \) at \( x = 0 \) clearly makes the onset of charge order. As is evident from the figure, this peak is more and more suppressed as Zn is doped into the compound and eventually is almost completely suppressed at a Zn-content \( x = 0.75 \).

Similar is found in the resistivity along the \( a \)-axis (see right panel of figure 6.14). However, apparently the Zn-doping influences \( \rho_a \) only in the charge ordered state since \( \rho_a \) (300 K) is the same for all Zn-contents and clear differences between the curves only evolve below the charge ordering transition.

It is very apparent from this observation that the charge ordered state is gradually destroyed as Zn is doped into the system. Since \( \ell_h \), i.e. the magnon-hole scattering component of \( l_{\text{mag}} \) is strongly affected by the charge ordering (see in details section 6.3), the discrepancies between \( l_{\text{mag}} \) and \( l_{\text{mag}}^* \) at higher temperature have to be related directly to this fact. This is particularly evident at the higher doping levels \( x = 0.5 \) and \( x = 0.75 \), where \( l_{\text{mag}} \) only slightly and constantly increases as the temperature is lowered from 300 K to \( \sim 100 \text{K} \). This only weak temperature dependence indicates that \( \ell_h \) in these cases is only weakly temperature dependent as well. It should be noted, however, that due to the small \( d_{\text{Zn-Zn}} \) at these high doping levels the temperature dependence of \( \ell_h \) only faintly affects the total \( l_{\text{mag}} \).

**Conclusion**

The development of \( \kappa_{\text{mag}} \) on Zn-doping investigated above is consistent with the general expectation that magnetic defects as induced by the Zn-ions lead to a reduction of the magnetic heat transport. It is remarkable, that apparently the kinetic model yields a reasonable order of magnitude for the defect distances if it is assumed that magnons are strongly scattered on these. In fact, this strongly corroborates that the simple kinetic model to describe \( \kappa_{\text{mag}} \) of the spin ladders is indeed a valuable analytic tool. It is natural to conclude that the model works well not only for Zn-doped materials discussed above but as well for \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) and \( \text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41} \), where it yields the aforementioned surprising high values of \( l_{\text{mag}} \approx 3000 \text{Å} \) at low temperature. It is mentioned that this is in strong contrast to the result from Alvarez and Gros [6] who found
a much lower $l_{\text{mag}}$ for Ca$_9$La$_5$Cu$_{24}$O$_{41}$ based on exact diagonalization calculations of the thermal Drude weight.

6.3 Spin ladders II – Ca doped Sr$_{14}$Cu$_{24}$O$_{41}$ ($x \leq 5$)

We now turn to the investigation of the importance of magnon-hole scattering in (Sr, Ca, La)$_{14}$Cu$_{24}$O$_{41}$ by influencing the hole content in the ladders via Ca-doping as proposed in the previous chapter.

6.3.1 Experimental results

In a figure 6.15 we present the $T$-dependence of the thermal conductivity parallel ($\kappa_c$) and perpendicular ($\kappa_a$, $\kappa_b$) to the ladders of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ ($x = 0, 2, 3, 4, 5$). The signature of the one-dimensional magnetic heat transport, i.e., the huge magnon peak at high temperature is most evident for $x = 0$. Similar magnon peaks are also observed for the Ca-doped materials with $x \leq 3$. It is, however, evident that with increasing $x$ the peak shifts gradually towards lower $T$ and its maximum strongly decreases. It is eventually absent completely for $x = 4$ and $x = 5$. Nevertheless, there is a pronounced anisotropy between $\kappa_a$ and $\kappa_c$ also at this higher doping level: for $T > 20$ K $\kappa_a$ monotonically decreases whereas $\kappa_c$ exhibits a minimum around 100 K and increases with further rising $T$, exceeding the phononic $\kappa_a$ by up to a factor of five at room temperature. We thus conclude that magnon heat conduction still contributes significantly to $\kappa_c$ also in these cases [12].

Due to the large spin gap [102, 134] the magnon thermal conductivity $\kappa_{\text{mag}}$ is negligible below $T < 40$ K [11]. This can be used to separate the phonon and magnon contributions. As before $\kappa_c$ has been fitted for $T < 40$ K with the usual model [137] and this fit has been extrapolated up to $T = 300$ K in order to obtain the phonon thermal conductivity $\kappa_{\text{ph}}$ (solid lines in figure 6.15). Subtraction of $\kappa_{\text{ph}}$ from $\kappa_c$ yields $\kappa_{\text{mag}}$ which is shown in the top panel of figure 6.16.

