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Thermal conductivity and specific heat of the linear chain cuprate Sr_2CuO_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_2CuO_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/k_B is estimated to be $\simeq 2650$ K.

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.[1] One important conserved quantity is the energy current,[1,2] 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 nonintegrable 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 magnon thermal conductivity in the series $(Sr,Ca,La)_{14}Cu_{24}O_{41}$.[3,4] The structure of these materials contains two building blocks with 1D character, namely CuO_2 chains and Cu_2O_3 ladders, both oriented along the same direction. Unfortunately, the dimerization 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_2CuO_3, which is often considered as the best physical realization of the 1D Heisenberg $S=1/2$ model. The crystal structure of Sr_2CuO_3 contains chains formed by CuO_4 squares sharing oxygen corners.[5] The chains run along the b axis and, as shown in the inset of Fig. 2, 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/k_B, is between 2150 and 3000 K.[6–9] The ratio k_BT_N/J, where T_N is the 3D Néel temperature, is as small as 2×10^{-3}, 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 excitations (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.[10] For thermal transport measurements, three rectangular-bar-shaped samples of typical dimensions $2.5\times1\times1$ 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 χ was measured with a commercial SQUID magnetometer.

Small amounts of excess oxygen are known to be present in as-grown crystals of Sr_2CuO_3, giving rise to a Curie-Weiss term in the temperature dependence of the magnetic susceptibility[6] 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. 8. 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 1.8×10^{-4} for the unannealed sample #1 and 6×10^{-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. 1 as a plot of C_p/T versus T^2. The solid lines in Fig. 1 are fits to the data above 4 K using the approximation

$$C_p=\gamma T+\beta T^3+\delta T^5. \tag{1}$$

The parameter values are $\gamma=2.12\times10^{-3}$J mole^{-1} K^{-2}, $\beta=1.359\times10^{-4}$ J mole^{-1} K^{-4}, and $\delta=1.310\times10^{-7}$ J mole^{-1} K^{-6} for sample #1, and $\gamma=2.06\times10^{-3}$ J mole^{-1} K^{-2}, $\beta=1.531\times10^{-4}$ J mole^{-1}K^{-4}, and $\delta=1.310\times10^{-7}$ J mole^{-1} K^{-6} for sample #2.

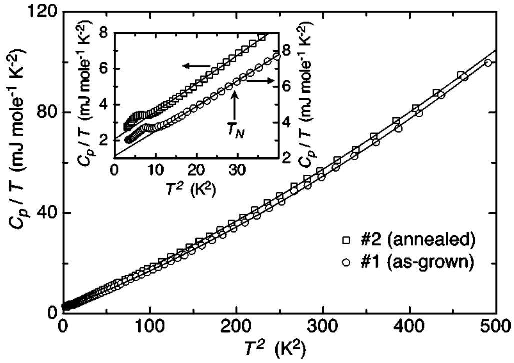

FIG. 1. Specific heat of Sr_2CuO_3 as C_p/T versus T^2. The solid lines represent the fit to Eq. (1). The inset shows the data at low temperatures. The value of T_N denoted by an arrow is from Ref. 18.

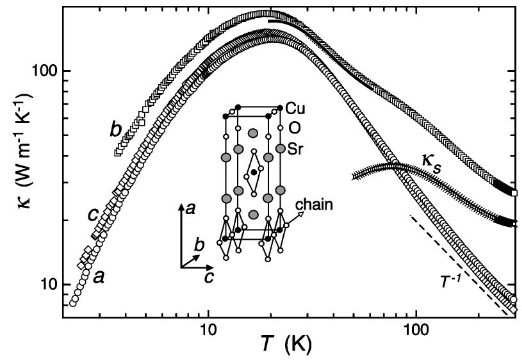

FIG. 2. Temperature dependence of the thermal conductivity of Sr_2CuO_3 along the a, b, and c axes. κ_s is the calculated spinon thermal conductivity along the b axis. The solid line is the estimated sum of spinon and phonon thermal conductivities assuming that the spinon mean free path is equal to the distance between bond defects (see text). The schematic crystal structure is shown in the inset.

