Directional point-contact Andreev-reflection spectroscopy of Fe-based superconductors: Fermi surface topology, gap symmetry, and electron–boson interaction

D Daghero, M Tortello, G A Ummarino and R S Gonnelli

1 Dipartimento di Fisica, Politecnico di Torino, 10129 Torino, Italy

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Abstract
Point-contact Andreev-reflection spectroscopy (PCAR) has proven to be one of the most powerful tools in the investigation of superconductors, where it provides information on the order parameter (OP), a fundamental property of the superconducting state. In the past 20 years, successive improvements of the models used to analyze the spectra have continuously extended its capabilities, making it suited to study new superconductors with ‘exotic’ properties such as anisotropic, nodal and multiple OPs. In Fe-based superconductors, the complex compound- and doping-dependent Fermi surface (FS) and the predicted sensitivity of the OP to fine structural details present unprecedent challenges for this technique. Nevertheless, we show here that PCAR measurements in Fe-based superconductors carried out so far have already greatly contributed to our understanding of these materials, despite some apparent inconsistencies that can be overcome if a homogeneous treatment of the data is used. We also demonstrate that, if properly extended theoretical models for Andreev reflection are used, directional PCAR spectroscopy can provide detailed information not only on the amplitude and symmetry of the OPs, but also on the nature of the pairing boson, and even give some hints about the shape of the FS.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

The order parameter (OP) is the most important quantity in a superconductor, since it determines how the charge carriers couple to form Cooper pairs. In the standard Bardeen–Cooper–Schrieffer (BCS) theory for superconductivity [1], the pairing potential is always attractive, does not depend on energy, is isotropic in space and is due to the interaction between electrons and phonons (in other words, phonons are the ‘mediating boson’). The amplitude of the OP, $\Delta$, is also the ‘energy gap’ in the superconductor, i.e. the distance, in energy, between the condensate of Cooper pairs and the first single-particle excitation. A dependence on energy of the OP must be added, as in the so-called Eliashberg theory [2], to properly describe those superconductors, such as Pb, where the interaction between electrons and phonons is particularly strong. In the past decades, many superconductors have been discovered in which the OP is anisotropic (i.e. its amplitude shows some angular dependence) or can even change sign on energy, between the condensate of Cooper pairs and the first single-particle excitation. A dependence on energy of the OP must be added, as in the so-called Eliashberg theory [2], to properly describe those superconductors, such as Pb, where the interaction between electrons and phonons is particularly strong. In the past decades, many superconductors have been discovered in which the OP is anisotropic (i.e. its amplitude shows some angular dependence) or can even change sign to become negative in some directions (as in the so-called d-wave symmetry, common in copper-oxide superconductors); in some cases, like the well-known MgB$_2$, multiple OPs exist, related to different sets of bands that form separated ‘sheets’ of the Fermi surface (FS).

The recently discovered Fe-based superconductors present most of these unusual properties at the same time. The coupling of electrons with the mediating boson (whatever its nature is) seems to be intermediate to strong; the FS is made up of separated sheets, which are mostly 2D-like; there are probably multiple OPs that, in most cases, are expected to be isotropic but with opposite sign on hole-like and electron-like FS sheets [3]. Under some conditions, OPs that display a sign change on the same sheet of the FS are predicted to become energetically favorable [4, 5].

As usual when a new class of superconductors is discovered, the experimental study of the OP in Fe-based superconductors has immediately attracted the attention and expectations of the scientific community. Determining the number, the amplitude and the symmetry of the OPs is a necessary step to assess the coupling mechanism and to understand the details of how superconductivity occurs in these materials. Point-contact spectroscopy is one of the techniques that has been more useful in the investigation of the OP in these materials. Despite its apparent simplicity (it just consists in measuring the differential conductance of a very small, in principle point-like contact between a normal metal and the superconductor under study) it is a powerful and versatile, yet inexpensive, research tool generally based on a combination of quantum effects: the tunnel effect (dominant in high-resistance contacts) and the Andreev reflection (dominant in small-resistance contacts). Here we will concentrate on the latter. To explain in a simple way what Andreev reflection is, let us imagine an incident electron with total energy $E$ to travel towards the interface in the N (normal) side of a ideal, barrierless S–N junction ($S = $ superconductor). If it finds vacant electronic states at the same energy on the S side, the electron will simply propagate in S. If instead its energy is smaller than the energy gap $\Delta$ in S, it cannot propagate in S, so it forms a Cooper pair with another electron excited from the Fermi sea in S. This leaves a hole in S that crosses the interface and travels backwards in N (see [6–8] for more accurate descriptions). From the point of view of N, things happen as if the electron was reflected as a hole. This ‘reflection’ causes a doubling of the conductance with respect to an N–N junction in which Andreev reflection cannot take place. This doubling occurs only as long as the energy of the injected electron (equal to $eV$ if $V$ is the voltage difference between N and S) is smaller or equal to $\Delta$. Thus, a measurement of the junction conductance as a function of $V$ allows determining the gap, i.e. the amplitude of the OP. In unconventional superconductors, the shape of the conductance curves can provide information not only on the amplitude of the OP, but also on its angular dependence (i.e. symmetry in reciprocal space) and, under particular conditions, on the shape of the FS and on the spectral function of the boson that mediates the superconducting pairing, as we will discuss in section 2.3.