Prior to discussing the effect of Ca-doping on $\kappa_{\text{mag}}$ we briefly recall the differences between $\kappa_{\text{mag}}$ of Sr$_{14}$Cu$_{24}$O$_{41}$ with a finite hole content in the ladders and $\kappa_{\text{mag}}$ of La$_5$Ca$_9$Cu$_{24}$O$_{41}$, which contains undoped ladders (see figure 6.16, top panel). The apparent strong suppression of $\kappa_{\text{mag}}$ in Sr$_{14}$Cu$_{24}$O$_{41}$ at high temperatures must be related to scattering of the magnons on holes, since structural defects due to different ions on the Sr-site are known to not influence $\kappa_{\text{mag}}$ and therefore the hole doping is the only difference with respect to the undoped ladders. Since both $\kappa_{\text{mag}}$
Figure 6.15: $\kappa_c (\bullet)$ and $\kappa_a (\circ)$ of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ ($x = 0, 2, 3, 4, 5$) as a function of temperature. Solid lines represent the estimated phononic background of $\kappa_c$. For $x = 0$ also $\kappa$ along the $b$-axis is shown (open square). From [138].
6.3 Spin ladders II – Ca doping ($x \leq 5$)

Figure 6.16: Top: $\kappa_{\text{mag}}(T)$ of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ ($x = 0, 2, 3, 4, 5$) and of La$_5$Ca$_9$Cu$_{24}$O$_{41}$. Inset: enlarged representation for $x = 3, 4, 5$. Bottom: $l_h(T)$ for $x = 0, 2, 3, 4, 5$. The effect of possible errors in $l_0$ (cf. text) is shown as an example for $x = 3$ by the shaded area. Inset: doping dependence of $l_h$ at 300 K. The error bars arise due to an estimated error of 50% for the phonon background. The solid line represents the mean hole distance as calculated from Ref. [109]. From [138].

curves are almost identical below $T_0 \approx 100$ K, this scattering mechanism obviously becomes completely unimportant below $T_0$ and unfurls its full strength above a characteristic temperature $T^* \approx 240$ K. The comparison with $\kappa_{\text{mag}}$ of the Ca-doped samples (see figure 6.16, top panel) reveals that $T_0$ and $T^*$ are gradually shifted towards lower $T$; i.e., the temperature region where $\kappa_{\text{mag}}$ is suppressed extends and magnon-hole-scattering also becomes important at low $T$. Apparently, at $x = 4, 5$ this region becomes so wide that even the peak at low $T$ is suppressed.
6.3.2 Analysis and Discussion

In order to elucidate the origin of this interesting observation $\kappa_{mag}$ of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ has been analyzed and the temperature dependence of $l_{mag}$ has been calculated with the kinetic model discussed in the previous sections. Firstly, $\kappa_{mag}$ is fitted at low $T$ with equation 5.7, yielding the spin gap $\Delta_{\text{ladder}}$ and $l_0$, i.e., the low-$T$ value of $l_{mag}$ which is assumed to be constant in the fitting range (cf. section 5.2). $l_{mag} = l_0$ arises when scattering on quasiparticles freezes out and magnon-defect scattering dominates. Again, the second step of the analysis comprises the calculation of $l_{mag}(T)$ by comparing experimental and theoretical data of $\kappa_{mag}$ using equation 5.4 with a known value for $\Delta_{\text{ladder}}$. Due to the strong suppression of $\kappa_{mag}$ in the higher Ca-levels, such a determination of $\Delta_{\text{ladder}}$ and $l_0$ is only reasonable for $x \leq 2$. Therefore, we use $\Delta_{\text{ladder}}/k_B = 377$ K as known from neutron scattering [102, 134] for the calculation of $l_{mag}(T)$ for $x \geq 3$.

