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## Heat transport in Bismuth and electron-doped cuprate superconductors

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A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

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à ma famille,

- à tous ces yeux noirs qui vous emmènent sur le versant ensoleillé de la vie,
- à l'Europe naissante.



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Résumé

La conductivité thermique s'avère très puissante pour sonder les quasiparticules électroniques, surtout à basse température. À plus haute température, elle renseigne sur le comportement des phonons et des électrons, mais les deux contributions se distinguent moins clairement.

Nous avons mené une étude comparative de la conductivité thermique dans les cuprates dopés aux trous et aux électrons, centrée sur  $Bi_2Sr_2CaCu_2O_8$  (dopé aux trous) et  $Pr_{1.85}Ce_{0.15}CuO_4$  (aux électrons). Un examen de la littérature a montré que l'apparente symmétrie entre ces deux familles (diagramme de phase, structure présentant des similitudes) contraste avec des propriétés physiques différentes.

Nous avons détecté la présence d'un fluide normal résiduel dans  $Bi_2Sr_2CaCu_2O_8$ , en accord avec la théorie pour les supraconducteurs *d*-wave, et montré son absence dans  $Pr_{1.85}Ce_{0.15}CuO_4$ , indication d'un gap sans zero. A plus haute temperature nous avons fait la première observation d'un pic à  $T_c$  dans la conductivité thermique de  $Pr_{2-x}Ce_xCuO_4$ .

## ABSTRACT

Thermal conductivity is a powerful probe of electronic quasiparticles, especially at low temperatures. At higher temperatures it gives very useful information on the behavior of quasiparticles and phonons, however both contributions are more difficult to identify precisely.

We carried out a comparative study of the thermal conductivity in the hole and electron-doped cuprates, focussed on  $Bi_2Sr_2CaCu_2O_8$  (hole-doped) and  $Pr_{1.85}Ce_{0.15}$ -CuO<sub>4</sub> (electron-doped). After a brief review of the literature it was clear that these families show very different physical properties, although they present similar features in their structure and phase diagram.

We detected the presence of a residual normal fluid in  $Bi_2Sr_2CaCu_2O_8$ , in rather good agreement with the theory for *d*-wave superconductors, and showed its absence in  $Pr_{1.85}Ce_{0.15}CuO_4$ , firm indication of a nodeless gap. At higher temperatures we observed for the first time a peak below  $T_c$  in the thermal conductivity of  $Pr_{1.85}Ce_{0.15}CuO_4$ .

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## INTRODUCTION

1

In 1986, the discovery of superconductivity at about 30 K in  $La_{2-x}Sr_xCuO_4$  [1] was the origin of an ever growing interest in high temperature superconductivity. Indeed, high temperature superconductivity constitutes a very challenging intellectual problem and has enormous potential for technological applications. The latter point leads scientists to search for always higher critical temperatures, the record so far being ~ 133 K for a compound in the Hg-Ba-Ca-Cu-O system (at normal pressure).

The high  $T_c$  cuprate superconductors have a layered perovskite-like structure consisting of conducting  $CuO_2$  planes separated by insulating layers. These  $CuO_2$  planes, where are believed to reside the charge carriers, are considered as playing a major role in superconductivity. The charge carriers can be holes (in hole-doped cuprates) or electrons (in electron-doped cuprates). After 12 years, the symmetry of the superconducting order parameter and the identity of the electron pairing mechanism appear to be close to being established. However, some fundamental questions remain unanswered. For instance, the hole and electron doped cuprates have the common aspects described above in their structure and have an apparently symmetric phase diagram. However, they display surprisingly many different physical properties and their order parameter seems to be of different symmetry. The first difficulty arises from experimental considerations. Whereas a consensus begins to exist about the symmetry of the gap in the hole-doped superconductors, because of materials problems, only two types of experiments have been able to give some information on this topic in electron-doped cuprates. Thermal conductivity, by probing normal quasiparticle at very low temperatures, can reliably give insight into the problem.

Thus we present in this thesis a comparative study of the thermal conductivity in the hole and electron-doped cuprates. We have investigated three hole-doped compounds,  $Bi_2Sr_2CaCu_2O_8$  in particular but also  $YBa_2Cu_3O_{6.9}$  and  $La_{1.83}Sr_{0.17}CuO_4$ , as well as the electron-doped  $Pr_{1.85}Ce_{0.15}CuO_4$ .

Another point to be mentioned is the current interest in the low temperature thermal conductivity of  $Bi_2Sr_2CaCu_2O_8$ , because anomalies induced by magnetic field or magnetic impurities have been reported. At low temperatures, the contributions to the thermal conductivity arising from phonons and electrons can be extracted reliably, which enabled us to participate in the debate on the interpretation of the anomalous features reported in the literature.

However, at higher temperatures thermal conductivity also gives very useful information on the behavior of quasiparticles and phonons, even if both contributions are more difficult to identify precisely.

In this thesis, we review in chapter 2 some aspects of the theory of thermal conductivity in normal metals and superconductors. Then we review in chapters 3 and 4 the main properties of the hole-doped cuprate  $Bi_2Sr_2CaCu_2O_8$  and the electron-doped  $Pr_{2-x}Ce_xCuO_4$ , respectively. Each of these two chapters is ended by a review of the charge and heat conduction. Chapter 5 is a discussion about experimental aspects of this work, restricted in the temperature range 1.5–150 K. Indeed, I haven't directly participated in the experiments at temperatures below 1 K, achieved with a dilution fridge (see the acknowledgements). In chapter 6 we present and discuss our results for the thermal conductivity both below 1 K and above, before concluding.

## 2

#### THEORETICAL REVIEW

## 2.1 Thermal conductivity

#### 2.1.1 Definition

In an isotropic solid, the thermal conductivity  $\kappa$  is simply defined as the coefficient of proportionality between the heat flow vector  $\vec{H}$  and the temperature gradient  $\vec{\nabla}T$  [2]:

$$\vec{H} = -\kappa \vec{\nabla} T \tag{2.1}$$

 $\vec{H}$  measures the heat flow rate through a unit cross-section perpendicular to it. A negative sign is necessary to indicate that heat flows down a temperature gradient from the hotter to the colder region.

In crystals without cubic symmetry, the equation becomes :

$$H_i = -\kappa_{ij} \frac{\Delta T}{\Delta x_j} \tag{2.2}$$

where the coefficients  $\kappa_{ij}$  form a second-rank tensor.

In a solid, heat is conducted by electrons, phonons, magnetic excitations, etc., and  $\kappa$  is the sum of the various contributions :

$$\kappa = \kappa_e + \kappa_{ph} + \dots \tag{2.3}$$

#### 2.1.2 Electrons and the Wiedemann-Franz law

The electron gas in solids is a quantum gas. The electronic states are indexed by their band number n and their momentum vector  $\vec{k}$ . This gas is described with the distribution function  $f_n(\vec{r}, \vec{k}, t)$ . If the external fields are weak enough one can

neglect inter-band transitions and let the index n be implicit. The evolution towards equilibrium (disturbed by a thermal gradient, for instance) is governed by collisions. The Boltzmann equation is usually used to account for this process. In the semiclassical model [2] it has the form :

$$\frac{\partial f}{\partial t} + \frac{\vec{F}}{\hbar} \vec{\nabla}_k f + \vec{v}_k \cdot \vec{\nabla}_r f = \left(\frac{\partial f}{\partial t}\right)_{coll}$$
(2.4)

with  $\vec{v}_k = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \varepsilon_{\vec{k}}$  the velocity and  $\vec{F}$  the external force. The left-hand side of (2.4) is simply obtained by differentiation, from the fact that in absence of collision  $f\left(\vec{r} + d\vec{r}, \vec{k} + d\vec{k}, t + dt\right) = f\left(\vec{r}, \vec{k}, t\right)$ . The right-hand side takes into account the effects of collisions. The Boltzmann equation is valid provided that the duration of a collision is much smaller that the time  $\tau$  between two collisions ( $\tau_c \ll \tau$ ), and that  $\hbar/\tau$  be much smaller than the typical energy of the system (in the case of metals, the condition is  $\hbar/\tau \ll \varepsilon_F$ ). The principal effect of the term  $\left(\frac{\partial f}{\partial t}\right)_{coll}$  is to let f relax towards a local equilibrium function, namely a local Fermi-Dirac function  $f^{(0)} = \left(\exp\left(\frac{\varepsilon_E - \mu(\vec{r}, t)}{k_B T(\vec{r}, t)}\right) + 1\right)^{-1}$ . The exact form of the collision integral  $\left(\frac{\partial f}{\partial t}\right)_{coll}$  depends on the scattering mechanism involved. Guidelines to calculate it will be given in section (2.1.4). However, the matrix elements are difficult to evaluate and one often makes the relaxation time approximation :

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f(\vec{r}, \vec{k}, t) - f^{(0)}(\vec{r}, \vec{k}, t)}{\tau_{\vec{k}}}$$
(2.5)

where  $f^{(0)}$  is the local Fermi-Dirac function and  $\tau_{\vec{k}}$  is the collision time. The significance of this approximation is the assumption that the effect of collisions is to let fevolve towards  $f^{(0)}$ , exponentially with a relaxation time of the order of the collision time  $\tau$ . In the case of isotropic impurity scattering and spatially uniform temperature gradient and electromagnetic fields, the distribution function doesn't depend on  $\vec{r}$ . If the Fermi surface is isotropic,  $\tau$  depends only on  $\|\vec{k}\|$  and (2.5) simply becomes :

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f_k - f_0}{\tau_k} \tag{2.6}$$

where  $f_0$  is the global equilibrium distribution function (the Fermi-Dirac function).

Now we want to calculate the thermal conductivity  $\kappa$  in those conditions (isotropic Fermi surface and scattering). The thermal current density is given by

$$\vec{j_q} = \int \frac{d\vec{k}}{4\pi^3} \varepsilon_k \vec{v_k} \left( f_k - f_0 \right) \tag{2.7}$$

Using the relaxation-time approximation (eqns. 2.4 and 2.6), in the absence of electromagnetic forces ( $\vec{F} = 0$ ), and in a steady-state regime ( $\frac{\partial f}{\partial t} = 0$ ), the Boltzmann equation writes

$$-\frac{f_k - f_0}{\tau_k} = \vec{v_k} \cdot \vec{\nabla_r} f_k \tag{2.8}$$

Setting  $f_k = f_0 + f^{(1)}$  (where  $f_0$  is the Fermi-Dirac function) and neglecting the second order terms, we get

$$f_{k} - f_{0} = -\tau_{k}\vec{v_{k}} \cdot \vec{\nabla_{r}}f_{0} = -\tau_{k}\vec{v_{k}} \cdot \vec{\nabla}T\frac{\partial f_{0}}{\partial T} = +\tau_{k}\frac{\varepsilon_{k}}{T}\frac{\partial f_{0}}{\partial \varepsilon_{k}}\vec{v_{k}} \cdot \vec{\nabla}T$$
(2.9)

Replacing in (2.7) gives

$$\vec{j_q} = \frac{1}{T} \int \frac{d\vec{k}}{4\pi^3} \varepsilon_k^2 \frac{\partial f_0}{\partial \varepsilon_k} \tau_k v_k^2 \cos\theta \vec{\nabla} T$$
(2.10)

where  $\theta$  is the angle with respect to the temperature gradient axis. Replacing by an integration over energy and carrying out the angular integration, we obtain [2]:

$$\vec{j}_q = \left\{ v_F^2 \tau \frac{1}{3T} \int_0^{+\infty} \varepsilon^2 \frac{\partial f_0}{\partial \varepsilon} N(\varepsilon) d\varepsilon \right\} \vec{\nabla} T$$
(2.11)

Replacing by

$$c_V = \frac{d}{dT} \int \varepsilon N(\varepsilon) f_0(\varepsilon) d\varepsilon = -\frac{1}{T} \int \varepsilon^2 N(\varepsilon) \frac{\partial f_0}{\partial \varepsilon} d\varepsilon$$
(2.12)

we get

$$\kappa_e = \frac{1}{3} c_V v_F^2 \tau \tag{2.13}$$

With the same type of derivation, we find for the charge conduction :

$$\sigma = \frac{ne^2\tau}{m} \tag{2.14}$$

With

$$c_{V} = -\frac{1}{T} \int \varepsilon^{2} N(\varepsilon) \frac{\partial f_{0}}{\partial \varepsilon} d\varepsilon = \frac{\pi^{2}}{9} N(\varepsilon_{F}) k_{B}^{2} T + O\left(\frac{k_{B}T}{\varepsilon_{F}}\right)$$
(2.15)

and assuming the same scattering time for both thermal and electrical relaxation processes, one gets

$$\frac{\kappa_e}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} \tag{2.16}$$

Equation 2.16 is called the Wiedemann-Franz (WF) law while the ratio  $\frac{\kappa_e}{\sigma T}$  is the Lorenz number. The constant  $\frac{\pi^2 k_B^2}{3e^2} = L_0 = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$  is the Sommerfeld value. The validity of the WF law will be discussed in section 2.1.4.

#### 2.1.3 Phonons

Once again, by using the Boltzmann equation formalism in the relaxation-time approach, the thermal conductivity for phonon heat carriers can be derived (see [3]):

$$\kappa_{ph} = \frac{k_B}{2\pi^2 v_{ph}} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \qquad (2.17)$$

with  $\theta$  the Debye temperature,  $v_{ph}$  an average phonon velocity and  $x = \hbar \omega / k_B T$ . The scattering time  $\tau(x)$  is simply the inverse of the sum of the various scattering rates (Matthiessen's rule, see section 2.1.4.) relevant to the crystal under investigation. The average phonon velocity  $v_{ph}$  is given by  $v_l(2s^2 + 1)/(2s^3 + 1)$  (see [3]) where s is the ratio of longitudinal to transverse phonon velocity,  $v_l/v_t$ . In general, integrals of the form (2.17) have to be evaluated numerically. Using

$$C(x)dx = \frac{3k_B}{2\pi^2 v^3} \left(\frac{k_B}{\hbar}\right)^3 T^3 \frac{x^4 e^x}{(e^x - 1)^2} dx$$
(2.18)

and  $\tau(x) = l(x)/v(x)$ , equation (2.17) can be written as

$$\kappa = \frac{1}{3}v \int l(x)C(x)dx \qquad (2.19)$$

which is a logical extension of the simple kinetic equation

$$\kappa = \frac{1}{3} l c_V v_{ph}. \tag{2.20}$$

#### 2.1.4 Sources of thermal resistance

In each heat channel, the conduction is limited because the mean free path of the heat carriers is reduced by various scattering mechanisms.

#### Scattering of electrons.

The main sources of scattering for electrons are the following:

1. Impurities and crystal defects. The scattering is elastic since the change of energy of the impurity  $([\Delta P]^2/2M$ , where M is the mass of the crystal) is much smaller than the initial energy of the electron.

Just as an example we will now give some guidelines to calculate the scattering rate in this case (see for instance [4].) The probability of transition from  $|\vec{k}\rangle$  (supposed occupied) to  $|\vec{k'}\rangle$  (supposed empty) is given by Fermi's Golden rule:

$$W_{\vec{k}\vec{k}'} = \frac{2\pi}{\hbar} |\langle k' | V | k \rangle|^2 \delta(E_k - E_{k'})$$
(2.21)

The collision integral is given by

$$\begin{pmatrix} \frac{\partial f}{\partial t} \end{pmatrix}_{coll} = \sum_{k'} [ \text{ \# of electrons having a transition from } \left| \vec{k'} \right\rangle \text{ to } \left| \vec{k} \right\rangle$$

$$- \text{ \# of electrons having a transition from } \left| \vec{k} \right\rangle \text{ to } \left| \vec{k'} \right\rangle ]$$

$$= \sum_{k'} \left[ W_{\vec{k}\vec{k'}} f_{\vec{k'}} (1 - f_{\vec{k}}) - W_{\vec{k'}\vec{k}} f_{\vec{k}} (1 - f_{\vec{k'}}) \right]$$

One can express the scattering rate  $\frac{1}{\tau_k}$  as a function of the collision integral through equation (2.6). Since this process is elastic its scattering rate (and consequently the electrical resistivity associated to it) is independent of temperature. Thus  $\kappa_e$  will have the same behavior as the electronic heat capacity (linear in T at low temperatures).

