Spin Thermal Conductivity of the Haldane Chain Compound Y_2BaNiO_5

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We have measured the thermal conductivity of the spin $S = 1$ chain compound Y_2BaNiO_5. Analyzing the anisotropy of the thermal transport allows us to identify a definite spin-mediated thermal conductivity κ_s along the chain direction. The calculated spin-related energy diffusion constant $D_E(T)$ shows a broad peak around 120 K. Close to room temperature, $D_E(T)$ approaches the theoretically predicted high-temperature value, while scattering of spin excitations by magnetic impurities seems to be the major limiting factor of κ_s at low temperature.

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A broad class of low-dimensional quantum spin systems is expected to exhibit anomalous transport properties due to the integrability of the corresponding model Hamiltonians [1–3]. A particularly well studied example is the one-dimensional Heisenberg antiferromagnetic (1D HAF) $S = 1/2$ XXZ model, for which several theoretical works find finite Drude weights in the frequency spectra of the thermal $\kappa(\omega)$ and the spin conductivity $\sigma(\omega)$ (see the recent review article [4] and the references therein). This, in turn, results in ballistic, dissipationless thermal and spin conductivities. These predictions are supported by experimental observations of enhanced energy diffusion constants D_E and spin diffusion constants D_S in several physical realizations of the $S = 1/2$ 1D HAF model [5–8]. In contrast, in $S = 1$ HAF chains, the first excited state is separated from the singlet ground state by an energy gap Δ, and the system is not integrable [9]. This excludes infinite conductivities, but anomalous diffusion constants may still be expected [10]. Experimental results on the thermal transport in $S = 1$ chain compounds are scarce. The existence of spin-mediated energy transport in the $S = 1$ chain compound $AgVP_2S_6$ has been reported [11], but the sample quality did not allow for unambiguously resolving whether the cause of the relatively low values of the spin-mediated thermal conductivity is of intrinsic origin or is caused by defects.

In this Letter, we report a study of the anisotropic thermal conductivity of large high-quality single crystals of Y_2BaNiO_5, which represents a nearly ideal realization of the spin $S = 1$ HAF chain. The basic building blocks are chains of NiO_6 octahedra with Ni^{2+} ions ($S = 1$) running along the a axis of the orthorhombic structure with lattice parameters $a = 3.76$ Å, $b = 5.76$ Å, and $c = 11.33$ Å (space group Immm). The 1D character of the magnetic properties is well established by susceptibility and inelastic neutron scattering measurements yielding $J \approx 250$–280 K, $\Delta \approx 100$ K, and $|J_\perp/J| \leq 10^{-4}$ for the in-chain superexchange coupling, the Haldane gap, and the ratio between out-of-chain and in-chain coupling, respectively [12–15]. Our thermal conductivity data provide clear evidence for a sizeable spin-mediated energy transport along the chain direction, which is absent along both perpendicular directions. In agreement with theoretical expectations, the derived energy diffusion constant shows a qualitatively different temperature dependence as those found for various $S = 1/2$ chain compounds. Our data also suggest that magnetic impurities provide the dominating scattering mechanism for magnons at low temperatures.

The single crystals of Y_2BaNiO_5 were grown by a self-flux method [16]. Out of one crystal, a bar-shaped sample was cut with dimensions $0.89 \times 0.79 \times 0.77$ mm^3 along the principal axes a, b, and c, respectively. For the $\kappa(T)$ measurements, we used a standard steady-state method [17]. The thermal gradient of $\Delta T \simeq 0.1$ K has been determined using a differential Chromel-Au + 0.07%Fe thermocouple. Unaccounted heat losses due to the connecting leads and the sample surface radiation are estimated to be negligible below about 200 K although at higher temperatures, they can lead to somewhat overestimated values of κ. For each orientation, a few $\kappa(T)$ runs have been made with removing and reattaching the thermal contacts to the sample. Different runs gave qualitatively similar temperature dependencies, but different absolute values varying up to $\pm 10\%$ for each orientation. This mainly arises from the uncertainty in determining the exact distance of the thermocouple junctions. Up to 14 T, we did not find any magnetic-field dependence of the thermal conductivity.

