Evidence for a large magnetic heat current in insulating cuprates

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There is growing experimental evidence that spin excitations may contribute significantly to the heat current in low-dimensional spin systems. This seems to be well established for one-dimensional (1D) systems\textsuperscript{1,2,4,5}. For example, in the insulating spin-ladder material Sr\textsubscript{14−x}Ca\textsubscript{x}Cu\textsubscript{24}O\textsubscript{41} a large magnetic contribution \(k_m\) to the thermal conductivity \(k\) can be derived from a pronounced double-peak structure of \(k\) along the ladder direction\textsuperscript{2,4}. The situation is less clear in two-dimensional (2D) spin systems. These are, however, of particular importance due to their relevance for high-temperature superconductivity\textsuperscript{6,7}. A double-peak structure comparable to that in 1D systems is found in the in-plane thermal conductivity of insulating 2D cuprates such as La\textsubscript{2}CuO\textsubscript{4} (LCO) and YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6} (YBCO) (Ref. \textsuperscript{8,9,10}). This may indicate a sizable magnetic contribution to the heat current at high temperatures\textsuperscript{8}. However, the phononic thermal conductivity \(k_{ph}\) may show a double-peak structure also, as a result of pronounced (resonant) scattering in a narrow temperature range. Such scattering may arise from the presence of local magnetic excitations, as was recently shown for the 2D spin-dimer system SrCu\textsubscript{2}(BO\textsubscript{3})\textsubscript{2} (Ref. \textsuperscript{11}), or it may arise from the presence of soft phonon modes\textsuperscript{12}. The latter was suggested for LCO and YBCO, in which soft modes e.g. associated with tilt distortions of the CuO\textsubscript{2} polyhedra are known to be present\textsuperscript{2,12}. An additional complication arises from a strong sensitivity of the double-peak structure to light oxygen doping\textsuperscript{2,12}.

A material of particular interest in this context is Sr\textsubscript{2}Cu\textsubscript{2}O\textsubscript{2}Cl\textsubscript{2} (SCOC). It is structurally very similar to LCO: It contains CuO\textsubscript{2}-layers as in LCO, but the out-of-plane oxygen ions at the apices of the CuO\textsubscript{6}-octahedra are replaced by Cl and La by Sr. The material has several advantages compared to LCO and YBCO (see e.g. Ref. \textsuperscript{11}). (1) SCOC does not exhibit any distortion from tetragonal symmetry down to at least 10K so that there is no structural instability associated with soft tilting modes. (2) Because of the absence of tilt distortions the magnetic properties are simpler than those of LCO. For example, there is no Dzyaloshinskii-Moriya exchange interaction. Thus, SCOC is believed to represent the best realization of a two-dimensional square-lattice \(S = 1/2\) Heisenberg antiferromagnet. (3) In contrast to LCO and YBCO, SCOC cannot be doped easily with charge carriers.

In this paper we present measurements of the in-plane thermal conductivity \(k\) of SCOC. We identify a double-peak structure from a pronounced high-temperature shoulder around 230 K. Analysis of these data and a comparison to LCO and YBCO shows that it is very unlikely that the double peak structure arises from anomalous phonon damping due to scattering on soft lattice modes or magnetic excitations. The data indicate instead a large magnetic thermal conductivity at high temperatures as an intrinsic feature of the insulating 2D cuprates.

We studied a single crystal of Sr\textsubscript{2}Cu\textsubscript{2}O\textsubscript{2}Cl\textsubscript{2} of rectangular form (1 × 3 × 4 mm\textsuperscript{3}) with the short direction along the crystallographic \(c\) axis. It was grown by the traveling-solvent floating zone method. The thermal conductivity was measured with the heat current within the CuO\textsubscript{2} planes by a conventional steady-state method using a differential Chromel-Au+0.07\%Fe-thermocouple. Typical temperature gradients were of the order of 0.2 K. The absolute accuracy of our data is restricted by uncertainties in the sample geometry whereas the relative accuracy is of the order of a few \%.\textsuperscript{13}

We show in Fig. 1 the in-plane thermal conductivity of SCOC as a function of temperature. We identify a maximum at \(\approx 30\) K and a shoulder at high temperatures around 230K. The pronounced low-temperature maximum of \(k\) indicates a high crystal quality. We note that \(k\) is independent of a magnetic field (\(\leq 8\) Tesla) applied within the CuO\textsubscript{2} planes perpendicular to the heat current. For comparison we show in Fig. 1 the in-plane thermal conductivity of a single crystal of LCO measured by Nakamura et al.\textsuperscript{6}. These data also reveal a double-peak structure. The absolute value of \(k\) at the low-temperature maximum is smaller than in SCOC. One reason may be that LCO is more sensitive to defects, resulting e.g. from excess oxygen, which introduces lattice defects and hole doping and thus reduces the mean free path of the heat-carrying excitations.