Point-contact Andreev-reflection (PCAR) spectroscopy measurements in Fe-based superconductors have been carried out by various groups. Early measurements suffered from the unsatisfactory quality of the first samples and indeed gave contradicting and sometimes unrepeatable results. This might have given the impression that PCAR does not provide reliable results in these compounds. We will show in section 3 that, instead, when PCAR experiments in good-quality samples are carried out with all the necessary precautions by different groups and even in samples of different forms (single crystals, polycrystals, films) they do provide surprisingly consistent results. The sometimes contradicting conclusions arise from the interpretation of the data rather than from the data themselves. We will thus show that, in the most studied 1111 and 122 compounds, the available PCAR results, if analyzed in a homogeneous way, agree rather well on the amplitude of the OPs, on their temperature dependence and on their symmetry (the $\pm$ one, with isotropic OPs with sign reversal between hole-like and electron-like FS sheets [3]. Under some conditions, OPs that display a sign change on the same sheet of the FS are predicted to become energetically favorable [4, 5].

As usual when a new class of superconductors is discovered, the experimental study of the OP in Fe-based superconductors has immediately attracted the attention and expectations of the scientific community. Determining the number, the amplitude and the symmetry of the OPs is a necessary step to assess the coupling mechanism and to understand the details of how superconductivity occurs in these materials. Point-contact spectroscopy is one of the techniques that has been more useful in the investigation of the OP in these materials. Despite its apparent simplicity (it just consists in measuring the differential conductance of a very small, in principle point-like contact between a normal metal and the superconductor under study) it is a powerful and versatile, yet inexpensive, research tool generally based on a combination of quantum effects: the tunnel effect (dominant in high-resistance contacts) and the Andreev reflection (dominant in small-resistance contacts). Here we will concentrate on the latter. To explain in a simple way what Andreev reflection is, let us imagine an incident electron with total energy $E$ to travel towards the interface in the N (normal) side of a ideal, barrierless S–N junction ($S = $ superconductor). If it finds vacant electronic states at the same energy on the S side, the electron will simply propagate in S. If instead its energy is smaller than the energy gap $\Delta$ in S, it cannot
in various Fe-based superconductors seem to follow a universal trend as a function of the critical temperature ($T_c$) of the samples. Both $2\Delta_1/k_BT_c$ and $2\Delta_2/k_BT_c$ remain approximately constant down to $T_c \approx 30$ K, then tend to increase in compounds with lower $T_c$—even though further measurements in the low-$T_c$ region would be necessary to confirm this trend. We will propose a possible explanation of this behavior that essentially relies on the fact that the mediating boson is an electronic excitation (for example, spin fluctuations) and thus is subject to a 'feedback effect' of the condensate on the electron–boson spectral function.

2. Multiband 3D models for directional Andreev-reflection spectroscopy

2.1. The ‘standard’ 1D and 2D Blonder–Tinkham–Klapwijk models

We already presented in a recent review [9] the explicit expressions for the normalized conductance of a point contact between a normal metal (N) and a superconductor (S) in the case of a 2D geometry of the FSs of the latter. Let us briefly summarize these equations here, since in section 2.3 we will use them as the starting point to extend the Blonder–Tinkham–Klapwijk (BTK) model to particular 3D shapes of the FS and to particular directions of current injection. In the following we will call ‘2D BTK model’ the generalization of the original, ‘1D’ BTK theory [6], introduced in 1996 by Tanaka and Kashiwaya [7]. In their paper they first wrote the normalized conductance $G(E) = (dI_{NS}/dV)/(dI_{SN}/dV)$ at $T = 0$ (where $I_{NS}$ and $I_{SN}$ are the currents flowing through the interface when the material under study is in the superconducting and in the normal state, respectively) as a function of the two quantities $N_q(E) = E/\sqrt{E^2 - \Delta^2}$ and $N_p(E) = \Delta/\sqrt{E^2 - \Delta^2}$, whose real parts are the BCS quasiparticle and pair density of states, respectively.

Here we will immediately generalize these expressions to the strong-coupling regime, where the order parameter $\Delta$ is a complex function of energy resulting from the solution of the Eliashberg equations, and to the presence of inelastic quasiparticle scattering processes at the N/S interface. In the latter case it has been shown [10] that the resulting (and dominant) extrinsic reduction of the quasiparticle lifetime can be properly taken into account by including in the model an imaginary part of the energy described by the broadening parameter $\Gamma$, i.e. $E \rightarrow E + i\Gamma$. As a consequence, from now on $N_q(E, \Gamma) = (E + i\Gamma)/\sqrt{(E + i\Gamma)^2 - \Delta^2}$ and $N_p(E, \Gamma) = \Delta/(E + i\Gamma)^2 - \Delta^2$. Note that we have allowed $\Delta$ to depend on energy for the sake of generality, even though we will use this dependence explicitly only in section 2.4.

