Thermal Conductivity of the Hole-Doped Spin Ladder System $Sr_{14-x}Ca_xCu_{24}O_{41}$

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The thermal conductivity of the spin-1/2 ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x = 0$, 2, and 12) has been measured both along (κ_c) and perpendicular to (κ_a) the ladder direction at temperatures between 5 and 300 K. While the temperature dependence of κ_a is typical for phonon heat transport, an unusual double-peak structure is observed for $\kappa_c(T)$. We interpret this unexpected feature as a manifestation of quasi-one-dimensional magnon thermal transport mediated by spin excitations along the ladders.

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The physics of low-dimensional systems attracts much attention because in many cases rigorous theoretical predictions can be made. A particularly interesting system in this respect is $(Sr, Ca, La)_{14}Cu_{24}O_{41}$, where Cu-O bonds form both Cu-O chains and Cu-O two-leg ladders. Apart from the observation of pressure induced superconductivity in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$ [1], the particular geometrical arrangement of the Cu atoms provides a playground for magnetic studies of this type of material [2].

The crystal structure of $Sr_{14}Cu_{24}O_{41}$ consists of CuO_2 and $SrCu_2O_3$ layers, alternatingly stacked along the b axis [3]. The CuO_2 layers contain linear chains of Cu ions linked by two nearly 90° Cu-O-Cu bonds. The Cu_2O_3 subunit contains two-leg ladders in which Cu ions are linked by 180° Cu-O-Cu bonds which provide strong antiferromagnetic coupling between the ladder Cu ions. Both chains and ladders run along the c axis.

The formal valency of Cu in $Sr_{14}Cu_{24}O_{41}$ is +2.25, suggesting six holes per formula unit of the stoichiometric compound. Most holes are localized in the CuO_2 chains at oxygen sites, and are each coupled to a copper spin to form a Zhang-Rice singlet. The remaining magnetic Cu ions form dimers which develop a long-range ordered structure. The dimer ground and excited states are separated by a gap $\Delta_{\mathrm{chain}} \sim 11$ meV with a small dispersion amplitude of the order of 1 meV [4,5].

The copper spins on the same rung of a ladder adopt a singlet ground state separated from the triplet excited state by an energy gap Δ_{ladder}. Both inelastic neutron scattering and recent NMR measurements imply a value of the gap between 350 and 380 K [6,7]. The dispersion of the ladder spin excitations has been found to be very steep along the ladder direction but flat for the rung direction [8].

Replacing Sr by isovalent Ca initiates a transfer of holes from the chains to the ladders, leading to a change of the temperature dependence of the c-axis resistivity from semiconducting to metallic at $x \sim 6$–8. The substitution does not change Δ_{chain}, but the ordered state of dimers in the chains becomes unstable [4]. NMR measurements [9] indicate that the ladder spin gap decreases with Ca substitution, whereas recent inelastic neutron scattering results [8] suggest that Δ_{ladder} does not change with hole doping.

In this Letter, we report the observation of an unusual and unexpected contribution to the thermal conductivity $\kappa_c(T)$ along the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$, and suggest that it is due to an energy transport via magnetic excitations.

The single crystals of $Sr_{14}Cu_{24}O_{41}$, $Sr_{12}Ca_2Cu_{24}O_{41}$, and $Sr_2Ca_{12}Cu_{24}O_{41}$ (further referred to as Ca0, Ca2, and Ca12, respectively) were grown by a traveling-solvent floating-zone method [10]. Rectangular-bar-shaped samples of typical dimensions $2 \times 1 \times 0.6$ mm^3 with the long dimension parallel to either the a or the c axes were cut from the same crystal of each composition. The thermal conductivity was measured by a conventional steady-state method. The temperature gradient along the sample was monitored by differential Chromel-Au + 0.07% Fe thermocouples. The thermocouple junctions were soldered to two copper wires, which were glued to the sample a small distance apart, providing thermal contact while insulating electrically. The temperature difference ΔT between the two thermometers was typically chosen to be 1% to 3% of the absolute average temperature. The absolute accuracy of the measurements was ±10% because of uncertainties in sample geometry.

