Thermal conductivity and specific heat of the linear chain cuprate Sr$_2$CuO$_3$: Evidence for thermal transport via spinons

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We report measurements of the specific heat and the thermal conductivity of the model Heisenberg spin-1/2 chain cuprate Sr$_2$CuO$_3$ at low temperatures. In addition to a nearly isotropic phonon heat transport, we find a quasi one-dimensional excess thermal conductivity along the chain direction, most likely associated with spin excitations (spinons). The spinon energy current is limited mainly by scattering on defects and phonons. Analyzing the specific heat data, the intrachain magnetic exchange \( J/\kappa_B \) is estimated to be \( \approx 2650 \) K.

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There is a considerable theoretical interest in one-dimensional (1D) Heisenberg spin-1/2 systems because they exhibit a number of properties that are entirely dominated by quantum-mechanical behavior and have no analogues in three-dimensional systems. In particular, it has been shown that the Heisenberg \( S=1/2 \) chain represents an integrable system characterized by a macroscopic number of conservation laws. One important conserved quantity is the energy current, implying an ideal (infinite) thermal conductivity along the chains at nonzero temperatures, if perturbations from impurities, phonons, or an interchain coupling, which always lead to non-integrable models, are negligible. It is an open question, to what extent a real material may be regarded as an ideal integrable system. Probably, the most obvious evidence for the predicted anomalous heat transport is the recent observation of an unusually high quasi-1D magnetic thermal conductivity in the series (Sr,Ca,La)$_{14}$Cu$_{24}$O$_{53}$. The structure of these materials contains two building blocks with 1D character, namely CuO$_3$ chains and Cu$_2$O$_3$ ladders, both oriented along the same direction. Unfortunately, the dimerisation within the chains and a non-negligible interchain interaction in this system complicate the analysis of the observed features in terms of an integrable model.

In this work, we have searched for anomalies in the thermal transport of Sr$_2$CuO$_3$, which is often considered as the best physical realization of the 1D Heisenberg \( S=1/2 \) model. The crystal structure of Sr$_2$CuO$_3$ contains chains formed by CuO$_4$ squares sharing oxygen corners. The chains run along the \( b \) axis and, as shown in the inset of Fig. 1, the CuO$_4$ squares lie in the \( ab \) plane. The intrachain exchange interaction between neighboring Cu$^{2+}$ ions connected via 180° Cu-O-Cu bonds, measured as \( J/\kappa_B \), is between 2150 and 3000 K. The ratio \( k_B T_N/J \), where \( T_N \) is the 3D Néel temperature, is as small as \( 2 \times 10^{-5} \), reflecting an extremely small ratio \( J'/J \), \( J' \) representing the interchain interaction.

Our observations indicate an excess thermal conductivity along the chain direction, provided by quasi-1D spin excitation (spinons). According to our analysis presented below, its magnitude is limited by scattering of spinons on defects and phonons. We find no evidence for a mutual scattering between spin excitations and hence it seems to be absent or at least negligibly small, in agreement with theoretical predictions for integrable models.

The specimens used in these experiments were cut from a single crystal that had been grown by the traveling solvent floating zone method. The details of crystal growth and structural characterization are described elsewhere. For thermal transport measurements, three rectangular-bar-shaped samples of typical dimensions \( 2.5 \times 1 \times 1 \) mm$^3$ with the longest dimension parallel to either the \( a \), \( b \) or \( c \) axis were prepared. Two additional samples, #1 and #2, cut from the same piece, were used for specific heat measurements. The thermal conductivity was measured using a conventional steady-state method as described in Ref. 3. A standard relaxation technique was employed for the specific heat measurements. The magnetic susceptibility \( \chi \) was measured with a commercial SQUID magnetometer.

Small amounts of excess oxygen are known to be present in as-grown crystals of Sr$_2$CuO$_3$, giving rise to a Curie-Weiss term in the temperature dependence of the magnetic susceptibility due to uncompensated Cu \( S=1/2 \) spins. In order to study the influence of excess oxygen, we annealed sample #2 at 870°C for 72 h under argon atmosphere, as described in Ref. 3. From the results of our measurements of \( \chi(T) \), the ratio of the number of residual spin-1/2 impurities to the total number of Cu ions was estimated to be \( 1.8 \times 10^{-4} \) for the unannealed sample #1 and \( 6 \times 10^{-5} \) for the annealed sample #2.