The main steps in the calculation of the normalized conductance $G(E)$ consist in the determination of the barrier transparency when the material under study is in the normal state ($\tau_N$) and in the superconducting state ($\sigma_S(E)$). These quantities are actually transmission probability distributions and are obtained by solving the Bogoliubov–de Gennes equations with the only condition that the component of the wavevector $k$ parallel to the interface is conserved in all processes, for any direction of the incoming electron from the N side. In the pure 2D case here discussed, where we suppose the interface to coincide with a plane parallel to the $z$-axis, the incoming electrons lie in the $xy$-plane and have a wave vector $k_{FS}$ which forms an angle $\theta_N$ with respect to the unitary vector $\hat{n}$ normal to the interface. In principle, if the Fermi velocity is different in the N and S side, the charge carriers experience a ‘refraction’ when crossing the interface (i.e. the wavevector of the quasiparticles in the S side of the junction $k_{FS}$ could be different from $k_{FN}$) so that the direction of propagation of quasiparticles in the S side could form an angle $\theta_S$ different from $\theta_N$ with respect to the normal to the interface. Under these conditions, electrons incident on the interface with suitable angles can experience a normal reflection even in the absence of a barrier potential $U_0$ located at the interface, and the normal transmission coefficient $\tau_N$ is no longer identically 1. In the most general case when $U_0$ is present, the normal transparency of the barrier is

$$\tau_N = \frac{4(k_{FN} \cdot \hat{n})(k_{FS} \cdot \hat{n})}{(k_{FN} \cdot \hat{n} + k_{FS} \cdot \hat{n})^2 + 4Z^2k_{FN}^2},$$

where $Z = U_0/hv_F$ is the dimensionless parameter which accounts for the potential barrier.

From now on we will restrict the analysis to the case $k_{FN} = k_{FS} = k_F$ from which it follows $\theta_N = \theta_S = \theta$. As a matter of fact, while properly taking into account the Fermi velocity mismatch at the interface in the 2D case is a non-straightforward but feasible task (see [9]), it becomes an extremely complex problem in the full 3D case we will discuss in section 2.3, when the true shape of the FS will be considered. Under the previous restrictive hypothesis the normal transparency becomes

$$\tau_N(\theta) = \frac{\cos^2 \theta}{\cos^2 \theta + Z^2}.$$  

It is clear that, for $Z = 0$, the normal transmission probability is identically 1 for any direction of the incoming electron, i.e. for $-\pi/2 < \theta < \pi/2$. When $Z \neq 0$, instead, the barrier transparency depends on the direction of the incoming electron in the N side; for $Z = 10$ (tunneling regime) the transmission probability is always small and highly directional. It can be shown that the relative transparency of the barrier in the superconducting state is given by [7]

$$\sigma_S(E, \theta) = \frac{1 + \tau_N(\theta)|\gamma(E)|^2 + (\tau_N(\theta) - 1)|\gamma(E)|^2}{1 + (\tau_N(\theta) - 1)|\gamma(E)|^2},$$

where $\gamma(E) = [N_q(E) - 1]/N_p(E)$ and finally the normalized conductance at $T = 0$ is

$$G_{2D}(E) = \frac{\int_{-\pi/2}^{\pi/2} \sigma_S(E, \theta) \tau_N(\theta) \cos \theta d\theta}{\int_{-\pi/2}^{\pi/2} \tau_N(\theta) \cos \theta d\theta}.$$  

Both in the numerator and denominator of equation (4) the integration extremes are $-\pi/2$ and $\pi/2$ since the current
injection occurs in the whole positive half-space for which \(0 \leq \cos \theta \leq 1\). The standard BTK theory [6] is the 1D limit of this model, in which all the electrons from the N side are injected in the same direction perpendicular to the interface. Obviously, the normal-state transmission probability in this case is simply obtained by putting \(\theta = 0\) in equation (2), i.e. \(\tau_N = 1/(1 + Z^2)\). By doing the same also in equations (3) and (4) the expression for the 1D BTK conductance \(G_{1D}(E) = \sigma_S(E, 0)\) is thus recovered. Instead, the 2D BTK model itself is the limit of the more general 3D model (see section 2.3) if the gap is isotropic and the FS is spherical (i.e. the system has a rotational symmetry around the axis normal to the interface).

