Thermal conductivity of doped La$_2$CuO$_4$ as an example for heat transport by optical phonons in complex materials

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Abstract. We investigate the phonon thermal conductivity $\kappa_{\text{ph}}$ of doped La$_2$CuO$_4$ based on out-of-plane thermal conductivity measurements. When room temperature is approached the temperature dependence of $\kappa_{\text{ph}}$ strongly deviates from the $T^{-1}$-decrease which is usually expected for heat transport by acoustic phonons. Instead, $\kappa_{\text{ph}}$ decreases much weaker or even increases with rising temperature. Simple arguments suggest that such unusual temperature dependencies of $\kappa_{\text{ph}}$ are caused by heat transport via dispersive optical phonons.

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The thermal conductivity $\kappa$ is an interesting tool in order to probe dissipation and scattering of any propagating excitation in a solid. A recent example is $\kappa$ of complex materials with low-dimensional spin structures where magnetic excitations provide an unusual transport channel of heat [1,2,3,4,5]. Such magnetic heat conduction can in general only be measured in parallel with the phononic heat transport of the underlying crystal lattice. A thorough understanding of the phonon thermal conductivity $\kappa_{\text{ph}}$ is therefore essential to identify and separate a magnetic contribution $\kappa_{\text{mag}}$.

In early experiments on magnetic materials clear deviations from a low-temperature scaling as $T^3$, which as $T \rightarrow 0$ is expected for $\kappa_{\text{ph}}$, were assessed as one important indication of $\kappa_{\text{mag}}$ [6,7,8]. Recently, experiments have been performed on materials where magnetic coupling and velocities of magnetic excitations are several orders of magnitude larger than in these early studies. Significant $\kappa_{\text{mag}}$ is in these cases present at much higher temperatures where $\kappa_{\text{ph}}$ is expected to follow a $T^{-1}$ behavior. Prominent examples are the spin-ladder system (Sr,Ca,La)$_{14}$Cu$_{24}$O$_{41}$ and the two-dimensional antiferromagnetic La$_2$CuO$_4$, where pronounced peaks are observed in $\kappa$ at high $T$ [1,2,3,4,5]. These high-$T$ anomalies reflect the dimensionality of the underlying magnetic structure, i.e., they are only observed when $\kappa$ is measured along the direction of ladders or, in the case of La$_2$CuO$_4$, parallel to the magnetic planes. However, it is not a priori clear that such anomalies result from magnetic heat transport. Just as well, it is possible that dispersive optical modes provide a thermal transport channel which could generate an unusual high-$T$ behavior of $\kappa_{\text{ph}}$. Even the observed anisotropies could be explained in such a scenario, since low-dimensional magnetic structures often originate from lattice sub-structures with a similar low dimensionality. It is therefore essential to carefully investigate the origin of high $T$ anomalies. A firm proof that indeed magnetic heat conduction is present, is for example obtained if the analysis of the additional contributions yields characteristic magnetic properties like the spin gap of the ladders or magnetic defect distances [1,2,3].

The actual relevance of heat conduction by optical phonons has, however, never been studied systematically. It is the purpose of this paper to initiate future work in this field by pointing out that optical phonons provide a substantial transport mechanism of heat in doped La$_2$CuO$_4$. Our estimation for the heat conductivity by optical phonons $\kappa_{\text{opt}}$ is based on realistic values for the phonon energies and velocities in this material. We find that at room temperature $\kappa_{\text{opt}}$ can amount to about 40% of the total phonon thermal conductivity $\kappa_{\text{ph}}$.

The experimental data which give reason for our considerations is the out-of-plane thermal conductivity $\kappa_c$ of La$_{1.8-x}$Eu$_{0.2}$Sr$_x$CuO$_4$ single crystals with $x = 0, 0.08, 0.15$ and $0.2$. Fig. 1 displays $\kappa_c$ as a function of $T$. Prior to discussing the high-$T$ behavior of $\kappa_c$ in more detail, we briefly summarize the most important facets of the doping- and temperature dependence of $\kappa_c$ which have been elaborately discussed in Ref. [9]. Details of the experiment are also described there. Unlike the in-plane-thermal conductivity $\kappa_{ab}$ of doped La$_2$CuO$_4$ which, depending on doping, consists of phononic, magnetic and...
Fig. 1. Out-of-plane thermal conductivity $\kappa_c$ of La$_{1.8-x}$Eu$_{0.2}$Sr$_x$CuO$_4$ ($x = 0, 0.08, 0.15, 0.2$) as a function of temperature.