2. Phonons. For the electron-phonon scattering, using Einstein model, where each atom oscillates like an independent harmonic oscillator of energy  $E_{\lambda}$ , of probability  $P_{\lambda}$ , the transition probability is of the type  $W_{kk';\nu\nu'}$  with  $\nu' = \nu \pm 1$ . Electron-phonon scattering is inelastic. A clear temperature dependence for the scattering rate in this case exists for  $T \ll \theta_D$  and  $T \gg \theta_D$ . At high T,  $\rho \sim T$  and  $\kappa \sim T^0$  (WF law). However since the Debye temperatures of the elements or compounds we have studied lie above the range of our measurements, we are mainly concerned in the low temperature limit. For  $T \ll \theta_D$ ,



Figure 2.1: Electrical conductivity  $\sigma$  and electronic thermal conductivity  $\kappa^{\epsilon}$  of a metal as function of temperature. The upper curves in each case are for more perfect specimens than the lower curves. after [3]

 $\frac{1}{\tau_k} \sim T^3$  but low temperature electron-phonon scattering is one of the cases for which the resistivity is not simply proportional to  $\frac{1}{\tau_k}$ , and actually  $\rho \sim T^5$  [2]. Directly following equation (2.13), since  $c_V \sim T$ ,  $\kappa_e \sim T^{-2}$ .

3. *Electrons*. Electron-electron scattering plays a minor role in the theory of conduction in normal metals (at low temperatures it is dominated by impurity scattering and at higher temperatures by electron-phonon scattering), except in exceptionally pure crystals. However, as we shall see later, electron-electron interactions are very important in high-temperature cuprates.

Figure 2.1 illustrates the behavior as a function of temperature of electrical and electronic thermal conductivities of a normal metal, set by the dominant scattering mechanisms. At high temperatures electron-phonon scattering is dominant, with a rate proportional to the lattice vibrational energy, which is proportional to T. Thus  $\sigma \sim 1/T$ . From equation (2.13),  $\kappa_e \sim T^0$ . As the temperature is decreased, collisions are less effective in limiting the mean free path and  $\sigma$  increases faster than the 1/Tlaw ( $\kappa \sim 1/T^2$ ). Eventually the electronic mean free path reaches a constant value determined by impurities and other punctual defects. In this range  $\kappa_e$  is linear in temperature.

So far in this section we have presented the main mechanisms causing the scattering of electrons. Then as an illustration we have seen the usual behavior of the charge and electronic thermal conductivities in normal metals (which doesn't necessarily apply to the cuprate superconductors).

#### Scattering of phonons.

Now we will go on by a review of the main sources of scattering for phonons in single crystals, followed by the schematic behavior of the thermal conductivity in an *insulating* crystal. For more details see [3] and [5].

- 1. Boundaries. At low temperatures the phonon mean free path l becomes large enough to be comparable to the crystal size. Then, owing to the scattering of the lattice vibrations at the surface, l is limited by the smallest dimension of the sample (for a single crystal). The scattering rate is independent of frequency and the corresponding thermal conductivity is proportional to the phonon specific heat. Thus, at low temperatures,  $\kappa_{ph} \sim T^3$  when the conduction is limited by boundary scattering.
- 2. Electrons. When the phonon conduction is limited by conduction electrons, the scattering rate is proportional to  $\omega^1$  and the thermal conductivity is proportional to  $T^2$ .
- 3. Point defects. A defect which extends over a volume with linear dimensions much smaller than the phonon wavelength can be considered as a point defect. As a rough rule of thumb, the wavelength of the dominant phonons is equal to  $\theta/T$  interatomic distances. Point defects have a  $\omega^4$  dependence on the scattering rate leading to  $\kappa \sim 1/T$ .
- 4. Other phonons. Phonon-phonon collisions obey energy conservation (they are elastic processes) and the momentum conservation writes:  $\vec{q_1} + \vec{q_2} = \vec{q_3} + \vec{g}$ , where  $\vec{g}$  is a reciprocal lattice vector. When  $\vec{g} = 0$  the collision is called a normal or N-

process and it doesn't change the effective direction of the energy flow, thereby not limiting the heat transport. If  $\vec{q_1}$  and  $\vec{q_2}$  are such that  $\vec{g} \neq 0$ , the collision is called umklapp or U-process and in this case thermal energy is transported in a quite different direction. Such a drastic change in  $\vec{q}$  is a very effective source of thermal resistance. At high temperatures  $(T \geq \theta_D)$  the number of phonons which take part in U-processes is proportional to T and since  $c_V$  is constant, the thermal resistance is proportional to T, thus  $\kappa \sim 1/T$ . A more precise treatment leads to  $\kappa \sim 1/T^x$  with x between 1 and 2. At temperatures well below  $\theta_D$ , only an exponentially small fraction of the phonons will have large enough wavevectors to take part in U-processes, and  $\kappa \sim T^3 exp(\theta/bT)$  with  $b \approx 1$ .

- 5. Tunneling states. Atoms or groups of atoms tunnel between equilibrium positions at almost the same energy, with a smooth distribution over energy difference of the number of levels between which tunneling is possible. This model would apply to disordered systems in general and scattering of phonons by these tunneling modes implies a  $T^2$  variation in thermal conductivity.
- 6. Other mechanisms, such as sheet-like faults, dislocations, etc., don't play a very important role in single crystals.

Figure 2.2 shows the dominant scattering mechanisms in an insulating crystal, and the schematic behavior of thermal conductivity associated to them. At high temperatures, because of phonon-phonon scattering  $\kappa_{ph}$  is inversely proportional to T. When the temperature reaches a point where the fraction of phonons taking part in Uprocesses imposes the exponential behavior of thermal conductivity, the conductivity increases so rapidly with decreasing temperature that the phonon mean free path soon becomes comparable to the mean free path due to the scattering by lattice defects. As temperature decreases phonons with longer wavelengths are excited, that are unaffected by disorders on the atomic scale and are scattered by the sides of the sample. In this range  $c_v \sim T^3$  and  $\kappa$  is proportional to  $T^3$ .



Figure 2.2: Thermal conductivity of a non-metallic crystal. The upper curve is for a crystal of larger diameter than the lower curve. The dominant phonon-scattering mechanism are indicated along the abscissa. after [3]

When there are more than one scattering mechanisms, each independent of the others, the total scattering rate,  $1/\tau$ , is the sum of the several scattering rates from different mechanisms (Matthiessen's rule):

$$\frac{1}{\tau} = \sum_{i} \frac{1}{\tau^{i}} \tag{2.22}$$

#### Validity of the Wiedemann-Franz law.

The Wiedemann-Franz law holds when the dominant scattering is elastic. Then energy is conserved and both electrical and thermal currents are degraded in the same way (a change of momentum of the electron). However, inelastic scattering provides a degradation mechanism of the heat current (change of the thermal "charge" carried) that has no equivalent in the electrical conduction, causing the law to break down. Thus at low temperatures when the dominant electronic scattering is against impurities, it holds. At intermediate temperatures because of electron-phonon scattering the WF law breaks down. However it turns out that at high temperatures, especially owing to Umklapp processes, the law also holds because the change of energy of each electron involved in a collision with the lattice vibrations is small compared to  $k_BT$ .



Figure 2.3: Superconducting density of states for a BCS superconductor as a function of the quasiparticle energy.

## 2.2 Thermal conductivity of conventional superconductors

To begin it may be useful to discuss what is understood as a conventional superconductor. Their behavior has been very successfully described by the theory of Bardeen, Cooper and Schrieffer (BCS) [6]. For a review of this theory see [7]. BCS showed that in the presence of an attractive potential between electrons, the fundamental state of the system is unstable relative to a linear combination of normal-state configurations  $(k\uparrow, -k\downarrow)$ , which are both either occupied or unoccupied. This instability causes the opening of a gap  $\Delta$  of order  $k_BT_c$  in the excitation spectrum,  $E(\vec{k}) = [\varepsilon(\vec{k})^2 + \Delta(\vec{k})^2]^{\frac{1}{2}}$ , where  $\varepsilon(\vec{k})$  is the energy of an electron of wave-vector  $\vec{k}$  in the normal state. For thermal properties, this gaps leads to an exponentially activated behavior at low temperatures. The density of states is shown in figure 2.3. Superconductors are called conventional or BCS superconductor when they satisfy :

- 1. The attractive interaction between electrons is mediated via the exchange of virtual phonons.
- 2. The actual form of the attractive potential  $V_{kk'}$  chosen in the theory has no angular dependence (s-wave potential). This implies that the gap is isotropic

(s-wave gap) and finite everywhere.

After those recalls we can discuss the heat conduction. There are two fundamental aspects of the superconducting condensate which have effects on the thermal conductivity of the superconductor :

- Cooper pairs carry no entropy.
- Cooper pairs do not scatter phonons.

The first condition means that the electronic thermal conductivity decreases with decreasing temperature more rapidly in the superconducting state than in the normal state. Since  $\kappa_e \propto nvl_e$ , the number of quasiparticles decreases with temperature and goes to zero at T = 0, thus  $\kappa_e \sim \exp(-\Delta/kT)$  at low temperature. The second condition has a more subtle effect : provided that the mean-free path of phonons  $l_{ph}$  at  $T > T_c$  is limited by electron scattering, the phonon thermal conductivity will rise on passing into the superconducting state, because the number of quasi-particle excitations rapidly decreases—leading to an enhancement in the mean-free-path of phonons  $l_{ph}$ . A competition between the rapidly diminishing  $\kappa_e$  on the one hand and the increasing  $\kappa_{ph}$  on the other hand will determine the overall dependence of the total thermal conductivity of a given superconductor. In the vast majority of cases  $\kappa$  falls rapidly as the material goes superconducting. However, in some alloys, sufficiently disordered so that  $\kappa_e$  is small and  $\kappa_{ph}$  accounts for a large fraction of the normal-state thermal conductivity, one may observe a rise in the total conductivity as the sample enters into its superconducting state (as in the lead-10% bismuth alloy [8]).

The theory of heat transport in conventional superconductors has been first published by Bardeen, Rickayzen and Tewordt (BRT) [9]. We will now briefly sketch this theory, and to begin with, the equation of thermal conductivity.

#### 2.2.1 Electronic thermal conductivity

First, we only consider electron-impurity scattering. Here we will only quote the basic results of the theory. Applying the Boltzmann equation (2.4) to the heat transport,

we obtain the electronic heat current :

$$j_q = -\frac{2}{T} \sum \mu_i^2 E_k^2 \frac{\partial f_0}{\partial E_k} v_k^2 \tau_k \tag{2.23}$$

where  $E_k$  is the quasiparticle energy,  $v_k$  the group velocity of the quasiparticles in the superconducting state,  $\tau_k$  the relaxation time and  $\mu_i = \cos\theta$  where  $\theta$  is the angle with respect to the temperature gradient axis. The quasiparticle velocity is found to be

$$v_{k} = \left|\frac{\varepsilon_{k}}{E_{k}}\right| v_{F} = \frac{N(0)}{N_{s}(E)} v_{F}$$
(2.24)

with N(0) the density of states at the Fermi level in the normal state and  $N_s(E)$ the quasiparticle density of states. Thus at the Fermi level  $(k \rightarrow k_F \text{ or } \varepsilon_k \rightarrow 0)$ ,  $v_k \rightarrow 0$ : in addition to the loss of quasiparticle density in the superconducting state, their velocity is greatly reduced in the limit of low energies. Assuming an isotropic gap, and applying the relaxation-time approximation, Bardeen *et al.* compute the scattering time as

$$\tau_s = \left| \frac{E_k}{\varepsilon_k} \right| \tau_N = \frac{N_s(E)}{N(0)} \tau_N \tag{2.25}$$

where  $\tau_N$  is the relaxation time in the normal state. As  $\varepsilon_k \to 0$ , the scattering time  $\tau_s$  diverges : impurities have very little influence on low energy quasiparticles. Comparing equations (2.24) and (2.25), we see that the drop of the group velocity is compensated by the absence of impurity scattering and as a result, the mean free path  $l = v\tau$  is not affected by the superconducting transition<sup>1</sup> :  $l_s = l_N$  for quasiparticles of energy  $\varepsilon_k \to 0$ . Inserting equations (2.25) and (2.24) into (2.23) and changing the sum into an integral, we obtain:

$$\kappa_{e,s} = \frac{1}{3T} v_F^2 \tau_N N(0) \int_{\Delta(T)}^{+\infty} dE E^2 \left(-\frac{\partial f}{\partial E}\right)$$
(2.26)

<sup>&</sup>lt;sup>1</sup>This compensation doesn't occur in superconductors with nodes in the gap function. Indeed, near a node  $v_k \rightarrow v_F$  because  $E = \varepsilon$ . Thus keeping a scattering time described by eqn. (2.25) would yield an unphysical, infinite mean free path at low energies. As we shall see later, in the case of the high- $T_c$  cuprates, one has to assume on the contrary strong, multiple scattering in order to account for the experimental data.



Figure 2.4: Ratio of superconducting to normal thermal conductivity for aluminum as a function of  $T/T_c$  (after Satterthwaite [10]). The solid lines represent the BRT calculation in the presence of impurity scattering for three values of the gap parameter, namely 2  $\Delta(0) = 3.00, 3.25$ , and 3.52 times  $k_BT_c$ .

By letting  $\Delta \to 0$ , we still find equation (2.13) for the normal state thermal conductivity  $\kappa_{e,n}$ . Dividing  $\kappa_{e,s}$  by  $\kappa_{e,n}$  we get

$$\kappa_{e,s}(T)/\kappa_{e,n} = \int_{\Delta(T)}^{+\infty} dE E^2 \frac{\partial f}{\partial E} / \int_0^{+\infty} d\varepsilon \varepsilon^2 \frac{\partial f}{\partial \varepsilon}$$
(2.27)

A plot of the theoretical  $(\kappa_{e,s}/\kappa_{e,n})$  versus  $(T/T_c)$ , together with a plot of experimental data of aluminum, for three samples of varying impurity concentration, is provided in fig. (2.4). As one can see, there is excellent agreement between this theory and experiment.

For completeness, let us briefly consider the case of electron-phonon scattering, which can be dominant in the case of very pure crystals. Kadanoff and Martin [11], have presented a theory in good agreement with experimental data. When the conductivity is limited by phonon scattering,

$$\kappa_e = \frac{\pi^2}{3} \frac{n}{m} k_B^2 T [\Gamma + v_F / l]^{-1}$$
(2.28)

There exist two contributions to the thermal resistance: 1)  $\Gamma$ , which results from phonon absorption and emission and is proportional to  $T^3$ , and 2)  $v_F/l$ , which is due to impurity scattering and is independent of T, and adds to the thermal resistance.

#### 2.2.2 Lattice thermal conductivity

Phonon heat transport is not much affected by the superconducting state except via electron-phonon scattering. In this case, in BRT theory [12], the thermal conductivity is given by:

$$\kappa_{gs} = D(\frac{T}{\Theta})^2 \int_0^\infty \frac{u^3 du}{(e^u - 1)(1 - e^{-u})g(u)}$$
(2.29)

where D is a constant independent of temperature, u the reduced energy  $\hbar v/k_B T$ , and

$$g(u) = \frac{1 - e^{-u}}{u} \int dE \left| \frac{EE'}{\varepsilon \varepsilon'} \right| (1 - \frac{\varepsilon_0^2}{EE'}) f(E) f(-E').$$
(2.30)

Energies are measured in units of  $k_BT$  and g(u) represents physically the ratio of the relaxation time of electrons in the normal state  $\tau_{e,n}$  to that of quasiparticles in the superconducting state  $\tau_{e,s}$ . Therefore, it tends to 1 above  $T_c$ . In the superconducting state, it gives us the information about: 1) the number of electrons that scatter phonons, which decreases as temperature goes down. 2) the scattering matrix element including the coherence factor.

