this implies a total coupling equal to $\lambda_{tot} = 2.24$[1]. All the free parameter are now fixed and the critical temperature can be reproduced very well if a feed-back effect [144, 145] of the condensate is considered.

Now the bosonic structure can be analyzed. From the sign-changed first derivative (the upper curve in Figure 5.10(a)) of the experimental data, by subtracting the greater gap from the peak position (i.e the first peak at energy higher than Δ_{e2}), we obtain the representative bosonic energy $\Omega_0 \sim 11 - 13$ meV. This is a first signal that the structure considered can be a resonance of the strong electron-boson interaction. Then one can follow this structure in temperature (see Figure 5.10(b)), this result again supports the idea of an unconventional mechanism, indeed it goes to zero at the critical temperature and obviously this rules out phonons as mediating bosons.

Finally, within a BTK model including the energy-dependent order parameter obtained from the Eliashberg model, the original Andreev-reflection spectrum can be reproduced (all the parameters are summarized in Table 5.4). As can be appreciated by looking at the orange curve in Figure 5.9, the fit in the central part of the spectrum has been improved and now the bosonic resonance appears at the right energy. The disagreement in the amplitude of the EBI shoulders in the theoretical curve and in the experimental spectrum is not so worrying since, as explained elsewhere [146], the normalization of the experimental spectra in the case of films is somehow arbitrary. A different choice for the normalization curve could well give rise to higher shoulders that could, in turn, be better reproduced by the theoretical curve. The horizontal position (i.e. the energy) of the shoulders instead is not affected by the normalization and is therefore a true "robust" quantity.

In conclusion we proved that the structure that appears in the PCARS curve at energies higher than the gaps has a bosonic origin. Moreover we used, to reproduce the experimental data, a spectral function with a energy peak value that is in agreement with the experimental representative energy of antiferromagnetic spin fluctuations [9] and this fact strongly supports this mechanism to be responsible of superconductivity in this material.

5.5   The normal state: thin films vs single crystals

Nowadays very high-quality thin films are available and this allows using them for fundamental studies as well as for more technological applications [147–151]. In particular, Co-doped BaFe$_2$As$_2$ films of high quality can be readily fabricated

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[1]These are the only free parameters, the remaining coupling constants are fixed by the relation $\lambda_{ji} = \nu_{ij}\lambda_{ij}$, with $\nu_{ij} = N_i/N_j$ where N_i is the DOS at the Fermi level of the i-band. In this case from fist principle calculation we have $\nu_{12} = 1.856$ and $\nu_{13} = 7.386$.

	BTK-BCS	Eliashberg
Δ_h	7.6 meV	7.4 meV
Δ_{e1}	4.0 meV	3.6 meV
Δ_{e2}	-	10.1 meV
T_c	25.4 K	25.3 K
$\lambda_{h,e1}$	-	0.50
$\lambda_{h,e2}$	-	1.65
λ_{tot}	-	2.24
Ω_0	-	11 meV
W_h	0.55	0.50
W_{e1}	-	0.45
Γ_h	3.60	2.20
Γ_{e1}	2.02	2.15
Γ_{e2}	-	2.30
z_h	0.36	0.06
z_{e1}	0.17	0.26
z_{e2}	-	0.06

Table 5.4: Parameters used for creating the theoretical curves reported in Figure 5.9. In the left table there are the value of the three gaps together with the critical temperature, the coupling constants and the representative bosonic energy. On the right there are the parameter related to the BTK model: W_i are the weight of the bands, obviously $W_n = 1 - \sum_{i=1}^{n-1} W_i$, Γ_i are lifetime broadening parameters and z_i are the parameters that characterizes the potential barrier.

by pulsed laser deposition (PLD) and are thus one of the most suitable materials for these purposes. The investigation of the effects of the substrate in thin films is thus a hot topic and a particular attention has been paid to the strain-dependent critical temperature [152, 153]. Here we present the study of the resistivity measured on $Ba(Fe_{1-x}Co_x)_2As_2$ thin films grown on CaF_2 substrates and with different nominal cobalt content (namely 8%, 10% and 15%) in comparison with analogous measurements on single crystals taken from literature [154].

In an analogous way to LiFeAs we propose here a model that contains two different kinds of carriers (holes and electrons) as suggested by the presence of several sheets in the Fermi surface and by the tendency of the $\rho(T)$ curves to saturate at high temperature, as already observed in other iron-based compounds [110, 118, 155]. On the basis of experimental evidences, we assume that the temperature dependence of the resistivity is dominated by the coupling between electrons and spin fluctuations. This simple model allows us to fit very well the resistivity of single crystals by adjusting the free parameters (in particular the characteristic boson frequency Ω_0) in agreement with the results obtained by inelastic neutron scattering and optical measurements [104, 156]. In the case of thin films, the $\rho(T)$ curves can be fitted with a set of parameters that agrees

