THERMAL CONDUCTIVITY AND GRAIN SIZE OF CERAMIC $La_{1.8}Sr_{.2}CuO_4$

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Abstract

In order to study the importance of Casimir phonon scattering on the thermal conductivity of $La_{1.8}Sr_{.2}CuO_4$, we measure the thermal conductivity between 1 and 30K on samples of different grain size. We conclude that it starts to be important in this temperature range for grain sizes $d < 10\mu$. The other phonon scattering mechanisms to understand the thermal conductivity temperature dependence are scattering against stacking faults or twin walls and tunneling system analogous to those found in glasses.

High temperature superconductors present an unusual low temperature thermal conductivity for superconducting materials. In $YBa_2Cu_3O_{7-x}$ a T^3 dependence is obtained for low density, small grain (d~1μ) ceramic samples[1]. While for high density, large grain (d~200μ) samples a T^2 with a much higher value is measured[2]. And at lower temperatures low density, medium grain size (d~10μ) yield a temperature dependence[3] similar to that of ceramic insulators[4]. The situation is clarified by measurements on monocrystals[5] that yield a T^2 law from .1 to 10K. In $Bi_2Sr_2CaCu_2O_{8+x}$ monocrystals[6] a similar dependence is obtained. While in the $La_{2-x}Sr_xCuO_{4-y}$, where no measurements have been performed on superconducting monocrystals, all groups find the same $T^{1.5}$ dependence[7] on ceramic samples of different origin and grain sizes. The curious insulator-like dependence is also observed at lower temperatures[8]. The actual understanding of these measurements can be summarized as follows. Casimir phonon scattering against grain boundaries is responsible for the T^3 seen in the small grain samples while other unknown and not yet well studied mechanisms yield the ceramic insulator-like behavior at low temperature. The T^2 dependence[5,6,9] observed in monocrystals and high density samples is the only "intrinsic" and is probably related to a mechanism similar to that of tunneling systems (TS) found in glasses and in certain disordered crystals, as first proposed by M. Núñez Regueiro et al.[10].

Well oxygenated and superconducting $La_{2-x}Sr_xCu_{4-y}$ monocrystals are extremely hard to prepare, rendering the determination of its intrinsic thermal conductivity almost impossible. What we have enterprised in the work presented in this communication is to try to determine what size of grain allows the measurement in dense ceramics of an intrinsic behaviour for the thermal conductivity. We have then made samples of different grain size by different methods and measured their thermal conductivity. We conclude that Casimir scattering is important for grain sizes smaller than 10μ and that, besides a T^2 probably due to TS, a term due to scattering against stacking faults is necessary to understand our data.

Samples 171, 172 and 174 were made by mixing the oxides and carbonates in the stoichiometric proportions and grinding them by hand in an agate mortar. After firing them at $1100^{\circ}C$ they were thoroughly regrinded and sintered at $1100^{\circ}C$ in an oxygen atmosphere for 2 hours (sample 171). While samples 172 and 174 were left longer to ensure grain enlargement. However, a good oxygenation was difficult to perform in them due to their grain size as seen from their low superconducting Tc. Sample 3μ was sintered from superconducting 3μ grains obtained by liophilization and carefully oxygenated at $1000^{\circ}C$ while the $S\mu1$ sample was done by sintering submicronic powder obtained from coprecipitation techniques and oxygenated at $1000^{\circ}C$ for two hours. The samples were characterized by resistive measurements and scanning electron microscopy.

The experimental setup for measuring the thermal conductivity is as follows. The sample was heated by a current passing through a metal-film resistor attached by silver paste to one end of the sample while the other end was glued also with silver paste to the heat sink. Two small calibrated carbon resistors served as thermometers to measure the thermal gradient, using a method described elsewhere (ref.11) which corrects for spurious heat flow and allows the use of one thermometer to calculate the temperature difference and the absolute temperature. The thermal conductivity of the measured samples is shown in Figure 1 and summarized in

Table 1. Values were corrected for density according to Landauer's formula[12]. We observe a neat tendency towards bigger powers with smaller grain size. This can be qualitatively explained in the following way: as the grain becomes smaller the importance of Casimir grain boundary scattering becomes bigger and the thermal conductivity tends to a T^3 behavior. However, we have done a more thorough analysis taking into account several different processes that can exist in this material whose interaction can yield the observed dependence. To calculate the thermal conductivity we use the expression

$$K(T) = \frac{1}{3} \int C(\omega,T)\ v^2\ \tau(\omega) d\omega$$

where $c(\omega,T)$ is the specific heat for phonon mode of frequency ω, v is a mean sound velocity and τ is the phonon scattering rate. In general the phonon scattering rate can be written