The results of the specific heat \( (C_p) \) measurements in the temperature range between 1.5 and 22 K are presented in Fig. 4 as a plot of \( C_p/T \) versus \( T^2 \). The solid
The inset of Fig. 1 reveals anomalies of the specific heat with onsets below approximately 3.5 K for both samples, indicating some sort of phase transition. For the annealed sample the anomaly is shifted to lower temperatures with respect to the peak for the as-grown sample. Both anomalies occur at lower temperatures than the Néel temperatures $T_N$ found by $\mu$SR ($4.15 < T_N < 6$ K) and neutron scattering ($T_N = 5.4$ K) measurements, respectively. One possible explanation for this disagreement is that, besides the transition to an antiferromagnetically (AFM) ordered state at $T_N = 5.4$ K, not reflected in $C_p(T)$, there is another transition at $T < 3.5$ K. Recently, two subsequent magnetic phase transitions at $T_1 = 5.0$ K and $T_2 = 1.5$ K were observed for SrCuO$_2$, containing similar spin-1/2 chains but assembled pairwise in arrays of zigzag chains. The more likely possibility that is consistent with our observations is that our anomalies reflect the AFM transition reported in Refs. 17 and 18 but now shifted to lower temperatures because of a smaller number of impurities in the samples. It has been shown that nonmagnetic impurities interrupting the spin-1/2 chains enhance staggered spin-spin correlations a common feature of various low-dimensional Heisenberg spin systems. A convincing manifestation of this feature is the stabilization of the long-range AFM order by replacing Cu$^{2+}$ with non-magnetic ions in the spin-ladder system SrCu$_2$O$_3$ (Ref. 24) and the spin-Peierls system CuGeO$_3$ (Refs. 25,26). Recently, a field-induced staggered magnetisation near impurities was also observed in Sr$_2$CuO$_3$ by NMR measurements. Therefore, it seems quite likely that the experimentally observed Néel temperatures are always enhanced via the influence of impurities and exceed the value that is given by the ratio $J'/J$ itself. Indeed, for Sr$_2$CuO$_3$ calculations considering only dipolar interchain coupling yield a value of $T_N$ as low as 0.028 K.

The results of the thermal conductivity $\kappa$ along the $a$, $b$, and $c$ axes are presented in Fig. 2. For both directions perpendicular to the chain direction, $\kappa(T)$ shows a peak at $T_{\text{max}} \sim 20$ K and a decrease with increasing temperature, tending to a $T^{-1}$ variation above $T \geq 200$ K. This behavior is typical for phonon thermal transport. The thermal conductivity along the chain direction, $\kappa_a$, exhibits the same temperature dependence at $T \lesssim T_{\text{max}}$ but obviously not so at higher temperatures. We suggest that this difference is caused by an additional quasi-1D heat transport along the chain direction, provided by spin excitations. For insulators the phonon–phonon scattering mechanism leads to $\kappa \propto T^{-n}$ ($n \sim 1$) at $T \geq \Theta_D$. For layered structures, such as Sr$_2$CuO$_3$, where the layers are perpendicular to the $a$ axis, one may expect that in this temperature region the ratio between the in-plane and the out-of-plane phonon conductivity is larger than the anisotropy of $\kappa(T)$ along two different in-plane
Since the difference between \( \kappa_c \) (in-plane) and \( \kappa_e \) (out-of-plane) is very small, the difference between \( \kappa_b \) and \( \kappa_e \) (both in-plane) should even be smaller. This argument is, of course, not valid for the temperature region near and below \( T_{\text{max}} \), where the influence of sample boundaries and various defects is important and, therefore, the behavior of \( \kappa(T) \) is, to some extent, sample-dependent. Our fitting of \( \kappa_c(T) \) and \( \kappa_a(T) \) of \( \text{Sr}_2\text{CuO}_3 \), employing the Debye model of phonon thermal conductivity in a similar way as described in Ref. 3, has shown that the influence of boundary scattering on the thermal conductivity is negligible at \( T \geq 50 \text{ K} \). The same calculation indicates that an enhanced phonon contribution to \( \kappa_b \) below 50 K may mostly be traced back to an enhanced phonon mean free path which is limited by boundary and defect scattering. Based on all these arguments presented above, we make the crucial assumption that the phonon thermal conductivity at \( T \geq 50 \text{ K} \) is almost isotropic.