The results are presented in Fig. 1. The thermal conductivity along the a axis (κ_a) exhibits a low-temperature peak and, at higher temperatures, the temperature dependence is close to $\kappa_a \propto T^{-1}$. This behavior is typical for phonon heat transport [11]. The electronic thermal conductivities κ_e along both directions, estimated from the resistivities ρ by applying the Wiedemann-Franz law $\kappa_e = LT/\rho$, with the Lorenz number $L = 2.45 \times 10^{-8}$ W Ω/K^2, were found to be negligible for semiconducting Ca0 and Ca2 and less than 3% of the total measured thermal conductivity for Ca12. At temperatures below ~30 K the thermal conductivity along the c axis (κ_c) follows the same temperature dependence as κ_a with an almost constant and small anisotropy ratio κ_c/κ_a, as shown in the inset of Fig. 1. This suggests that also the c-axis thermal transport is predominantly phononic in this temperature region and that the same types of phonon scattering determine the behavior of both $\kappa_c(T)$ and $\kappa_a(T)$. At temperatures exceeding 40 K, κ_c/κ_a increases for all

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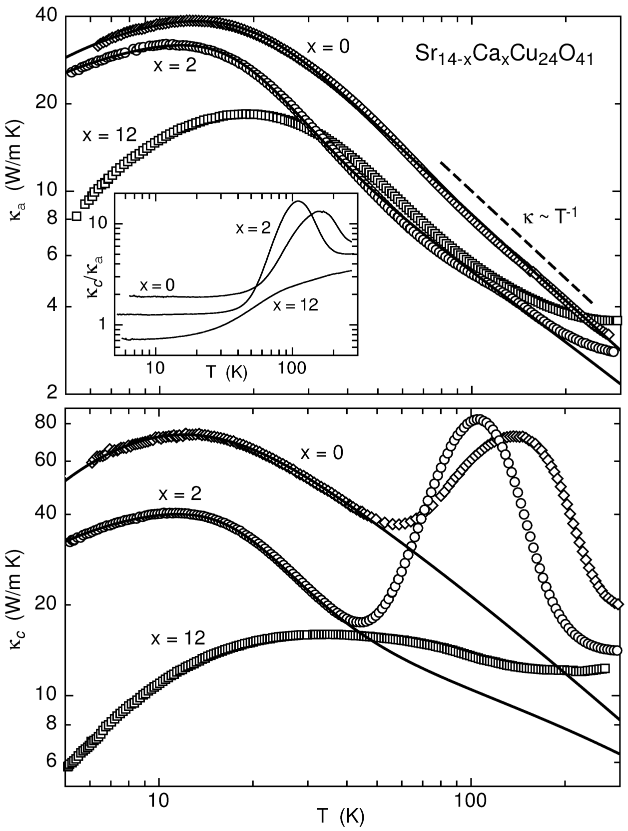

FIG. 1. Temperature dependence of the thermal conductivity of $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x = 0$, 2, and 12) along the a axis (κ_a) and along the c axis (κ_c). The solid lines represent the calculated phonon thermal conductivities. The inset shows the temperature dependences of anisotropy ratio κ_c/κ_a.

compositions investigated, and $\kappa_c(T)$ is qualitatively different from $\kappa_a(T)$, especially for Ca0 and Ca2. For these compositions, $\kappa_c(T)$ reveals an excess thermal conduction exhibiting peak values above 100 K, representing the most significant new observation made in this work.