%Co	T_c^{10} (K)	T_c^{90} (K)	ΔT_c (K)
0.08 (TF)	24.2	25.6	1.4
0.10 (TF)	24.6	26.6	2.0
0.15 (TF)	23.3	24.8	1.5
0.10 (SC)	21.4	22.8	1.4

Table 5.5: Critical temperatures of thin films (TF) [146] and single crystals (SC) [154] determined from electric transport measurements. T_c^{10} and T_c^{90} are the temperatures at which the resistance (the resistivity) is respectively 10% and 90% of the normal-state value immediately before the transition. ΔT_c is defined here as $T_c^{90} - T_c^{10}$.

with the experimental data available in literature only if the SF spectrum is depleted at low energy, resulting in a transfer of spectral weight to higher energies. Thanks to the interaction between phonons and spin fluctuations, this effect can be ascribed to the phonon hardening induced by the reduction of the unit-cell volume [157] caused by the presence of the CaF$_2$ substrate [158].

5.5.1 Experimental details

The Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ ($x = 0.08, 0.10, 0.15$) epitaxial thin films with a thickness of the order of 50 nm were deposited on (001)CaF$_2$ substrates by pulsed laser deposition (PLD) [158] using a polycrystalline target with high phase purity [158, 159]. The surface smoothness was confirmed by in-situ reflection high energy electron diffraction (RHEED) during the deposition; only streaky pattern were observed for all films, indicative of a smooth surface. The details of the structural characterization and of the microstructure of these high-quality epitaxial thin films can be found in Ref. [158]. Standard four-probe resistance measurements in van der Pauw configuration were performed in a ^{4}He cryostat to determine the $\rho(T)$ curve as well as the transport critical temperature and the width of the superconducting transition [146] (both reported in Table 5.5).

5.5.2 Reduction of a multiband model to a two-band model

Since the Fermi surface of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ presents several sheets, at least in principle a multi-band model should be necessary to explain superconducting and normal-state properties. However one can wonder what is the minimum number of bands to be considered. In the superconducting state, most of the experiments show only two gaps, but in Eliashberg theory a two-band model is not enough to explain the experimental data and the hypothesis of more than two gaps is necessary (the observation of only two distinct gaps can thus be explained by experimental resolution limits and by the similar amplitudes of some of these

gaps). Three- and four-band Eliashberg models have been proposed to describe
the superconducting phenomenology. On the other hand, in the normal state the
situation appears to be simpler. In order to investigate the electrical resistivity,
we group the hole and the electron bands, and we propose a model containing
only two different kinds of carriers, as explained in Section 4.4.1. Incidentally,
the confirmation that this is the *minimum* model comes from the fact that a
single-band model[2] is unable to fit the experimental $\rho(T)$ curve, as shown in
Figure 5.11. Considering that the electron-phonon coupling in all the compounds
that belong to the class of iron-based superconductors is weak [85], it is logical
to consider (as already done for LiFeAs) that another mechanism contributes to
the transport properties; taking into account the superconducting properties of
the iron pnictides, the antiferromagnetic spin fluctuations are the best candidate
to play the role of the principal actor also in the normal state.

As explained in the previous chapter, the electron-SF transport spectral functions
$\alpha_{tr}^2(\Omega)F_{tr}(\Omega)$ are similar to the standard Eliashberg $\alpha^2(\Omega)F(\Omega)$ [112], but for
$\Omega \to 0$ they behave like Ω^3 and not like Ω.

Therefore, the condition

$$\alpha_{tr}^2(\Omega)F_{tr}(\Omega) \propto \Omega^3 \tag{5.11}$$

should be imposed in the range

$$0 < \Omega < \Omega_D, \text{ with } \Omega_D = \Omega_0/10 \tag{5.12}$$

the relation between Ω_D and Ω_0 is based on phenomenological assumptions [112]
and Ω_0 is the representative bosonic energy.Then

$$
\begin{aligned}
\alpha_{tr}^2(\Omega)F'_{tr}(\Omega) &= A\,\Omega^3\Theta(\Omega_D - \Omega) \\
&+ B\left[\frac{\Omega_0\Omega}{\Omega^2 + \Omega_0^2}\,\Theta(\Omega_c - \Omega)\right]\Theta(\Omega - \Omega_D)
\end{aligned}
\tag{5.13}
$$

where Θ is the Heaviside function and the constants A and B have been fixed by
requiring the continuity in Ω_D and the normalization.The factor in the squares
brackets has the functional form of the theoretical AFM spin fluctuations spectral
function in the normal state [100], peaked at Ω_0 that reproduces the experimental
normal-state dynamical spin susceptibility [104], here Ω_c is a cut-off energy (in
these calculations $\Omega_c = 1$ eV).