In Fig. 1, we present typical results for $\kappa^i(T)$ ($i = a, b, c$) of Y_2BaNiO_5. Near 20 K, $\kappa^i(T)$ for all three crystal directions exhibits a low-temperature peak, which is typical for insulators where thermal transport is of phononic origin. The peak signifies a gradual change of the dominant phonon scattering mechanism from sample boundaries and extended defects at low temperatures to phonon-phonon scattering at high temperatures [18]. Another feature, which is observed only for the a direction, is a shoulder-like feature between about 80 and 140 K. Such an anisotropy has been observed in various low-dimensional spin systems such as 2D $S = 1/2$ materials [17,19–24], $S = 1/2$ ladder compounds [25–27], and $S = 1/2$ chain com-

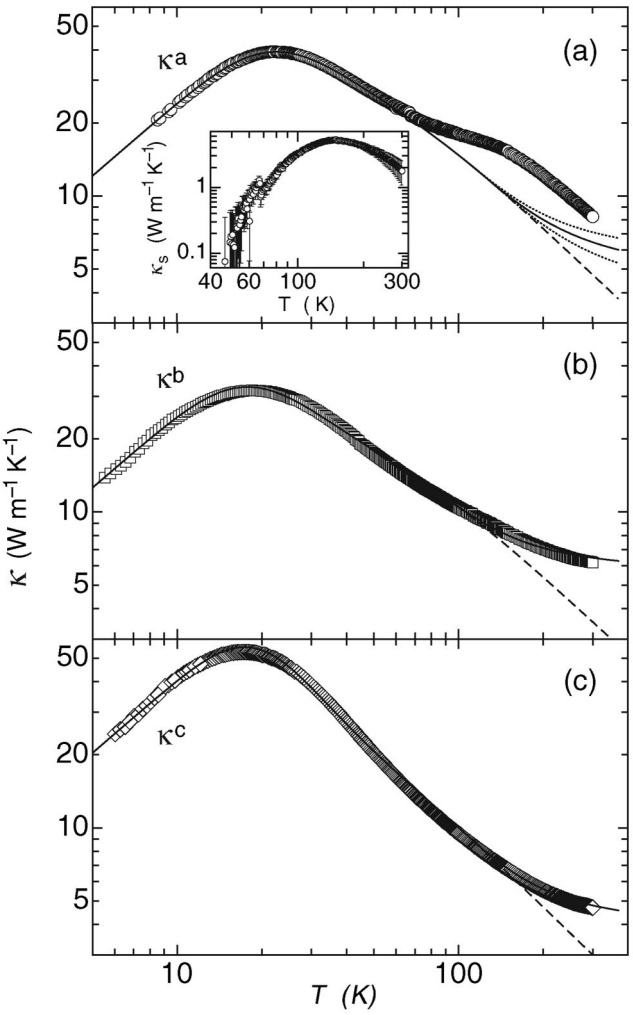

FIG. 1. Thermal conductivity of Y_2BaNiO_5 along (a axis) and perpendicular (b and c axis) to the spin chains. The solid (dashed) lines represent calculations of the phonon contributions with (without) taking into account a minimum phonon mean free path. The inset shows the spin contribution to the thermal conductivity along the chain direction (see text).

pounds [7,28–30]. The conventional explanation is the existence of an extra contribution to the thermal conductivity, beside the phonon conductivity ($\kappa_{\rm ph}$), coming from spin excitations (κ_s), such that along the direction(s) of strong magnetic exchange $\kappa^{\parallel} = \kappa_{\rm ph} + \kappa_s$. Because of weak interactions perpendicular to the chains or planes, κ_s is negligible in these directions, that is $\kappa^{\perp} \approx \kappa_{\rm ph}$. However, one has to be careful in associating any high-temperature anomaly in $\kappa^{\parallel}(T)$ with the spin transport because similarly looking features can also appear in a purely phononic thermal conductivity as a result of scattering via spin-lattice interaction in certain temperature regions [31], as well as being caused by additional thermal transport via optical phonon modes [32]. There are no obvious reasons, however, for these purely phononic mechanisms to show up only along the spin-chain direction. Thus, the most likely origin of the high-temperature feature in $\kappa^a(T)$ of Y_2BaNiO_5 is the spin contribution κ_s.