In summary, we have seen that a pairing between electrons gives rise to superconductivity and that a gap opens up between the ground state and the first excited state. We have defined conventional superconductors as materials in which the pairing is caused by electron-phonon interactions, leading to an isotropic *s*-wave gap. We have presented a theory for the electronic thermal conductivity based on impurity scattering, which accounted for the exponential activated behavior of  $\kappa_e$  seen experimentally, as we showed on Al. We mentioned that the phonon contribution is not much affected by the transition except via electron-phonon scattering. To conclude this section, we want to display the thermal conductivity of Nb (figure 2.5), which illustrates this last point, in addition to the exponential drop of  $\kappa$  below  $T_c$ . In nio-



Figure 2.5: Thermal conductivity of niobium in the normal (triangles) and superconducting (circles) state (After [13]). The solid lines through the experimental data points are guides to the eye. The lowest curve is the result expected from the BRT theory. Notice the peak at low temperature arising from the phonon contribution.

bium, the critical temperature is 9.1 K, 8 times higher than in aluminum. Because of the exponential behavior in BRT theory, the electronic contribution is negligible at temperatures below 2 K. The phonon contribution, enhanced by the disappearance of electron scattering, becomes dominant and peaks at low temperature. As temperature is lowered the decrease in the number of phonon eventually wins over the increase of the phonon mean free path, all the easier since the latter is limited by boundary scattering.

#### 2.3 Unconventional superconductors

## 2.3.1 Quasiparticle transport in superconductors with nodes in the gap function

For an account of the theory of electronic thermal conductivity in unconventional superconductors see [14]. For a clean superconductor with an order parameter that vanishes along a line on the Fermi surface the density of states increases linearly as a function of the excitation energy at low energies :  $N(E) \sim N_f E/\Delta_0$ . However, because of impurities, the density of states is approximately constant below a certain energy  $\gamma$ , and is therefore non-zero at zero energy.  $\gamma$  can be viewed as arising from a broadening of nodes by impurities. The energy scale  $\gamma$ , and thus the density of states at zero energy N(0), depend on both the impurity concentration,  $n_{imp}$ , and the scattering phase shift<sup>1</sup>  $\delta_0$ . However, whatever the phase shift, for any finite concentration of impurities (and as a consequence for any physical crystal),  $\gamma$  and N(0) are finite.

The presence of impurities causes additional Cooper pairs to break, thus an increase of the impurity concentration  $n_{imp}$  is accompanied by an increase of the residual normal fluid density  $n_n$ , which gives a greater contribution to the thermal conductivity (*i.e.*  $N(0) \sim \gamma$ ). Parallel to this the scattering of each quasiparticle by impurities diminishes the mean free path for heat conduction in the zero temperature limit (*i.e.*  $l \sim 1/\gamma$ ). The two phenomena happen to compensate exactly in gaps with a line of zero in the direction of transport, so that  $\kappa(T \rightarrow 0)$  doesn't depend on the impurity concentration : it is universal, as first shown by Lee [15]. The dependence of  $\gamma$  on the phase shift, mentioned above, is very strong. In the limit when  $\delta_0 = \pi/2$ ,  $\gamma \sim \sqrt{\pi \Delta_0 \Gamma/2}$  where  $\Gamma$  is the normal state scattering rate, while in the opposite limit (when  $\delta_0 = 0$ ),  $\gamma \sim 4\Delta_0 \exp(-\pi \Delta_0/2\Gamma)$ . We remark that  $\gamma$  is larger for unitary scattering, making universality easier to be achieved in this case. The theoretical values

<sup>&</sup>lt;sup>1</sup>The scattering phase shift specifies the strength of impurity scattering. The limit when  $\delta_0 = 0$ (Born limit) describes a weak scattering whereas the other limit,  $\delta_0 = \pi/2$  (unitary limit), applies to strong, resonant, multiple scattering.

expected for some precise gap topology and symmetry of interest will be reviewed in chapters 3 and 6 and compared to experimental data.

#### 2.3.2 Lattice thermal conductivity for High-Tc superconductors

At sufficiently low temperatures for the phonon conductivity to be in its asymptotic  $\kappa_{ph} \sim T^3$  regime, equation (2.20) can be used (which is convenient since in this range the coefficient  $\kappa_{ph}/T^3$  is approximately constant). For higher temperatures, Tewordt and Wölkhausen have employed the BRT theory [12] for the lattice thermal conductivity limited by electron scattering (see section 2.2.2), and have supplemented it by taking into account additional scattering processes of the phonons by static imperfections. They have written the final equation in a form convenient for fitting experimental data :

$$\kappa_{ph}(t) = At^3 \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} \times [1 + \alpha t^4 x^4 + \beta t^2 x^2 + \delta t x + \gamma t x g(x, y)]^{-1}$$
(2.31)

where  $t = \frac{T}{Tc}$  is the reduced temperature,  $x = \hbar w/k_B T$  is the reduced phonon energy,  $y = \frac{\Delta(T)}{k_B T}$  is the parameter containing the energy gap. The coefficients correspond to the different scattering mechanisms (by boundaries, point defects, sheet-like faults, dislocations, and phonons). This theory is presented in full details in reference [16].

## 3

## THE HOLE-DOPED CUPRATE BI<sub>2</sub>Sr<sub>2</sub>CACU<sub>2</sub>O<sub>8</sub>

## 3.1 Structure and doping

Superconducting cuprates appear as complex systems. However they show common structural features which are rather simple : their structures can be regarded as a superposition along the crystal c-axis of metallic CuO<sub>2</sub> planes and insulating block layers. The CuO<sub>2</sub> planes are believed to play a major role for superconductivity whereas the insulating layers, composed of oxygen and a metal like Y, Ba, La, Tl or Bi, are considered as "charge reservoirs" that supply charge carriers for the planes. The electronically passive role played by the insulating layers gives to most of the high- $T_c$  cuprates a quasi two-dimensional character in their metallic and superconducting properties. The mobile charge carriers can be holes (hole-doped cuprates) or electrons (electron-doped cuprates).

In this thesis we will study an electron-doped compound (see chapter 4) and the  $Bi_2Sr_2CaCu_2O_8$  hole-doped compound (BSCCO). However a comparison will often be made with two other hole-doped compounds,  $La_{2-x}Sr_xCuO_4$  (LSCO), the first high temperature superconductor discovered, and  $YBa_2Cu_3O_{7-\delta}$  (YBCO), the most widely studied because high quality single crystals can be prepared (see for example [17]). The crystal structures of LSCO, YBCO and BSCCO are shown in figure 3.1. In this figure the structure of BSCCO is idealized ; in fact there is a mismatch between the BaO-BiO-BiO-BaO and the CuO<sub>2</sub> layers, which produces a stretching of the Bi layers, giving rise to an incommensurate modulation in the a direction, with a period  $\approx 5a$ . Thus BSCCO is slightly orthorhombic (a = 5.41Å, b = 5.42Å, c = 30.9Å). As in



Figure 3.1: Crystal structures and unit cell parameters of the hole-doped high- $T_c$  superconductors we have investigated (After [18]). a)  $La_{2-z}Sr_zCuO_4$ , tetragonal : a=b=3.779 Å, c=13.226 Å,  $T_c \simeq 40$  K; b) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, orthorhombic : a=3.818 Å, b=3.884 Å, c=11.683 Å,  $T_c \simeq 94$  K; c) Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (Bi-2212), slightly orthorhombic : a=5.409 Å, b=5.420 Å, c=30.930 Å,  $T_c \simeq 89$  K. Structure (c) is also that of the Thalium compound Tl-2212 and the elements corresponding to BSCCO (Bi and Sr) are those indicated in parentheses.

YBCO, there is a bilayer of CuO<sub>2</sub> planes in the unit cell of BSCCO, as opposed to a single layer in LSCO and the electron-doped cuprates of figure 4.1). As indicated in ref. [19], the CuO<sub>2</sub> planes of the bilayers in YBCO and BSCCO are separated by about 3.2 Å, the distance between two bilayers being respectively about 8.2 and 12 Å. In LSCO the single CuO<sub>2</sub> planes are separated by about 6.6 Å (as well as in the electron-doped compounds). Thus the number of CuO<sub>2</sub> planes per unit length along the c-axis is respectively  $\approx 0.13$ , 0.15 and 0.17 Å<sup>-1</sup> in BSCCO, LSCO and YBCO. We should also mention that the presence of holes could be explained by the overlap of the Bi 6s and the Cu d<sub>x<sup>2</sup>-y<sup>2</sup></sub> bands at the Fermi level [20].
The proximity of antiferromagnetism (AFM) seen in the schematic phase diagram (figure 3.2) suggests that the electron pairing mechanism leading to superconductivity in the cuprates may be mediated by antiferromagnetic spin fluctuations. Actually



Figure 3.2: Schematic temperature-dopant concentration phase diagram for cuprates. After [21]. The solid lines labeled  $T_N$  and  $T_C$  delineate the antiferromagnetic and superconducting regions, respectively. The "hatched" line denoted  $T^{\bullet}$  represents the crossover into the pseudogap state (see below).

a number of theoretical models (reviewed in [21]) based on AFM spin fluctuations predict *d*-wave superconductivity with  $d_{x^2-y^2}$  symmetry for the cuprates, precisely the symmetry of the order parameter consistent with most of the experiments in *hole*-doped cuprates, as we shall see in the next section.

The most important aspects of this section are probably, first, the presence of the  $CuO_2$  planes, which contain the charge carriers and are believed to play a key role in superconductivity. The number of adjacent planes in the structure of the cuprates is related to the transition temperature. Secondly, the presence of the antiferromagnetic region close to the superconducting phase suggests antiferromagnetic spin fluctuations as mechanism for the pairing of electrons.

## 3.2 Gap symmetry

Since the symmetry of the order parameter in high- $T_c$  superconductors provides clues to identify the pairing mechanism, it is a key question to answer in order to develop the theory of high-temperature superconductivity. To understand fully the symmetry of the order parameter  $\Delta_0(\vec{k})$ , one needs to know both its amplitude and its phase. Some of the experiments giving information on  $\left|\Delta_0(\vec{k})\right|$  are listed below. The linear temperature dependence of the microwave penetration depth [22] (or [23] in BSCCO), the  $T^3$  power law at low temperature of the NMR longitudinal relaxation rate  $1/T_1$  [24], the results of angle-resolved photoemission spectroscopy (ARPES) measurements [25], Raman scattering [26] (in BSCCO : [27]), the residual linear term in thermal conductivity [28], all<sup>1</sup> are consistent with a  $d_{x^2-y^2}$  or extended s-wave symmetry for hole-doped cuprates such as YBCO, LSCO and BSCCO. To distinguish between the two, information on the phase is needed. Experiments sensitive to the phase, which have mainly been performed on YBCO, all involve the Josephson effect (see for instance [7]). They are reviewed in the preprint by M. B. Maple [21]. Most of them, like SQUID interferometry, indicate a  $d_{x^2-y^2}$  symmetry. Some of them, like c-axis Josephson tunneling, predict in addition a significant s-wave component. The best candidate for Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> is the order parameter with  $d_{x^2-u^2}$  symmetry. Its Fermi-surface gap function as well as density of state is shown in figure 3.3 (along with that of s-wave or extended s-wave symmetry). The gap has zero amplitude for lines on the Fermi surface, at angles  $\Phi = m\pi/4(m = 1, 3, 5, 7)$ . The density of states  $N(E) \sim E$  at low temperatures (however, see section 2.3.1).

Thus, a number of experiments firmly suggest an order parameter with  $d_{x^2-y^2}$  symmetry in the hole-doped cuprates YBCO, BSCCO and LSCO.

<sup>&</sup>lt;sup>1</sup>In fact, since the linear term in thermal conductivity has also been observed to be universal, this experiment favors *d*-wave as opposed to anisotropic *s*-wave symmetry. Indeed, according to the theory [15], universal transport wouldn't be observed in a superconductor with *s*-wave gap symmetry.



Figure 3.3: Fermi-surface gap functions and densities of states of a tetragonal superconductor for various pairing symmetries. The gap functions are plotted in the  $k_z = 0$  plane. N(E) shown below each gap function is the density of states for one-quasiparticle excitations. Unlike the classic *s*-wave case, the extended *s*-wave and the *d*-wave gap functions have a linear density of states at very low temperatures. After [29].

## 3.3 Transport

#### 3.3.1 Normal state properties

As in the other hole-doped cuprates, the in-plane resistivity in BSCCO is linear in temperature over the measured temperature range :

$$\rho_{ab}(T) \approx \rho_{ab}(0) + cT \tag{3.1}$$

This behavior is unusual in a normal metal where the generic low-temperature resistivity is closer to  $\rho = A + BT^5$  and the linear dependence appears only at high temperatures ( $T \simeq \theta_D/4$ ), as seen in section 2.1.4. Although the usual formula of phonon-limited resistivity happens to give a reasonable fit to the  $\rho(T)$  curve, it is known that the linear temperature dependence is due to electron-electron correlations (see [30]). In the particular case of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> at optimal doping the c-axis resistivity seems to have a semiconductive behavior well reproduced by the following formula [31],[32] :

$$\rho_{\rm c}(T) = \frac{a}{T} e^{\frac{\Delta}{T}} + b \tag{3.2}$$

where a, b and  $\Delta$  are constant and for optimal doping according to the data of Watanabe *et al.* [31],  $a \simeq 20 \text{ m}\Omega \text{cmK}$ ,  $b \simeq 6 \Omega \text{cm}$  and  $\Delta \simeq 200 \text{ K}$ . Watanabe *et* 

al. find an out-of/in-plane anisotropy ratio  $\rho_c/\rho_{ab} \approx 510^3$  consistent with Yoshizaki et al.'s  $\rho_c/\rho_{ab} \approx 10^4$  [32]. Such a large anisotropy may be explained by the fact that there are as many as 4 insulating layers between the CuO<sub>2</sub> planes (for only 3 in YBCO for instance). Another explanation could be the macroscopic structure of the BSCCO material, which looks like a superposition (along the c-axis) of mikalike sheets, possibly reducing the conductivity by tunneling between two sheets. In addition, it is difficult in those conditions to evaluate whether the current distribution is uniform in the sample, or only takes place in some sheets of the material representing only a fraction of the sample.

One remarkable aspect of the normal state in  $Bi_2Sr_2CaCu_2O_8$  is the existence of a pseudogap (a suppression of certain but not all excitations) in the low energy spin, but also charge excitation spectra. ARPES measurements [25] on BSCCO have revealed that the symmetry of the pseudogap is consistent with the symmetry of the gap. The pseudogap appears to be intimately related to the superconducting energy gap, being in some way its precursor.

#### 3.3.2 Review of thermal conductivity

#### High temperature range (T > 1 K).

Figure 3.4 displays the thermal conductivity data obtained in Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> by N. P. Ong *et al.*. The main feature is the broad peak just below the transition. This kind of peak has also been observed in many other hole-doped cuprates, like LSCO and YBCO (see [34], [35]). Two scenarios are "a priori" possible to interpret it. The first one is the increase of the phonon mean free path following the loss of electronic scatterers by pairing. The second one is a dramatic rise of the quasiparticle mean free path below  $T_c$ , which would more than compensate the decrease of electronic carriers density. Two experiments have given insight into the problem in YBCO and convinced that most of the peak had to be attributed to the electronic heat carriers. By a thermal hall effect experiment, a way of isolating the electronic thermal conductivity  $\kappa_e$ , Krishana *et al.* [36] have seen a peak of  $\kappa_e(T)$  below  $T_c$ . This result is



Figure 3.4: Thermal conductivity of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> in zero field and in a 14.1 T magnetic field [33].

consistent with the microwave conductivity measurements of Bonn *et al.* [30]. They have observed a broad peak in the microwave surface conductivity, indicative of a rapid suppression of the electronic scattering rate below  $T_c$ . The data of Bonn *et al.* have revealed that strong electron-electron scattering dominates the charge conduction in the normal state. As charge carriers condense in the superconducting state, the dominant inelastic scattering goes with them. Given that the same broad peak as in YBCO has been obtained in microwave measurements of the real part of the conductivity in BSCCO [37] (meaning a suppression of the quasiparticle scattering rate below  $T_c$ ), and that the two materials show otherwise very similar properties, there is no reason to think of a different scenario than in YBCO to explain the peak of  $\kappa$  below the transition.