As mentioned above, in these compounds the electronic structure consists of
electron and hole pockets (hereafter indicated respectively by the indices 1 and
2). Then, in order to keep the number of free parameters as low as possible
and taking into account that just one carrier is not enough, we consider a model

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[2]Owing to the symmetry of the superconducting state, in the single-band model the coupling
should be mediated by phonons, whose spectral function is reported in the inset of Figure 5.11.
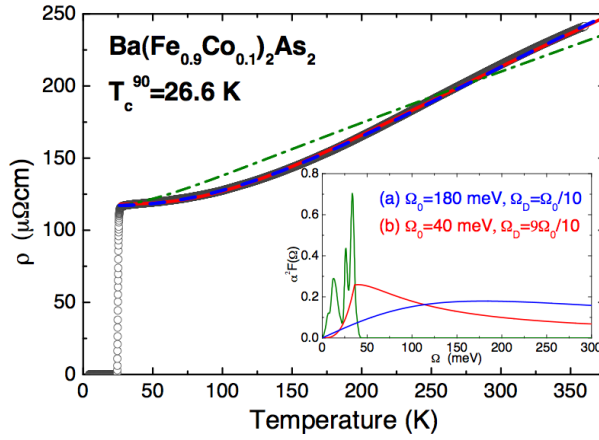
Figure 5.11: Temperature dependence of the resistivity of the thin film with $x=0.10$. The dash-dotted green line is the curve obtained within a model containing only one kind of carriers and a phonon mediated coupling. The dashed blue curve represents the fit obtained with $\Omega_0 = 180$ meV and $\Omega_D = 0.1\Omega_0$; the solid red line is the fit obtained with $\Omega_0 = 40$ meV and $\Omega_D = 0.9\Omega_0$. The relevant normalized electron-boson spectral functions are shown in the inset with the corresponding color.

containing two different kinds of carriers. Within this model the electron-boson coupling constants $\lambda_{tr,1}$ and $\lambda_{tr,2}$, the impurities scattering rates γ_1 and γ_2, the plasma energies $\omega_{p,1}$ and $\omega_{p,2}$ and the representative bosonic energy Ω_0 of the transport electron-boson spectral functions are the free parameters. Specific properties of each compound and experimental data allow to establish some of them. For instance, Ω_0 can be provided by inelastic neutron scattering experiments, while the values of $\omega_{p,1}$ and $\omega_{p,2}$ can be obtained, at least in the case of ideal single crystal by first principle calculations. Moreover, ARPES and de Haas-van Alphen data suggest that for Co-doped Ba-122 the transport is dominated by the electronic bands and that the hole bands are characterized by a smaller mobility [154, 156]. This means that within our model:

(i) the transport coupling is much stronger in the electron band, so that, at least as a first approximation, $\lambda_{tr,2}$ can be fixed to be zero and

(ii) the effects of the impurities are mostly concentrated in the hole band, i.e. $\gamma_2 \gg \gamma_1$. In this way one contribution to the resistivity (the hole one) results to be temperature independent, as can be noticed by looking at equation (4.19), and the other is responsible for the slope of the resistivity with the temperature. Moreover the values of γ_2 and γ_1 are related to the value of the residual resistivity ρ_0 through the plasma frequencies, therefore the number of the degrees of freedom is decreased by one. In the best case, this simplified model contains only two free parameters ($\lambda_{tr,1}$ and, for example, γ_2), however for $Ba(Fe_{1-x}Co_x)_2As_2$ thin films there are not enough experimental data to fix Ω_0 in the normal state,
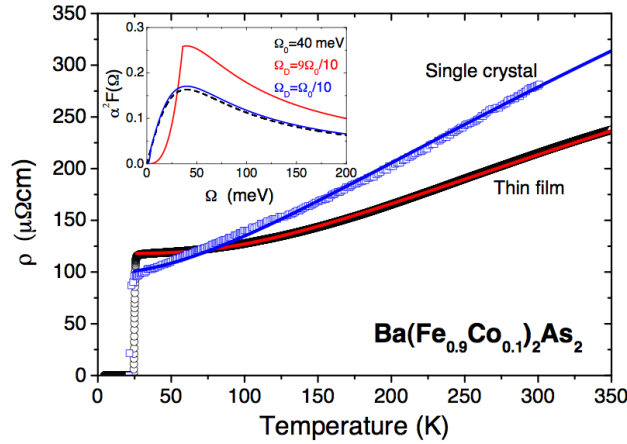
Figure 5.12: Comparison between the resistivity of Ba(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ thin film (black circles and solid red line) and single crystal (blue squares, taken from [154], and solid blue line). The fit (line) has been obtained in both cases with $\Omega_0 = 40$ meV. The inset shows the two spectral functions that have been used to fit the experimental data with the corresponding colors and the antiferromagnetic spin fluctuations spectral function in the normal state (dashed black line) without the change of behavior at low energy.

it is expected to change with the cobalt content. On the other hand, the combination of various factors such as the doping homogeneity and the strain do to the substrate make the ab-initio calculation of $\omega_{p,1}$ and $\omega_{p,2}$ somehow unreliable and arbitrary. Therefore we decided to keep $\omega_{p,1}$ and $\omega_{p,2}$ as adjustable parameters, but we assume they non to deviate too much from the values determined in the optimal-doping case in the same films [156]. and then $\omega_{p,1} \sim 1.1$ eV and $\omega_{p,2} \sim 0.7$ eV. This approximation is plausible considering that, in the films considered, the variation of T_c with respect to the optimal value is less than 2 K, and the variation of the cobalt content is at most 0.05. Then, since we are far from the phase transitions (for example metal-insulator transitions), we think that there should not be any radical change in the fundamental electronic properties of the material.