For Ca0 and Ca2, the experimental data of $\kappa_a(T)$ at all temperatures and of $\kappa_c(T)$ below 30 K were fitted to the formula given by the Debye model of phonon thermal conductivity

$$\kappa_{\mathrm{ph}} = \frac{k_{\mathrm{B}}}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\tau(\omega, T)\, dx\,, \tag{1}$$

where $\tau(\omega, T)$ is the mean lifetime of a phonon, ω is its frequency, and $x = \hbar\omega/k_{\mathrm{B}}T$. The average sound velocity v was calculated from the value of the Debye temperature $\Theta_D = 296$ K (data of Ref. [12]) using the expression $\Theta_D = v(\hbar/k_{\mathrm{B}})(6\pi^2 n)^{1/3}$, where n is the number density of atoms. No fitting of the Ca12 data was attempted because at present no information about the Debye temperature or the phonon spectrum of $Sr_{14-x}Ca_xCu_{24}O_{41}$ with large x is available.

The phonon relaxation rate was approximated by

$$\tau^{-1} = v/L + A\omega^4 + BT\omega^3 \exp\left(-\frac{\Theta_D}{bT}\right) + \tau_{\mathrm{res}}^{-1}. \tag{2}$$

Here, the four terms correspond to phonon scattering at sample boundaries, at point defects, due to phonon-phonon U processes, and via resonant scattering, respectively; L, A, B, and b are free parameters. The first three terms in Eq. (2) were sufficient to fit $\kappa_a(T)$ for Ca0 reasonably well, but to reproduce the deviations from the T^{-1} dependence for Ca2 we had to consider resonant phonon scattering. The best fit was obtained by assuming that the resonant scattering of phonons occurs via magnetic two-level systems [13] with

$$\tau_{\mathrm{res}}^{-1} = C\frac{\omega^4}{(\omega_0^2 - \omega^2)^2} F(T)\,, \tag{3}$$

where $F(T)$ describes the difference of thermal populations of the excited and the ground state and C is a free parameter. For singlet-triplet excitations of dimerized states in both ladders and chains,

$$F(T) = 1 - \frac{1 - \exp(-E/T)}{1 + 3\exp(-E/T)}\,, \tag{4}$$

where $E = \hbar\omega_0/k_{\mathrm{B}}$ is the average excitation energy. The parameters C and E were obtained by fitting the $\kappa_a(T)$ data of Ca2 and subsequently assumed to be the same for $\kappa_c(T)$ of this material. The fit values of the free parameters are presented in Table I.

In view of the simplicity of the model calculation, the numerical values of the parameters should be considered as preliminary. The parameters L describing the boundary scattering are close to the smallest dimensions of the samples. The value of the parameter E is of similar magnitude as the excitation energy of 11 meV (127 K) of the coupled dimer system of chain Cu spins [4]; the resonant scattering is negligible for Ca0. It may be that the resonant scattering occurs via isolated rather than interacting dimers. Neutron scattering experiments of Eccleston *et al.* [14] on $Sr_{11.2}Ca_{2.8}Cu_{24}O_{41}$ revealed both the 11 meV peak due to interacting dimers and a narrow peak at about 4 meV (46 K) which has not been observed for Ca-free samples. The 4 meV peak was attributed to singlet-triplet excitations of isolated dimers. It was also shown that the substitution of Ca for Sr in $Sr_{14}Cu_{24}O_{41}$ disturbs the long-range order of chain dimers [4], increasing the number of isolated dimers.

For $T \geq 40$ K the measured $\kappa_c(T)$ deviates substantially from the extrapolated phonon thermal conductivity. Two scenarios may account for the deviation: either a very anomalous temperature dependence of phonon scattering has to be considered, or an additional channel of thermal transport, which is negligible at low temperatures, opens up rapidly for $T \geq 40$ K and produces the peak feature at $T > 100$ K.

TABLE I. Parameters of the fitting of $\kappa(T)$ data to Eqs. (1)–(3).