In order to analyze $\kappa_s(T)$, one has to subtract the phonon contribution $\kappa^a_{\rm ph}(T)$ from the total measured $\kappa^a(T)$ along the a direction. Assuming that the same scattering mechanisms influence $\kappa^i_{\rm ph}$ along all directions, we first analyzed $\kappa^b(T)$ and $\kappa^c(T)$, assumed to be purely phononic, in order to establish the main phonon scattering mechanisms. Then we applied the same analysis to $\kappa^a(T)$ at low temperatures where the spin contribution $\kappa_s(T)$ is expected to be negligibly small due to the spin gap, and extrapolated $\kappa^a_{\rm ph}(T)$ to higher temperatures. For this analysis, we employed the standard model of phonon thermal conductivity [18]:

$$\kappa_{\rm ph} = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\,\tau(\omega, T)\,dx, \quad (1)$$

where $x = \hbar\omega/k_B T$, ω is the frequency of a phonon, $\tau(\omega, T)$ is the relaxation time, Θ_D is the Debye temperature, $\upsilon = \Theta_D(k_B/\hbar)(6\pi^2 n)^{-1/3}$ is the mean sound velocity, and n is the number density of atoms. Because of the low $\kappa(T) \simeq 1\ \mathrm{W\,m^{-1}\,K^{-1}}$ at high temperatures, which is comparable to κ values of amorphous materials [33], we took into account a lower limit for the phonon mean free path $\ell_{\rm min}$. The underlying idea is that the phonon mean free path cannot be smaller than roughly the size of the unit cell. Such an $\ell_{\rm min}$ is also observed in crystalline materials at high temperatures [34]. Thus, the equation for τ was put in the form $\tau(\omega, T) = \max\{\tau_\Sigma(\omega, T), \ell_{\rm min}/\upsilon\}$. We now assume that all phonon scattering mechanisms act independently, such that $\tau_\Sigma^{-1} = \sum \tau_i^{-1}$, where each term τ_i^{-1} corresponds to an individual scattering mechanism. We found that two scattering mechanisms, namely phonon scattering by extended two-dimensional defects and phonon-phonon scattering in the form

$$\tau_\Sigma^{-1} = A\omega^2 + B\omega^2 T \exp(-\Theta_D/bT), \quad (2)$$

are sufficient to approximate $\kappa^b(T)$ and $\kappa^c(T)$. We used $\Theta_D = 390$ K estimated from the low-temperature specific heat [35]. The parameters A, B, b, and $\ell_{\rm min}$ were treated as freely adjustable parameters; the fit values are presented in Table I. The fits of $\kappa^i_{\rm ph}(T)$ for $i = b$ and c are shown in Fig. 1(b) and 1(c) as solid lines. The dashed lines are obtained for the same values of A, B, and b, but setting $\ell_{\rm min} = 0$. This demonstrates that $\ell_{\rm min}$ does not influence

TABLE I. Parameters of the fits of $\kappa^i(T)$ to Eq. (1).

Parameter	a axis	b axis	c axis
A (10^{-17} s)	4.0	3.8	2.4
B (10^{-18} s K^{-1})	9.1	12.0	14.9
b	6.7	8.1	6.1
$\ell_{\rm min}$ (Å)		18.3	12.8
Temperature region (K)	5–50	5–300	5–300

$\kappa^i_{\rm ph}(T)$ below about 100 K. Hence, only the parameters A, B, b can be adjusted by the fit of $\kappa^a_{\rm ph}(T)$ in the temperature range $T < 50$ K. We do not attribute much significance to the absolute values of the fit parameters for two reasons: (i) the Debye model is a crude estimate of the phonon spectrum of a real material, and (ii) the fit is only used to estimate the phonon background contribution, which has to be subtracted in order to separate the spin-mediated thermal conductivity.