In a similar way, also Ω_0 is allowed to change, however it has to assume reasonable value, i.e. compatibly with experimental measurements of inelastic neutron scattering (i.e. Ω_0=40 meV).

These constrains, combined with the condition on γ_i and the particular shape of the experimental resistivity curves as functions of temperature strongly limit the range of values for the parameters that allow a good fit of the $\rho(T)$ curve. Then only small variations around each parameter are allowed and these are not significant for the discussion here presented, in fact even considering the larger variation possible no difference can be obtained in the conclusions that are going to be shown.

5.5.3 "Hardening" of the electron-boson spectral function

The first step was to apply this model to the resistivity of the $Ba(Fe_{1-x}Co_x)_2As_2$ thin film with 10% of cobalt (see Figure 5.11). If the spectral functions are kept with the form of the equation (5.13), with $\Omega_D = \Omega_0/10$ and the peak is fixed to assume a value $\Omega_0 \sim 40$ meV, there is no way to adjust the other input parameters to reproduce the experimental curve. This is true even if very different plasma frequencies with respect those mentioned above are considered.

In contrast, with these input parameters we can reproduce very well the $\rho(T)$ curve of the single crystals with the same doping, as can be appreciated by looking the Figure 5.12. Clearly, the thin-film configuration is more complex and this is surely also reflected in the shape of the resistivity curve.

To reproduce the low-temperature behavior of the $\rho(T)$ curve in thin films, we were forced to allow some more changes and in particular to act on the shape of the electron-boson spectral function.

If the functional form is kept as defined in the equation (5.13), still considering valid that $\Omega_D = \Omega_0/10$, then the representative bosonic energy increases drastically, up to $\Omega_0 = 180$ meV for the best fit, as depicted by the red solid line in Figure 5.11. Such a high energy-value of the the mediating boson looks unreasonable [104] The only other possibility is to keep Ω_0 to the same value used in single crystals and to change the range where the spectral function follows a Ω^3 trend, i.e. to act on Ω_D and increase is well above the usual value of $\Omega_0/10$. Within this assumption a very good fit of the $\rho(T)$ curve for the film with 10% of cobalt content can be obtained. The resultsare reported in Figure 5.11 and in Figure 5.12 and all the parameters used for this fit are reported in Table 5.6 It is important to underline that we have also tried to fit the same $\rho(T)$ curve with very different values of the plasma frequencies and reasonable physical values for the other parameters, but even in these cases it was impossible to reproduce the low-temperature behavior of the resistivity curve. An analogous procedure has been applied also to thin films with different cobalt content, $Ba(Fe_{0.92}Co_{0.08})_2As_2$ and to $Ba(Fe_{0.75}Co_{0.15})_2As_2$ as shown in Figure 5.13 and Figure 5.14. Also in these cases the resistivity was initially reproduced with an unphysical high bosonic energy and then, following the same reasoning, the shape of the spectral function was changed and a good fit was obtained with the values reported in Table 5.7. This leads to similar conclusions and supports the idea that in the case of thin films the spectral function should have a Ω^3 behavior in a wider range than in single crystals. In other words, there is a "hardening" of the electron-boson spectral function, with a transfer of spectral weight from energies smaller than Ω_0 to energies higher than Ω_0. Probably this effect is so striking because the main mechanism is not phononic. In fact the strain produced by the substrate on the film can create changes in the electronic structure and in the Fermi surface nesting that is crucial for raising superconductivity mediated by

Ba(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$

		Thin film		Single Crystal
	1-band model	2-band model (a)	2-band model (b)	2-band model
Ω_0 (meV)	-	180 ± 3	40 ± 3	40 ± 3
$\lambda_{tr,1}$	0.20	0.65 ± 0.02	0.33 ± 0.01	0.35 ± 0.02
$\lambda_{tr,tot}$	0.20	0.26	0.13	0.14
γ_1 (meV)	37	21	24	16
γ_2 (meV)	-	69 ± 2	100 ± 6	80 ± 8
$\omega_{p,1}$ (meV)	1550	1060 ± 20	1180 ± 8	1110
$\omega_{p,2}$ (meV)	-	102 ± 20	1020 ± 30	700