In order to separate scattering effects due to holes from the total $l_{mag}$ we apply Matthiesen’s rule $1/l_{mag} = 1/l_0 + 1/l_h$, where $l_h$ denotes the hole-scattering part of $l_{mag}$ and is a measure for the importance of magnon-hole scattering. $l_h$ is related to the mean distance of holes $d_h$ via the effective scattering probability $\gamma_h$ by $l_h = d_h/\gamma_h$. While $l_0$ is known from fits of the low-$T$ increase of $\kappa_{mag}$ for $x \leq 2$ [25], $l_0 = 3000 \pm 1000$ Å has been assumed.\(^2\)

$l_h(T)$ of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ is depicted in the bottom panel of figure 6.16. Obviously, $l_h$ systematically decreases with increasing Ca-content which is strong evidence for the growing importance of magnon-hole scattering upon Ca-doping, i.e., with increasing hole content in the ladders. All curves also decrease with rising $T$ and saturate around 50-80 Å, which is of the same order of magnitude as the mean distance of holes $d_h \approx 30$ Å [109] (cf. inset of figure 6.16). At room temperature magnons appear to be strongly scattered on holes with a scattering probability $\gamma_h = d_h/l_h = 0.5 - 1$, which is also consistent with the pronounced suppression of $\kappa_{mag}$ above $T^*$. Note that in this high-$T$ range the uncertainty in $\kappa_{ph}$ leads to a relative error in $l_h$ of about 50% which explains the apparent non systematic high-$T$ behavior of $l_h$.

It is possible to read off the characteristic temperature $T^*$ from these curves for $x \leq 3$, since it separates an almost constant high-$T$ behavior from a steep $T$-dependence at low $T$. This $T$-dependence is clearly correlated with the electrical resistivity $\rho$ as is evident from our measurements along the $c$- and $a$-axes ($\rho_c$ and $\rho_a$) depicted in figure 6.17. For

\(^2\)We emphasize that $l_{mag}$ strongly decreases with growing $T$ and therefore the large estimated error $\Delta l_0 = 1000$ Å significantly affects $l_h$ only at low $T$ (cf. figure 6.16), playing no role in the following analysis.
6.3 Spin ladders II – Ca doping (x ≤ 5)

Figure 6.17: Temperature dependence of the electrical resistivity along the ladders \( \rho_c \) (left) and perpendicular \( \rho_a \) (right) of \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41} \) \( (x = 0, 2, 3, 4, 5, 6, 8, 9, 11, 12) \).

For \( x ≤ 2 \) the highly similar \( T \)-dependence of \( \rho \) and \( l_h \) is apparent. In order to show this correlation of \( l_h \) and \( \rho \) also for higher doping levels \( (x ≤ 5) \), we compare in figure 6.18 the logarithmic derivatives of \( l_h \) and \( \rho_c \), i.e., \( \delta_h = \frac{d}{d(1/T)} \ln l_h \) (open circles) and \( \delta_e = \frac{d}{d(1/T)} \ln \rho_c \) (full circles).\(^3\) As is obvious from the figure, \( \delta_h \) and \( \delta_e \) exhibit a very similar \( T \)-dependence for all \( x \). This proves unambiguously that the magnon heat transport and the electric transport are closely linked to each other and that charge degrees of freedom are by far the strongest scatterers of spin excitations. Since the peaks in \( \delta_e \) are signatures of the charge ordering in this material [131], the freezing-out of magnon-hole scattering has to be attributed to the formation of this charge ordered state.

It is however very surprising that this scattering channel vanishes completely in the charge ordered state. In the framework of our model there are two possible scenarios to interpret this intriguing finding. Since \( \kappa_{\text{mag}} \) selectively probes the magnetic excitations in the ladders, either the relevant hole concentration in the ladders decreases drastically below

\(^3\)Note that by this choice of derivatives it is not intended to imply any conclusions about activated transport in the material. However, with respect to other representations which similarly show the correlations between \( \rho \) and \( l_h \), the signatures of charge order are most clearly visible with this choice.
Chapter 6: Results

Figure 6.18: Temperature dependence of $\delta_h$ ($\circ$) and $\delta_e$ ($\bullet$) in Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ ($x = 0, 2, 3, 4, 5$).

$T^*$, or the scattering probability $\gamma_h$ vanishes upon charge ordering in the ladders.

The first scenario seems to be supported by a recent $^{17}$O-NMR study [141]. A strong change of the electrical field gradient is observed below $T^*$ which the authors interpret in terms of a complete transfer of holes from the ladders to the chains below $T^*$. This interpretation, however, is not supported by preliminary x-ray absorption spectroscopy (XAS) data on these compounds [142], which clearly show that the spectra of the charge ordered state differ drastically from the spectra of undoped ladders. The XAS data do indeed exhibit some clear cut changes at $T^*$; however, the change of the hole distribution between ladders and chains as signalled by these data is only subtle, if present at all.