$$\tau(\omega) = (\alpha\omega^2 + \beta\omega^2 + \gamma\omega + \delta)^{-1}$$

The first term is due to the scattering[13] of phonons by electrons (K^e_{ph}) in the case that the phonon wave length λ_{ph} is longer than the electronic mean free path l_e. This possibility is sustained by the proposal of Uher and Cohen[8] that uncondensed electrons exist below Tc. The second term is originated by phonon scattering against stacking faults[14] (β is proportional to the stacking fault density N_p), that can be easy to form in this layered material. The third term is due to the scattering of phonons against TS, γ being proportional to the product of thier density coupling constant, $\bar{P} = Pg^2$ (See e.g. ref. 10). And the fourth one is due to incoherent phonon scattering against grain walls (Casimir scattering where δ is related to the mean grain size $\bar{d}$). Other scattering mechanisms such as point defects, dislocations, etc., have been ignored either because they will not give the desired temperature dependence (point defects), or because the magnitudes obtained by approximative fits gave unphysical quantities (e.g. too many dislocations). On the other hand a linear in T contribution by uncondensed electrons can be important at low temperatures, but not at the measured temperatures[8]. Phonons are, then, the sole heat carriers in this temperature range. An extremely good fit can be obtained with all the parameters at the same time, but the number of parameters renders such a fit useless for determining the important trends for the different samples. We have chosen then to consider only two at a time. If we choose an ω and a constant term (phonon electron or stacking faults and Casimir) we obtain a K_{ph}^{e} that misses the scaling[13] with temperature and residual resistivity by almost two order of magnitude. Scattering against uncondensed electrons can be then properly dismissed. If, however, we consider that the ω term comes from stacking faults we obtain values for their density of about onestacking fault each ~200 layers, which is a very plausible value. The δ term gives a value of the average grain size $\bar{d}$. We see that for the large grain samples the real d is ~10 times bigger, while for the smaller grain samples the value obtained from K(T) is closer to the real value the crossover roughly taking place for the 10μ sample. This means that for the larger grain samples the important scattering mechanism is another one, e.g. γ_{Ts}, while for smaller grain samples Casimir scattering is relevant. The other pair of parameters that can be taken together are the ω^2 and ω ones. The ω and the constant term alone cannot yield the observed dependence. The interplay of the N_p^{-1} and P seems to indicate that for about 10μ the Casimir term starts to be important. In fact if we suppose that TS are due to disorder of oxygen vacancies[15], we would indeed expect a lower P for the samples 171 that is better oxygenated, than for the samples 172 and 174, that are slightly deoxygenated. As we do not observe such behaviour we can assume that Casimir scattering (which is not taken into account in this last fit) causes a not real increase in the TS term. This is also seen in the smaller grain samples. A word should be said here on what can be the origin of the stacking faults. Though stacking faults in the strict sense can be expected in these compounds, the most commonly accepted planar defects are twin walls. It is impossible for the moment to distinguish between the two type of defects. This same process may be important for T > 10K in $YBa_2Cu_3O_{7-x}$ and may be at the origin of the T dependence found in $Bi_2Sr_2CaCu_3O_{8+x}$ for T > 1K.[6,16]

In conclusion, measurements of the thermal of ceramic samples of $La_{1.8}Sr_{.2}CuO_4$ of different grain sizes seem to indicate that the principal sources of phonon scattering are stacking faults, tunneling systems, and for samples of grain dimension smaller than approximately 10μ Casimir scattering against grain boundaries.

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TABLE I

SAMPLE	METHOD	GRAIN SIZE	DENSITY	T^n
3M	Liophilization	3	5.55	1.8
Sμ1	Coprecipitation	5	5.62	1.5
171	Grinding	10	6.21	1.4
174	Grinding	50	6.25	1.2
172	Grinding	100	6.72	1.2

TABLE II

SAMPLE	d	$K^{e}_{ph}(1K)$	$N_p^{-1}(1)$	$\bar{d}$	$N_p^{-1}(2)$	P
3μ	3	0.67	1600	1.7	5500	7.8
Sμ1	5	0.87	2100	5.0	2500	2.3
171	10	0.56	1300	3.8	2000	1.3
174	50	0.39	900	14	1100	0.56
172	100	0.47	1100	13	1300	0.52