Table 5.6: Values of the parameters used for the fit of the resistivity of the Ba(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ thin film reported in Figure 5.11 and for the fit of the resistivity of the single crystal reported in Figure 5.12. In all the cases $\lambda_{tr,2} = 0$, so that $\lambda_{tr,tot} = (N_1 \lambda_{tr,1})/(N_1 + N_2)$. γ_1, γ_2, $\omega_{p,1}$, $\omega_{p,2}$ are not independent parameters because they are related to ρ_0.
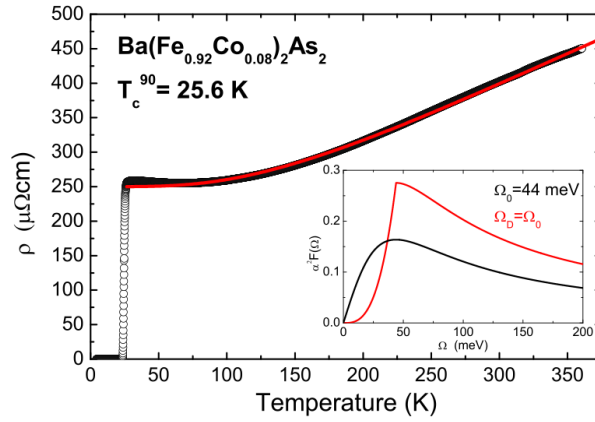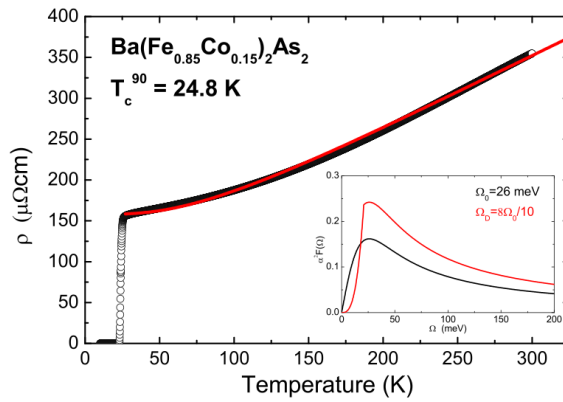
Figure 5.13: Temperature dependence of the resistivity of the $Ba(Fe_{1-x}Co_x)_2As_2$ thin film with $x = 0.08$. The solid red curve represents the fit obtained with $\Omega_0 = 44$ meV. In the inset two different electron-boson spectral functions are reported: the red curve is that used to fit the experimental data, the black one is the antiferromagnetic spin fluctuations spectral function in the normal state without changing the low-energy behavior.

$Ba(Fe_{1-x}Co_x)_2As_2$ thin films

	$x=0.08$	$x=0.1$	$x=0.15$
Ω_0 (meV)	44 ± 1	40	26
Ω_D (meV)	$(0.98 \pm 0.02)\,\Omega_0$	$(0.9 \pm 0.02)\,\Omega_0$	$(0.8 \pm 0.02)\,\Omega_0$
$\lambda_{tr,1}$	0.32 ± 0.01	0.33 ± 0.01	0.34 ± 0.01
$\lambda_{tr,tot}$	0.13	0.13	0.14
γ_1 (meV)	32	24	26
γ_2 (meV)	190 ± 10	100 ± 10	600 ± 30
$\omega_{p,1}$ (meV)	970 ± 12	1180 ± 8	1140 ± 5
$\omega_{p,2}$ (meV)	$780 \ \pm 30$	1020 ± 30	1140 ± 30

Table 5.7: Values of the parameters used for the fit of the $\rho(T)$ curves of $Ba(Fe_{1-x}Co_x)_2As_2$ thin films with three different Co contents ($x = 0.08, 0.10, 0.15$). In all the cases $\lambda_{tr,2} = 0$.

spin fluctuations [160]. The effect of the substrate can be assimilated to that of a uniaxial pressure and in particular [153] the substrate used here (CaF_2) has the largest effect on the volume cell of the Co doped Ba-122 because of the mismatch of the dimension of the unit cells. From a qualitative point of view we know that even if for the "122" family the phonon coupling is small and basically negligible at zero pressure, a reduction of the unit cell volume causes an increase of phonon frequencies especially for the superconducting compounds [157]. Concerning the parent compound, it has been argued that under pressure the interaction between the lattice structure and the magnetism is no longer negligible even in the normal state [161], i.e the spin-phonon coupling may play an important role. The central point is that the A_{1g} vibration of the arsenic ions slightly distort

Figure 5.14: Temperature dependence of the resistivity of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ thin film with x=0.15. The solid red curve represents the fit obtained with $\Omega_0 = 26$ meV. In the inset two different electron-boson spectral functions are shown: the red curve is the one used to fit the experimental data, the black one is the antiferromagnetic spin fluctuations spectral function in the normal state without changing the low-energy behavior.

the AsFe$_4$ tetrahedron and this has effects even in the normal state. This could cause a "hardening" of the transport spectral function.

5.5.4   Comparison with cuprates

Incidentally, it is interesting to note, as shown in Table 5.8 and in Figure 5.15, that the representative energy of the electron-boson spectral function in the normal state decreases with increasing the cobalt content in the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ thin films. The same table also highlights that in this compound (no matter if in the form of crystal of thin film) as well as in LiFeAs [162] and in other iron-based superconductors [118] the normal and superconducting states are characterized by very different values of the typical energy of the electron-boson spectral function and of the total electron-boson coupling constant. In particular, the typical energy of the electron-boson spectral function systematically increases going from the superconducting to the normal state (in agreement with inelastic neutron scattering experimental data [104]) while the total electron-boson coupling constant significantly decreases. The very different properties of the mediating boson in the normal and superconductive state can be a unifying principle at the root of superconductivity in the iron-based materials. Moreover the same property has been observed in HTCS [66], this may suggest that iron-based compounds share some characteristics with cuprates.