The second scenario, i.e., the reduction of the scattering probability at constant hole content, is reasonable if the charge order is connected with a periodic modulation of the spin density. Though possible, it seems unlikely that the periodic arrangement of the holes is the only reason for the strong suppression of scattering. In order to be compatible with the large $\kappa_{mag}$ and $l_{mag}$ at low temperature the charge order would have to be perfect on a unrealistically large lengthsacle with a correlation length $\xi > l_0$. 
Further studies are necessary to clarify the origin of the drastic change of $l_{\text{mag}}$ at $T^*$. For example, one might speculate that hole pair formation and/or a change of the orbital character of the ladder’s hole states, as could be signalled by the NMR and XAS data, play a relevant role in the magnetic heat transport. Besides these uncertainties, however, there are also clear-cut conclusions to be made from our data. Firstly, charge ordering is indeed present in the ladders of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$. This charge ordering is strongly linked to magnetic degrees of freedom. Finally, measuring the magnon heat transport is a valuable tool to study the interaction of charge and spin degrees of freedom.

### 6.4 Spin ladders II – Ca doped $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ ($x \geq 5$)

#### 6.4.1 Experimental results

Figure 6.19 presents $\kappa_a$ and $\kappa_c$ of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ for the doping levels $x = 6, 8, 9, 11$ and 12. Unlike the strong doping dependence observed at low doping levels, the development of $\kappa_a$ and $\kappa_c$ upon doping is more subtle in this doping regime. As revealed by figure 6.19, some high temperature anisotropy between $\kappa_a$ and $\kappa_c$ persists also here: While $\kappa_a$ in all cases exhibits a typical phononic $T$-dependence with $\kappa_c$ monotonically decreasing at $T > 20$ K, $\kappa_c$ is roughly constant ($x = 11$), exhibits a second peak ($x = 8$) or monotonically increases ($x = 6, 9, 12$) with rising temperature. Hence, it is also for these cases concluded that magnetic heat conduction plays a significant role in the high-$T$ behavior of $\kappa_c$. According to the Wiedemann-Franz law based on the resistivity data in figure 6.17, electronic contributions are very small and only become significant in $\kappa_c$ at $x = 12$, where they are smaller than $0.8 \text{ Wm}^{-1}\text{K}^{-1}$.

#### 6.4.2 Discussion

Figure 6.20 shows $\kappa_c$ of the complete series with each curve shifted with respect to the others for clarity. In this representation it becomes apparent that the high temperature increase of $\kappa_c$ only varies rather weakly when the Ca-doping is changed. Much more pronounced changes concern the phononic low temperature peak. While this peak is well developed for $x = 6$ and $x = 8$ it appears slightly less pronounced at $x = 9$ and is almost not present for $x \geq 11$. In principle, two qualitative different situations could result in such a behavior. Firstly, one of the possible contributions to $\kappa_c$ could develop more weight between 50 and 100 K. This appears to be supported by the particular shape of $\kappa_c$ at $x = 12$.
Figure 6.19: Thermal conductivity of \( \text{Sr}_{14-x} \text{Ca}_x \text{Cu}_{24} \text{O}_{41} \) \( (x = 6, 8, 9, 11, 12) \) along c- and a-axes denoted by solid \( (\kappa_c) \) and open \( (\kappa_a) \) circles, respectively, as a function of temperature. The solid lines represent the estimated phononic background of \( \kappa_c \) at the low temperature maximum. The thermal conductivity \( \kappa_{c-el} \) for \( x = 12 \) after subtract the electronic contributions is represented by the open square.
in this temperature region. In fact, the electronic contributions revealed by the Wiedemann-Franz law are largest in this temperature region (cf. Open square in figure 6.19 and solid line adept to the plot in figure 6.20). Secondly, the disappearance of the phonon peak could be related to a suppression of $\kappa_{\text{ph}}$ in the vicinity of the peak. In order to investigate this we plot in figure 6.21 the maximum value of $\kappa_c$ in the peak as a function of doping. As becomes clear from the plot, this value depends only weakly of the Ca content and slightly decreases with increasing $x$. This is just opposite to the expectation of a growing phonon peak with increasing Ca-content at least for $x \geq 7$ since the number of impurities, i.e., the amount of Sr on the Ca-site (related to a hypothetical parent compound $\text{Ca}_{14}\text{Cu}_{24}\text{O}_{41}$) is decreasing with increasing $x$. Intriguingly, the expected increase is indeed observed for the maximum of the phonon peak of $\kappa_a$, whose doping dependence is also shown in figure 6.21. This unusual anisotropic development of the phononic peak suggests that the phononic peak of $\kappa_c$ is indeed suppressed with increasing Ca-content.
Figure 6.21: Phononic maxima of $\kappa_c$ (full symbols) and $\kappa_a$ (open symbols) of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ($x = 6, 8, 9, 11, 12$). The error bars account for geometrical errors of about 10%.