In figure 1(a) a comparison of the normalized conductances \(G_{1D}(E)\) (solid lines) and \(G_{2D}(E)\) (dashed lines) is shown at \(T = 0\) and \(\Gamma = 0\) as a function of the normalized energy \(E/\Delta\) for different values of the barrier parameter \(Z\). Looking at the form of \(\tau_N(\theta)\) (equation (2)), one expects the 1D BTK normalized conductance to coincide with the 2D one when \(Z = 0\) (i.e. when \(\tau_N = 1\) and \(\sigma_S(E) = 1 + |\gamma(E)|^2\)) and when \(Z \to \infty\) (i.e. when \(\tau_N \to 0\) and \(\sigma_S(E) \to (1 - |\gamma(E)|^2)/|1 - \gamma(E)|^2\)). This is clearly shown in the curves at \(Z = 10\) and \(Z = 0\). The maximum deviations between the predictions of the two models occur for \(Z \approx 0.3-0.5\) which, incidentally, is the range of values commonly observed in experiments in Fe-based superconductors. It is very easy to demonstrate that, in practice, each \(G_{2D}(E)\) curve almost coincides with the \(G_{1D}(E)\) calculated for a properly enhanced \(Z\) value and, thus, the 1D BTK model can be efficiently used instead of the 2D one provided that the gap is isotropic, the FS is spherical and one is not interested in the precise determination of the \(Z\) values.

All the equations seen up to now are calculated at \(T = 0\). The effect of a finite temperature \(T\) can be properly taken into account by simply convolving the normalized conductance with the Fermi function at that temperature, as shown in detail in [9] and by including in the calculations the proper temperature dependence of the gap. Figure 1(b) shows the temperature dependence of the normalized conductances \(G_{1D}(E)\) (solid lines) and \(G_{2D}(E)\) (dashed lines) for \(\Delta = 3.0\) meV, \(\Gamma = 0\), \(Z = 0.3\) and \(T_c = 20\) K. The BCS temperature dependence of the gap \(\Delta(T)\) used in the calculations is shown in the inset. This kind of curves is what is expected in the best PCAR experiments (\(\Gamma = 0\)) on a single-band isotropic BCS superconductor.

### 2.2. Symmetry of the order parameter

In order to understand the profound changes occurring in the normalized conductance of a point contact when the symmetry of the OP is not s-wave, it is necessary to briefly describe in greater detail the physical processes that take place at the NS interface. When an electron coming from the N side reaches the potential barrier at the interface, four different processes can occur depending on the electron energy and on the height of the barrier: (A) the electron is reflected as a hole in N (Andreev reflection); (B) the electron is specularly reflected as an electron in N (normal reflection); (C) the electron is transmitted in S as an electron-like quasiparticle, ELQ (normal transmission); (D) the electron is transmitted in

**Figure 1.** (a) Theoretical PCAR normalized conductance of a single-band s-wave superconductor as function of reduced energy \(E/\Delta\) at \(T = 0\) and \(\Gamma = 0\) for different \(Z\) values from the pure Andreev-reflection regime \((Z = 0)\) to the tunneling one \((Z = 10)\). The solid curves are calculated using the 1D BTK model, while the dashed ones use the 2D BTK one (see text). (b) Temperature dependence of the theoretical PCAR normalized conductance of panel (a) for \(\Delta = 3\) meV, \(\Gamma = 0\) and \(Z = 0.3\). Also in this case solid curves represent the results of the 1D BTK model and dashed ones the results of the 2D BTK one. In the inset the BCS temperature dependence of the gap is shown. The curves in (a) and (b) are vertically offset for clarity.
S as a hole-like quasiparticle, HLQ (anomalous transmission). Due to the charge conservation this last process results in two electrons ‘reflected’ back in N for every incoming electron. The probabilities of these processes strongly depend on the energy of the incoming electron and on the Z parameter. In particular, processes C and D are forbidden for $E < \Delta$ (where there can be no transmitted quasiparticles), process B is present at any energy when $Z > 0$ and process A is also present at any energy (but is very small for $E > \Delta$) only if $Z$ values are not too large (in practice $Z < 10$). Equation (4) properly takes into account all these probabilities, but only in the case of an isotropic OP, i.e. in s-wave symmetry. When the OP is anisotropic, i.e. its amplitude and possibly its sign change as a function of the direction in reciprocal space, the situation is more complex. As a matter of fact, the wavevector of the ELQ $k_1^\alpha$ and that of the HLQ $-k_1^\gamma$ have now different direction, yet still having the same component parallel to the interface. In other words, the two vectors in the S side form the angles $\theta$ and $-\theta$ with respect to the unitary vector $n$, respectively [7]. In this situation and depending on the orientation of the anisotropic OP with respect to $n$ the ELQs and the HLQs can feel different OPs.