The interpretation of the peak as an electronic feature mustn't hide the importance of the phonon contribution at other temperatures, and we are going now to compare the relative importance of both contributions to the thermal conductivity at various temperatures. In the normal state, most of the heat is shown to be carried by phonons (in YBCO  $\kappa_e/\kappa_{ph} \approx 0.1$  [33]). The electron contribution is limited by strong electron-electron scattering. Below the transition because of the pairing of electrons the electronic scattering rate is suppressed and the quasiparticle mean free path increases. In YBCO  $\kappa$  at the peak is more than twice the normal state value [34]. Since most of the peak magnitude is attributed to electrons,  $\kappa_e$  at the peak dominates  $\kappa_{ph}$ . However in less pure crystals like BSCCO or LSCO, the importance of impurity scattering limits the increase of  $\kappa_e$  (see section 6.2). In these conditions it is unlikely that the electronic contribution dominates the transport of heat at the peak. The peak is the result of the competition between the decrease of the quasiparticle density and the concomitant increase of the quasiparticle mean free path, the latter being restricted to a value determined by impurity scattering. Thus at some point the electronic contribution at the peak  $\kappa_{ph}$  is "again" dominant (assuming  $\kappa_e$  was the main contribution at the peak). However at very low temperatures  $\kappa_e \sim T$  while  $\kappa_{ph} \sim T^3$  (see chapter 2) and at some temperature (of the order of 100 mK as seen in chapter 6) the quasiparticles become the main carriers of heat.

#### Low temperature range (T < 1 K).

In ref. [33], Krishana *et al.* have reported an anomaly in the low temperature thermal conductivity of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (T < 25K), also seen later by Aubin *et al.* [38] : at a transition field  $H_0$ , a sharp break in the slope of  $\kappa$  occurs, followed by a plateau region in which it is constant with increasing field. In ref. [39], a possible interpretation of this anomaly is given, in the form of an electronic phase transition from the  $d_{x^2-y^2}$  state towards a d+id state, induced by the magnetic field. In this context, R. Movshovich *et al.* have published another paper claiming a new phase transition in low temperature thermal conductivity of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> [40], which A. V. Balatsky has explained by a possible transition towards a  $d_{x^2+y^2} + id_{xy}$  state, induced by magnetic impurities [41]. In their article, Movshovich *et al.* evaluate that the heat is mainly carried by electrons at the temperature of the transition and thus attribute it to a sudden suppression of quasiparticle heat transport. We will discuss this result in chapter 6 and show why it is not consistent with our data and interpretation. In summary, some kind of electronic mechanism for inelastic scattering dominates transport properties in the normal state and is suppressed below the superconducting transition at the same time as the quasiparticle density. In particular, this causes a peak in the thermal conductivity. We have also stressed the importance of the phonon contribution to the heat transport in the cuprate superconductors. To finish, we have noticed that a few anomalies have recently been reported in the low temperature thermal conductivity of the  $Bi_2Sr_2CaCu_2O_8$  compound, induced by a magnetic field or magnetic impurities.

# 4

## The electron-doped cuprate $Pr_{2-x}Ce_xCuO_4$

### 4.1 Structure and doping

In 1989, Tokura *et al.* [42] have discovered materials that, unlike the hole-doped cuprates, have to be doped by electrons in order to become superconducting. In this family of compounds,  $\text{Re}_{2-x}\text{Ce}_x\text{CuO}_4$  where Re is a rare earth element (Pr, Nd, Sm or Eu), electrons are introduced by substituting  $\text{Re}^{3+}$  ions by a small percentage of  $\text{Ce}^{4+}$  ions. The material crystallizes into the T'-structure (simply the name given to the structure of figure 4.1a), close from the T-structure (fig. 4.1b) of their parent hole-doped compound  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO). In the electron-doped cuprates, the CuO<sub>2</sub>



Figure 4.1: Crystal structures of (a)  $\text{Re}_{2-x}\text{Ce}_x\text{CuO}_4$  in the T'-structure, after [42]. The arrangement is tetragonal. For NCCO the unit cell parameters are a=b=3.95 Å, c=12.09 Å, for PCCO a=b=3.96 Å, c=12.16 Å. (b)  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  in the T-structure. The arrow and X in (a) indicate the approximate position of the empty apical site in the T'-structure.

planes, considered as being responsible for superconductivity, are all equidistant (like in LSCO : they are both part of the "single-layer" group). The difference between the structure of  $\operatorname{Re}_{2-x}\operatorname{Ce}_{x}\operatorname{CuO}_{4}$  and  $\operatorname{La}_{2-x}\operatorname{Sr}_{x}\operatorname{CuO}_{4}$  resides in the arrangement of the insulating layers, the oxygen atoms lying in the lanthanide planes and in-between in the T and T' cases respectively. In the T'-structure, there are no so-called apical oxygens (oxygen atoms at the boundary with the insulating layers, shown by the arrow in figure 4.1). This absence of apical oxygen atoms places the Cu ions in a planar environment shared with only four O ions as nearest neighbors, to be compared with an octahedral and tetrahedral arrangement in LSCO and YBCO, respectively. Another characteristic of the  $Re_{2-x}Ce_xCuO_4$  family is that the maximum amount of Ce doping allowed (solubility limit) varies as a function of the lanthanide used [43]. The greater the ionic radius of  $Re^{3+}$  (Pr, Nd, Sm, Eu from greatest to lowest), the greater the volume of the unit cell and the greater the solubility limit. To illustrate this, the compound  $\operatorname{Re}_{2-x}\operatorname{Ce}_x\operatorname{CuO}_4$  with  $\operatorname{Re}=\operatorname{Gd}$  (the rare earth next to Eu in the periodic table) is not superconducting at normal pressure because the ionic radius of Gd is too small and causes a static distortion of the T'-structure (see [43]).

Figure 4.3 shows the superconducting phase diagram of  $Pr_{2-x}Ce_xCuO_4$  compared to  $Nd_{2-x}Ce_xCuO_4$  and figure 4.2 the more complete typical qualitative phase diagram of an electron-doped cuprate (here that of  $Nd_{2-x}Ce_xCuO_4$ ) compared to that of  $La_{2-x}Sr_xCuO_4$ . Let us first draw general conclusions from figure 4.2. The most striking feature is the close symmetry of the two diagrams, with the presence of antiferromagnetism (AFM) followed, when the charge carriers concentration x is increased, by the superconducting (SC) region, with a maximum  $T_c$  for  $x \simeq 0.15$ . The main difference may be the relative size of these two regions, the AFM one being narrow and the SC one wide in the hole-doped compound, and the reverse in the electron-doped material. The AFM doping range extends up to x = 0.12-0.14 in  $Nd_{2-x}Ce_xCuO_4$  and only 0.05 in  $La_{2-x}Sr_xCuO_4$ . Another difference is that superconductivity directly replaces antiferromagnetism in  $Nd_{2-x}Ce_xCuO_4$ , whereas in  $La_{2-x}Sr_xCuO_4$  the two phases are separated by a spin glass region.



ELECTRON-HOLE SYMMETRY (QUALITATIVE)

Figure 4.2: Temperature-dopant phase diagram for the hole-doped  $La_{2-x}Sr_xCuO_4$  and electrondoped  $Nd_{2-x}Ce_xCuO_4$  systems. AFM=antiferromagnetic phase, SG=spin glass phase, and SC=superconducting phase. After [44].



Figure 4.3: Phase diagram of  $Nd_{2-z}Ce_zCuO_4$  polycrystals (squares) from [42] and  $Pr_{2-z}Ce_zCuO_4$  thin films (circles) of Patrick Fournier [45].

The phase diagram of figure 4.3 seems to be characteristic of electron-doped cuprates since varying the substituent (Th for Ce) or the rare earth (Pr, Nd, Sm, Eu) doesn't really change it [45], [44]. An important feature of this diagram is the sharp increase of  $T_c$  between x=0.13 and x=0.15, which is a problem for making sam-

ples of intermediate  $T_c$ . Furthermore it worsen the consequences of inhomogeneities in the crystals. Skelton *et al.* [46] have determined using a micron-sized X-ray beam the Ce homogeneity as a function of position along the c-axis of a 100  $\mu$ m thick crystal. Their observation indicate that the material grows layer by layer with smoothly varying Ce for Nd substitution. Because  $T_c$  is so sharply peaked around x=0.15, the transport properties measured along the ab-plane of such a crystal might not represent exactly the properties of the material with the nominal concentration (say, x=0.15). There might be ab-planes in the crystal with different  $T_c$ 's, leading to stairsshaped multiple transitions. A prescription against this is to use thinner crystals, for instance of thickness of the order of 10  $\mu$ m.

Another feature of this phase diagram, as already mentioned, is the narrowness of the doping range that allows superconductivity. For completeness we should mention that Brinkmann *et al.* [47] have reported a wider doping range of superconductivity in PCCO than shown in figure 4.3. The authors found superconductivity within 50 to 100  $\mu$ m thick Pr<sub>2-x</sub>Ce<sub>x</sub>CuO<sub>4</sub> crystals with  $0.05 \le x \le 0.10$  which reached a  $T_c$  of 25 to 28K. However inhomogeneous Ce distribution over the thickness could lead to such observations.

In this section we have seen that the electron-doped cuprate superconductors all crystallize in the same structure, different from that of LSCO only by the absence of apical oxygen atoms. The superconducting phase diagram displays an evident electron-hole symmetry, with a range of dopant concentration delimiting the superconducting phase being however narrower in the electron-doped compounds.

### 4.2 Gap symmetry

The similarity of the phase diagrams of  $La_{2-x}Sr_xCuO_4$  and  $Nd_{2-x}Ce_xCuO_4$  (fig. 4.2), with appearance of optimal superconductivity at the same doping suggests an electronhole symmetry in most of the physical properties. However, most of their normal state and superconducting properties are very different. And to begin with, the order para-



Figure 4.4: Microwave penetration depth measurements from D. H. Wu et al. [49] and A. Andreone et al. [48] compared to a fit using the s-wave exponential model (solid line).

meter doesn't seem to have the same symmetry. Whereas many different experiments are consistent with a *d*-wave gap in hole-doped superconductors (see previous chapter), only<sup>1</sup> microwave measurements of the penetration depth and Raman scattering have so far given limited information about the symmetry of the gap in electron-doped cuprates, and they haven't shown evidence for nodes in it. The results of penetration depth measurements in Nd<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>4</sub> performed by A. Andreone *et al.* [48] and D.H. Wu *et al.* [49] are shown<sup>2</sup> in fig. (4.4). There is a very good agreement with an exponential dependence of the penetration depth with  $2\Delta_0/k_BT_c \approx 4$  for both sets of data. Note however that J. R. Cooper has suggested [50] that the value of  $\delta\lambda$ extracted from microwave measurements has to be corrected when the permeability  $\mu_r$  diverges, which is the case in NCCO because of the large Nd moments. Taking this into account, he found an extracted value of  $\delta\lambda(T)$  quadratic in T (dirty *d*-wave behaviour). Another sensitive experiment which has revealed the anisotropic order parameter in hole-doped cuprates (see chapter 3) is Raman scattering. Displacement

<sup>&</sup>lt;sup>1</sup>apart from the work presented in this thesis

<sup>&</sup>lt;sup>2</sup>The frequency difference  $\delta f$  plotted in the figure is proportional to  $\delta X_s$  where  $X_s$  is the surface reactance.  $\delta \lambda$  is related to  $X_s$  by  $\delta X_s(T) = \mu_0 \omega \delta \lambda(T)$ .

of low frequency spectral weight to higher frequencies as the sample is cooled down below  $T_c$  is attributed to the opening of the gap. Using two different polarization configurations, one can deduce a superconducting gap and evaluate its anisotropy. However in NCCO, Stadlober *et al.* find that the spectra are consistent with an *s*wave order parameter [51].

It would be very useful to have other ways available of probing the electronic system, but many problems arise [45]. The large magnetic moment of the Re<sup>3+</sup> ion in Re-Ce-Cu-O prevents from measuring any relaxation rate of nuclear moments in NMR. Tunneling experiments haven't given very reproducible data so far because of material issues [52]. Owing to the difficulty of making good Josephson junctions, it hasn't been possible yet to perform SQUID-type experiments, which are sensitive to the phase of the gap. The resolution in ARPES [53] is about 6 meV, which is not sufficient for measurements of  $2\Delta_0 \sim 8$  meV ( $2\Delta_0/k_BT_c \sim 4$  with  $T_c \approx 20$  K).

Thus the existing data tend to favor a nodeless s-wave gap in the electron-doped cuprates. However the information on the gap symmetry is still limited, mainly because of material issues. In this context, thermal conductivity (being a bulk probe, its reliability is not critically affected by the sample quality) can give a very useful contribution to the question (see our results in chapter 6).

### 4.3 Transport

#### 4.3.1 Normal state properties

While the resistivity is linear in temperature over a large temperature range in hole-doped superconductors (see previous chapter), its behavior is very different in electron-doped cuprates. Patrick Fournier reports a nearly  $T^2$  dependence of  $\rho_{ab}$  in both  $Pr_{1.85}Ce_{0.15}CuO_4$  [45] and  $Nd_{1.85}Ce_{0.15}CuO_4$  [54] thin films, with a residual resistivity  $\rho_0$  of the order of 70 and 60  $\mu\Omega$ cm respectively. Similarly, according to data obtained by Y. Dalichaouch *et al.*, both  $\rho_{ab}$  and  $\rho_c$  of optimally doped  $Re_{1.83}Ce_{0.17}CuO_{4-y}$  single crystals (Re=Nd and Sm) vary as  $T^2$  [55]. Thus the intrinsic temperature de-



Figure 4.5: **LEFT**: Temperature dependence of  $\kappa$  for PCCO and NCCO sintered samples [56]. Solid lines denote curves fitted to the theory of Tewordt and Wölkhausen [16]. **RIGHT**: Temperature dependence of  $\kappa_{ab}$  of  $\Pr_{2-x}Ce_xCuO_4$  ( $x \sim 0.145$ ) single crystal [57]. Here again, solid lines denote curves fitted to the theory of Tewordt and Wölkhausen.

pendence of the electrical resistivity in electron-doped cuprates seems to be  $T^2$  (as confirmed in section 6.1). The  $T^2$  temperature dependence with fairly high residual resistivity could be consistent with electron-electron scattering with a large elastic scattering contribution (defects such as impurities, lattice defects, vacancies...).

Hall coefficient measurements in PCCO and NCCO have revealed another holeelectron asymmetry. An upturn of  $R_H$  towards positive values is observed in those compounds at optimal doping (while  $R_H \sim 1/T$  at optimal doping in hole-doped cuprates), suggesting the presence of two types of charge carriers (holes and electrons) in these systems which might have to be described by a two-carrier model [45] [54]. At x = 0.2 in  $\Pr_{2-x}Ce_xCuO_4$ , the Hall coefficient is positive in all the temperature range (up to room temperature) : the electron-like character has disappeared, while the sample is still superconducting.

#### 4.3.2 Heat transport

This review of heat transport in electron-doped cuprates and in particular in PCCO is limited by the amount of literature existing on this topic. Figure 4.5 represents the in-plane thermal conductivity  $\kappa(T)$  in a sintered sample of  $\Pr_{1.85}Ce_{0.15}CuO_4$  (left) and  $\kappa(T)$  in single crystals (right). Evaluating the maximum electronic thermal conductivity with the Wiedemann-Franz law, both of these authors find that  $\kappa$  is mostly phononic in the temperature range of the experiment and shows a pronounced maximum around 30-40K, unrelated to the superconducting transition. Again, the absence of any feature at the transition may be a consequence of bad sample quality. The one order of magnitude difference compared to LSCO (higher in PCCO) is attributed by both authors to the absence of apical oxygen in the T'-structure. H. Ogasawara *et al.* suggest that the presence of apical oxygen atoms in  $La_{2-x}Sr_xCuO_4$  favours tunneling state scattering, thereby reducing the thermal conductivity due to phonons. The thermal conductivity of PCCO will be compared to that of its parent compound LSCO in chapter 6.

In conclusion, electron-doped cuprates present charge transport properties (quadratic resistivity, upturn in  $R_H$ ) not seen in the electron-doped materials. The heat conduction is much better in PCCO and NCCO than in LSCO, as will be discussed later.