The spin thermal conductivity along the chains $\kappa_s(T) = \kappa^a - \kappa^a_{\rm ph}$ is plotted in the inset of Fig. 1(a). For $\kappa^a_{\rm ph}(T)$, we used the solid line of Fig. 1(a), which is calculated for the fit parameters of Table I and $\ell_{\rm min} = 15.5$ Å, which is the average of the $\ell_{\rm min}$ values for the b and c axes. The dotted lines are obtained for $\kappa^a_{\rm ph}(T)$ if the individual values of $\ell_{\rm min}$ for b and c are used. One can see that the errors of $\kappa^a_{\rm ph}$ due to the uncertainty of $\ell_{\rm min}$ are negligible below about 140 K and reach about $\pm 10\%$ at 300 K. Below about 70 K, κ_s is not well resolved because the difference between the total measured κ^a and the estimated phonon contribution $\kappa^a_{\rm ph}$ becomes of the order of relative experimental errors. Therefore, we will consider only the κ_s data above this temperature. The maximum of $\kappa_s(T)$ amounts to about 5 $\mathrm{W\,K^{-1}\,m^{-1}}$. That is about 5 times higher than that observed for the only other Haldane system $AgVP_2S_6$ ($J \simeq 780$ K; $\Delta \simeq 240$ K) for which thermal conductivity has been investigated so far [11]. From our $\kappa_s(T)$ data, we calculated the spin-related energy diffusion constant $D_E(T) = \kappa_s(T)/(C_s(T)a^2)$, where $C_s(T)$ is the specific heat of the spin chain and a the lattice constant along the chain. For $C_s(T)$, the numerical results for the ideal HAF $S = 1$ chain with $J/k_B = 280$ K, calculated within the quantum nonlinear σ-model (NLσM) [36], were used.

The results of the present study together with the data for $AgVP_2S_6$ are shown in Fig. 2(a). It is remarkable that not only the absolute values, but also their temperature dependencies are similar for both materials. An important observation is that, for both $S = 1$ materials, $D_E(T)$ remains rather low in the whole investigated temperature region. This is in stark contrast to the $S = 1/2$ chains where $D_E(T)$ increases by about 2 orders of magnitude with decreasing temperature, as is also shown in Fig. 2(a).

The question is whether this is a generic difference, related to the integrability of the $S = 1/2$ and the nonintegrability of the $S = 1$ chain model, or is it caused by extrinsic influences. To our knowledge, theoretical calculations for the energy diffusion in $S = 1$ HAF chains at $T \lesssim J/k_B$ are absent. The early analysis by Huber *et al.* gives the high-temperature limiting value for $D_E^{\rm ht} \sim 2J/\hbar$ [37], while a recent numerical study suggests a higher value of $D_E^{\rm ht} \approx 5.6J/\hbar$ [10]. Indeed, at high temperatures $D_E(T)$ of Y_2BaNiO_5 is close to this limiting value, see Fig. 2(a). The fact that $D_E(T)$ approaches $D_E^{\rm ht}$ calculated for purely intrinsic interactions [10] suggests that intrinsic

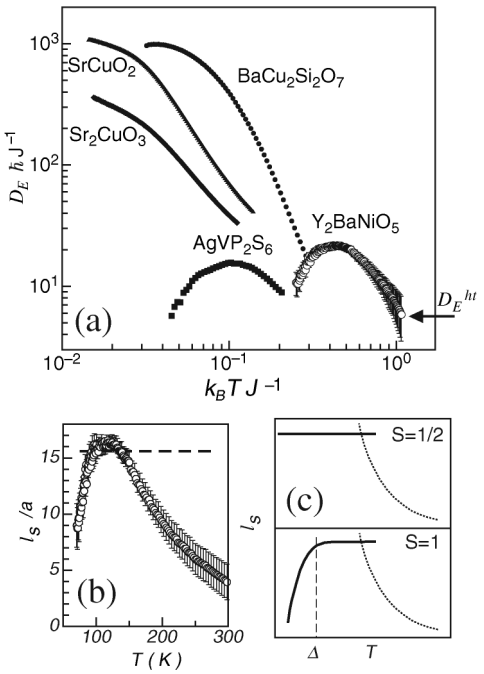

FIG. 2. (a) The energy diffusion constant $D_E(T)$, calculated from the thermal conductivity data of Y_2BaNiO_5. For comparison, we also show $D_E(T)$ of the $S = 1$ chain compound $AgVP_2S_6$ and of the $S = 1/2$ chain compounds $BaCu_2Si_2O_7$, Sr_2CuO_3, and $SrCuO_2$ (data from Refs. [7,8,11]). The arrow corresponds to the high-temperature limit $D_E^{\rm ht}$ calculated in [10]. (b) The normalized mean free path of the spin excitations calculated from the thermal conductivity data. The lower limit $\ell_{\rm min}^{\rm segment}$ of the average chain segment length estimated from the susceptibility data is shown by the dashed line. (c) Illustration of the expected differences in defect scattering in the $S = 1/2$ and $S = 1$ chains. The solid lines correspond to the mean free path for spin excitations when defect scattering is dominant. The dotted lines corresponds to a temperature-dependent scattering which is expected to become dominant at high temperatures, such as interaction between spin excitations or interactions with phonons.

processes largely determine the energy diffusion in Y_2BaNiO_5 at high temperatures.