The sum $\beta T^3+\delta T^5$ in Eq. (1) is a common low-temperature approximation for the lattice specific heat. The fit values of the parameter β result in values of the Debye temperature of $\Theta_D=441\pm10$ K and 424 ± 10 K for samples #1 and #2, respectively. Since Sr_2CuO_3 is an insulator, the linear in T contribution is not due to itinerant electrons but is ascribed to spin degrees of freedom.

The elementary excitations of a 1D Heisenberg spin-1/2 antiferromagnetic system are not $S=1$ magnons but $S=1/2$ topological excitations,[11] now commonly called ''spinons.'' The applicability of the spinon model has been demonstrated experimentally for several $S=1/2$ chain systems, including Sr_2CuO_3.[12,13] The corresponding specific heat at $T\ll J/k_B$ is given by[14–16]

$$C_s=\frac{2Nk_B^2}{3J}T, \tag{2}$$

where N is the number of magnetic ions in the system. The fit values of the parameter γ give $J/k_B=2620\pm100$ K and 2690 ± 100 K for samples #1 and #2, respectively. This may be compared with $J/k_B\simeq2200$ K deduced from magnetic susceptibility data[8,9] and a somewhat larger value of $J/k_B=2850$ K, as obtained from the analysis of an optical absorption spectrum.[7,17] The cited susceptibility measurements covered a wide temperature range between 5 and 800 K, whereas the absorption spectrum presented in Ref. 7 has been recorded at low temperatures (32 K). Hence the discrepancy between the values of J may be ascribed to its possible decrease with increasing temperature.[18] Our rather large low-temperature values of J are compatible with this suggestion.

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 μSR (Ref. 19) ($4.15<T_N<6$ K) and neutron scattering[20] ($T_N=5.4$ 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 $T_c<3.5$ K. Recently, two subsequent magnetic phase transitions at $T_{c1}=5.0$ K and $T_{c2}=1.5$ K were observed for $SrCuO_2$, containing similar spin-1/2 chains but assembled pairwise in arrays of zigzag chains.[21] The more likely possibility that is consistent with our observations is that our anomalies reflect the AFM transition reported in Refs. 19 and 20, 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,[22] a common feature of various low-dimensional Heisenberg spin systems.[23] A convincing manifestation of this feature is the stabilization of the long-range AFM order by replacing Cu^{2+} with nonmagnetic ions in the spin-ladder system $SrCu_2O_3$ (Ref. 24) and the spin-Peierls system $CuGeO_3$ (Refs. 25,26). Recently, a field-induced staggered magnetization near impurities was also observed in Sr_2CuO_3 by NMR measurements.[27] 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_2CuO_3, calculations considering only dipolar interchain coupling[6] yield a value of T_N as low as 0.028 K.

The results of the thermal conductivity κ 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 $T_{max}\sim20$ K and a decrease with increasing temperature, tending to a T^{-1} variation above $T\geqslant200$ K. This behavior is typical for phonon thermal transport.[28] The thermal conductivity along the chain direction, κ_b, exhibits the same temperature dependence at $T\leqslant T_{max}$ 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 $\kappa\propto T^{-n}$ ($n\sim1$) at $T\geqslant\Theta_D$. For layered structures, such as Sr_2CuO_3, where the layers are perpendicular to the a axis, one may expect that in this temperature region the ratio between an in-plane and the out-of-plane phonon conductivity is larger than the anisotropy of $\kappa(T)$ along two different in-plane directions.[29] Since the difference between κ_c (in-plane) and κ_a (out-of-plane) is very small, the difference between κ_b and κ_c (both in-plane) should even be smaller.