### EXPERIMENTAL DETAILS

5

Our YBCO sample is a single crystal grown by a self-flux method (see [17]) at the beginning of this project, with the advice of R. Gagnon. The tetragonal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub> crystal is oxygenated for 5 days at 500°C in O<sub>2</sub> atmosphere, giving an orthorhombic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> superconducting crystal. As a consequence of the tetragonal  $\rightarrow$  orthorhombic transformation, domains of dominant  $\vec{a}$  or  $\vec{b}$  orientation (twins) take place in the crystal. They are removed by applying an uniaxial pressure on the sample (at 550°C for 30 min). Under the stress the slightly larger b-axis is favored perpendicularly to the axis of pressure. In the YBCO sample we investigated the pressure has been applied parallel to the length of the crystal, and we measured transport along the a-axis (in this way we don't have a direct contribution from Cu-O chains present along the b-axis). The other samples are all single crystals sent from elsewhere (see tables 6.1 and 6.2).

### 5.1 Sample characterization

#### 5.1.1 Electrical resistivity

For each crystal investigated, we have measured the resistive superconducting transition with a low frequency resistance bridge (LR-700 form Linear Research Inc) or a lock-in (SR-830 from Standford Research Systems). An electric current was directed along the sample's length via contacts at its both ends, and the voltage was measured between two points via contacts on its surface. In this configuration the current doesn't go through the contacts, avoiding to have their resistance included in the measurement. The contacts for the electric current were made of 100  $\mu$ m silver wires glued on the sample by silver epoxy before being annealed. The contacts for the voltage leads were made the same way but with 50  $\mu$ m silver wires in order to reduce the uncertainty on the geometric factor. The annealing time and temperature depend on the compound. The electrical resistance of these contacts was typically ~ 100 and 3.5 m $\Omega$  at room temperature and helium temperatures. In our setup we were able to measure the electrical resistivity with the same contacts as those used for the thermal conductivity. The advantage of this design is to obtain the Lorenz number without any geometric factor uncertainty.

#### 5.1.2 Magnetic susceptibility

A magnetic susceptibility measurement facility was also available for the determination of  $T_c$ . This method presents the advantage of not requiring any special preparation (*e.g.* contacts), and it is more sensitive than resistivity to possible inhomogeneities. The susceptibility apparatus is shown in fig. (5.1).

While the sample is in the normal state, its susceptibility is negligible, and as the temperature drops below the transition point, magnetic flux is screened out of the sample and the effective volume of that secondary coil drops, which results in a change in the total e.m.f. picked up.

#### 5.1.3 Scanning electron microscopy

We used Scanning Electron Microscopy (SEM) to measure the sample's dimensions and to examine its macroscopic structure. The length L and section S are needed to calculate the geometric factor L/S which gives the absolute value of the conductivity (thermal and electrical) from the conductance.

# 5.2 The <sup>4</sup>He cryostat

The cryogenic apparatus we used was a "dipstick", insertable in a liquid <sup>4</sup>He storage dewar, which enabled us to reach temperatures down to 1.5 K by pumping on a small liquid helium reservoir. The characteristics of this <sup>4</sup>He cryostat can be found



Figure 5.1: Susceptibility apparatus: one resistance bridge is used for reading the thermometer and another bridge to measure the susceptibility in mutual inductance mode.

in reference [58]. It has the qualities of low helium consumption, fast cool-down and warm-up times and good temperature stability from 1.3 K to room temperature. The portion which is inserted into the Dewar is shown in fig. 5.2.

• <u>Wiring</u>: Our setup uses 38 wires connected to two 19-pin electrical feedthroughs sealed hermetically on the upper portion of the cryostat. The wires are contained in the tube used for evacuating the can. In order to restrict the heat flow from room temperature down into the can, they are anchored at 2 stages : on top of the vacuum can (4.2 K) and on the sample stage. The material and size of the wires have also been chosen in this purpose : the 16 wires used to measure voltages are made of constantan (to limit thermal conductance) gauge 36, and the 20 used for the intensity are copper, gauge 36 (for low electrical resistance). The 2 remaining, assigned to carry stronger currents leading to the heater, are in copper, gauge 30. The sample stage is connected to the internal pot by a brass threaded rod, which provides an appropriate thermal link for the



Figure 5.2: Low-temperature portion of the <sup>4</sup>He insertable cryostat. The tubes marked  $C_1$  and  $C_2$  are capillary feed-through tubes for use with a continuous fill capillary.

smooth control of the sample temperature.

- <u>Heater and thermometer</u>: the temperature was controlled by a temperature controller (from Lakeshore) working with two possible calibrated thermometers : Pt (30-150 K) or Ge (1.0-75 K). We used the Ge thermometer from 1.5 to 60 K and then the Pt from 50 to 150 K. Originally heater and thermometer were fixed on the sample stage (position H and T in figure 5.2). We have displaced them on the sample holder to improve the thermal contact between them and the sample holder.
- <u>Vacuum can</u>: as shown on top of fig. 5.2, a tapered grease seal is used for the vacuum can. Very convenient to seal hermetically the vacuum can, it takes in addition only a small fraction of the available cross-sectional area. We used a diffusion pump to achieve pressures as low as 10<sup>-7</sup> torr necessary for the measurement of thermal conductivity (see below).
- Cooling procedure: From a ground temperature of 4.2 K, temperatures as low

as 1.5 K can be reached by pumping on a pot of liquid helium which is filled by pressurizing helium gas. Continuous refill of the pot is provided by a thin capillary attached to the pot, the other end being immersed in the liquid helium of the storage dewar. Although this refill facility is very simple in principle, it has surprisingly taken some months before getting it to work properly. Most of the time, some air trapped in the capillary must have blocked it upon freezing below 77 K, and deprived from the refill, the pot was empty after only an hour of experiment. The procedure which eventually enabled us to maintain a temperature of 1.5-1.6 K as long as desired with the pot remaining full is described below. The pumping tube going to the pot was connected with a "T" (via two valves) to a primary pump at one end, to a tube providing helium gas at the other end. This helium gas tube was not to be removed before the end of the experiment, to avoid any air contamination into the pot that could risk to block the capillary. In the same purpose, a cold trap was inserted in the helium gas circuit in between the bottle and the dipstick. First, the bottle being closed, all the helium gas circuit was pumped to remove air and other particles present. Then the trap was filled with liquid nitrogen. In the next stage, the pot was pressurized at about 14 psi with the clean helium gas free from possible impurities that had condensed in the cold trap. With a surpressure in the pot no air was to penetrate through the capillary and the dipstick could be immersed into the dewar, where it was out of air contamination danger. Thus at this stage it was possible to remove the surpressure in the pot, the liquid helium in the dewar being very pure. Then the stick was progressively dipped down to the bottom of the dewar, which took less than an hour if exchange gas had been previously inserted in the sample chamber. Once at liquid helium temperature vacuum was made in the sample chamber. Clean helium gas was pressurized in the pot at about 6 psi, to fill the pot with liquid helium (it takes about 20 minutes). If the vacuum in the chamber is sufficient, one can then pump on the pot to lower the temperature down to about 1.5-1.6 K.

# 5.3 Thermal conductivity setup

#### 5.3.1 Description

To measure thermal conductivity we used the so-called longitudinal steady-state method (see for example [3]). For every recorded point, the temperature of the sample is stabilized at some temperature  $T_0$ , and then a constant heating power is applied to one end of the sample. At equilibrium, the temperature gradient across the sample is measured and thermal conductivity is given by:

$$\kappa = \frac{\text{power}}{\text{temperature gradient}} \times \text{geometric factor}$$
(5.1)

The setup is illustrated schematically in fig. (5.3). It is a 4-probe method (requiring a cold bath at one end, a heater at the other and two thermometers in between). Four silver wires are attached to the sample with silver epoxy, two of 50  $\mu$ m diameter connected to the thermometers, and two of 100  $\mu$ m diameter connected to the heater and heat sink. The heater is connected to its contact with non superconducting solder, so as to maintain a good thermal contact at any temperature.

For an accurate measurement of the thermal conductivity, all the heat dissipated by the heater has to go across the sample. Thus the setup is designed to limit heat losses through the wires, thermometers, heater, through the residual gas of the sample chamber or by radiation. We used manganin coils (~  $40\Omega$  of  $25 \mu m$ wire) to isolate thermally the thermometers and the heater from the Cu base. The two thermometers were both 20  $\Omega$  Cernox resistors from Lakeshore, with a size of  $1 \times 1.5 \text{ mm}^2$ . These sensors have a semiconductive temperature dependence but they are still sensitive above room temperature, and thus in the whole range of our experiments (1.5–150 K). The heater was chosen to be a semiconductor-film resistor of 1.5 k $\Omega$ , for its weak temperature dependence (except at temperatures below 10 K, where its resistance increases fast), and its small size (1.5 × 1.5 mm<sup>2</sup>—the radiative heat loss is proportional to the surface area). The heater's resistance is much higher than that of the manganin coils (1.5 k $\Omega \gg 40\Omega$ ), thus the power is dissipated almost entirely in the heater.



Figure 5.3: Schematic drawing of the thermal conductivity apparatus. Ag wires are glued with epoxy along the sample, perpendicular to the direction of current, the manganin coils are connected to the electrical leads of the probe.

#### 5.3.2 Estimation of heat losses

The thermal conductivity of the high- $T_c$  materials being in general rather low, the risks of heat losses mentioned in the previous section are increased. To make sure that they don't affect appreciably our results, we will try to estimate quantitatively the losses at some points of the setup. For a study of the losses concerning the data obtained in the fridge, see the PhD thesis of B. Lussier ([59]). Here we discuss the losses in the dipstick setup only. Points 2 and 3 of the calculations (conduction in a gas and radiation) are based on a study of heat exchange in the book by G. K. White [60].

1. Losses through the wires. They are limited by manganin coils (40 gauge). The thermal conductivity of manganin at 150 K is 13 Wm<sup>-1</sup>K<sup>-1</sup> [60], from which we deduce its conductance  $4.2 \times 10^{-8} WK^{-1}$ . Among the samples we have investigated, the worse thermal conductance K was found in the very thin BSCCO samples. At 150 K, K is typically of the order of  $10^{-4}$  WK<sup>-1</sup> and at 1.5 K it is  $7 \times 10^{-6}$  WK<sup>-1</sup>. Thus even at 1.5 K, the heat loss through these coils is negligible compared with the heat flow through the sample. If we now include

the thermal resistance of the contacts between heater and sample, and between sample and heat sink, which are around  $10^4 \text{ W}^{-1}\text{K}$ , we get a total conductance of  $\frac{1}{3} \times 10^{-4} WK^{-1}$ , still much higher than that of manganin coils.

2. Losses through the surrounding gas. Good vacuum must be maintained in the can to reduce heat exchange with the residual gas present in the sample chamber. Since the pressure in the sample chamber is typically less than  $5 \times 10^7$  mbar, the mean free path of the gas molecules is larger than the dimensions of the can. In this case, according to [60], the power lost by conduction through the residual gas is given by :

$$\dot{Q}_{\text{conduction}} = \frac{constant}{\sqrt{T}} \times a_0 p \left(T_2 - T_1\right) \text{ W/m}^2 \tag{5.2}$$

where p is the pressure of the gas,  $T_1$  and  $T_2$  are the temperatures of the two points between which heat is exchanged, and  $a_0$ , called the accommodation coefficient, is always smaller than 1. For conduction in air,  $constant/\sqrt{T} \simeq$ 1.2 at room temperature, thus it is about 1.7 at 150 K. There is a constant heat exchange between the sample holder at 150 K and the wall of the can at 4.2 K. However here we want to calculate the extra conduction generated by the power dissipated in the heater, relative to the Cu base temperature. Thus  $T_2 - T_1 = \Delta T_{\text{heater}}$ . In our experiments at T = 150 K we had  $\Delta T_{\text{heater}} \approx 15$  K (estimated as being a little more than the 12 K temperature difference between the hot thermometer and the Cu base). With a pressure of  $5 \times 10^{-5}$  Pa, we get  $\dot{Q}_{conduction} < 1.3 \text{ mW/m}^2$ . The heat is exchanged through a heater surface area of  $2 \times (1.5 \text{ mm} \times 1.5 \text{ mm}) = 4.5 \times 10^{-6} \text{ m}^2$ , so the power lost is less than 6 nW. Compared to the typical heat flow through the sample  $\kappa \Delta T$  of the order of 1 mW, it also turns out to be a negligible effect.

3. Losses by radiation. They are more significant at high temperatures and limit the temperature range of our experiments. For two plane parallel surfaces of emissivities  $\varepsilon_1$  and  $\varepsilon_2$  at temperatures  $T_1$  and  $T_2$ , the heat transfer by radiation from an area A per unit time is [60]

$$\dot{Q}_{radiation} = \sigma A \left[ (T_2)^4 - (T_1)^4 \right] \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2}$$
(5.3)

where  $\sigma$  is not the electrical conductivity but Stephan's constant,  $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4$ . Again we estimate the extra radiation caused by the power in the heater, relative to the sink temperature. Thus  $T_1=150 \text{ K}$  and  $T_2 = T_1 + \Delta T_{\text{heater}}$ . Assuming both emissivities equal to 1 (the worst possibility), and with  $A \simeq 5 \text{ mm}^2$  and  $\Delta T_{\text{heater}} \simeq 15 \text{ K}$  we find  $\dot{Q}_{radiation} = 0.07 \text{ mW}$  at 150 K. In our BSCCO measurements the power dissipated by the heater was about 1 mW at this temperature, and it was about 3.5 mW for the YBCO experiment. Thus this upper estimation of losses by radiation represents 7% of the heat flow across a BSCCO sample. Of course, emissivities are certainly less than one and these losses are certainly actually less than 5% of the heater power. However considering the  $T^4$  dependence of the losses it sounds reasonable to stop the experiments at 150 K.

# 5.4 Experimental procedure

The experiment is directed by an interactive program written with the "Labview" software. For each point once the sink temperature adjusted by the temperature controller<sup>1</sup> is stable, one waits for equilibrium in the sample. The sample is considered as being in thermal equilibrium when the slope of the resistance of both Cernox thermometers (calculated over the last 10 data points) is below a value fixed by the program. At this stage the sink temperature  $T_{\rm sink}$  and the voltage of both Cernox thermometers<sup>2</sup>  $V_{\rm cold}(Q = 0)$  and  $V_{\rm hot}(Q = 0)$  are recorded. Q stands for the heat coming from the heater. These data are needed to make a calibration of the Cernox

<sup>&</sup>lt;sup>1</sup>A Lakeshore DRC 93CA coupled to a calibrated Ge or Pt thermometer.

<sup>&</sup>lt;sup>2</sup>Measured by two SR-850 lock-in amplifiers from Standford Research Systems. The lock-in sends a low frequency ac voltage, which is converted into a current trough a 10 k $\Omega$  limiting resistor and the voltage across each thermometer is measured.

<sup>&</sup>lt;sup>3</sup>In absence of power dissipated by the heater both thermometers are at the same temperature but "cold" and "hot" make sense in presence of a temperature gradient in the sample.



Figure 5.4: Illustration of the analysis performed in order to extract the temperature of the thermometers. The solid and dashed lines are respectively the calibration curves for the hot and cold thermometers.

thermometers. Then a temperature gradient is applied in the sample. After equilibrium the program records the voltage U and intensity I of the heater, the new values  $V_{\text{cold}}(Q)$  and  $V_{\text{hot}}(Q)$  of the voltage in both thermometers, and  $T_{\text{sink}}$  to check that it hasn't increased appreciably. From the calibration curves V(T) of the Cernox resistors, one can deduct the temperatures  $T_{\text{cold}}$  and  $T_{\text{hot}}$  corresponding to  $V_{\text{cold}}(Q)$ and  $V_{\text{hot}}(Q)$  (*i.e.* when the heater dissipates a power  $U \times I$ ). This is illustrated in figure 5.4 where the data comes from the measurement of the sample BSCCO#2. The calibration is obtained by a fit with third or fourth order polynomials of the data "ln T versus  $\ln V(0)$ " of the temperature as a function of thermometers voltages. Then  $\ln V(Q)$  is inserted in the polynomial, giving the corresponding  $\ln T$ . The exponential is taken to get  $T_{\text{hot}}$  and  $T_{\text{cold}}$ . Our method is accurate only if  $\Delta T/T$  is not too large (otherwise one looses resolution in the measurement) or not too small (otherwise the noise takes too much relative importance). The program adjusts the heater power so that  $\Delta T/T$  remains close to 4%. The thermal conductivity  $\kappa$  at temperature  $\overline{T} = (T_{\text{cold}} + T_{\text{hot}})/2$  is then given by equation (5.1)

$$\kappa(\overline{T}) = \frac{U \times I}{T_{\text{hot}} - T_{\text{cold}}} \times \frac{L}{S}$$
(5.4)

where L and S are the length and the cross-section area of the sample.

