Universal behavior of spin-mediated energy transport in $S = 1/2$ chain cuprates: BaCu$_2$Si$_2$O$_7$ as an example

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Abstract. – The thermal conductivity $\kappa$ of the spin-1/2 chain cuprate BaCu$_2$Si$_2$O$_7$ was measured along different crystallographic directions in the temperature region between 0.5 and 300 K. The thermal conductivity along the chain direction considerably exceeds that along perpendicular directions. Near the antiferromagnetic transition at $T_N = 9.2$ K the data indicates enhanced scattering of phonons by critical fluctuations in the spin system. A comparison of the data above $T_N$ with available results on similar materials reveals similarities in the main features of the temperature dependence of the mean free path of itinerant spin excitations. This universal behavior is most likely caused by the spin-lattice interaction.

According to theoretical predictions, the energy transport in several types of $S = 1/2$ one-dimensional (1D) antiferromagnetic (AFM) spin systems is expected to be remarkably different from similar three-dimensional (3D) systems. In 3D systems, the thermal conductivity of magnetic origin can be large only much below the long-range ordering transitions, where the itinerant spin excitations are well-defined quasiparticles (magnons). At temperatures close to but below the 3D ordering transition, the spin-mediated thermal conductivity $\kappa_1$ is considerably reduced because of enhanced magnon-magnon scattering [1, 2]. Above the transition, the energy transport by spin excitations is small and has diffusive character, such that in real materials other carriers of energy, most notably phonons and, in electrical conductors, electronic quasiparticles, dominate the heat transport. In strictly 1D spin systems, no long-range order exists at nonzero temperatures, and naively one could expect a rather small thermal conduction via the spin system. However, for 1D $S = 1/2$ spin systems described by the Heisenberg AFM XXZ Hamiltonian

$$H = J \sum_i (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z)$$ (1)

with $-1 < \Delta \leq 1$, the heat transport turns out to be of ballistic type and therefore, $\kappa_1$ is infinite for infinite-length systems. Anomalous behavior of energy transport in Heisenberg...
S = 1/2 AFM XXZ chains has been predicted a long time ago \[3,4\]. It was recently associated with the integrability of the underlying model, because the energy density appears to be one of the numerous constants of motion of integrable systems \[5\]. Very recently, thermal transport in integrable models of several 1D spin systems was analyzed employing the Kubo formalism and adopting the notion of a “thermal” Drude weight with a similar meaning as the Drude weight in the standard theory of electrical transport \[6,7\]. The thermal conductivity can thus be written as \[7\]

\[
\kappa_s(T) = \kappa^{th}(T) \tau, \tag{2}
\]

where \(\kappa^{th}\) is the thermal Drude weight (in ref. \[6\] the thermal Drude weight is denoted as \(\tilde{\kappa} \equiv \pi \kappa^{th}\)) and \(\tau\) is the lifetime of the eigenstates of the spin system. The Drude-weight can be calculated exactly, e.g., by the Bethe Ansatz method. For a system described by the Hamiltonian in eq. \[1\], different methods of calculation give consistent values of \(\kappa^{th}(T)\) \[6,7,9,10,11\]. The relaxation time \(\tau\) is infinite for an ideal integrable 1D system but turns finite if the influence of external perturbations, such as defects, phonons, interchain coupling, cannot be neglected. Theoretical work concerning the features of \(\tau\) for different types of perturbation is scarce. Below, we describe an experimental attempt to investigate details of energy transport relaxation in 1D Heisenberg \(S = 1/2\) XXZ model materials.

We have measured the thermal conductivity \(\kappa\) of the \(S = 1/2\) spin-chain compound BaCu$_2$Si$_2$O$_7$ along different crystallographic directions and at temperatures between 0.5 and 300 K. BaCu$_2$Si$_2$O$_7$ has an orthorhombic crystal structure with lattice parameters \(a = 6.862\) Å, \(b = 13.178\) Å, and \(c = 6.897\) Å \[12\]. Important structural elements are chains of corner-sharing CuO$_4$ tetrahedra, running along the \(c\)-axis. Cu$^{2+}$ ions with spins \(S = 1/2\) are connected along the chain direction via 124° Cu–O–Cu bonds. The magnetic properties of individual chains can be well described by the isotropic form of the Hamiltonian of eq. \[1\], i.e., \(\Delta = 1\) and \(J = 24.1\) meV \[13\]. The interchain interactions are two orders of magnitude smaller \[14\] and lead to a 3D AFM ordering transition at \(T_N = 9.2\) K. Below \(T_N\), the spins are oriented along the \(c\)-axis. Applying a magnetic field along the easy axis leads to an exotic two-stage spin-flop transition \[15\]; the origin of this anomalous behaviour is not completely understood \[16,17\]. Recent interest in BaCu$_2$Si$_2$O$_7$ was also stimulated by the speculation that below \(T_N\) the “longitudinal mode”, a long-lived spin wave with a polarization parallel to the direction of the ordered moments, might be observed \[18\].