Even though the growing importance of electronic contributions to $\kappa_c$ could qualitatively contribute to the "disappearance" of this phononic peak of $\kappa_c$ the electronic contributions only play a minor role since they are very small.

The origin of this unusual suppression of $\kappa_c$ seems unclear. However, some qualitative considerations allow further conclusions. On one hand a relation to enhanced scattering of phonons due to static disorder is rather unlikely to be the case, since such scattering normally is isotropic but the suppression occurs only along the $c$-direction. On the other hand it appears natural to relate the anisotropic suppression to low-energetic one-dimensional excitations in the ladder or chain structures which cause umklapp-scattering of phonons in three- or four-particles processes. The exact type of this excitations, however, remains unclear. Thinkable excitations in this regard are hole-pair propagations and quasiparticles carrying one hole and a spin 1/2 [123]. Also charge density wave excitations as reported reported recently [18, 19, 20] or excitations of the chains could play a role here.
6.4 Spin ladders III – Ca doping ($x \geq 5$)

Figure 6.22: Magnon thermal conductivity $\kappa_{\text{mag}}$ of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ ($x = 5, 6, 8, 9$) as a function of temperature.

Magnon thermal conductivity

Due to strong suppression of the phononic peak in $\kappa_c$ discussed above, a reasonable estimation of the phononic background by fitting the phononic peak and extrapolating this fit towards high temperatures can only give reasonable results for $x \leq 9$. Therefore the estimation of $\kappa_{\text{ph}}$ and the extraction of $\kappa_{\text{mag}}$ has been done only for these cases. The fits are represented in figure 6.19 by solid lines. Figure 6.22 presents the resulting $\kappa_{\text{mag}}$ for $x = 6, 8, 9$ as a function of temperature in comparison with $\kappa_{\text{mag}}$ of $x = 5$. As is evident from the figure, the differences between these curves are only marginal. One exception is found at $x = 8$ where $\kappa_{\text{mag}}$ is slightly larger than in the other cases. It is unclear whether this is intrinsic to this doping level or rather a particularity of the sample that has been investigated.\(^4\) The fact that the curves for $x = 5, 6$, and $9$ are very similar

\(^4\)A further possibility should be mentioned in this regard. It has been observed previously [25] as well as in the presented measurements that $\kappa_c$ of (Sr, Ca, La)$_{14}$Cu$_{24}$O$_{41}$
suggests the latter to be the case.

Qualitatively this observation shows that $\kappa_{\text{mag}}$ does not significantly change in this high doping ranges ($x > 5$), i.e., in the doping regime where the holes become mobile since the charge ordering in the ladders is destroyed and resistivity decreases. The calculation and investigation of the magnon mean free path in this region is therefore abandoned. The data are consistent with a $\kappa_{\text{mag}}$ with dominating magnon-hole scattering. Apparently the strength of this scattering does not significantly change even though the resistivity decreases by several orders of magnitude.