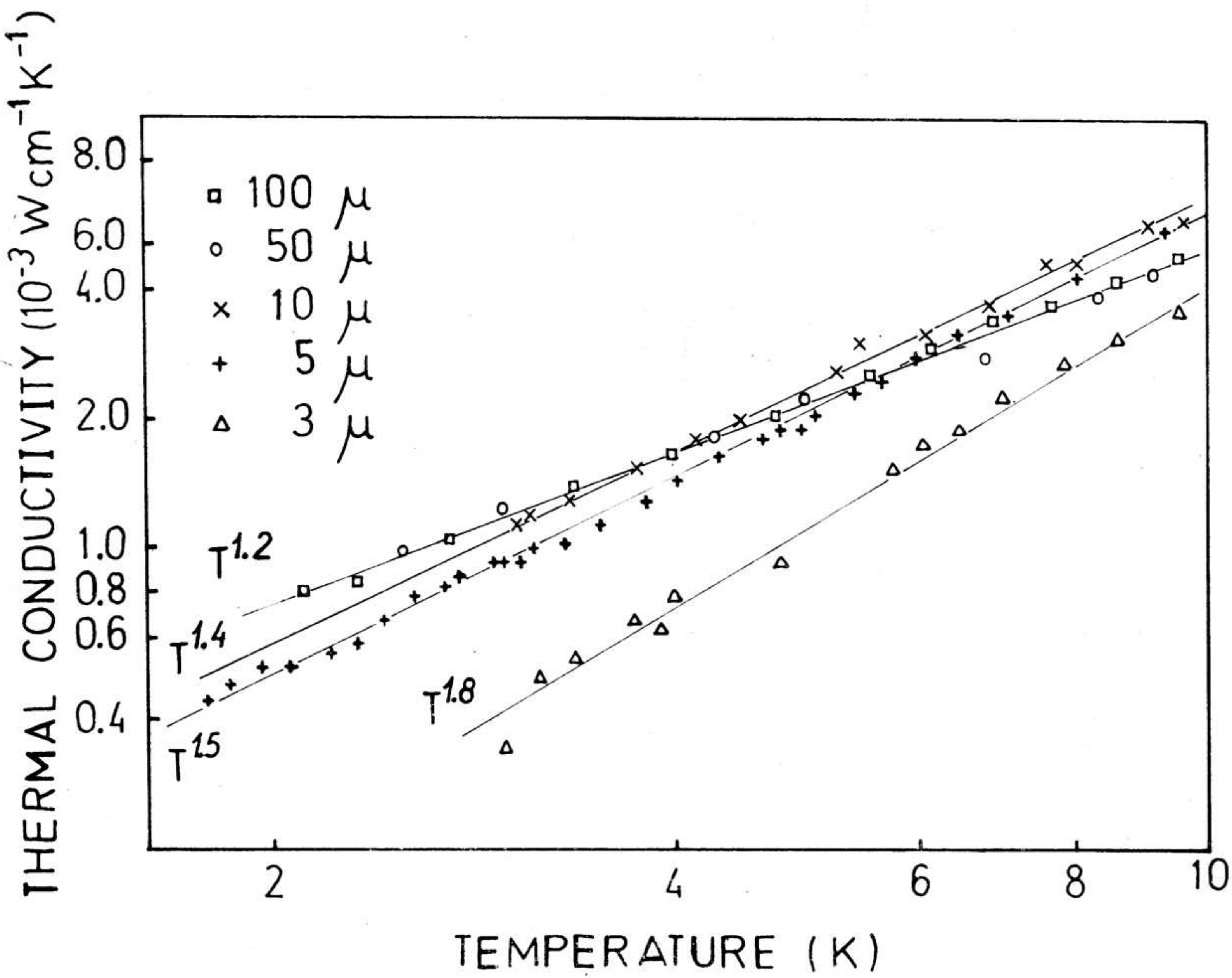
Figure Captions

Figure 1: Thermal conductivity of $La_{1.8}Sr_{0.2}CuO_{4-y}$ for different grain sizes is shown (Δ sample 3μ, + sample sμ1, × sample 171, o sample 174, □ sample 174. Samples were carefully oxygenated although samples 172 and 174 are slightly deoxygenated due to large grain sizes. Density corrections were made for all samples. The results show a temperature dependence that tends to higher powers with smaller grain sizes.

Table Captions

Table 1: Sample preparation is indicated and described in text. Mean grain size, in microns, was determined by scanning electron microscopy. The samples' densities were determined through volume and weight measurements and are given in grams per cubic centimeters. The powers for an $A.T^n$ fit show a tendency towards Casimir's regime as grain size becomes smaller (see text).

Table 2: The parameters of the two different fits discussed in the text are shown for each sample of mean grain size d (in microns). From the first fit we obtained the thermal conductivity of phonons against electrons K_{ph}^{e} (1K) shown at 1 K in 10^{-3} Watts K^{-1} cm^{-1}, the mean distance between stacking faults N_p^{-1} (1) in Å and the mean grain size $\bar{d}$ in microns. From the second fit, the distance between stacking faults N_p^{-1}(2) and the product of the density of tunneling states and coupling constant $\bar{P}$ in 10^6 erg cm^{-3} were calculated.


THERMAL CONDUCTIVITY (10^{-3} W cm^{-1} K^{-1})
8.0
6.0
4.0
2.0
1.0
0.8
0.6
0.4
100 μ
50 μ
10 μ
5 μ
3 μ
$T^{1.2}$
$T^{1.4}$
$T^{1.5}$
$T^{1.8}$
2
4
6
8
10
TEMPERATURE (K)