Let us extend the equations for the 2D BTK model to this case. Let us assume that the system has a translational invariance along $k_z$, i.e. the FS is a cylinder, the OP has a $k$ dependence only in the $k_x,k_y$ plane (as it happens in cuprates) and the current injection occurs in the same plane (ab-plane contact). We can now introduce the angle misalignment $\alpha$ between the crystallographic a-axis in S and the normal to the interface $n$. As a consequence of gap anisotropy and of this misalignment, ELQs feel the order parameter $\Delta(E, \theta, \alpha) = \Delta(E, \theta - \alpha)$, while HLQs feel $\Delta(E, \theta, -\alpha) = \Delta(E, -\theta - \alpha)$. In this case the relative transparency of the barrier in the superconducting state becomes [7]

$$
\sigma_s(E, \theta) = 1 + \frac{\tau_n(\theta)[\gamma_+(E, \theta)]^2 + (\tau_n(\theta) - 1)[\gamma_+(E, \theta)\gamma_-(E, \theta)]^2}{[1 + (\tau_n(\theta) - 1)[\gamma_+(E, \theta)\gamma_-(E, \theta)\exp(i\varphi_d)]^2]},
$$

(5)

where

$$
\gamma_{\pm}(E, \theta) = \frac{(E + i\Gamma) - \sqrt{(E + i\Gamma)^2 - |\Delta(E, \theta)|^2}}{|\Delta(E, \theta)|},
$$

(6)

and

$$
\varphi_d = -i \ln \left[ \frac{\Delta(E, \theta)|_{+}}{\Delta(E, \theta)|_{-}} \right]
$$

(7)

is the phase difference (function of $\theta$) seen by the HLQs with respect to the ELQs. Of course, $\tau_n(\theta)$ remains the same (indeed it only describes processes B and C in a N–N junction) and thus, simply by introducing the new expression for $\sigma_s(E, \theta)$ (equation (5)) into equation (4) and performing the proper integration in $\theta$ one can obtain the normalized conductance at $T = 0$ for any symmetry of the OP in the $k_x,k_y$ plane. This symmetry is of course expressed by the specific $\theta$ dependence of the functions $\Delta(E, \theta)|_{\pm}$.

In this review we are interested in the symmetries that have been considered plausible for Fe-based superconductors. The $\pm$ symmetry, with isotropic OPs of different signs on the hole-like and on the electron-like FS sheets [3], is the most likely for the majority of the systems. If interband interference effects [11] are negligible, this phase change is not detectable by PCAR and gives the same spectra as a multiband s-wave symmetry. Under suitable conditions, which seem to be related to fine structural parameters [4, 5], anisotropic or nodal symmetries are expected to become more energetically favorable. As a consequence, apart from the s-wave, we will discuss here the cases of fully anisotropic s-wave symmetry (with zeros in the gap) and the $d_{x^2-y^2}$-wave one. The two expressions for the OP are $\Delta_{ab}(E, \theta) = \Delta(E)\cos[2(\pm\theta - \alpha)]$ and $\Delta_d(E, \theta) = \Delta(E)\cos2(\pm\theta - \alpha)$, respectively [7, 12]. In the first case the pair potential is zero in four directions but never changes sign, while in the second case the sign change typical of d-wave symmetry is present, as shown in the insets of figure 2.

Figure 2(a) reports the theoretical 2D Andreev reflection (AR) normalized conductance curves obtained from the integration of equation (4) for fully anisotropic s-wave symmetry, at finite temperature ($T = 1.5\, \text{K}$) and different $Z$ values. Upper and lower panels refer to the cases $\Gamma = 0$ and $\Gamma = \Delta/4$, respectively. Figures 2(b) and (c) report the corresponding conductance curves obtained for a d-wave symmetry, where $\alpha = \pi/4$ and $\alpha = \pi/8$, respectively. Without entering too much into details, the main message coming from these calculations is the following. For current injection in the ab-plane, and when $Z$ is sufficiently small, a maximum of the conductance at zero bias appears both in anisotropic s- and d-wave symmetries (top panels). These maxima however have a somewhat different physical origin in the two symmetries. In fully anisotropic s symmetry, they come only from the angular integration over OPs that can assume any value between the maximum $\Delta(E)$ and 0. In d-wave symmetry, the zero-bias maximum has the same origin only for $Z = 0$, while for finite $Z$ values it considerably grows (becoming much higher than 2 in the tunneling regime) because of an additional effect, i.e. the constructive interference of ELQs and HLQs that feel a phase difference of the pair potential. This interference effect (described by the $\exp(i\varphi_d)$ term in the denominator of equation (5)) is the only one responsible for the zero-bias conductance peak (ZBCP) present in the d-wave case for $\alpha = 0$ and large $Z$, a peak that is totally absent in the anisotropic s case.

In principle, the different shapes of the conductance curves for the two symmetries at low $Z$ shown in the upper panels of figure 2 would allow one to identify the true OP symmetry. In practice, however, even a relatively small amount of broadening, i.e. $\Gamma = \Delta/4$, is sufficient to prevent the correct determination of the OP symmetry, as shown in the lower panels of figure 2, unless $Z$ is sufficiently large. At low $Z$, the ZBCP typical of the d-wave symmetry, smoothed by $\Gamma$, can be confused with the zero-bias maximum of the anisotropic s-wave one. Thus, in the presence of a zero-bias maximum in the experimental curves of ab-plane point contacts in the AR regime (i.e at low $Z$) what we can only say is that the OP is zero along some directions. Only ab-plane measurements in the tunneling regime would...
allow us to distinguish the two situations but, apparently, they are not so easy to obtain in Fe-based compounds with point-contact or scanning tunneling microscopy (STM) techniques.