However, the experimental energy diffusion constant for $S = 1$ chains does not scale as T/J, although such a scaling should hold for intrinsic diffusion. This scaling is also absent for the $S = 1/2$ case where predominantly external perturbations, such as spin-phonon interaction [38], determine the behavior of spin-mediated heat transport. This suggests that, at least for a part of the excitation spectrum of the $S = 1$ chains, external perturbations are also important. Besides phonons, magnetic impurities, that is ions with spin $S \neq 1$, are also expected to contribute to the scattering of spin excitations. If, in a certain temperature range, this type of scattering dominates, one may expect the magnon mean free path ℓ_s to be close to the average distance between the impurities in the chains. Information about the concentration of magnetic impuri-

ties can be obtained from the low-temperature increase of the magnetic susceptibility, if the type of impurities is known [39,40]. For our sample, this is not known, but we can estimate the lower limit of the average chain segment length $\ell_{\mathrm{min}}^{\mathrm{segment}}$ by assuming that all magnetic impurities have $S = 1/2$ and are situated in the chains. A corresponding fit of the susceptibility data (not shown) of our sample yields $\ell_{\mathrm{min}}^{\mathrm{segment}} \sim 60$ Å. In Fig. 2(b), the mean free path of the spin excitations, estimated via $\ell_s = \kappa_s/(C_s v_s)$ where v_s is the average velocity of spin excitations, is compared with $\ell_{\mathrm{min}}^{\mathrm{segment}}$. In our calculations, we used $v_s(T) = (Z\hbar)^{-1} \int \varepsilon_k' f(\varepsilon, T) dk$, where $Z = \int f(\varepsilon, T) dk$, $f(\varepsilon, T) = (\exp(\varepsilon/k_B T) - 1)^{-1}$, and $\varepsilon(k)$ is the dispersion relation. For magnons in the $S = 1$ chain, we used the corresponding relations from the NLσM, $\varepsilon(k) = [V^2(ka)^2 + \Delta(T)^2]^{1/2}$ with $\Delta_0 = 0.41$ J, and $V = 2.49$ J [41].

At low temperatures, $\ell_s(T)$ approaches $\ell_{\mathrm{min}}^{\mathrm{segment}}$ suggesting that magnetic impurities are indeed one of the most important sources of magnon scattering. For several $S = 1/2$ chain compounds, a saturation of $\ell_s(T)$ at low temperatures is observed [8]. This is intuitively understood as resulting from scattering by defects, in analogy with the boundary scattering in conventional systems. However, after reaching a peak around 120 K, the derived $\ell_s(T)$ of Y_2BaNiO_5 decreases again with further decreasing temperature; a similar behavior was also observed for the $S = 1$ compound $AgVP_2S_6$ [11]. Yet, this behavior does not contradict the assumption that impurities are the dominant scatterers at low temperatures, since in gapped 1D spin systems, impurities are expected to give a constant mean free path only at high temperatures [42]. At $T \ll \Delta$, the scattering efficiency of point defects is energy dependent and the low-energy spin excitations are scattered by impurities stronger than high-energy excitations [42]. This should lead to a mean free path decreasing with decreasing temperature for $T \lesssim \Delta$ in the $S = 1$ chains, in contrast to the gapless $S = 1/2$ chains, as is illustrated in Fig. 2(c). This expectation is in apparent agreement with our experimental results.

In conclusion, our study of the anisotropic thermal conductivity of the $S = 1$ Haldane chain system Y_2BaNiO_5 permits an evaluation of the contribution of spin excitations to the heat transport along the chain direction. The corresponding energy diffusion constant is found to be close to the predicted high-temperature limiting value. With decreasing temperature, the spin-related energy diffusion constant of Y_2BaNiO_5 increases much less than those of $S = 1/2$ chain compounds in agreement with theoretical expectations. The absolute values and the temperature dependence of the magnon mean free path suggest that magnetic impurities provide the dominating scattering mechanism for magnons at low temperatures.

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