Compound	T_c	Ω_0	Ω_0^{sup}	$\lambda_{tr,tot}$	$\lambda_{sup,tot}$
LiFeAs	18.0	47	8	0.77	2.00
$Ba_{0.68}K_{0.32}Fe_2As_2$	38.5	40	18	0.87	1.89
$Ba(Fe_{0.9}Co_{0.1})_2As_2$	22.8	40	9	0.14	2.83
TF-$Ba(Fe_{0.92}Co_{0.08})_2As_2$	25.5	44	10	0.13	2.22
TF-$Ba(Fe_{0.9}Co_{0.1})_2As_2$	26.6	40	11	0.13	2.22
TF-$Ba(Fe_{0.75}Co_{0.15})_2As_2$	24.8	26	9	0.14	1.82

Table 5.8: Summary of characteristic parameters obtained in this work for $Ba(Fe_{1-x}Co_x)_2As_2$ thin films (TF) and single crystals [154], in a similar work done on LiFeAs [162] and taken from literature for the case of $Ba_{0.68}K_{0.32}Fe_2As_2$ [118]. The values of T_c, of the characteristic spin-fluctuation energy (in the normal and in the superconducting state, Ω_0 and Ω_0^{sup}), and of the total coupling constant (in the normal and in the superconducting state, $\lambda_{tr,tot}$ and $\lambda_{sup,tot}$) are shown. The critical temperatures are expressed in kelvin and the energies in meV.
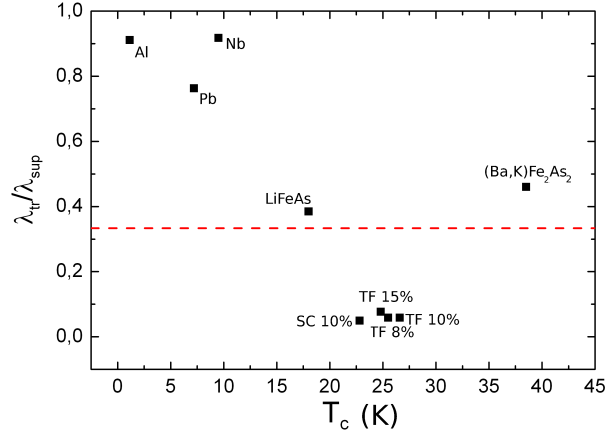
Figure 5.15: Summary of values of the ratio $\lambda_{\text{tr}}/\lambda_{\text{sup}}$ for some iron compounds and some "conventional" supeconductors. The labels SC 10%, TF 8%, TF 10% and TF 15% mean single crystal and thin films of $Ba(Fe_{1-x}Co_x)_2As_2$ at the doping indicated. The red dashed line marks the order of magnitude that this ratio assumes in cuprates[66].

5.6 Conclusions

In the first part of this chapter results of PCAR experiments in $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals and films with $x = 0.08$ and in $Ca(Fe_{1-x}Co_x)_2As_2$ single crystals with $x = 0.06$ have been presented. The PCAR spectra have been analyzed within 3D version of the BTK model that accounts for the shape of the FS including an analytical model for the real FS obtained from ab intio calculations within DFT. The results indicate that the two systems, although belonging to the same 122 family of Fe-based compounds, show major differences in the shape

of the spectra, and this is a symptom of a difference in the symmetry of the order parameters. In Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$, a zero-bias peak or maximum is always observed and can be explained considering a strong anisotropy of the smaller gap. DFT calculations show that the hole-like FS sheet undergoes a topological transition at 6% Co content and splits into separated closed pockets. This can be interpreted as an extreme consequence of the increasing-with-doping warping of this FS sheet, which is predicted to be accompanied by the emergence of 3D nodes in the relevant gap. Indeed, a fit of the spectra is possible by assuming either a d-wave [133] or an anisotropic symmetry of the small gap, to mimic the possible evolution of these 3D nodes when the topological transition occurs. In the case of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ at $x = 0.08$, the calculated FS shows markedly warped hole-like sheets but no topological transitions. The spectra taken in single crystals with the current injected along the *ab*-plane can be fitted with two isotropic gaps; the agreement between model and data is limited to the central region of the spectra because of additional structures around 20 meV that are due to the strong electron-boson coupling [126, 140] and cannot be reproduced within this approach. Instead, the fit of the *c*-axis spectra measured in thin films with the same model is unsuccessful around zero bias, where the so-called Z-enhancing effect due to the shape of the FS produces a strong depression of the conductance which is not observed experimentally. This might be the sign of the presence of gap minima [28] whose existence has been inferred from Raman spectroscopy results [132].