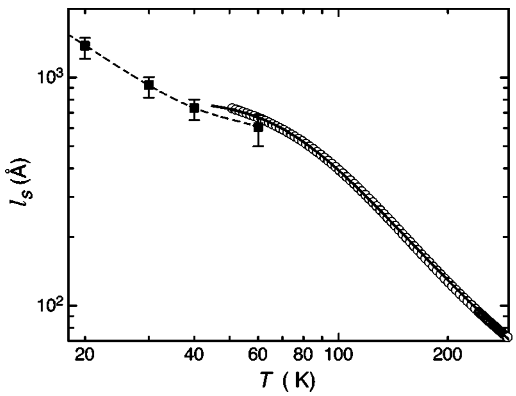

FIG. 3. Spinon mean free path for Sr_2CuO_3. The solid line is a fit to Eq. (4). The solid squares represent the distance between two neighboring bond defects (from Ref. 30) and the dashed line is a polynomial fit to these data.

This argument is, of course, not valid for the temperature region near and below $T_{\max}$, 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 Sr_2CuO_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 $T \geqslant 50$ K. The same calculation indicates that an enhanced phonon contribution to κ_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 $T \geqslant 50$ 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 $T \geqslant 50$ K, was subtracted from the experimental data of κ_b. The resulting spin part κ_s is also plotted in Fig. 2. 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[11] $v_s = Ja\pi/2\hbar$, where a is the distance between the spins along the chain direction. Since $T \ll J/k_B$ still holds, Eq. (2) for the specific heat is valid, and thus the thermal conductivity of spinons is given by the simple equation

$$\kappa_s = N_s a \frac{k_B^2 \pi}{3\hbar} l_s T, \tag{3}$$

where N_s is the number of spins per unit volume. Equation (3) has been shown to also be valid for 1D magnon systems.[30]

We calculated l_s using Eq. (3) and taking into account small (maximum 6.5% at 300 K) deviations[31] 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 $\Sigma l_{s,i}^{-1}$ of the inverse mean free paths produced by each scattering mechanism. It turns out that

$$l_s^{-1} = AT \exp(-T^*/T) + L^{-1}, \tag{4}$$

with the parameters $A = 8.2 \times 10^5$ m^{-1} K^{-1}, $T^* = 186$ K, and $L = 7.86 \times 10^{-8}$ 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 $J/k_B \sim 2600$ K. Since T^* is close to $\Theta_D/2 = 220$ 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 2×10^4 Å between $S = 1/2$ impurities, estimated from the Curie-Weiss-type term of the magnetic susceptibility. A similar discrepancy has also been encountered in the interpretation of NMR measurements on Sr_2CuO_3.[27] Recently, in order to explain some peculiar features of NMR spectra of Sr_2CuO_3, Boucher and Takigawa[32] 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,[32] is shown in Fig. 3. We note a reasonably good overlap with our data of l_s 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 $T \leqslant 50$ K. However, the idea that the 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 ($\kappa_{\mathrm{ph}} + \kappa_s$) along the b axis at temperatures between 20 and 60 K assuming, first that κ_{ph} is isotropic also in this temperature range and equal to the average of κ_c and κ_a and, second that l_s is equal to the distance between neighboring bond defects given in Ref. 32 (the dashed line in Fig. 3). The resulting temperature dependence of κ_b shown by the solid line in Fig. 2 is in qualitative agreement with the experiment.[33]

Concluding this paper, we return to the question whether the present results are relevant vis à vis integrable models. We argue that a sizeable quasi-1D thermal transport mediated by spin excitations does exist in Sr_2CuO_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.[1] 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_2CuO_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**, 11 029 (1997).
[2] Th. Niemeijer 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. L. 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. Misochko *et al.*, Phys. Rev. B **53**, 14 733 (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**, 13 681 (1997).
[19] A. Keren *et al.*, Phys. Rev. B **48**, 12 926 (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**, 10 866 (1992); Phys. Rev. Lett. **75**, 934 (1995).
[23] M. Laukamp *et al.*, Phys. Rev. B **57**, 10 755 (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 B **215**, 164 (1995).
[27] M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **55**, 14 129 (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.