Fig. 2. $\kappa_c$ of La$_{1.8-x}$Eu$_{0.2}$Sr$_x$CuO$_4$ ($x = 0, 0.08, 0.15, 0.2$) as a function of temperature (open circles). The solid lines extrapolate the $T$-dependence of $\kappa_c$ in the LTT-phase to high $T$ (cf. text).

electronic contributions, $\kappa_c$ is purely phononic for all Sr-contents. This is concluded from the very low out-of-plane electrical conductivity and the negligible magnetic coupling along the c-axis. A usual low-$T$ phonon peak is present in $\kappa_c$ for all doping levels. The gradual suppression of the peak upon Sr-doping is straightforwardly understood in terms of scattering by impurities which are induced by the Sr-ions. For $x \leq 0.15$ a step-like decrease is present at $T_{LT} \approx 130$ K which may be seen more clearly in Fig. 2 where the high-$T$ behavior of $\kappa_c$ is shown separately for each compound. At $T_{LT}$ a structural phase transition occurs between the so-called LTO- (Low-Temperature-Orthorhombic, $T \geq T_{LT}$) and LTT-phases (Low-Temperature-Tetragonal, $T \leq T_{LT}$). Soft tilting modes of the CuO$_6$-octahedra enhance the scattering of acoustic phonons in the LTO-phase, which generates the step at $T_{LT}$.

As revealed from Fig. 2 the $T$-dependence of $\kappa_c$ in the LTO-phase apparently evolves from ($x = 0, 0.08$) an almost constant behavior with a slight decrease at high $T$ into a clear increase with increasing $T$ ($x = 0.15, 0.2$). This obviously conflicts with the expected decrease of $\kappa_{ph}$ (ideally following $T^{-1}$). Strong deviations from the expected behavior could in principle arise from structural peculiarities of the LTO-phase. This can, however, be ruled out since in the case of $x = 0.2$ the LTT-, the LTO- and in addition the so-called HTT-structures (High-Temperature-Tetragonal) are successively passed through with rising $T$ without any influence on the increase of $\kappa_c$. Furthermore, $\kappa_{ph}$ of the LTO-phase should never be equal to and never exceed $\kappa_{ph}$ of the LTT-phase, where additional phonon-scattering by the aforementioned soft tilting modes does not exist. Yet this is the case for $x = 0.15$ and $x = 0.2$. For $x = 0$ and $x = 0.08$, a similar situation is present concerning a hypothetical $\kappa_{ph}$ of the LTT-phase which is extrapolated into the LTO-phase (solid lines in Fig. 2). These extrapolations have been obtained by fitting $\kappa_{ph}$ of the LTT-phase with $\kappa = a/T + b$, $b > 0$ and extrapolating this function to high $T$. In all cases these extrapolations are considerably smaller than the measured $\kappa_c$ just slightly above $T_{LT}$. We therefore conclude that in addition to the usual heat conductivity by the acoustic phonons, $\kappa_{acst}$, a further transport channel for heat is present. Electronic and magnetic contributions to $\kappa$ can be excluded as already mentioned above. The additional heat transport must therefore arise due to optical phonons. This is remarkable since in practice optical phonons are neglected in the analysis of phonon heat transport.

It is commonly argued that optical phonons have dispersion curves at high energy with almost no slope. In that case the number of excited phonons is small and these phonons do not propagate. Their ability to transport heat is therefore negligibly small. The situation is different in the case of doped La$_2$CuO$_4$ where it is well established that numerous optical phonons have a high velocity [12,13]. Considerable transport of heat by such optical phonons should therefore be possible if their energy is not too high to be excited at temperatures relevant here, i.e. at $T \lesssim 300$ K. In the following we therefore investigate this possibility based on a simple kinetic model for the phononic heat transport.

Following standard linearized Boltzmann-theory the thermal conductivity of a single phonon branch (labelled by $i$) in a crystal with cubic symmetry is given by [14]

$$\tau^i = \frac{1}{3} \frac{1}{(2\pi)^3} \int v_{k}^i \eta_k^i \frac{d}{dT} \eta_k d^3 k, \quad (1)$$