2.3. Shape of the Fermi surface and directionality

In this subsection we will extend the 2D BTK theory to arbitrary shapes of the FS and will show what is expected when the current is injected either in the $ab$-plane or along the $c$-axis. Under a few restrictive hypotheses (still present in this approach), the final result will be the full 3D generalization of the BTK model to any anisotropic feature both of the FS and of the pair potential symmetry.

The first obvious generalization, essential for the interpretation of the results in Fe-based superconductors, is to consider the multiband nature of superconductivity in these compounds and the multiple sheets of the FS arising from the crossings of the Fermi energy by the different bands. This problem gained for the first time importance and popularity ten years ago with the discovery of MgB$_2$, the first well-known multiband, multigap superconductor [13, 14]. At the level of AR data analysis and in order to have a limited number of fitting parameters the standard approach is to consider a two-band, two-gap system where the values of $\Delta_i$, $Z_i$ and $\Gamma_i$ of every band ($i = 1, 2$) have to be determined by the best fit of theoretical curves to the experimental ones. The total normalized conductance is thus written as $G_{tot}(E) = w_1 G_1(E) + (1 - w_1) G_2(E)$, where $G_i(E)$ is the normalized conductance of the $i$th band (1D or 2D depending on the selected model) and $w_1$ is the relative contribution of band 1 to the total conductance. The drawback here is that, apart from a few lucky cases [14], the weight factor $w_1$ is also a parameter of the fit. We will see later that this is not the case in the full 3D model where the weighting factors come automatically from the complex interaction between the FS shape and the direction of current injection.

A simple extension of the 2D BTK theory to the 3D case can be realized under the hypothesis of a spherical FS in the $S$ side of the junction (the $N$ side is always supposed to have a spherical FS) as shown in [15]. The main point here is to express $\tau_N$, $\sigma_\delta(E)$ and $\Delta(E)$ (if the OP is anisotropic) as a function of both the azimuthal and inclination angles $\theta$ and $\phi$ defined with respect to a Cartesian reference frame chosen as in [15]. Of course the specific expressions depend on the direction of current injection and on the particular symmetry of the pair potential. As an example, for an $ab$-plane contact (always with no mismatch of Fermi velocity at the interface, here chosen to coincide with the $yz$-plane) it is rather easy to show that

$$\tau_{N,\delta}^{sp}(\theta, \phi) = \frac{\cos^2 \theta \sin^2 \phi}{\cos^2 \theta \sin^2 \phi + Z^2}$$

and $\Delta(E, \theta, \phi)_{\parallel}$ are the expressions of the pair potential seen by the ELQs and HLQs, respectively, for the specific symmetry considered. By introducing $\Delta(E, \theta, \phi)_{\parallel}$ into the

**Figure 2.** (a) Reduced energy dependence of the normalized conductance of a single-band superconductor with full anisotropic $s$ symmetry of the OP for different $Z$ values at $T = 1.5$ K, $\alpha = \pi/4$ and $\Gamma = 0$ (upper panel) and at $T = 1.5$ K, $\alpha = \pi/4$ and $\Gamma = \Delta/4$ (lower panel). (b) The same as in panel (a) but for a single-band superconductor with $d_{x^2-y^2}$ symmetry of the OP. (c) The same as in panel (b) but for $\alpha = \pi/8$. The insets in all the panels represent the symmetry of the pair potential (red and blue colors mean positive and negative values, respectively) while the black arrows indicate the direction of current injection.
above formulae for $\gamma_{k}$ and $\varphi_{d}$ (equations (6) and (7)), and then inserting $\tau^{ph}_{S\xi}(\theta, \phi)$ and the obtained $\gamma_{k}(E, \theta, \phi)$ and $\varphi_{d}(\theta, \phi)$ into equation (5) it is finally possible to integrate on the two angles arriving at the normalized conductance:

$$
G^{ph}_{3D}(E) = \frac{\int_{0}^{\pi/2} \int_{-\pi}^{\pi/2} \bar{\sigma}_{S\xi}(E, \theta, \phi) \tau^{ph}_{S\xi}(\theta, \phi) \cos \theta \sin^2 \phi \, d\theta \, d\phi}{\int_{0}^{\pi/2} \int_{-\pi}^{\pi/2} \bar{\tau}^{ph}_{N\xi}(\theta, \phi) \cos \theta \sin^2 \phi \, d\theta \, d\phi}.
$$

(8)

The model discussed so far is still implicitly based on the assumption of a spherical FS. The problem then arises of how to express the $c$-axis or $ab$-plane conductance in a superconductor with a quasi-2D FS. This is the case of cuprates or of Sr$_{2}$RuO$_{4}$. A possible solution, though not really general, is to restrict the integration in $\phi$ to a narrow angular range around $\pi/2$ as in [15]. In this way, the spherical FS of the model is reduced to a almost cylindrical belt that locally approximates the true, cylindrical FS. In the following, we will instead derive and present a more general approach to a full 3D case, with an FS of arbitrary shape.