In order to single-out the heat transport due to spin excitations, the phonon thermal conductivity, averaged over the \( a \)- and \( c \)-directions at \( T \geq 50 \text{ K} \), was subtracted from the experimental data of \( \kappa_b \). The resulting spin part \( \kappa_s \) is also plotted in Fig. 3. In a first approximation, valid for any system of quasiparticles, the 1D thermal conductivity is given by the simple kinetic expression

\[
\kappa_s = C_s v_s l_s,
\]

where \( C_s \) is the specific heat, \( v_s \) is the velocity, and \( l_s \) is the mean free path of the spin excitations. The velocity of spinons is

\[
v_s = J a \pi / 2 \hbar,
\]

where \( a \) is the distance between the spins along the chain direction. Since \( T \ll J/k_B \) still holds, Eq. (4) for the specific heat is valid, and thus the thermal conductivity of spinons is given by the simple equation

\[
\kappa_s = N_s a^2 k_B^2 \pi l_s T, \tag{3}
\]

where \( N_s \) is the number of spins per unit volume. Eq. (3) has been shown to also be valid for 1D magnon systems.

We calculated \( l_s \) using Eq. (3) and taking into account small (maximum 6.5% at 300 K) deviations of \( C_s(T) \) from linearity. The calculated spinon mean free path is shown in Fig. 3. It tends to reach a constant value at low temperatures and decreases with increasing temperature. Assuming that the different scattering mechanisms act independently, the inverse total mean free path of spinons \( l_s^{-1} \) may be written as a sum \( \sum l_s^{-1} \) of the inverse mean free paths produced by each scattering mechanism. It turns out that

\[
l_s^{-1} = A T \exp(-T^*/T) + L^{-1}, \tag{4}
\]

with the parameters \( A = 8.2 \times 10^5 \text{ m}^{-1}\text{K}^{-1} \), \( T^* = 186 \text{ K} \), and \( L = 7.86 \times 10^{-8} \text{ m} \), reproduces our results in the whole temperature region between 50 and 300 K with high accuracy, as may be seen in Fig. 3. If the first term on the right-hand side of Eq. (4) is to represent Umklapp processes, spinon-spinon scattering may be ruled out because this case would require \( T^* \) to be of the order of \( J/k_B \sim 2600 \text{ K} \). Since \( T^* \) is close to \( \Theta_D/2 = 220 \text{ K} \), spinon-phonon Umklapp processes are the most likely choice for this contribution.

The second and constant term in Eq. (4) is attributed to scattering of spin excitations on defects interrupting the Cu-O chains. In that case the value of the parameter \( L \) is a measure for the mean distance between the defects. Surprisingly, this distance is much shorter than the average distance of \( 2 \times 10^4 \ \text{Å} \) between \( S=1/2 \) impurities, estimated from the Curie-Weiss-type term of the magnetic susceptibility. A similar discrepancy has also

![FIG. 2. Temperature dependence of the thermal conductivity of \( \text{Sr}_2\text{CuO}_3 \) along the \( a \), \( b \), and \( c \) axes. \( \kappa_s \) is the calculated spinon thermal conductivity along the \( b \) axis. The solid line is the estimated sum of spinon and phonon thermal conductivities assuming that the spinon mean free path is equal to the distance between bond-defects (see text). The schematic crystal structure is shown in the inset.](image-url)

![FIG. 3. Spinon mean free path for \( \text{Sr}_2\text{CuO}_3 \). The solid line is a fit to Eq. (3). The solid squares represent the distance between two neighboring bond-defects (from Ref. 30) and the dashed line is a polynomial fit to these data.](image-url)
been encountered in the interpretation of NMR measurements on Sr$_2$CuO$_3$. Recently, in order to explain some peculiar features of NMR spectra of Sr$_2$CuO$_3$, Boucher and Takigawa introduced the concept of mobile “bond-defects”, which are not related to interstitial excess oxygen. The calculated mean distance between two neighboring bond-defects, consistent with the NMR data between 20 and 60 K, is shown in Fig. 3. We note a reasonably good overlap with our data of $l_d$ at $T = 60$ K. The model of Boucher and Takigawa predicts that at lower temperatures the interaction between defects is important and the number of bond-defects decreases with increasing temperature. If our parameter $L$ in Eq. (4) indeed represents the distance between bond-defects, it ought to be temperature-dependent below 50 K. Unfortunately, a quantitative check of this conjecture is difficult because of the uncertain subtraction of the phonon background at $T \leq 50$ K. However, the idea that bond-defects are the main source of spinon scattering at low temperatures is, at least qualitatively, consistent with the temperature dependence and the anisotropy of the thermal conductivity also below 50 K. To demonstrate this, we calculated the total thermal conductivity ($\kappa_{\text{ph}} + \kappa_s$) along the $b$ axis at temperatures between 20 and 60 K assuming, first that $\kappa_{\text{ph}}$ is isotropic also in this temperature range and equal to the average of $\kappa_c$ and $\kappa_a$ and, second that $l_d$ is equal to the distance between neighboring bond-defects given in Ref. 32 (the dashed line in Fig. 3). The resulting temperature dependence of $\kappa_b$ shown by the solid line in Fig. 3 is in qualitative agreement with the experiment.