6.5 Conclusion

The above investigations show that magnon-hole scattering is an important scattering mechanism in both the two dimensional antiferromagnet La$_2$CuO$_4$ and the spin ladder compound Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$. There are, however, distinct differences. While magnon-hole scattering in doped La$_2$CuO$_4$ is temperature independent and even stronger than scattering on static magnetic defects leading to an almost complete suppression of $\kappa_{\text{mag}}$, it depends strongly on the hole mobility in the case of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$. For Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ at $x \leq 5$ drastic temperature and doping dependent changes in $\kappa_{\text{mag}}$ and $l_{\text{mag}}$ have been found to be clearly correlated with anomalies of electronic transport. In this doping regime the data suggest charge ordering in the ladders, which has a strong impact on magnetic degrees of freedom. In particular, magnon-hole scattering is unimportant in the charge ordered phase but becomes the dominating scattering process in the presence of mobile holes. At higher doping ($x \geq 5$) $\kappa_{\text{mag}}$ basically remains unchanged, with magnon-hole scattering being the dominating scattering process in the whole investigated temperature range ($\sim 50$ to $300$ K). Here, a suppression of the phononic peak of $\kappa_c$ at high doping ($x > 9$) indicates scattering of phonons with one dimensional excitations from the ladder or chain substructures.

frequently is subject of variations which occur from measurement to measurement and whose origin is not fully understood. It stressed that the curves presented here have been identically obtained in both cooling and heating measurements. For detailed discussion of this phenomenon see Ref. [25].
Chapter 7

Summary

In this work the magnetic thermal conductivity $\kappa_{\text{mag}}$ of low dimensional quantum spin systems with $S = 1/2$ with a focus on magnon hole scattering and its relevance for the magnetic heat transport has been investigated experimentally.

One system under investigation was the two dimensional Heisenberg antiferromagnet $\text{La}_2\text{CuO}_4$, doped with a slight amount of Sr corresponding to 1% hole doping. This doping leads to a drastic suppression of the magnon thermal conductivity observed in the pure material. Nevertheless, a slight anisotropy between the in-plane and the out-of-plane thermal conductivity of this material indicates that a small magnetic heat conduction is still present. The possible $\kappa_{\text{mag}}$ has been extracted and analyzed with a simple kinetic model which previously was used to analyze $\kappa_{\text{mag}}$ of pure and Zn-doped $\text{La}_2\text{CuO}_4$ and which allows to calculate the magnon mean free path $l_{\text{mag}}$. The upper bound of $l_{\text{mag}}$ has been extracted from the data and compared with values found in the pure and Zn-doped material. Remarkably, $l_{\text{mag}}$ is much shorter than in all other cases which shows that in this material magnons are strongly scattered. This is particularly evident in the direct comparison between this hole doped case and Zn-doped $\text{La}_2\text{CuO}_4$, each with a doping level of 1%. While in the Zn-doped case, i.e., in the presence of static magnetic defects, $l_{\text{mag}}$ is roughly equal to the mean unidirectional distance of Zn-impurities $d_{\text{Zn-Zn}}$ ($l_{\text{mag}} \approx d_{\text{Zn-Zn}}$), it is at least a factor of about two smaller in the hole doped case, where the holes are in principle mobile defects which delocalize and distort the antiferromagnetic correlations in a larger scale.

The other material studied in this thesis was pure and Zn-doped $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$, which contains antiferromagnetic two-leg spinladders. The aim of the investigation of Zn-doped $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ was a quantitative test of a kinetic model which forms the basis of the analysis of $\kappa_{\text{mag}}$ in these compounds. Similar to the two-dimensional case $l_{\text{mag}} \approx d_{\text{Zn-Zn}}$
has been found, which shows that the model is indeed suitable for the quantitative analysis of $\kappa_{\text{mag}}$. Furthermore, $\kappa_{\text{mag}}$ has been investigated of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ in a wide range of Ca-contents ($x = 0...12$). The measurements revealed at low doping levels ($x \leq 5$) a strong doping and temperature dependence of $\kappa_{\text{mag}}$ which by comparison with electrical transport measurements could unambiguously be related to charge ordering in the ladder subunits of the material. Interestingly, the magnon-hole scattering strength is much different than in the two dimensional case described above. Strong magnon-hole scattering is only present in the case of mobile holes. As soon as charge ordering sets in, this scattering mechanism freezes out and becomes completely unimportant at low temperatures. At higher doping levels ($x \geq 5$) the doping dependence of $\kappa_{\text{mag}}$ is only weak. Here the anisotropic suppression of the phononic thermal conductivity at low temperatures indicates a new doping-induced one dimensional scattering process of phonons.
Bibliography


Abstract

The magnon thermal conductivity $\kappa_{\text{mag}}$ of the low dimensional quantum spin systems $\text{La}_2\text{CuO}_4$ and $(\text{Sr, Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ with a focus on magnon hole scattering and its relevance for the magnetic heat transport has been investigated experimentally. In the two dimensional Heisenberg antiferromagnet $\text{La}_2\text{CuO}_4$ already slight hole doping ($\sim 1\%$) almost completely suppresses $\kappa_{\text{mag}}$. Comparison with $\kappa_{\text{mag}}$ of Zn-doped $\text{La}_2\text{CuO}_4$ reveals that magnon-hole scattering is even stronger than scattering on static magnetic defects.