Just for simplicity we will still limit the calculations to the contribution of only two bands (thus the band index $i$ assumes only the values 1 and 2). For the directionality of the contact, we consider here current injections along the $x$-axis ($yz$-plane interface) and along the $z$-axis ($xy$-plane interface), being representative of the typical experimental conditions in single crystals of the Fe-based compounds, i.e. the $ab$-plane and the $c$-axis contacts, respectively.

The particular shape of the $i$th FS is described by the wave vector $k_{F,i}(\theta, \phi)$, while the unitary vector perpendicular to the FS at any point of the reciprocal space is simply given by $n_{F,i}(\theta, \phi) = (\partial k_{F,i}(\theta, \phi)/\partial \theta) \times (\partial k_{F,i}(\theta, \phi)/\partial \phi)$ whose calculation is trivial once the shape of $i$th FS has been chosen.

Under the additional (but reasonable) hypothesis that the points on the FS are close to the points of maximum symmetry of the energy bands (i.e. they are close to the top or the bottom of parabolic-like bands) one can express the Fermi velocity at any point as a function of the component of $k_{F,i}$ perpendicular to the FS at that point:

$$
v_{F,i}(\theta, \phi) = \frac{\hbar k_{F,i}^{2}(\theta, \phi)}{m^{*}} n_{F,i}(\theta, \phi) = \frac{\hbar k_{F,i}(\theta, \phi) \cdot n_{F,i}(\theta, \phi)}{m^{*}},
$$

where $m^{*}$ is the effective mass of quasiparticles. Finally, the components of the Fermi velocity along a given direction can be simply obtained by projecting $v_{F,i}(\theta, \phi)$ along that direction, i.e. $v_{F,i}(\theta, \phi) = v_{F,i}(\theta, \phi) \cdot \hat{i}$ and $v_{F,i}(\theta, \phi) = v_{F,i}(\theta, \phi) \cdot \hat{k}$ where, of course, $\hat{i}$ and $\hat{k}$ are the unitary vectors of the $x$- and $z$-axis, respectively. We now have all the ingredients required to calculate the normalized conductance.

By following the approach originally developed in [14, 16] and recently summarized in [9], and by neglecting possible interference effects between bands that can lead to the formation of bound states at the surface [11], we obtain the normalized conductance for current injection along the $x$-axis:

$$
G_{3D}(E) = \left[ \sum_{i} \int_{0}^{\pi/2} \int_{0}^{2\pi} \sigma_{S\xi,i}(E, \theta, \phi) \tau_{N\xi,i}(\theta, \phi) \right] \times \left[ \frac{v_{F,i}(\theta, \phi)}{v_{F,i}(\theta, \phi)} \right] k_{F,i}(\theta, \phi) \sin \phi \, d\theta \, d\phi.
$$

(9)

where

$$
\tau_{N\xi,i}(\theta, \phi) = \frac{4v_{F,i}(\theta, \phi) v_{N\xi}}{[v_{F,i}(\theta, \phi) + v_{N\xi}]^{2} + 4Z_{z,i}^{2} v_{N\xi}^{2}}
$$

and $\sigma_{S\xi,i}(E, \theta, \phi)$ has the same expression shown in equation (5) but now contains the band-associated functions $\gamma_{k}(E, \theta, \phi)$ and $\varphi_{d}(\theta, \phi)$ given by equations (9) and (10). In this way, of course, the condition of no mismatch of Fermi velocities across the interface translates here into $v_{F,i}(\theta^{*}, \phi^{*}) = v_{N\xi}$ where $\theta^{*}$ and $\phi^{*}$ define a point on the FS (usually in the $k_{z}k_{y}$-plane) where we suppose the two velocities to be equal. By imposing this condition, we eliminate the need to know the term $\bar{h}/m^{*}$ which multiplies all the elements at numerator and denominator of equations (9) and (10). In this way, of course, we neglect the small deviation of the quasiparticles in crossing the interface due to the modest mismatch of Fermi velocities in N and S simply arising from the geometry of the FS in S. In equations (9) and (10) $v_{N\xi} = v_{N\xi} \cdot \hat{i} = v_{N\xi} \cos \theta \sin \phi$ and $Z_{z,i}$ is the barrier height parameter for current injection along the $x$-axis in the $i$th band. Finally, the limits of integration in $\phi$ ($\phi_{min}$ and $\pi - \phi_{min}$) are fixed in such a way that the integration is restricted to the first Brillouin zone.