Parameter	$x = 0$ a axis	$x = 2$ a axis	$x = 0$ c axis	$x = 2$ c axis
L (10^{-4} m)	8.1 ± 2	12.3 ± 3	5.8 ± 3	12.9 ± 2.5
A (10^{-42} s^3)	8.7 ± 2.5	13.6 ± 2.5	2.5 ± 1	9.6 ± 1.2
B (10^{-31} K^{-1} s^2)	19.6 ± 0.2	19.5 ± 0.5	5.6 ± 1	3.1 ± 1
b	6.5 ± 0.4	6.5 ± 0.4	12.3 ± 1.5	16 ± 8
C (10^{11} s^{-1})		6.6 ± 1.5		6.6 ± 1.5
E (K)		82 ± 20		82 ± 20

The first possibility is very unlikely because the elastic moduli of $Sr_{14-x}Ca_xCu_{24}O_{41}$ in the *ac* plane are only weakly anisotropic [15]. Thus a phonon scattering mechanism affecting strongly the thermal conductivity along the c direction should also produce a significant effect along the a direction. This is definitely not the case for Ca0 and Ca2, as may be seen in Fig. 1. Taking into account that there is no phase transition in the considered temperature region, a dramatic and transient weakening of phonon scattering along the c axis seems quite unlikely.

Since phonons and electrons cannot account for the observed anomalous temperature dependence of κ_c, itinerant magnetic excitations ought to be considered. The singlet-triplet (magnon) excitations of the chains exhibit a flat dispersion [4] and, therefore, their contribution to heat transport should be small. On the contrary, the strong interaction between ladder Cu spins results in a very high velocity of ladder magnon excitations in the c direction [6], so the ladder spin system may participate substantially in thermal transport.

For analyzing the additional thermal conductivity, the extrapolated $\kappa_{c,\mathrm{ph}}$ (see Fig. 1) has been subtracted from the total measured κ_c. The result is plotted on a logarithmic scale versus $1/T$ in the inset of Fig. 2. The lower limit of 0.4 W m^{-1} K^{-1} is set by the experimental uncertainty at these temperatures. It may be seen that between 40 and 65 K the excess thermal conductivities vary as $\exp(-\Delta_\kappa/T)$ with $\Delta_\kappa = 355 \pm 40$ and 363 ± 40 K for Ca0 and Ca2, respectively. Because Δ_κ coincides with Δ_{ladder}, the suggestion of thermal transport by magnetic excitations gains additional support. For estimating the magnon mean free path, we employed a kinetic expression for a one-dimensional magnon thermal conductivity $\kappa_{m,1\mathrm{D}}(T) = (2\pi)^{-1} \int C_m(q) v_m(q) l_m(q)\, dq$, where C_m, q, v_m, and l_m are the specific heat, wave vector, group velocity, and mean free path of a magnon, respectively. If l_m is independent of q, then the magnon thermal conductivity of the system of spin ladders along the ladder direction is

$$\kappa_m(T) = N \frac{k_{\mathrm{B}}^2}{\pi \hbar} l_m T \int_{x_0}^{x_{\max}} \frac{x^2 \exp(x)}{[\exp(x) - 1]^2}\, dx\,, \quad (5)$$

where N is the number of ladders crossing a unit area in the *ab* plane, $x = \varepsilon_m/k_{\mathrm{B}}T$, $x_{\max} = \varepsilon_{\max}/k_{\mathrm{B}}T$, $x_0 = \Delta_{\mathrm{ladder}}/k_{\mathrm{B}}T$, ε_m is the magnon energy, Δ_{ladder} is the spin gap, and $\varepsilon_{\max}$ is the band maximum. Fitting the additional magnon thermal conductivity to Eq. (5), using the experimental temperature dependence [8] of Δ_{ladder}, results in the values of l_m shown in Fig. 2. For both Ca0 and Ca2, l_m is weakly temperature dependent up to 80–100 K, then decreases rapidly and tends to saturate at $T \geq 250$ K. The number of holes per Cu ion on a ladder, as evaluated using optical conductivity data, is 0.07 for Ca0 and 0.11 for Ca2 [16]. In case of a uniform distribution of holes, the mean distance between them along the c axis is 28 and 18 Å for Ca0 and Ca2, respectively. These distances are smaller but of the same order of magnitude as the calculated l_m values near room temperature, suggesting that holes are the main scatterers of magnetic excitations. Below 250 K, holes have been found to form pairs which at lower temperatures eventually localize [17,18]. Since a triplet excitation propagating along the ladder can pass through a hole pair [19], the decreasing number of unpaired holes below ≈250 K should enhance the mean free path of magnetic excitations, in agreement with our plot shown in Fig. 2. The almost constant magnon mean free path at $T \leq 80$ K is probably due to defects and remaining unpaired holes.