# 5.5 Test on an Al sample

In order to test our experimental setup we measured the resistance and thermal conductance of a 18.5 mm long aluminum wire of 50  $\mu$ m diameter and of purity 99.99%. The resistivity (resistance divided by geometric factor) and thermal conductivity (conductance multiplied by geometric factor) are plotted in figures 5.5 and 5.6 as a function of temperature. One finds the features characteristic of normal metals



Figure 5.5: Resistivity versus temperature of Al. The sample is 99.99% pure. The inset shows a focus on the region of constant resistivity at low temperature.

described in fig. (2.1.4) : at high temperature  $\sigma \sim 1/T$  and thus  $\rho \sim T$ . In this range  $\kappa_e$  is constant. However the phonon contribution has to be taken into account and a slight upward slope is expected for  $\kappa$ . As temperature is decreased electrons begin to be less scattered by phonons and  $\rho$  decreases more slowly, while  $\kappa$  increases. At low temperature  $\rho$  eventually reaches a constant determined by impurity scattering (inset of fig. 5.5). The phonon contribution to the thermal conductivity is negligible and  $\kappa \simeq \kappa_e \sim T$ . Thus in this range the Wiedemann-Franz law holds and our data should verify  $\kappa = (L_0/\rho)T$ , or  $K = (L_0/R)T$  (which is equivalent since the geometric factors cancel out). Figure 5.7 shows a focus between 1.5 and 3.5 K of the thermal



Figure 5.6: Thermal conductivity versus temperature of an Al wire in the whole range of our experiments.



Figure 5.7: Linear fit of the thermal conductance of a 50  $\mu$ m diameter 18.5 mm long Al wire between 1.5 and 3.5 K. The slope K/T multiplied by the residual resistance  $R = 0.497 \Omega$  is in theory equal to the Sommerfeld value of the Lorenz number  $L_0$ .

conductance K versus temperature. Note that in our setup R and K are measured with the same contacts, which eliminates any uncertainty due to the need of geometric factors. The linear fit gives a slope of  $4.67 \times 10^{-5}$  WK<sup>-2</sup>. With a residual resistance R = 0.497 m $\Omega$ , we find  $L_0 = 2.32 \times 10^{-8}$  W $\Omega$ K<sup>-2</sup>. The WF law is verified with only 5% discrepancy relative to the Sommerfeld value.

Figure 5.8 represents the experimental Lorenz number  $L = \kappa \rho/T$  compared to the Sommerfeld value (straight line), in the whole range of our experiments. As just pointed out, at low temperature, L is close to  $L_0$ . As a result of inelastic scattering (section 2.1.4), L moves away from  $L_0$  at intermediate temperatures. However it is



Figure 5.8: Plot of the ratio  $L = \kappa/\sigma T$  for the Al wire. At low temperatures  $\kappa \simeq \kappa_e$  and the curve is an illustration of the Wiedemann-Franz law. The Sommerfeld value  $10^8 \times L_0 = 2.44 \text{ W}\Omega \text{K}^{-2}$  is indicated by a line. In the high temperature part of the range the phonon contribution has to be taken into consideration.

expected to tend to  $L_0$  again at high temperature. As opposed to this, the figure shows that L becomes greater than  $L_0$ . This has to be attributed mostly to the withtemperature-increasing phonon contribution  $\kappa_{ph}$ , which is absent from the WF law but not negligible in this range. A part of this discrepancy with the WF law could also come from heat losses by radiation, as mentioned earlier in this chapter.

Thus, we have verified the Wiedemann-Franz law at low temperature, proving the reliability of our setup.

# 6

# **RESULTS AND DISCUSSION**

We have characterized a few pure single crystals of  $Pr_{1.85}Ce_{0.15}CuO_4$ ,  $YBa_2Cu_3O_{6.9}$ , Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>, and La<sub>1.83</sub>Sr<sub>0.17</sub>CuO<sub>4</sub> (by resistivity measurements and for some of them magnetization). All of them are optimally doped, which means that their dopant concentration is that allowing the highest possible  $T_c$  in each compound. As explained in the previous chapter, the YBCO sample is a detwinned crystal and the data have been taken for charge and heat current along the *a* direction, in order to avoid a direct contribution from the CuO chains. Among those samples, one sample of LSCO, one of YBCO, two of BSCCO and two of PCCO have been chosen for further investigation. Their characteristics are summarized in tables (6.1) and (6.2). In these tables is also indicated for each sample the uncertainty on the geometric factor, which is the main source of uncertainty in our measurements. Uncertainty information being given in the tables, we haven't inserted error bars in our figures, in order to keep them clearer.

### 6.1 Resistivity

One  $\rho(T)$  curve for each compound studied is shown in fig. (6.1). Our PCCO samples display a ~  $T^2$  resistivity, consistent with the existing data (section 4.3.1). The three hole-doped compounds (YBCO, BSCCO and LSCO) present a linear resistivity  $\rho = A + BT$  in the whole range starting close above the transition. However in the case of LSCO there is a slight change of slope around 160 K. A is mostly associated with impurity scattering and B with inelastic scattering (varying the amount of impurities changes A but not B). The values of  $A = \rho_0$  (extrapolation at T = 0 of the normal state resistivity) and the slope  $B = d\rho/dT$  are summarized in table (6.1). In a Table 6.1: The geometric factor,  $T_c$  and resistivity of the hole-doped compounds. The second column indicates the name and provenance of the samples, with (PF) standing for Patrick Fournier at University of Maryland, (NPO) has been sent by N. P. Ong from Princeton University and the growth of the sample labeled (RG) was, under the supervision of Robert Gagnon, a part of this master's work. The geometric factor G is the length divided by the section of the crystal (the resistivity is given by the resistance divided by G). The relative uncertainty on G is indicated in parentheses.  $T_c$  has been taken as the middle of the resistive transition and  $\Delta T_c$  is the interval in which resistivity falls from 90 to 10%.  $\rho_0$  and  $d\rho/dT$  have been obtained from a linear fit of the resistivity versus temperature curve in the range 70-200K in LSCO, and 130-250K in BSCCO and YBCO.

Compound	Sample	Geometric	T <sub>c</sub>	$\Delta T_{c}$	$ ho_0$	<u>dp</u> dT
	(provenance)	Factor				
		$(m^{-1})$	(K)	(K)	$(\mu\Omega cm)$	$(\mu\Omega cmK^{-1})$
$La_{1.83}Sr_{0.17}CuO_4$	(NPO)	3631(7%)	39	9	39	1.29
$Bi_2Sr_2CaCu_2O_8$	#1 (PF)	?	89	3.5	—	—
	#2 (PF)	35294(25%)	89	2.5	12	1.15
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.9</sub>	15-5-97a-axis	15556(12%)	93.6	0.4	-10	1.10
	or a#3 (RG)					

Table 6.2: The geometric factor,  $T_c$  and resistivity of the electron-doped compounds. The second column indicates the name and provenance of the samples, with (PF) standing for Patrick Fournier at University of Maryland. The geometric factor G is the length divided by the section of the crystal (the resistivity is given by the resistance divided by G). The relative uncertainty on G is indicated in parentheses.  $T_c$  has been taken as the middle of the resistive transition and  $\Delta T_c$  is the interval in which resistivity falls from 90 to 10%.  $\rho_0$  has been obtained from a second order polynomial fit of the resistivity versus temperature curve in the range 50-250K.

Compound	Sample	Geometric	T <sub>c</sub>	$\Delta T_{c}$	$ ho_0$
	(provenance)	Factor			
		$(m^{-1})$	(K)	(K)	$(\mu\Omega cm)$
Pr <sub>1.85</sub> Ce <sub>0.15</sub> CuO <sub>4</sub>	#2 (PF)	44578(16%)	19	5.5	39
	#3 (PF)	97166(12%)	20	4	19



Figure 6.1: Resistivity as a function of temperature of the samples PCCO#3, YBCO, BSCCO#2 and LSCO. See tables (6.1) and (6.2) for quantitative details.

very simple model we may use Drude formula (eqn. (2.14)) to express the inelastic scattering rate  $1/\tau_{inel}$ , and since the resistivity  $1/\sigma$  is linear in T,

$$\frac{1}{\tau_{\text{inel}}} = \frac{(N\delta)e^2}{m^*} \left(\frac{d\rho}{dT}\right) T \tag{6.1}$$

where  $\delta$ , the filling factor, is the number of itinerant holes per Cu(2) ions (*i.e.* the Cu ions of the CuO<sub>2</sub> planes) and N is the density of Cu(2) ions. A quantity related to N is the linear density  $N_{\text{planes}}$  of CuO<sub>2</sub> planes along the c-axis. Thus in order to compare the scattering rate in this model for our hole-doped samples, we want to compare the ratio of the quantity  $N_{\text{planes}} \delta \frac{d\rho}{dT}$ . In section 4.1, we saw that  $N_{\text{planes}}$  is respectively about 0.15, 0.13 and 0.17 in LSCO, BSCCO and YBCO.  $\delta$  is 0.25 in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (thus probably a bit less in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub>) and 0.17 in LSCO [61]. With the values of  $d\rho/dT$  listed in table (6.1), we find 1.0 / 1.1 / 1.4 for the ratio of  $1/\tau_{\text{inel}}$  in LSCO/BSCCO/YBCO, very similar in the three samples. Thus there may be a common inelastic scattering mechanism, suggested from the results from D. A. Bonn *et al.* in YBCO (see section 3.3.2) to be strong electron-electron interactions [30]. We also remark that  $d\rho/dT$  has the same value to within 20% in the



Figure 6.2: Resistive superconducting transition of : (□) PCCO#2 ; ● PCCO#3.

3 samples. All these results ( $\rho \sim T$  with a similar slope in hole-doped compounds) are consistent with existing data (see section 3.3.1). In particular, the more or less equivalent scattering rate in several cuprates is also found in infrared spectroscopy (see [62]).

However the residual resistivity of the samples we have measured is rather lower for each compound than in most samples reported in the literature, showing their comparatively high quality. Among "our" samples, the purest and most homogeneous one is the YBCO crystal, characterized by a very sharp transition (less than 0.4 K) and a negative residual resistivity. The growth process is very well mastered and all the samples have nearly the same  $\rho$ , sharp transition and a 93.2 K  $< T_C < 93.8$  K. Although the two Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> crystals we have selected show a linear resistivity with a sharp transition (about 3 K) and a low  $\rho_0$ , homogeneity and oxygen concentration are more difficult to control in this mika-like compound. So one of the samples we received presents a rounded resistivity curve. In the case of Pr<sub>2-x</sub>Ce<sub>x</sub>CuO<sub>4</sub> it hasn't been achieved at this stage to grow repeatedly high quality crystals. As pointed out in section 4.1, the consequences of inhomogeneous dopant concentration are enhanced by the sharpness of the superconducting phase diagram, favoring multiple and broad transitions. This is the case in our samples, as shown by their resistive transition in fig. (6.2). PCCO#2 (squares) presents a transition in three stages and its residual resistivity is the double than in the other sample. Anyway in both  $La_{1.83}Sr_{0.17}CuO_4$ and  $Pr_{1.85}Ce_{0.15}CuO_4$ , superconductivity requires 15% impurities, moving the crystals away from stoichiometry and yielding large residual resistivities. In addition they suffer from inhomogeneities in the concentration of dopant.

In this section we have presented our results for the resistivity (linear in temperature in hole-doped compounds, quadratic in PCCO), in accordance with previous data (see section 4.3.1). We have also discussed the materials quality, very high in YBCO, reasonable in BSCCO, and comparatively rather poor in LSCO and PCCO.

# 6.2 Thermal conductivity at high temperature (T > 1 K)

We present in this section the thermal conductivity versus temperature of Bi<sub>2</sub>Sr<sub>2</sub>Ca-Cu<sub>2</sub>O<sub>8</sub> and Pr<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>4</sub> in the range 1.5 K to 120–150 K. These data will also be compared to those for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> and La<sub>1.83</sub>Sr<sub>0.17</sub>CuO<sub>4</sub>.  $\kappa(T)$  in Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> is displayed in fig. (6.3). The curve presents the same qualitative features as that



Figure 6.3: Thermal conductivity of  $Bi_2Sr_2CaCu_2O_8$  versus temperature. ( $\triangle$ ) BSCCO#1; ( $\diamond$ ) BSCCO#2. The difference of magnitude between the two curves lies within the uncertainty on the geometric factor.

from Ong et al. (fig. (3.4)) : a kink at about 10 K and the well known peak below  $T_c$  also seen in YBCO and LSCO (see figures (6.4) and (6.5)). This peak is attributed to a suppression of the quasiparticle scattering rate below the transition,



Figure 6.4: Thermal conductivity versus temperature in YBCO and BSCCO. The left-side scale corresponds to the left-side legend (circles). In order to be able to distinguish all the features of  $\kappa(T)$  in BSCCO, the data of the solid circles curve has been plotted on a different scale (small plus signs, BSCCO zoom, right-side scale). The arrows indicate the scale associated to each curve.



Figure 6.5: Thermal conductivity versus temperature in LSCO and PCCO. The left-side scale corresponds to the left-side legend (diamonds). Because the heat conduction is much better in PCCO than is LSCO, the data of the solid diamonds curve has been plotted on a different scale (small plus signs, LSCO zoom, right-side scale). The arrows indicate the scale associated to each curve.



Figure 6.6: Normalized thermal conductivity  $\kappa/\kappa(T_c)$  versus normalized temperature  $T/T_c$ . Comparison between BSCCO#1 and YBCO.



Figure 6.7: Normalized thermal conductivity  $\kappa/\kappa(T_c)$  versus normalized temperature  $T/T_c$ . Comparison between LSCO and PCCO#3.



Figure 6.8: Thermal conductivity versus temperature in our two  $Pr_{1.85}Ce_{0.15}CuO_4$  samples. Sample #3 (solid diamonds), which has a lower residual resistivity, shows a feature at  $T_c$  contrary to sample #2 (empty diamonds).

as explained in section 3.3.2. Quantitatively our measurements also agree with the data of Ong *et al.* within the uncertainty on the geometric factor. The geometric factor for sample #1 has been estimated from the resistivity data, in such a way that  $d\rho(T)/dT$  is equal in samples #1 and #2. Since the peak is believed to be due to a rapid increase of the electronic mean free path below the transition, it should be affected by the level of impurity scattering. In this respect, it is interesting to compare the magnitude of the peak below  $T_c$  in the hole-doped compounds (figures (6.6) and (6.7) are convenient for this comparison), and relate it to  $\rho(T_c)/\rho(0)$ , ratio which underlines the relative importance of inelastic and elastic scattering. From microwave conductivity data [63],  $\rho(T_c)/\rho(0) \sim 100$  in YBCO. From table (6.1), one can estimate  $\rho(T_c)/\rho_0 \sim 10$  in BSCCO and  $\sim 2$  in LSCO. This scales nearly exactly with the magnitudes of the peak below  $T_c$  of respectively 115, 10 and 3% of the normal state value in YBCO, BSCCO and LSCO. Thus most of the discrepancy in the peak magnitudes can be explained by the different levels of purity (from cleanest to dirtiest) in YBCO, BSCCO and LSCO samples.

Fig. (6.8) shows  $\kappa(T)$  for PCCO. Three main features are observed in this figure : a broad peak in the normal state, interrupted by a small peak just below  $T_c$ , and a large absolute value of the thermal conductivity compared with the other compounds
(a factor of 5 to 10 relative to LSCO, as seen in fig. (6.5)). Let us now comment on these features, beginning with the normal state.

Because of inelastic scattering the Wiedemann-Franz law doesn't hold in this temperature range and  $\kappa_e/\sigma T < L_0$ . Thus  $L_0\sigma T$  is an upper estimate of the electronic thermal conductivity. Let us calculate it just above  $T_c$ :  $\frac{1}{\sigma} = \rho \simeq 25 \ \mu\Omega$ cm and  $T_c = 20$  K, which gives  $\kappa_e < L_0\sigma T = 2 \ \mathrm{Wm^{-1}K^{-1}}$ . We estimate then  $\kappa_e$  to represent less than 5% of the total conduction, the rest being attributed to phonons. Thus the broad peak in the normal state has to be phononic.