Both compounds, SCOC and LCO, are antiferromagnetic insulators. In an insulator the heat is usually carried by phonons. The typical behavior of \(k_{ph}\) of a crystalline insulator is shown by the solid lines in Fig. 1. These curves represent fits to the low-temperature maximum of \(k\) (fitted below about 50 K) of SCOC and LCO using the standard Debye model for the thermal conduc-
conductivity $k_c$ of LCO behaves as the in-plane thermal conductivity $k$ at low temperatures, but $k_c$ shows no indication of a high-temperature maximum. Such strongly temperature dependent anisotropy is not expected for purely phononic heat conduction.

Additional phonon scattering, active in a narrow temperature range close to the minimum of $k$, may in principle cause a double-peak structure. However, resonant scattering on local magnetic excitations as in SrCu$_2$(BO$_3$)$_2$ (Ref. 11) cannot be the correct explanation in the present case: In the 2D square-lattice cuprates the dispersion of magnetic excitations ranges from $\approx 0$ to $2J/kB \gtrsim 2000$ K ($J$ is the in-plane exchange constant) so that there is no reason that scattering on magnetic excitations should be most pronounced in a narrow temperature interval around 100 K. Note, in particular, that in the 2D cuprates scattering on magnetic excitations should not disappear above the Néel-temperature $T_N$, because the relevant energy scale is set by $J \gg T_N$ (see below). Additional phonon damping from scattering on soft lattice modes as suggested in Ref. 8 is also unlikely as a cause of the double peak: (1) There are no lattice instabilities in SCOC, rendering this mechanism unimportant for this material. (2) The double-peak structure is also present in the tetragonal low-temperature phase of Eu-doped LCO, in which no soft tilting modes should be present either. (3) The absence of a double-peak structure of $k_c$ in LCO (Ref. 8) implies that anomalous phonon scattering would have to be active only for $k$. Such strong anisotropy of the phonon-phonon scattering is not expected. Finally, note that the finding $k_c < k$ in LCO (Ref. 8) provides evidence against any scattering scenario as a cause of the double peak structure: for such scattering, if active only for $k$, but absent for $k_c$, implies $k < k_c$, in contradiction to the experimental results.

The data of Fig. 1 (in particular $k > k_c$) are most naturally explained, if an additional channel of heat transport for the in-plane thermal conductivity is present. In an undoped insulating 2D Heisenberg antiferromagnet with an electronic gap $\gtrsim 1.5$ eV, the only candidate for heat transport next to phonons are magnetic excitations. Their thermal conductivity $k_m$ adds to that of the phonons, i.e. $k = k_{ph} + k_m$. In order to extract $k_m$ from the data we subtract $k_{ph}$ as obtained from the fit of the low-temperature maximum. Note that $k_m$ cannot be obtained at $T \lesssim 100$K in this way, because Eq. 1 was fitted to the total $k$ below 50 K. Remarkably, $k_m$ is of comparable magnitude (roughly of the order 10 W/Km) in both compounds (see inset Fig. 1). The maximum of $k_m$ is at $\approx 245$ K in SCOC and at $\approx 285$ K in LCO.

Is a magnetic contribution of this size reasonable? We estimate $k_m$ using the kinetic equation in 2D,

$$k_m = \frac{1}{2} c_m v_m \ell_m.$$  

Here $c_m$ is the magnetic specific heat and $\ell_m$ the mean free path of the magnetic excitations. The velocity $v_m$ of long-wavelength spin waves is $v_m \approx 1.06 \cdot 10^5$ m/s.
and \( c_{m}^{\text{LCO}} \approx 1.16 \times 10^{5} \text{ m/s} \), which is obtained from \( v_{m} = \sqrt{8SZ_{c}Ja/h} \). Here \( Z_{c} \) is the Oguchi correction.  

Values of \( J_{m} \) for Fig. 1 show that the high-temperature maximum of \( k_{m} \) is determined by the large in-plane exchange interaction \( J \) and not by the inter-plane interactions. Therefore, no significant anomaly of \( k_{m} \) is expected at \( T_{N} \).