Three bar-shaped samples with typical dimensions of about \(0.4 \times 0.5 \times 2\) mm$^3$ were cut from the same single crystal grown using the floating-zone image-furnace technique. For each sample, the longest dimension was oriented along one of the main crystallographic axes. The thermal conductivity was measured employing the standard uniaxial heat flow technique. The heat input into the sample was provided by the Joule heat of a RuO$_2$ resistor. The temperature gradient was monitored using a system of Chromel-Au +0.07% Fe thermocouples in the temperature region between 2 and 300 K, and by a couple of RuO$_2$ thermometers in the temperature regime between 0.5 and 3 K.

The \(\kappa(T)\) data measured along the \(a\), \(b\) and \(c\)-axes are shown in Fig. \[1\]. Between 2 and 32 K, they are in qualitative agreement with unpublished results of Takeya et al. \[19\] but our \(\kappa\)-values are somewhat higher and the distinct features around \(T_N = 9.2\) K, clearly visible in the insets of fig. \[1\] are absent in the data of ref. \[19\]. We suspect that this is due to the improved quality of the samples that were used in our study. Dips in \(\kappa(T)\) upon magnetic ordering have often been observed in magnetic materials, and can be attributed to the scattering of phonons by enhanced fluctuations of the order parameter \[12\]. Below about 2 K, the thermal conductivity is almost isotropic and the temperature dependence is \(\kappa \propto T^{2.5}\). The anisotropy of \(\kappa(T)\) is also weak above about 170 K where, for all directions, \(\kappa \propto T^{-0.5}\). The anisotropy
ratio $\kappa^b/\kappa^a$ for heat transport perpendicular to the chain direction is close to 1 and almost temperature-independent across the entire covered temperature range. It seems reasonable to assume that perpendicular to the spin chain direction, the phonon heat transport dominates and therefore, the weak anisotropy can easily be attributed to a weak anisotropy of the elastic constants and uncertainties in the evaluation of the sample geometry.

At intermediate temperatures the thermal conductivity $\kappa^c$ along the chain direction significantly exceeds those along the perpendicular directions. At 20 K, $\kappa^c/\kappa^a = 2.3$ and $\kappa^c/\kappa^b = 2.1$. This particular and temperature-dependent anisotropy cannot be attributed to anisotropic phonon heat transport. Considering the layered crystal structure of BaCu$_2$Si$_2$O$_7$ with CuO$_4$ layers separated by Ba and SiO$_4$ layers, which are stacked along the $b$-axis, it is expected that the phonon heat transport is weakest along the $b$-direction. Since this is not reflected in our observations, the anisotropy of the phonon heat transport is obviously very weak. A more detailed discussion of this point may be found in ref. [20].

The excess contribution to $\kappa$ along the $c$ direction is most naturally associated with the 1D energy transport by itinerant spin excitations (spinons). In electrically insulating materials, the total measured thermal conductivity along an $\alpha$-direction is $\kappa^\alpha(T) = \kappa^\alpha_{ph} + \kappa^\alpha_s$, where $\kappa^\alpha_{ph}$ and $\kappa^\alpha_s$ are phonon and spin contributions, respectively. For directions perpendicular to the direction of weakly interacting spin chains, $\kappa^\alpha_s, \kappa^\beta_s \approx 0$ because of the vanishingly small spinon velocities. To analyze the temperature dependence of $\kappa^\alpha_s$ (simply denoted as $\kappa_s$ below), we assumed that the phonon contribution $\kappa^\alpha_{ph}$ is nearly isotropic and subtracted $\kappa^\alpha_{ph} \approx (\kappa^\alpha^a + \kappa^\alpha^b)/2$ from the total measured $\kappa^\alpha(T)$. The resulting values of $\kappa_s(T)$ are shown in fig. 2. Since the measured values of $\kappa$ have maximum errors of about $\pm 10\%$ along all directions, the related absolute maximum of possible uncertainties in $\kappa_s(T)$, which are indicated by the shaded area in fig. 2 are very large at high and low temperatures, where the $\kappa^\alpha(T)$ curves for directions parallel and perpendicular to the chains differ only little. That is why we did not analyse the thermal conductivity in the AFM ordered state and restrict our analysis of $\kappa_s(T)$ to the
limited temperature region between $T_N$ and 80 K (see dashed vertical lines in fig. 2).