It is the first time that a feature at  $T_c$  in the thermal conductivity of  $Pr_{2-x}Ce_xCuO_4$ is reported, which confirms the comparative quality of this sample (PCCO#3). As displayed in fig. (6.8), no feature at  $T_c$  is to be seen in PCCO#2, showing the sensitivity of the peak to the scattering by defects. The  $T^2$  dependence of the resistivity suggests that the main inelastic scattering in the normal state is electron-electron scattering. Thus the peak could be explained, as in the hole-doped compounds, by the disappearance below  $T_c$  of electron-electron scattering, with here a large elastic scattering contribution (the small magnitude of the peak-2%- being related to the small ratio  $\rho(T_c)/\rho(0) \sim 1$ ). However we should note that this scenario is easier to be achieved in the hole-doped compounds than in PCCO, if we assume an exponential drop of the normal fluid density below  $T_c$  (as suggested by our low temperature PCCO data showed in fig. (6.10)). Indeed, the quasiparticle density decreases slower in a superconductor with nodes in the gap function. In fact, another possibility for the origin of the peak is that the phonon mean free path undergoes a small enhancement owing to the loss of electronic scatterers below  $T_c$ , thereby increasing  $\kappa_{ph}$ . However in this scenario it is more difficult to account for the absence of peak in PCCO#2.

The third feature we noticed in fig. (6.8) was the high absolute value of the thermal conductivity in PCCO (it is even higher in NCCO according to fig. (4.5) presented in a previous chapter). Since we attributed at least 95% of the heat conduction to phonons in the normal state, our question is why phonon conduction is much more effective in PCCO. Let us also consider the other compounds. The difference of mag-

	$v_l$	$v_t$	$< v_{ph} >$
YBCO	6000	3700	4000
BSCCO	4600	2800	3000
LSCO	6000	2900	3000
NCCO	7100	?	?

Table 6.3: Sound velocities in  $m/s : v_l$  is the longitudinal sound velocity,  $v_t$  the velocity of the faster of the two transverse modes and  $\langle v_{ph} \rangle$  is given by eqn. (6.5). The values are after [65].

nitudes of  $\kappa$  at 100 K are respectively about 20, 10, 4 and 4 for PCCO, YBCO, LSCO and BSCCO (see figures (6.4) and (6.5)). According to [64], the level of impurity affects only weakly the normal state thermal conductivity and can only account for a small part of the difference between the very pure YBCO sample and the BSCCO and LSCO ones. The sound velocity could be part of the clue. The larger the velocity of sound  $\langle v_{ph} \rangle$ , the larger the magnitude of  $\kappa^n$  (normal state thermal conductivity) in YBCO, BSCCO and LSCO (see table (6.3)). A comparison with fig. 6.1 shows hat PCCO is also much less resistive for the charge conduction than the three hole-doped compounds. A striking feature is that the PCCO and LSCO samples, which have nearly identical structures and are of similar quality, are the two extreme conductors of heat and of charge in figures (6.5) and (6.4), and (6.1). For the heat conduction, this underlines the role of the apical oxygens in the scattering of phonons. The electronic scattering of phonons could explain this feature, but the question to know why there would be more electrons or a stronger electron-phonon scattering in LSCO is not obvious.

In summary, the thermal conductivity in the range 1 to 150 K could respect an electron-hole symmetry by presenting the same general features : the normal state heat conduction is achieved in a large part by phonons, while the electronic contribution is restricted by some strong inelastic electronic mechanism. Below the transition this mechanism disappears, causing a broad peak, the magnitude of which is mainly related to the sample purity. However, we have noticed that the thermal conductivity is higher in the electron-doped than in the hole-doped compounds.

# 6.3 Thermal conductivity at low temperature (T < 1 K)

## 6.3.1 Introduction : universal heat conduction

The main purpose of our experiments at low temperatures (going down to  $T \simeq 50-70 \text{ mK}$ ) was to probe the density of quasiparticles as  $T \to 0$ . As seen in section 2.3.1, a superconductor with lines of nodes on the Fermi surface which has a finite concentration of impurities is predicted to have a finite density of excited states  $N(E) \simeq N(0)$ , approximatively constant below an energy scale  $\gamma$ , and above which  $N(E) \sim E$ . On the contrary, for a superconductor with a nodeless gap, N(E) = 0 below  $\Delta$ . Thus the presence or absence of a residual normal fluid gives information on the symmetry of the order parameter. In ref. [14], M. Graf *et al.* give the theoretical values of the electronic thermal conductivity in superconductors with a line node in the gap function, when  $k_BT \ll \gamma$ , for various possible gap symmetries. In all cases  $\kappa_e(T)|_{T\to 0} \propto T$ , the constant of proportionality depending on the gap symmetry. An advantage of working at low temperatures is that it is possible to isolate reliably  $\kappa_e$  and  $\kappa_{ph}$ , when the asymptotic  $T^3$  regime of the heat capacity has been reached. Then the phonon thermal conductivity (formula 2.20) writes  $\kappa_{ph} = bT^3$ , where b is approximatively constant and the theoretical thermal conductivity has the form

$$\kappa = aT + bT^3 \tag{6.2}$$

 $(aT \text{ and } bT^3 \text{ are respectively the contributions of quasiparticles and phonons}).$  In addition, as pointed out in section 2.3.1, for certain gap functions with appropriate topology and symmetry,  $\kappa_e$  (as well actually as the charge conductivity  $\sigma$ ) doesn't depend on the impurity scattering rate (as long as  $\hbar\gamma \ll \Delta_0$ , which won't apply if  $\Gamma$ is too large), *i.e.* the conduction by the residual normal fluid is universal.

Universal transport in a superconductor has been observed for the first time by L. Taillefer *et al.* [28]. They have measured the thermal conductivity at low temper-



Figure 6.9:  $\kappa/T$  versus  $T^2$  for two YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> single crystals along the a-axis, one insulating (y = 6.0; triangles) and one superconducting (y = 6.9; circles). Lines are fits to  $a + bT^2$  for T < 0.15 K. After L. Taillefer *et al.* [28].

atures of pure and Zn doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> single crystals, as well as an insulating (deoxygenated) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub> crystal. Their data, presented in fig. (6.9), could be fitted as  $\frac{\kappa}{T} = a + bT^2$  below  $T \simeq 150$  mK. For a 0.6%-Zn-doped sample, they found that the limit  $\frac{\kappa_0}{T}$  (*i.e.* for  $T \to 0$ ) was the same as in the pure sample, *i.e.* it is universal for small dopant concentrations. The comparison with the deoxygenated sample is also very enlightening. The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> sample presents a residual linear term in  $\kappa$ . Whereas the insulating sample shows as expected no residual linear term, its temperature dependence is similar to that of the metallic sample. The experimental data of Taillefer *et al.* illustrate nicely the predicted form of  $\kappa/T$  since the electronic contribution *a* vanishes when the electrons are removed and the phononic contribution  $bT^2$  is similar in both the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub> samples. They find a universal limit of 0.19 mWK<sup>-2</sup>cm<sup>-1</sup>, a result which is compared in their article with the predictions of the theory. For a *d*-wave gap of  $d_{x^2-y^2}$  symmetry, the T = 0 limit of  $\kappa/T$  along the *a* direction is [14]

$$\frac{\kappa_{00}}{T} \to \frac{\hbar k_B^2}{6e^2} \frac{\omega_p^2}{S} \tag{6.3}$$

where  $S = |d\Delta(\Phi)/d\Phi|_{node}$  is the slope of the gap at the node and  $\omega_p$  is the Drude plasma frequency. Assuming the standard *d*-wave gap  $\Delta_0 \cos(2\Phi)$  for which  $S = 2\Delta_0$ ,



Figure 6.10: Thermal conductivity divided by temperature at low temperatures. ( $\bigcirc$ ) PCCO#2; ( $\triangle$ ) BSCCO#2; ( $\Box$ ) YBCO; ( $\bigcirc$ ) LSCO

and a weak-coupling value  $\Delta = 2.14k_BT_c$ , there is agreement between the data and the theory if  $\omega_p = 1.5$  eV.  $\omega_p$  has been estimated from infrared measurements to be  $\simeq 1.3$  eV (see reference in [28]).

# 6.3.2 Experimental results

In this thesis we present measurements of the low temperature thermal conductivity in the ab-plane in other cuprates, namely pure samples of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>, La<sub>1.83</sub>Sr<sub>0.17</sub>CuO<sub>4</sub> and Pr<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>4</sub>. The results are presented in fig. (6.10) where they are compared to pure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> data. First we want to draw general conclusions and then we shall analyze the Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> data in more detail. As appearing clearly from the  $\kappa/T$  versus  $T^2$  plot, the data can be fitted as  $\frac{\kappa}{T} = a + bT^2$  below  $T \approx 140$  mK, as in [28]. Solid lines are a linear fit of the data points below about 130 mK. Again, aT and  $bT^3$  are respectively the electronic and phonon contributions. The most striking point of fig. (6.10) is the following : the thermal conductivity of the three hole-doped compounds (empty triangles, squares and circles) present a residual

	$\omega_p$	S	$\kappa_0/T \ (\mathrm{mWcm^{-1}K^{-2}})$	
	(eV)	(meV)	experiment	theory
YBCO	1.3	35 $(T_c)$	0.12	0.1
		$\approx 40 \; (\text{STM})$		0.09
BSCCO	1.1-1.2	20–21 (δλ)		0.12-0.15
		33 $(T_c)$	0.15	0.08-0.09
		$\approx 65$ (ARPES)		0.04
LSCO	0.80.9	15 $(T_c)$	0.02	0.09-1.1

Table 6.4: Electronic term. Experimental values and estimates (from eqn. (6.3)) of  $\kappa/T$  in the zero temperature limit. The references can be found in the text.

linear term whereas in the case of the electron-doped  $Pr_{1.85}Ce_{0.15}CuO_4$  (solid circles),  $\kappa/T$  extrapolates to zero. The residual linear term, signature of the presence of quasiparticles at very low temperatures means that there are gap nodes in the ab-plane of the Fermi surface. The presence of this normal fluid at T = 0 is a consequence of impurity scattering, causing pair-breaking at the nodes [66]. On the contrary, the absence of linear term in  $Pr_{2-x}Ce_xCuO_4$  indicates that this superconductor has a nodeless gap function. Our data are consistent with the other experiments which have given information on the gap symmetry (sections 3.2 and 4.2) and have predicted a *d*-wave order parameter in the hole-doped cuprates and a *s*-wave gap in the electrondoped cuprates. This result is particularly important in  $Pr_{2-x}Ce_xCuO_4$  where only few experiments can give information on the gap symmetry. Thus our data are maybe the strongest evidence for a nodeless gap in the electron-doped cuprates.

As we shall discuss later, another feature of fig. (6.10) is the similarity between the YBCO and BSCCO data, a being very close in both cases, as well as the temperature dependence in all the range of the figure. The results from a linear fit to the points included in the asymptotic region are summarized in tables (6.4) and (6.5) along with the theoretical estimations. For BSCCO the fit gives  $a = 0.15 \text{ mW/cmK}^2$ . The phonon coefficient b is 6.7 mW/cmK<sup>4</sup> in BSCCO, very close to the 7.5 mW/cmK<sup>4</sup>

	β	$< v_{ph} >$	$\Lambda_0$	$\kappa_{ph}/T^3 ~(\mathrm{mWcm^{-1}K^{-4}})$	
	$(mJ/K^4mol)$	(m/s)	$(\mu m)$	experiment	theory
YBCO	0.3-0.4	4000	300	7.5	11–14
BSCCO	0.9–0.12	3000	200	6.7	12.5–16.5
LSCO	0.3-0.4	3000	600	4.4	30–40
PCCO				20	

Table 6.5: **Phonon term.** Experimental values and estimates (from eqn. (6.6)) of the phonon coefficient in the asymptotic  $T^3$  regime. The references can be found in the text.

slope in YBCO. Now let us estimate for BSCCO the electronic and phononic coefficients from the theory.

# 6.3.3 Estimate of the thermal conductivity in $Bi_2Sr_2CaCu_2O_8$ .

<u>Electronic term</u>.

The theoretical elements we need for this estimation are presented in section 2.3.1. First we have to check that the energy for one-particle excitations is much less than the bandwidth  $\gamma$ , in which case the density of states N(E) is approximately constant. The energy of the one-particle excitations is  $k_BT$ , which in the region of our linear fit is less than  $k_B \times 140$ mK. Thus  $k_BT < 0.015$  meV. Then we need to calculate  $\hbar\gamma$ . In the unitary limit, it is given by  $\sqrt{\pi \Delta_0 \hbar \Gamma/2}$  while in the limit of weak scattering,  $\hbar\gamma \sim 4\Delta_0 \exp(-\pi \Delta_0/2\hbar\Gamma)$ , where  $\Gamma$  is the impurity scattering rate. It is generally assumed that impurity scattering in the cuprates is well described by taking the unitary limit [14], and this has been confirmed by the quantitative agreement between the theory and the data of L. Taillefer *et al.* [28]. In reference [23], T. Jacobs *et al.* indicate that the scattering rate at 130 K for his BSCCO single crystals is about 1.3  $10^{14}$  s<sup>-1</sup> (this is almost entirely inelastic since in very pure crystals the elastic contribution is very small, as shown by the work of Romero *et al.* [67]). In ref [28]  $\Gamma(T = 0)$  is evaluated from  $\Gamma(T = 100K)$  via the microwave conductivity result that the quasiparticle mean free path is known to increase by a factor of about 100 between 10 and 100 K. Microwave conductivity experiments ([23],[68]) have also shown this scattering suppression in BSCCO, but maybe with less amplitude, due to the lesser quality of the samples. To make a lower estimate of  $\hbar\gamma$ , we will assume a hundredfold decrease of the scattering rate from the normal state to low temperatures, yielding  $\hbar\Gamma < 10$  meV. With  $\Delta_0 = 2.14k_BT_c = 33$  meV in the weak coupling limit, one obtains  $\hbar\gamma \approx 5$  meV. Thus even for this lower bound estimate,  $k_BT \ll \hbar\gamma$  and we can use the zero temperature theoretical limits for  $\kappa_e$ . Since most of the experiments are consistent with a  $d_{x^2-y^2}$  order parameter in Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>, we will assume the gap to have this symmetry. In this case,  $[\kappa_e/T]_{T\to 0}$  is given by equation (6.3).

We adopt the values of the plasma frequency  $\omega_p = 1.1-1.2$  eV indicated in [14] (see references therein). We will use four ways to estimate the slope S of the gap at the nodes.

- 1. Thermal conductivity. Assuming  $\omega_p \simeq 1.1 \text{ eV}$ , we estimate S from eqn. (6.3) by inserting our experimental value of  $a = [\kappa_e/T]_{T\to 0} = 0.15 \text{ mWcm}^{-1}\text{K}^{-2}$ . We find  $S \simeq 17 \text{ meV}$ .
- 2. Weak-coupling approximation. Assuming the standard d-wave gap  $\Delta_0 \cos(2\Phi)$  for which  $S = 2\Delta_0$ , and a weak-coupling value  $\Delta_0 = 2.14k_BT_c$ , one finds  $S \simeq 33 \text{ meV}$   $(T_c = 89 \text{ K}).$
- 3. Angle-resolved photoemission spectroscopy (ARPES). Here we estimate S from the ARPES measurements of Ding et al. [53]. We can simply evaluate directly the slope at the node from the diagram of  $\Delta_0$  versus the angle, which gives  $\underline{S \approx 64 \text{ meV}}$ . Alternatively, we assume again the standard *d*-wave gap  $\Delta_0 \cos(2\Phi)$ , for which  $S = 2\Delta_0$ . Taking this time  $\Delta_0$  from the data of Ding et al., we find  $\underline{S \approx 66 \text{ meV}}$ .
- 4. Microwave measurements of the penetration depth. Another way of calculating the slope of the gap is from the linear slope of the penetration depth at low

temperatures obtained from microwave measurements. According to ref. [69],

$$\frac{\delta\lambda_{ab}(T)}{T} = \lambda_{ab}(0)\frac{2k_B\ln 2}{S}$$
(6.4)

 $\delta\lambda$  is the quantity obtained from the microwave measurements and the absolute penetration depth can be expressed as  $\lambda_{ab}(0) = c/\omega_p$  with c the speed of light and  $\omega_p$  the Drude plasma frequency. Assuming  $\omega_p = 1.1$  eV gives  $\lambda(0) = 1800$  Å. The results of T. Jacobs *et al.* [23] and S-F. Lee *et al.* [68] are very consistent for the linear behavior of the penetration depth : they find a slope  $\delta\lambda/T$  of 10.2 Å and 10 Å respectively. Replacing by these values in equation (6.4) gives  $S \simeq 21$  meV.