Note that an intersection between the measured and extrapolated curves also arises for extrapolation functions which decrease much weaker.
where \( v_i^k \), \( l_i^k \), \( c_i^k \) and \( n_i^k \) denote velocity, mean free path, energy and Bose function of a phonon. Frequently, a Debye-approximation with momentum independent mean free path is used, i.e. \( v_i^k \equiv v_i^0 \) and \( l_i^k \equiv l_i^0 \). In this case Eq. (1) simplifies to

\[
x_i^1 = \frac{1}{3} c_i^0 v_i^0 l_i^0
\]

with the specific heat \( c_i^0 \) of that phonon branch. The usual acoustic phonon thermal conductivity \( \kappa_{\text{acst}} \) is then obtained by summing up the contributions of the three acoustic phonon branches. Often the different branches of acoustic phonons are unified by employing an averaged phonon velocity and the Debye specific heat of phonons. Even though such an estimate for \( \kappa_{\text{acst}} \) is very crude, yet it is helpful to understand the \( T \) dependence of \( \kappa_{\text{acst}} \) in the low- and high-\( T \) limits: At low \( T \) the dominating scattering process is temperature independent scattering on crystal boundaries which leads to \( \kappa_{\text{acst}} \propto c_i \propto T^3 \). For \( T \to \infty \) the specific heat becomes constant while the phonon mean free path is inversely proportional to the number phonons that generate umklapp processes, i.e., \( \kappa_{\text{acst}} \propto T^{-1} \). These two limiting \( T \)-dependencies lead to the characteristic phonon-peak of \( \kappa_{\text{acst}} \) at low-\( T \) which arises when umklapp scattering becomes important and over-compensates the increasing number of phonons.

In order to obtain a description which takes optical phonon branches into account we take a summation over all relevant phonon branches (acoustic and optic), i.e.,

\[
\kappa = \sum_i x_i^1 = \frac{1}{3} \sum_i c_i^0 v_i^0 l_i^0,
\]

where we extract the velocities \( v_i^0 \) from linear approximations to the experimental \((0,0,q)\)-phonon dispersion relations as measured by inelastic neutron diffraction \[13\]. The specific heat \( c_i^0 \) of each branch is calculated with the usual Debye model where an energy gap \( \Delta_i \) has to be considered for the optical branches. Hence we have

\[
c_i^0 = 3 N_A k_B \left( \frac{T}{\Theta_D} \right)^3 \Gamma_i^0,
\]

where \( N_A \) and \( k_B \) are Avogadro’s and Boltzmann’s constants, \( \Theta_D \equiv v_i^0 h k_B^0 (6\pi^2 n)^{1/3} \) with \( n \) as the density of unit cells and

\[
\Gamma_i^0 = \frac{1}{\Theta_D^3} \int_0^{\delta_i} \frac{x \Delta_i}{T} \left[ x^2 \exp\left(x + \frac{\Delta_i}{T}\right) - \exp\left(x + \frac{\Delta_i}{T}\right) \right] dx.
\]

The different \( v_i^0 \), \( \Delta_i \) and \( \Theta_i^0 \) of the phonon branches which we used for our analysis are summarized in Table 1.

| Type    | \( \Delta_{\text{opt}}(K) \) | \( v_i^0 \) (ms\(^{-1}\)) | \( \Theta_D^i \) (K) |
|---------|-------------------------------|--------------------------|---------------------|
| acoustic 1+2 | 0 | 5423 | 280 |
| acoustic 3 | 0 | 12289 | 635 |
| optic A | 251 | 4263 | 220 |
| optic B | 333 | 3108 | 161 |
| optic C | 359 | 28041 | 1449 |

Table 1. Optical gaps \( \Delta_{\text{opt}} \), velocities \( v_i^0 \) and ‘Debye’ temperatures \( \Theta_D^i \) of the considered phonons.

and B already amount to about 80% of the Dulong-Petit value, i.e., the major part of these optical modes is already populated at this \( T \). Even though such an estimate for \( \kappa_{\text{acst}} \) is very crude, yet it is helpful to understand the \( T \) dependence of \( \kappa_{\text{acst}} \) in the low- and high-\( T \) limits: At low \( T \) the dominating scattering process is temperature independent scattering on crystal boundaries which leads to \( \kappa_{\text{acst}} \propto c_i \propto T^3 \). For \( T \to \infty \) the specific heat becomes constant while the phonon mean free path is inversely proportional to the number phonons that generate umklapp processes, i.e., \( \kappa_{\text{acst}} \propto T^{-1} \). These two limiting \( T \)-dependencies lead to the characteristic phonon-peak of \( \kappa_{\text{acst}} \) at low-\( T \) which arises when umklapp scattering becomes important and over-compensates the increasing number of phonons.