Another reason for the observed anisotropy of $\kappa$ might be an anisotropy in the scattering strength between phonons and spinons. Although such a scenario cannot be completely ruled out, two facts suggest that it is very unlikely. Firstly, the nearly isotropic heat transport at the highest temperatures reached in this study is not compatible with a strong anisotropy of the phonon thermal conductivity and thus, the phonon-spinon interaction. Secondly, the observed reductions of the thermal conductivities at $T_N$, directly related to the spin-lattice interaction $\kappa^c$, are approximately the same for all crystallographic directions. Consequently, the features of $\kappa(T)$ at $T_N$, clearly seen in the insets of fig. 1 are removed by subtracting $(\kappa^a + \kappa^b)/2$ from $\kappa^c$. All this suggests that, although the scattering of phonons by spin excitations may be relatively effective, $\kappa_{ph}$ remains, nonetheless, almost isotropic and hence the anisotropy of the measured $\kappa(T)$ is almost certainly due to heat transport by spin excitations along the $c$ direction.

From the values of $\kappa_s(T)$ and using eq. (2), we calculated the mean free path of the spin excitations $\ell_s = v_s \tau$, where $v_s(T)$ denotes the temperature-dependent average velocity of propagating spin excitations. Assuming that the excitations of the Hamiltonian in eq. (1) are spinons obeying Fermi-Dirac statistics and adopting an energy dispersion $\epsilon(k) = (J\pi/2) \sin kc$, where $c = 3.43 \times 10^{-10}$ m is the distance between neighboring spins in a chain, $v_s(T)$ can be calculated as

$$v_s(T) = \frac{\bar{\hbar}}{\hbar} \left[ \int \frac{\partial \epsilon}{\partial k} f(\epsilon, T) dk \right] / \left[ \int f(\epsilon, T) dk \right],$$

where $f(\epsilon, T) = (\exp(\epsilon/k_B T) + 1)^{-1}$. The temperature dependence of the thermal Drude weight $D^{th}(T)$, taken from ref. 6, served to calculate $\tau(T)$. The resulting values of $\ell_s(T)$ are shown in Fig. 3. The shaded area again denotes the uncertainty. We note a rapidly increasing $\ell_s(T)$ with decreasing temperature and a trend to saturation at low temperatures.

It is rather instructive to compare this $\ell_s(T)$ with available data for other similar insulating materials.
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Fig. 3 – Mean free path of spin excitations in BaCu$_2$Si$_2$O$_7$ in comparison with corresponding data for the spin-chain compounds Sr$_2$CuO$_3$ and SrCuO$_2$ [20], and the two-leg spin-ladder material Ca$_9$La$_5$Cu$_{24}$O$_{41}$ [25]. The intrachain spin-spin correlation length $\xi$, shown as the broken line, is from ref. [26].

Compounds. Apart from BaCu$_2$Si$_2$O$_7$, mean free paths of spin excitations have been evaluated for the $S = 1/2$ spin-chain compounds Sr$_2$CuO$_3$ and SrCuO$_2$ [20], CuGeO$_3$ [22, 23, 24], and also for the undoped spin ladder compound Ca$_9$La$_5$Cu$_{24}$O$_{41}$. The data for Sr$_2$CuO$_3$ and SrCuO$_2$ (data from [20]), and Ca$_9$La$_5$Cu$_{24}$O$_{41}$ [25] are shown in Fig. 3. For CuGeO$_3$, the temperature dependence of $\ell_s$ was not calculated, but it was noted that $\ell_s$ does not exceed the value of 1300 Å [23, 24]. It is remarkable that all $\ell_s(T)$ curves in fig. 3 reveal a similar trend, in particular the low-temperature saturation value is always of the order of $10^3$ Å. Also the high temperature features are similar and reveal a power law type $T^{-n}$ behavior with $n > 1$. It is important that, in spite of very different excitation spectra and therefore different temperature variations of $D^{th}(T)$ for spin chains and spin ladders [6, 7], the corresponding extrinsic parameters $\ell_s(T)$ exhibit similar features. This suggests that the relaxation mechanisms for spin excitations are the same in all these compounds.