In the second part of the discussion about Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ the resonances in the PCAR spectra are analyzed. First of all, following their behavior in temperature, it has been proven that they are bosonic resonances due to the strong electron-boson interactions. Then the shape of the spectra, with the bosonic resonances, has been reproduced within a 2D-BTK model that includes three different gaps with their complete energy dependence evaluated by solving the Eliashberg equations. In the Eliashberg model we considered a spectral functions that mimics the energy spectra of the spin fluctuations where Ω_0 has been extracted from the value of the critical temperature following the phenomenological relation $\Omega_0 = 4.65 k_B T_c$. The value obtained is 11 meV, in agreement with the experimental representative energy of antiferromagnetic spin fluctuations. All this discussion strongly support spin fluctuations to be responsible of superconductivity in this material.

Then, also the normal state properties Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ have been investigated, both in thin films and in single crystals at different value of cobalt doping. It is already known that, in thin films of iron-based compounds, the transport critical temperature is affected by the strain due to the substrate [153]. Here we have shown that this effect may also explain the different shape of the $\rho(T)$ curve in crystals and thin films of Co-doped Ba-122, even when the Co content

is the same. By using a simple effective two-band model for the transport, we have shown that the $\rho(T)$ curves of thin films can be fitted with the same characteristic boson energy Ω_0 used for single crystals only if some spectral weight is transferred from below Ω_0 to above Ω_0 in the transport electron-boson spectral function $\alpha_{tr}^2 F_{tr}(\Omega)$. In other words, $\alpha_{tr}^2 F_{tr}(\Omega)$ behaves like Ω^3 in a wider energy range than in single crystals. This effect is possibly induced by the indirect coupling between spin fluctuations and phonons [161], whose frequencies are increased by the compressive strain [157].

And finally, it was shown that the decrease (increase) in the electron-boson coupling constant (characteristic boson energy) between the superconducting and the normal state ($\lambda_{sup,tot} \gg \lambda_{tr,tot}$, $\Omega_0^{sup} \ll \Omega_0$) observed in crystals of various Fe-based compounds also holds in thin films of Co-doped Ba-122. This behavior is also common to HTSC [66] and may thus be a unifying principle at the root of superconductivity in iron-based materials and cuprates.

Chapter 6

Conclusions

In the present dissertation some members of the family of iron compounds have been invistigated. In particular the properties of LiFeAs and cobalt doped Ba-122, the representative compounds of the '111' and '122' classes, have been discussed both from the superconducting and the normal state point of view.

LiFeAs is a very peculiar compound, it is superconducting in its stoichiometric composition and there is no need of doping or pressure to induce the superconductivity. It seems to be non-magnetic and the presence of nesting is seriously questioned, opening in this way new doubts about the relation between the presence of nesting between different region of the Fermi surface and the antiferromagnetic spin fluctuations.

The electronic structure of this compound has been analyzed by ab initio calculations with Quantum Espresso and the results have been compared with that obtained by means of the Elk code. The Fermi surface presents five different sheets: three holonic bands centered in the Γ point and two electronic bands at the corner of the Brillouin zone. However the smaller holonic pocket has a very low density of the states and many ARPES measurements observe only two band in the center of the Brillouin zone. For these reason we decided to disregard this band and to propose a four band Eliashberg model in order to describe the superconducting properties of this compound and first of all the four different gap values reported by ARPES measurements at 8 K [96] and the critical temperature. Though, keeping in mind approximations supposed to be valid for iron compounds (i.e. considering the phonon coupling very small and that the spin fluctuation provide only interband coupling) it is not possible to reproduce the experimental gap values an in particular the very hight value of the larger one. Hence we were forced to introduce an intraband coupling that acts only on the first band. This could seem to be a phononic term and, if it were so, this would suggest an intrinsic incompatibility between this structure of the superconducting gaps and a purely spin-fluctuation mediated pairing.

A possible explanation may be linked to the very low Fermi energy of the band to which this gap is associated. A small value of the Fermi energy may cause the breakdown of the Migdal's theorem and then make inadequate the Eliashberg theory that in its common formulation disregards the vertex corrections, the effect of forcing the theory in a range of non validity would lead to fictitious increase of the intensity of the phononic pairing.

An analogous effect appears if we try to fit the experimental data of the upper critical field [109]. In this case we suppose that the effect of the breakdown of the Migdal's theorem can be reabsorbed in a fictitious enhancement of the value of the fermi velocity. Allowing $v_{F1}^{\|ab,c}$ as a free parameter implicitly implies that we are "phenomenologically" going beyond the first order contributions.
Then, as concern the superconducting state, the breakdown of the Migdal's theorem leads to use effective values of λ_{11} and v_{F1} different from real value because the framework of the theory is partially inadequate. And then our calculations show that LiFeAs presents peculiar features with respect to other iron compounds and it cannot be explained within the usual Eliashberg theory and a framework of a pure interband spin-fluctuation mediated superconductivity.