In order to obtain a description which takes optical phonon branches into account we take a summation over all relevant phonon branches (acoustic and optic), i.e.,

\[
\kappa = \sum_i x_i^1 = \frac{1}{3} \sum_i c_i^0 v_i^0 l_i^0,
\]

where we extract the velocities \( v_i^0 \) from linear approximations to the experimental \((0,0,q)\)-phonon dispersion relations as measured by inelastic neutron diffraction \[13\]. The specific heat \( c_i^0 \) of each branch is calculated with the usual Debye model where an energy gap \( \Delta_i \) has to be considered for the optical branches. Hence we have

\[
c_i^0 = 3 N_A k_B \left( \frac{T}{\Theta_D^i} \right)^3 \Gamma_i^0,
\]

where \( N_A \) and \( k_B \) are Avogadro’s and Boltzmann’s constants, \( \Theta_D^i \equiv v_i^0 h k_B^0 (6\pi^2 n)^{1/3} \) with \( n \) as the density of unit cells and

\[
\Gamma_i^0 = \frac{1}{\Theta_D^i} \int_0^{\delta_i} \frac{x \Delta_i}{T} \left[ x^2 \exp\left(x + \frac{\Delta_i}{T}\right) - \exp\left(x + \frac{\Delta_i}{T}\right) \right] dx.
\]

The different \( v_i^0 \), \( \Delta_i \) and \( \Theta_D^i \) of the phonon branches which we used for our analysis are summarized in Table 1.

It is evident from the table that the \( v_i^0 \) of the optical and acoustic branches are of comparable magnitude and therefore a significant propagation of the optical modes is present indeed. The degree of excitation of the optical modes is reflected by the specific heat, which is shown in Fig. 3 (a), for the different phonon branches. Remarkably, at \( T = 300 \) K the \( c_i^0 \) of the optical branches labelled A

\[2\text{ Since only a single phonon branch is considered, the Dulong-Petit value is } 24.9/3 \text{ Jm}^{-1}\text{K}^{-1} = 8.3 \text{ Jm}^{-1}\text{K}^{-1}.\]

\[3\text{ As a first approximation we assume for the calculation of } \kappa_{\text{acst}} \text{ and } \kappa_{\text{opt}} \text{ that the structural phase transition at } T_{LT} \approx 130 \text{ K does not affect the lattice dynamics.}\]
of the real dispersion relations which are present in some parts of the Brillouin-zone. Second, even though in the real material comparable dispersing optical phonon modes are present along all crystal directions, it is certainly not perfectly isotropic as implied by our approach. Third and finally, apart from the three acoustic branches we only take three optical branches into account. It is not clear whether the first two simplifications influence our estimation towards a smaller or larger result for $\kappa_{\text{opt}}$. Yet it is unlikely that the order of magnitude of $\kappa_{\text{opt}}$ is significantly smaller. Taking more optical branches into account, as required for a more realistic description, will certainly shift $\kappa_{\text{opt}}$ towards higher values.

Our data suggest a clear doping dependence of the ratio of $\kappa_{\text{opt}}$ and $\kappa_{\text{acst}}$ since the high-$T$ increase of $\kappa_{\text{c}}$ becomes more and more apparent with increasing Sr-content (cf. Fig. 2). We note in this context that for some of the dispersive optical phonon branches the optical gaps and the slopes of the dispersion curves change upon Sr-doping. Therefore, a growing importance of $\kappa_{\text{opt}}$ with increasing Sr-content could, for example, be related to decreasing optical gaps and increasing slopes of the dispersion curves [12,13]. However, in order to verify such a detailed interpretation, a more accurate description of $\kappa_{\text{ph}}$ than our simple approach is necessary. In principle, such can be achieved when the full set of $v_i^k$, $c_i^k$, and $l_i^k = v_i^k \tau_i^k$ (with the phonon life time $\tau_i^k$), accessible through neutron scattering experiments, is employed into the $\kappa$ in Eq. 1.

In conclusion, we have used a simple model in order to analyze the phononic out-of-plane thermal conductivity $\kappa_{\text{c}}$ of La$_{1.8-x}$Eu$_{0.2}$Sr$_x$CuO$_4$ in terms of contributions by acoustic and optic phonons. Heat conductivity by optical phonons turns out to be significant in this material, since according to our approach it amounts at room temperature to about 40% of the total phonon thermal conductivity. This result has important implications for studies on magnetic heat transport of low dimensional spin systems which are currently on debate [1,2,3,4,5,15,16,17]. Unusual $T$-dependencies of $\kappa$ which are hastily attributed to magnetic heat transport must carefully be excluded to stem from heat transport by dispersive optical phonons. We stress that more careful analysis of this usually underestimated mechanism of heat transport is desirable.

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