In $(\text{Sr, Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ a strong doping and temperature dependence of $\kappa_{\text{mag}}$ is present at low Ca-doping levels ($x \leq 5$). Here a unique relation between heat transport and charge ordering in the ladder subunits of the material has been shown. In the charge ordered state at low temperatures magnon-hole scattering is completely unimportant, while it becomes strong at high temperatures where in strength it is comparable with scattering of magnons on static magnetic defects induced by Zn-doping. At high Ca-doping ($x \geq 5$) the doping dependence of $\kappa_{\text{mag}}$ is only weak. However, an anisotropic suppression of the phononic thermal conductivity at low temperatures indicates a new doping-induced one dimensional scattering process of phonons.
Zusammenfassung

Die magnonische Wärmleitfähigkeit \( \kappa_{\text{mag}} \) der niedrigdimensionalen Quantenspinsysteme \( \text{La}_2\text{CuO}_4 \) und \( (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41} \) ist experimentell untersucht worden. Herbei wurde ein Schwerpunkt auf Magnon-Loch-Streuung und ihrer Relevanz für den magnetischen Wärmetransport gelegt. In dem zweidimensionalen Heisenberg-Antiferromagnet \( \text{La}_2\text{CuO}_4 \) wird \( \kappa_{\text{mag}} \) bereits bei einer sehr geringen Lochdotierung (\( \sim 1\% \)) fast vollständig unterdrückt. Der Vergleich mit \( \kappa_{\text{mag}} \) von Zn-Dotierung \( \text{La}_2\text{CuO}_4 \) zeigt, dass Magnon-Loch-Streuung deutlich stärker den Wärmetransport unterdrückt als Streuung an statischen magnetischen Defekten.

In \( (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41} \) herrscht bei niedrigen Ca-Gehalten \( (x \leq 5) \) eine starke Dotierungs- und Temperaturabhängigkeit von \( \kappa_{\text{mag}} \) vor. Hier ist ein klarer Zusammenhang zwischen Wärmetransport und Ladungsordnung in den Leiter-Substrukturen des Materials belegt worden. Im ladungsgeordneten Zustand bei niedrigen Temperaturen, ist Magnon-Loch-Streuung völlig unwichtig, wahingegen sie bei hohen Temperaturen bedeutend wird. Hier ist Magnon-Loch-Streuung von vergleichbarer Stärke wie im Fall der Streuung von Magnonen an statischen magnetischen Defekten, die durch Zn-Dotierung erzeugt werden können. Bei hohen Ca-Dotierungen \( (x \geq 5) \) ist die Dotierungsabhängigkeit von \( \kappa_{\text{mag}} \) nur schwach. Jedoch zeigt eine anisotrope Unterdrückung der phononischen Wärmleitfähigkeit bei niedrigen Temperaturen einen durch die Dotierung erzeugten eindimensionalen Streuprozess der Phononen an.
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List of publication


C.V.

Hanan Gouda ElHaes  Address: 33 Masged ElRady Str., Shoubra Elkhima, Elkalyoubia, Egypt;
Nationality: Egyptian;

23.02.1970 Born in Elkalyoubia;

May 1992 B.Sc. in Physics,
Faculty of Women for Arts, Science, and Education,
Ain Shams University;

April 1998 M.Sc. in Experimental Physics,
Faculty of Women for Arts, Science, and Education,
Ain Shams University;

8/1992 to 4/1998 Demonstrator in
Faculty of Women for Arts, Science, and Education,
Ain Shams University Cairo;

8/1998 to 7/1999 Assistant teacher in
Faculty of Women for Arts, Science, and Education,
Ain Shams University Cairo;

7/1999 to 10/1999 Goethe Institute, Bonn, Germany;

1999 to 2001 Diplom Preliminary Examinations,
RWTH-Aachen, Germany;

Since 2001 Ph.D Student in RWTH Aachen, Germany.