From these considerations we may draw several conclusions for the magnetic heat current: (1) We expect that \( k_{m} \) is determined by the large in-plane exchange interaction \( J \) and not by the inter-plane interactions. Therefore, no significant anomaly of \( k_{m} \) is expected at \( T_{N} \). (2) At least above \( T_{N} \), the heat-carrying magnetic excitations are not the familiar collective excitations of a magnetically ordered state (i.e. conventional magnons), but rather magnetic excitations (of triplet character) in a spin-liquid state. Note, however, that also at \( T < T_{N} \), the nature of the magnetic excitations of the 2D cuprates is under intensive debate.

A double-peak structure of \( k_{m} \) has also been reported for the insulating bilayer compound \( \text{YBa}_{2}\text{Cu}_{3}\text{O}_{6} \). As in LCO one observes pronounced anisotropy, i.e. \( k_{c} \) does not show a high-temperature maximum. Given the existence of a large \( k_{m} \) in the monolayer cuprates LCO and SCOC, the high-temperature maximum of YBCO is also likely to be of magnetic origin. This is consistent with the systematic variation of the temperature \( T_{H} \) of the high-temperature maximum of \( k \) with \( J \) for the three different insulating cuprates as shown in Tab. I.

The data in Fig. 1 show that the high-temperature maximum is more pronounced in LCO than in SCOC. A related observation is the weak high-temperature anomaly of \( k \) in \( \text{Pr}_{2}\text{Cu}_{4} \). In view of their rather similar magnetic properties one would expect a similar behavior of \( k_{m} \) in these compounds. However, doping with mobile charge carriers or static impurities influences the high-temperature maximum strongly. In particular, the high-temperature maximum in YBCO depends on a non-monotonic way on the oxygen concentration. Thus the different behavior of \( k_{m} \) might result from the fact that LCO and YBCO can easily be doped with charge carriers via variation of the oxygen content, whereas this is not possible in SCOC.

### Table I: Position \( T_{H} \) of the high-temperature maximum of \( k_{m} \), Neel-temperature \( T_{N} \), in-plane magnetic exchange coupling constant \( J \), and the ratio \( J/k_{B}T_{H} \) for three insulating 2D cuprates. Note that \( J/k_{B}T_{H} \) is very similar in all three compounds.

| Compound      | \( T_{H} \) (K) | \( T_{N} \) (K) | \( J/k_{B} \) (K) | \( J/k_{B}T_{H} \) |
|---------------|-----------------|-----------------|-------------------|-------------------|
| \( \text{YBa}_{2}\text{Cu}_{3}\text{O}_{6} \) | 200             | > 400           | 1125              | 5.6               |
| \( \text{Sr}_{2}\text{CuO}_{2}\text{Cl}_{2} \) | 245             | 260             | 1220              | 5.0               |
| \( \text{La}_{2}\text{CuO}_{4} \)        | 285             | 320             | 1390              | 4.9               |
Further experiments with a detailed control of the charge-carrier concentration could clarify this issue.

In summary, the in-plane thermal conductivity of Sr$_2$CuO$_2$Cl$_2$ shows an unusual temperature dependence with a pronounced shoulder at high temperatures, similar to the behavior found for La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_{6.9}$. There is no structural instability in Sr$_2$CuO$_2$Cl$_2$. Moreover, scattering on magnetic excitations is not restricted to a narrow temperature interval around the minimum of $k$ in these compounds. It is therefore unlikely that the double peak structure arises from strong damping of the phononic heat current by resonant scattering on soft lattice modes or magnetic excitations. The data rather indicate a large magnetic contribution to the heat current as an intrinsic property of the 2D cuprates.

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APPENDIX

To deduce $c(T)$ from the high-temperature series, this series is converted in a series for the entropy $s$ in the energy per site $e$ (Ref. 22). The extrapolations are stabilized by information on the ground state energy $e_0 = -0.669437(5)$ (Ref. 23), the maximum entropy $s = \ln 2$, and the expected low-energy power law $s(e) \propto (e - e_0)^{2/3}$. For the latter, Padé approximants are applied to $s'(e)/s(e) - 2/(3(e - e_0))$. Very good results are obtained (reliable error estimate $10^{-3}$ from comparing diagonal to non-diagonal Padé approximants). The result shown in the inset of Fig. 2 (error $10^{-3}$) is obtained by approximating

$$
\frac{(e - e_0) s'(e)}{s(e)} - \frac{2}{3} \ln \left( \frac{e - e_0}{1 - e_0} \right),
$$

which allows for multiplicative logarithmic corrections, yielding $c(T) \propto T^2(A + \ln^{-3}(1/T))$ with $A = 0$ and $\gamma = 1.05(5)$. We do not, however, exclude a small finite value of $A$ as found in spin-wave theory.

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