Moving on to the normal state, we analyzed the temperature dependence of resistivity measured in hight quality single-crystal [110] and we considered a model with two kind of carriers, grouping together holes and electrons. This approach reproduces accurately the experimental data, significantly better than previous attempts with a total coupling ($\lambda_{tr,tot} = 0.77$) consistent with expectations and sensibly smaller than the value of the of the superconducting coupling constants. Moreover the impurity scattering parameters seem to account properly for the high quality of the sample. We are aware that, in spite of the good fitting, this is still a rough simplification as compared to the more plausible situation where the two mechanisms coexist. However, it is clear from our analysis that the antiferromagnetic spin fluctuations must constitute the main contribution.
In conclusion, antiferromagnetic spin fluctuations play an important role not only in the superconducting state but also in the normal state, and by fitting the experimental resistivity relevant information on the energy peak of the spectral function and the total transport coupling constant have been extracted.

Then I discussed the properties of $Ba(Fe_{1-x}Co_x)_2As_2$ and $Ca(Fe_{1-x}Co_x)_2As_2$. As a starting point results of PCAR experiments both on thin films and in single crystal with $x = 0.08$ have been presented and analyzed within 3D version of the BTK model that accounts for the shape of the FS including an analytical model for the real FS obtained from ab intio calculations within DFT. Although the

two compounds belong to the same class of Fe-based compounds several differences appear in the shape of the spectra.

PCAR spectra measured in the samples of $CaFe_2As_2$ with 6% of cobalt content always show a zero-bias peak, manifestation of a strong anisotropy of the smaller gap. DFT calculations show that the hole-like FS sheet undergoes a topological transition at 6% Co content and splits into separated closed pockets, extreme consequence of the increasing-with-doping warping of this FS sheet, which is predicted to be accompanied by the emergence of 3D nodes in the relevant gap. Indeed, a fit of the spectra is possible by assuming either a d-wave [133] or (most likely) an anisotropic symmetry of the small gap, to mimic the possible evolution of these 3D nodes when the topological transition occurs.

In the case of $Ba(Fe_{1-x}Co_x)_2As_2$ at $x = 0.08$, the calculated FS shows markedly warped hole-like sheets but no topological transitions. The spectra taken in single crystals with the current injected along the *ab*-plane suggest the presence of two isotropic gaps. Instead, the fit of the *c*-axis spectra measured in thin films with the same model is unsuccessful around zero bias, where the so-called Z-enhancing effect due to the shape of the FS produces a strong depression of the conductance which is not observed experimentally.

In the second part of the discussion about $Ba(Fe_{1-x}Co_x)_2As_2$ the resonances in the PCAR spectra on thin film are analyzed. First of all, following their behavior in temperature, it has been proven that they are bosonic resonances due to the strong electron-boson interactions. Then the shape of the spectra, including the bosonic resonances, has been reproduced within a 2D-BTK model that includes three different gaps with their complete energy dependence evaluated by solving the Eliashberg equations and the spin fluctuation coupling is described by a lorentzian spectral function peaked at $\Omega_0 = 4.65 k_B T_c$.

As regards the normal state, the $\rho(T)$ curves of $Ba(Fe_{1-x}Co_x)_2As_2$ have been investigated, both in thin films and in single crystals at different value of cobalt doping, highlight more differences between the two systems due to the effects of the substrate, in fact it has been already proved that this can have huge influence on the critical temperature up to induce superconductivity in the parent compound. Here we have shown that this effect may also explain the different shape of the $\rho(T)$ curve in crystals and thin films of Co-doped Ba-122, even when the Co content is the same.

By using a simple effective two-band model for the transport, we have shown that the $\rho(T)$ curves of thin films can be fitted with the same characteristic boson energy Ω_0 used for single crystals only if some spectral weight is transferred from below Ω_0 to above Ω_0 in the transport electron-boson spectral function $\alpha_{tr}^2 F_{tr}(\Omega)$. In other words, $\alpha_{tr}^2 F_{tr}(\Omega)$ behaves like Ω^3 in a wider energy range

than in single crystals.

This effect is possibly induced by the indirect coupling between spin fluctuations and phonons [161], whose frequencies are increased by the compressive strain [157].

And finally, it was shown that the decrease (increase) in the electron-boson coupling constant (characteristic boson energy) between the superconducting and the normal state ($\lambda_{sup,tot} \gg \lambda_{tr,tot}$, $\Omega_0^{sup} \ll \Omega_0$) observed in crystals of various Fe-based compounds also holds in thin films of Co-doped Ba-122. This behavior is also common to HTSC [66] and may thus be a unifying principle at the root of superconductivity in iron-based materials and cuprates.

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List of publications

- G.A. Ummarino, S. Galasso and A. Sanna, *"A phenomenological multiband Eliashberg model for LiFeAs"*, J. Phys. Cond. Matter 25, 205701 (2013).

- G.A. Ummarino, Sara Galasso, A. Sanna, D. Daghero, M. Tortello and R.S. Gonnelli, *"Normal and superconducting properties of LiFeAs explained in the framework of four-band Eliashberg Theory"*, Phys. C 492, 21-24 (2013).

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