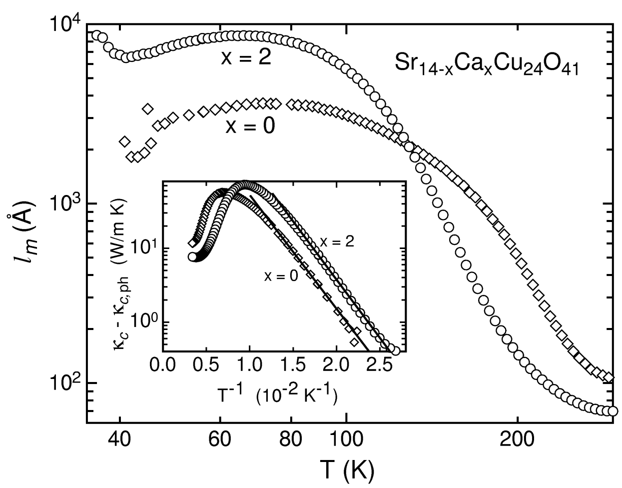

FIG. 2. Mean free path of spin excitations for $Sr_{14-x}Ca_x$-$Cu_{24}O_{41}$ ($x = 0$ and 2). The inset is $(\kappa_c - \kappa_{c,\mathrm{ph}})$ vs T^{-1}; the solid lines represent an exponential temperature variation of the type $\exp(-\Delta_\kappa/T)$.

The temperature dependence of the thermal conductivity of Ca12 along the ladder direction does not show the double-peak structure of the lightly hole-doped Ca0 and

Ca2. Nevertheless, the anisotropy ratio κ_c/κ_a also increases at temperatures exceeding 20 K. However, instead of a sharp peak as for Ca0 and Ca2, there is only a smooth increase in κ_c/κ_a in that temperature region. The obvious conjecture from this comparison is that for Ca12 the magnon thermal transport suggested above is also active but much stronger damped than that for Ca0 and Ca2 because of the enhanced number of itinerant holes. It has been pointed out that the electron-spin interaction strongly influences the electrical transport in $Sr_{14-x}Ca_xCu_{24}O_{41}$ [20,21]. The present study demonstrates that also the magnon thermal transport is sensitive to this interaction.

Our present results on $Sr_{14-x}Ca_xCu_{24}O_{41}$ may be compared with the corresponding results on layered cuprates. The unusual double-peak structure of the thermal conductivity in the *ab* plane observed on high-quality samples of insulating La_2CuO_4 and $(Y,Pr)Ba_2Cu_3O_{6+\delta}$ [22,23] is similar to but less pronounced than in our data set of $\kappa_c(T)$ for Ca0 and Ca2. It has been suggested [22] that the high-temperature peak in La_2CuO_4 may be caused by an additional magnon heat transport. The clear observation of magnon heat transport in $Sr_{14-x}Ca_xCu_{24}O_{41}$ supports this suggestion because the exchange interaction between Cu^{2+} spins in the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$ and in the CuO_2 planes of the layered cuprates is similar [24]. Our observation of a damped magnon thermal conductivity in conducting Ca12 raises the question whether this channel of heat transport is also present in doped high-T_c cuprates.

In conclusion, our study of the thermal conductivity of the spin-1/2 ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x = 0$, 2, and 12) provides evidence for an additional quasi-one-dimensional mechanism of heat transport parallel to the weakly anisotropic phonon thermal conductivity. This additional mechanism is ascribed to itinerant spin excitations in the ladders. The magnitude of this contribution is unexpectedly large.

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