Concluding this paper, we return to the question whether the present results are relevant vis à vis of integrable models. We argue that a sizeable quasi-1D thermal transport mediated by spin excitations does exist in Sr$_2$CuO$_3$. Its magnitude is not exceptional but the scatterers, i.e., defects and phonons, limiting the mean free path of spin excitations are extrinsic to the magnetic system. Our analysis indicates the absence or negligibly small influence of spinon-spinon scattering on the thermal conductivity, in agreement with the predictions made for integrable models. Our results imply that a dissipationless energy current, expected for systems that fulfill the assumptions of the integrable Heisenberg 1D $S=1/2$ model, is not robust if perturbations like defects and lattice excitations interfere. The very high value of the magnetic exchange interaction within the chains and the low temperature magnetic phase transition, identified via our specific heat measurements, confirm that Sr$_2$CuO$_3$ may, nevertheless, be considered as an excellent realization of a 1D $S=1/2$ Heisenberg antiferromagnet.

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1. X. Zotos, F. Naef, and P. Prelovšek, Phys. Rev. B 55, 11029 (1997).
2. Th. Nienhuis and H. A. W. van Vianen, Phys. Lett. 34A, 401 (1971).
3. A. V. Sologubenko, K. Giannò, H. R. Ott, U. Ammerahl, and A. Revcolevschi, Phys. Rev. Lett. 84, 2714 (2000).
4. K. Kudo et al., J. Low Temp. Phys. 117, 1689 (1999).
5. Chr. Teske and Hk. Muller-Büschbaum, Z. Anorg. Allg. Chem. 371, 325 (1969).
6. T. Ami et al., Phys. Rev. B 51, 5994 (1995).
7. H. Suzuura et al., Phys. Rev. Lett. 76, 2579 (1996).
8. N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. 76, 3212 (1996).
9. D. C. Johnston, Acta Phys. Pol. A 91, 181 (1997).
10. A. Revcolevschi, A. Vietkine, and H. Moudden, Physica C 282-287, 493 (1997).
11. L. D. Faddeev and L. A. Takhtajan, Phys. Lett. 85A, 375 (1981).
12. O. V. Mischko et al., Phys. Rev. B 53, 14733 (1996).
13. H. Fujisawa et al., Phys. Rev. B 59, 7358 (1999).
14. M. Takahashi, Prog. Theor. Phys. 50, 1519 (1973).
15. F. D. M. Haldane, Phys. Rev. Lett. 66, 1529 (1991).
16. W. McRae and O. P. Sushkov, Phys. Rev. B 58, 62 (1998).
17. J. Lorenzana and R. Eder, Phys. Rev. B 55, 3358 (1997).
18. M. Takigawa, O. A. Starykh, A. W. Sandvik, and R. R. P. Singh, Phys. Rev. B 56, 13081 (1997).
19. A. Keren et al., Phys. Rev. B 48, 12926 (1993).
20. K. M. Kojima et al., Phys. Rev. Lett. 78, 1787 (1997).
21. I. A. Zaliznyak et al., Phys. Rev. Lett. 83, 5370 (1999).
22. S. Eggert and I. Affleck, Phys. Rev. B 46, 10866 (1992); Phys. Rev. Lett. 75, 934 (1995).
23. M. Laukamp et al., Phys. Rev. B 57, 10755 (1998).
24. M. Azuma et al., Phys. Rev. B 55, 8658 (1997).
25. S. B. Oseroff et al., Phys. Rev. Lett. 74, 1450 (1995).
26. M. Hase et al., Physica (Amsterdam) 215B, 164 (1995).
27. M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B 55, 14129 (1997).
28. R. Berman, Thermal Conduction in Solids, (Clarendon, Oxford, 1976).
29. S. Y. Ren and J. D. Dow, Phys. Rev. B 25, 3750 (1982).
30. D. L. Huber, Prog. Theor. Phys. 39, 1170 (1968).
31. D. C. Johnston et al., Phys. Rev. B 61, 9558 (2000).
32. J. P. Boucher and M. Takigawa, Phys. Rev. B 62, 367 (2000).
33. Note that the possibility of an enhanced low-temperature phonon mean free path along the $b$ axis is not taken into account in this calculation.