Estimates of  $\kappa_0/T$  assuming  $\omega_p = 1.1-1.2$  eV and our different estimates of S are listed in table (6.4). While most of them are in good quantitative agreement with our experimental value of  $0.15 \text{ mW/cmK}^2$  (which has an experimental uncertainty of 25%), there is a factor of 4 discrepancy between that value and the ARPES result. This suggests that the form of the gap at the nodes could deviate from the standard *d*-wave relation  $\Delta_0 \cos(2\Phi)$  (S would be smaller than  $2\Delta_0$ ).

#### Phonon contribution.

Let us rewrite equation 2.20 in a form appropriate to measurements on single crystals at very low temperatures. The specific heat is given by  $c_v = \beta T^3$ . The phonon mean free path is determined by the size of the crystal and in high-quality crystals it can be taken as  $\Lambda_0 = \frac{2}{\sqrt{\pi}}\sqrt{wt}$ , which is the radius of a cylindrical crystal with the same section as the rectangular sample [70]. The sound velocity needs to be averaged over the longitudinal and transverse modes, and in single crystals [70], as seen in section 2.1.3,

$$\langle v_{ph} \rangle = v_l \frac{(2s^2 + 1)}{(2s^3 + 1)},$$
 (6.5)

where  $s = v_l/v_t$  and  $v_l$ ,  $v_t$  are respectively the longitudinal and transverse velocities. In summary,

$$\kappa_{ph} = \frac{1}{3} \beta \left\langle v_{ph} \right\rangle \Lambda_0 T^3 \tag{6.6}$$

First we want to calculate the average phonon velocity. According to [71], for the phonon wave vector  $\vec{q}//\vec{a}$ :

$$v_a^a = \sqrt{\frac{C_{11}}{\rho}}; v_a^b = \sqrt{\frac{C_{66}}{\rho}}; v_a^c = \sqrt{\frac{C_{55}}{\rho}}$$
 (6.7)

where  $v_q^{\epsilon}$  is the velocity in direction  $\vec{q}$  with polarization  $\epsilon$ , the  $C_{ii}$  being the elastic constants. The values of the elastic constants and the density  $\rho$  are listed in the review article by J. Dominec [65]. The longitudinal sound velocity is  $v_a^a$ . Taking only the faster of the two transverse modes (here  $v_a^b$ ), we find

$$v_l \simeq 4600 \,\mathrm{m/s} \; ; \; v_t \simeq 2800 \,\mathrm{m/s}$$
 (6.8)

and from equation (6.5)  $\langle v_{ph} \rangle \simeq 3000 \text{m/s}.$ 

A complete study of the specific heat has been done in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub> [72]. An estimate of the specific heat coefficient in BSCCO has been calculated from that in YBCO using the relation  $\beta \propto (T/\theta_D)^3$  via the ratio of Debye temperatures also listed in [65]. From  $\beta = 0.3-0.4$  mJ/molK<sup>4</sup> and  $\theta_D \simeq 400$  K in YBCO, with  $\theta_D \simeq 280$  K in Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>, one finds  $\beta = 0.9-1.2$ mJ/molK<sup>4</sup> =6.5-8.7 J/K<sup>4</sup>m.

For the sample BSCCO#2 measured at low temperatures,  $\Lambda_0 = 1.9 \ 10^{-4}$ m. Gathering those results in the equation for the phonon thermal conductivity gives  $b = \kappa_{ph}/T^3 = \frac{1}{3}\beta \langle v_{ph} \rangle \Lambda_0 = 12.5 - 16.5 \text{ mW/cmK}$ . Thus our theoretical estimate is twice the experimental value for b. The discrepancy probably lies mostly in the uncertainty on the Debye temperature (between 230K and 300K in the review article of Dominec) and the uncertainty on the dimensions of this sample.

After having discussed in the last two sections the contributions of phonons and normal electrons to the low temperature thermal conductivity, we are now able to evaluate their relative importance. Estimated and experimentally found contributions being reasonably consistent with each other, both approaches lead to the same qualitative conclusions. From our experimental results (see tables (6.4) and (6.5)) and eqn. (6.2), we find that  $\kappa_e$  is dominant at the lowest temperatures, below about 150 mK, where both contributions are equivalent. Above 140 mK the  $T^3$  dependence of  $\kappa_{ph}$  doesn't hold exactly but  $\kappa_{ph}$  still increases much faster than  $\kappa_e$ , and the thermal conductivity becomes rapidly dominated by phonons. All these phonons are responsible for the temperature dependence of  $\kappa/T$  seen in fig. (6.10), as shown by our  $a + bT^2$  fit and the accordance with the theory.

## 6.3.4 Summary

To summarize our low temperature results, we recall that the data could be fitted as  $\kappa/T = a + bT^2$  below  $T \approx 140$  mK. The electronic term *a* was found to be zero in PCCO, showing evidence for a gap without nodes and thus of *s*-wave symmetry. These data considerably reinforces the limited existing evidence for an *s*-wave gap in the electron-doped cuprates, as mentioned in section 4.2.

On the contrary we observed a non-zero linear term as  $T \rightarrow 0$  in the three holedoped compounds, signature of a residual normal fluid, and thus of nodes in the gap function. As in YBCO, the data for BSCCO was found to be in good agreement with the theory of universal transport in a superconductor with order parameter of  $d_{x^2-y^2}$ symmetry (which assumes strong, resonant scattering). Consistently with the existing information on Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>, this result suggests that the gap function possesses this symmetry, and thus that the residual linear term we obtained  $([\kappa/T]_{T\rightarrow 0} =$  $0.15 \text{ mWcm}^{-1}\text{K}^{-2})$  is universal. The phonon contribution  $\kappa_{ph}$  was found to be similar in BSCCO as in YBCO, and to dominate the low temperature heat conduction above  $T \approx 150 \text{ mK}$ .

Using data given in the article by Graf *et al.* [14], we also compared in table (6.4) our data for LSCO to the theory for  $d_{x^2-y^2}$  superconductors. Our zero temperature extrapolation of  $\kappa/T$  is a factor of 5 lower than the predictions of this theory, while the extrapolation from earlier measurements also cited in [14] are a factor of 10 higher than those predictions. As pointed by Graf *et al.* such discrepancies may be explained by deviations from the strong scattering limit.

### 6.3.5 Comment on the article of Movshovich et al..

The data obtained by R. Movshovich *et al.* are presented in fig. (6.11). The main body of the figure represents  $\kappa(T)/T$  in the range 70–500 mK for 3 samples of different



Figure 6.11: Thermal conductivity divided by temperature as a function of temperature for several Ni-doped Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> samples. ( $\diamond$ ) undoped,  $T_c = 89$  K; ( $\triangle$ )  $T_c = 74$  K; ( $\square$ )  $T_c = 77$  K,  $H \approx 200-300$  G. Inset : thermal conductivity of Bi<sub>2</sub>Sr<sub>2</sub>Ca(Cu<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub>O<sub>8</sub> sample with  $T_c = 77$  K. ( $\square$ )  $H \approx 0$  G; ( $\square$ )  $H \approx 200-300$  G.

Ni doping concentrations. The samples are labeled by their transition temperature (89K, 77K and 74K), the lowest values of  $T_c$  corresponding to the highest doping concentrations. The undoped sample presents no anomalous feature. The doping with Ni ions causes a dramatic drop of the thermal conductivity between  $T_c^* = 200 \text{ mK}$ and 160 mK. Intriguing result, the anomaly has disappeared in the  $T_c = 74$  K sample. Thus this transition is very sensitive to the level of doping. It is also very sensitive to magnetic field, as shown in the inset of fig. (6.11): a small magnetic field (200-300 Gauss) suppresses the effect. Quantitatively, this anomaly is characterized by a 80% drop of  $\kappa$  between 200 and 150 mK, indicating that it takes place within the main thermal transport channel of the system. In their article, Movshovich et al. evaluate that the heat is mainly carried by electrons in this temperature range and thus attribute the transition to a sudden suppression of quasiparticle heat transport. They interpret it as an evidence for the gapping of the nodes of the order parameter at the transition. Here we want to discuss three points mentioned in this article : the theoretical temperature dependence of  $\kappa$  at low temperature, the fact that the phonon term  $\kappa_{ph}$  could be neglected and the interpretation of the data as being an



Figure 6.12: Thermal conductivity divided by temperature in Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>. Comparison of our data (circles) with the data of R. Movshovich *et al.* [40] for their pure sample (diamonds). In both samples  $T_c = 89$  K. Left :  $\kappa/T$  vs T; right :  $\kappa/T$  vs  $T^2$ .

electronic feature.

Movshovich et al. describe their data below 300 mK as the sum of linear and quadratic terms. In a similar analysis as Krishana et al. in [33], they interpret the  $T^2$ term as following from the BRT theory (section 2.2.1) applied to a pure 2D d-wave superconductor in the limit  $T \ll \Delta$ . In the framework of this theory, the  $T^2$  dependence is obtained by replacing the density of state of a conventional superconductor by that of a pure *d*-wave superconductor, which is linear in energy (see fig. (3.3)). However as we have shown earlier in the chapter, in this temperature range (T < 300 mK), even for an undoped sample, one is in the regime where the density of states is approximately constant and the analysis of Movshovich et al. would be sound only at higher temperatures. Our analysis, described by equation (6.2), is remarkably well illustrated by our data in fig. (6.10). In figure (6.12), we have transferred the  $\kappa/T$ data of R. Movshovich et al. for their pure sample, and plotted it along with our data as a function of T (left) and  $T^2$  (right). As already seen in fig. (6.10), our data are linear below  $T \approx 140$  mK (or  $T^2 \approx 0.02$  K<sup>2</sup>) in the  $\kappa/T$  vs  $T^2$  plot. Consequently they show a (very) slight parabolic curvature in the  $\kappa/T$  vs T plot, which proves the absence of a quadratic term in  $\kappa$  in this temperature range. However Movshovich data are not consistent with this analysis, as seen in the right part of fig. (6.12) ( $\kappa/T$ 

vs  $T^2$ ), where it is obvious that no linear fit can be done. Actually they are not really consistent either with their analysis (a quadratic term in  $\kappa$ ) since in the  $\kappa/T$  versus T plot (look also at fig. (6.11)), deviations from the linear fit can be observed.

Secondly, using equation (6.6), the authors of [40] have made an upper limit estimate of the phonon contribution to the heat conduction. They conclude that  $\kappa_{ph}$ is only a small fraction of the total conductivity and comparing their estimate to a previous similar calculation in YBCO [28], that  $\kappa_{ph}$  is seven times smaller in BSCCO. Earlier in this section we have seen why the thermal conductivity should be written as  $\kappa = aT + bT^3$ , which implies that the temperature dependence of  $\kappa/T$  has to be attributed to phonons. Then, our data of fig. 6.10, where the temperature dependence of  $\kappa/T$  is very similar for YBCO and BSCCO, clearly show that the phonon contribution in BSCCO is of the same order as in YBCO. In ref. [28], the upper estimate for the phonon coefficient  $b = \kappa_{ph}/T^3$  is 17 mWK<sup>-4</sup>cm<sup>-1</sup>. Our value calculated for BSCCO, 13-16 mWK<sup>-4</sup> cm<sup>-1</sup>, very close to the YBCO value, completely disagrees with the assertion that the phonons contribute 7 times less in BSCCO than in YBCO in this range of temperatures. We estimated in section 6.3.3 that above T = 150 mK, the heat conduction is dominated by phonons : in the temperature range of Movshovich transition (between 160 mK and  $T_c^* \simeq 200$  mK) the phonon contribution is higher than the electronic one and obviously cannot be neglected.

The third point follows directly from the previous one. Movshovich *et al.* considering that the phonons cannot account for the observed 80% drop of the thermal conductivity since they estimate that the lattice only contributes to a small fraction of the conduction, attribute this feature to electrons. In the framework of our analysis, the anomaly seen in the plot of  $\kappa/T$  versus T in fig. (6.11) cannot be interpreted in this way. Indeed, we find that the electronic contribution to  $\kappa/T$  is nearly constant in the range of the experiments, all the temperature dependence, and therefore this anomaly, being attributed to phonons. However if the electronic thermal conductivity presents no anomalous feature, as implied by our analysis, there is no reason for the phonon conduction to drop at those temperature, and no more in a doped sample

than in a pure one. This leaves the interpretation of the data of Movshovich *et al.* an intriguing and unresolved problem.

Another point to mention is related to the extremely anisotropic character of BSCCO (in versus out-of-plane) and its structure in sheets, as noted in section 3.1. In order to have the heat passing through the whole bulk of the sample, it is important that the contact covers its entire end sections. In the experimental setup of Movshovich *et al.* the heat is introduced by separately turning on two heaters attached at different points along the sample (its end sections being attached to a thermometer and the heat sink). The heat coming from the surface of the sample, it is difficult to be sure that the temperature gradient is homogeneous along the c-axis of the crystal.

To finish we shall stress two weak points of the new phase observed by R. Movshovich *et al.*. First if the nodes of the order parameter were gapped at the transition, thereby suppressing the electronic heat conduction, there should be according to our results no finite linear term below the transition. Secondly, this anomaly is very weak, in the sense that it is extremely dependent on both doping and magnetic field, as mentioned at the beginning of this section.

In conclusion, because phonons dominate the heat conduction in this temperature range, the effect observed by R. Movshovich *et al.* can not be interpreted as an electronic feature, and is thus very puzzling. Their data for the pure sample, which show no anomaly, are consistent neither with the theory for *d*-wave superconductors nor with our data for pure BSCCO (actually one implies the other since our data are consistent with that theory).

# CONCLUSION

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In this study we have presented and compared the charge and heat conduction :

- in the Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> hole-doped cuprate, and we have compared it to YBCO, which has similar transport properties.
- in the  $Pr_{2-x}Ce_xCuO_4$  electron-doped cuprate, and compared it to LSCO, its parent compound from a structural point of view.

Despite the apparent symmetry of their phase diagram, we found that electron and hole-doped superconductors present very different transport properties, while the three hole-doped compounds show many common features. We obtained a linear temperature dependence of the resistivity in the hole-doped samples, and quadratic in PCCO, both in accordance with previous data.

As for the thermal conductivity in the range 1.5-150 K, hole and electron-doped cuprates seem to display the same general features. We found that heat is carried mainly by phonons in the normal state, where the electronic contribution is restricted by some strong electron-electron scattering mechanism. Below the transition the disappearance of this mechanism causes a broad peak, the magnitude of which is mainly related to the sample quality. We made the first observation of a peak below  $T_c$  in PCCO, and the  $T^2$  behavior of the resistivity suggests to interpret it by a suppression of electron-electron scattering, as in the hole-doped compounds.

Our low temperature data could be fitted as  $\kappa/T = a + bT^2$  below  $T \approx 140$  mK. The electronic term *a* was found to be zero in PCCO, showing evidence for a gap without nodes and thus of *s*-wave symmetry. These data considerably reinforces the limited

existing evidence for an s-wave gap in the electron-doped cuprates. On the contrary we observed a non-zero linear term as  $T \rightarrow 0$  in the three hole-doped compounds, signature of a residual normal fluid, and thus of nodes in the gap function. As in YBCO, the data for BSCCO was found to be in good agreement with the theory of universal transport in a superconductor with order parameter of  $d_{x^2-y^2}$  symmetry, consistent with the existing information on Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>. The phonon contribution was found to dominate the low temperature heat conduction above about 150 mK.

Having set those results, we showed that the anomaly in the low temperature thermal conductivity in Ni-doped samples of BSCCO could not possibly be an electronic feature, leaving its interpretation unresolved.

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