In view of the present lack of theoretical descriptions of relaxation processes in spin chain compounds, only qualitative suggestions can be made. The first straightforward result is that the mean free path of spinons is not limited by the spin-spin correlation length. The intrachain correlation length in spin chains varies as $\xi \propto T^{-1}$ with small logarithmic corrections [26]. The result of calculations for BaCu$_2$Si$_2$O$_7$ is shown as the dashed line in Fig. 3. The absolute values of $\ell_s$ at low temperatures are considerably larger than $\xi$, and we also note a much faster temperature-induced reduction of $\ell_s(T)$ than of $\xi(T)$ at elevated temperatures.

In ref. [27], a phenomenological approximation for the spinon mean free path was postu-
The first term on the right-hand side reflects the scattering of spinons by phonons, with the parameter $A_{sp}$ characterizing the spin-lattice interaction strength and $T^*$ representing a threshold energy typical for Umklapp-processes. The second and constant term is associated with the influence of magnetic defects due to non-$S = 1/2$ ions on the Cu sites, with $L_{sd}$ as the mean distance between them. Eq. (4) is equally well applicable to all data sets shown in Fig. 3. The solid lines in Fig. 3 are fits to eq. (4) with the parameter values given in Table I. If $L_{sd}$ indeed reflects the limitation of the mean free path by defects, the fit values of this parameter given in Table I are the consequence of similar densities of these defects in these materials. The exception is $\text{Sr}_2\text{CuO}_3$ where the smaller value of $L_{sd}$ might be due to the additional influence of bond-defects [27].

The relatively large value of the parameter $A_{sp}$ for $\text{BaCu}_2\text{Si}_2\text{O}_7$ indicates enhanced spinon-phonon scattering in this compound. This can be understood by taking into account that for this material, the intrachain exchange constant $J/k_B = 279$ K is close to the value of the Debye temperature $\theta_D$ which, from low-temperature specific heat data presented in ref. [28], is approximately 290 K. The near identity of the energy scales for spin and lattice excitations leads to stronger scattering processes between the two types of quasiparticles. For the other compounds, the values of $J/k_B$ are about an order of magnitude larger than $\theta_D$.

If the strongly increasing $\ell_s(T)$ with decreasing $T$ is indeed due to the reduction of spinon-phonon scattering, it may happen that at low enough temperatures the heat input into a sample will produce a temperature gradient in the crystal lattice only. Correspondingly, the spin system adopts a constant average temperature and does not participate in the energy transport processes [29]. In ref. [20] we estimated that for $\text{Sr}_2\text{CuO}_3$ and $\text{SrCuO}_2$ this happens quite abruptly in the temperature region between about 10 and 20 K. However, the wavevector dependence of the spinon-phonon interaction was not taken into account. Such a dependence would lead to a broadening of the transition from the high-temperature region, where $\kappa_s$ can be measured by our methods, to the low-temperature regime, where $\kappa_s$ is not observable in this way. In principle, the low-temperature saturation of $\ell_s(T)$ may reflect such a transition, instead of the influence of defects.

Although eq. (1) captures the main features of the temperature variation $\ell_s(T)$, it is not properly justified theoretically. A rigorous quantum mechanical analysis of the influence of the spin-lattice interaction on the energy relaxation in quantum spin chains would definitely be of great help.

In conclusion, the analysis of the experimental results of anisotropic heat transport in $\text{BaCu}_2\text{Si}_2\text{O}_7$ allowed for the evaluation of the mean free path $\ell_s(T)$ of itinerant spin excitations. A comparison with several other compounds containing isotropic Heisenberg $S = 1/2$ chain-type structural elements demonstrates that $\ell_s(T)$ of all these materials exhibit similar features, and indicates that a universal type of energy relaxation for spinons is dominant in these materials.

### Table I – Parameters of the fitting of $\ell_s(T)$ data to eq. (4)

| Parameter | $\text{Sr}_2\text{CuO}_3$ | $\text{SrCuO}_2$ | $\text{Ca}_2\text{La}_3\text{Cu}_{24}\text{O}_{11}$ | $\text{BaCu}_2\text{Si}_2\text{O}_7$ |
|-----------|-----------------|-----------------|---------------------------------|-----------------|
| $L_{sd}$ (nm) | $81 \pm 2$ | $242 \pm 2$ | $325 \pm 1$ | $216 \pm 2$ |
| $A_{sp}$ ($10^5$ m$^{-1}$) | $7.1 \pm 2$ | $6.7 \pm 1$ | $3.3 \pm 0.2$ | $41.4 \pm 2$ |
| $T^*$ (K) | $177 \pm 5$ | $204 \pm 2$ | $532 \pm 10$ | $80 \pm 2$ |
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