If all the previous considerations hold, writing the expression of the normalized conductance for current injection along the $z$-axis is straightforward:

$$
G_{3D}(E) = \left[ \sum_{i} \int_{0}^{\pi/2} \int_{0}^{2\pi} \sigma_{S\xi,i}(E, \theta, \phi) \tau_{N\xi,i}(\theta, \phi) \right] \times \left[ \frac{v_{F,i}(\theta, \phi)}{v_{F,i}(\theta, \phi)} \right] k_{F,i}(\theta, \phi) \sin \phi \, d\theta \, d\phi.
$$

(11)
...symmetry with zeros (figure 3) on the electron FS sheet at M, and a...is concerned, we will consider here an isotropic s-wave pair...surfaces in figures 3-8 (see text). In this case the OP on the electron FS sheet at M has isotropic s-wave symmetry while the one on the hole FS sheet at \( \Gamma \) has a fully anisotropic s-wave symmetry. (b) The same as in panel (a) but for a \( d_{x^2-y^2},z^2 \) symmetry of the OP on the hole FS sheet at \( \Gamma \).

Figure 3. (a) Reciprocal space representation of the shape of the FS sheets (matt surfaces) and of the pair potentials (semi-transparent gridded surfaces) used in the calculations whose results are shown in figure 4 (see text). In this case the OP on the electron FS sheet at M has isotropic s-wave symmetry while the one on the hole FS sheet at \( \Gamma \) has a fully anisotropic s-wave symmetry. (b) The same as in panel (a) but for a \( d_{x^2-y^2},z^2 \) symmetry of the OP on the hole FS sheet at \( \Gamma \).

Here, \( \tau_{SC},i(\theta,\phi) \) is obtained as in equation (10) but by projecting onto the \( z \) direction.

It is trivial to show that, in the presence of a single band and when not only the FS in N but also the one in S is spherical, equations (9) and (11) reduce to those of the 3D BTK model already discussed at the beginning of the present subsection.

We can now discuss the results of these calculations in a couple of cases of particular interest for Fe-based superconductors. In the typical 1111 or 122 compounds, the FS sheets can be approximated by more or less warped cylinders [17]. In some special cases, 3D pockets have been calculated, which can instead be approximately described as ellipsoids [18].

Surfaces that approximate reasonably well these FS sheets and that can be easily written in parametric form are the oblate or prolate spheroids and the one-sheeted hyperboloids of revolution. Here we will use two hyperboloids with different (negative) Gaussian curvatures to represent the hole and electron FS sheet of a hypothetical 1111 or 122 Fe-based compound. These theoretical FS sheets are shown as matt surfaces in figures 3(a) and (b). As far as the symmetry of OPs is concerned, we will consider here an isotropic s-wave pair potential on the electron FS sheet at M, and a \textit{fully anisotropic} s-wave symmetry with zeros (figure 3(a)) or a \( d_{x^2-y^2} \)-wave symmetry (figure 3(b)) for the hole-like FS sheet at \( \Gamma \). In figure 3 the OPs are represented as semi-transparent gridded surfaces with red grids where the pair potential is positive and blue ones where it is negative. A somewhat similar problem concerning the effect on the conductance curves of different OP symmetries on hole-like and electron-like FS sheets was discussed for the 2D case in [19].

Using these models for the geometry of FS sheets and symmetry of OPs shown in figure 3 and by working out equations (9) and (11) we obtain the theoretical normalized conductance for point contacts along the \( x \)-axis direction (\( ab \)-plane contacts) and along the \( z \)-axis one (\( c \)-axis contacts). This conductance is shown as a function of bias voltage at \( T = 0 \) and for different values of the parameters in panels (a) and (b) of figure 4, respectively. In all the simulations we used \( \Delta_1 = 4 \) meV (maximum absolute value of the anisotropic pair potential), \( \Delta_2 = 9 \) meV (value of the isotropic pair potential), \( \Gamma_3/\Delta_1 = \Gamma_2/\Delta_2 = 1/4 \) and \( Z_1 = Z_2 = 0.1 \). In practice, the small gap is on the hole FS and is anisotropic, with line nodes or zeros along four specific directions, while the large one is on the electron FS and is isotropic. In addition, \( Z \) values similar to the experimental ones and reasonably small (but not null) broadening parameters are used. The selected symmetries and parameters do not correspond to any actual Fe-based superconductor. Nevertheless, they are somewhat inspired by recent theoretical papers on hole-doped BaFe\(_2\)As\(_2\) [20] and on BaFe\(_2\)(As\(_1-x\)P\(_x\))\(_2\) [5], where 3D nodal structures are predicted to appear in the warped hole FS. Symmetries involving nodes on the electron FS (nodal s-wave) or on the hole FS (d-wave) have been discussed also for 1111 low-\( T_c \) compounds [4]. Figure 4(a) shows the normalized conductance curves of the \( ab \)-plane contacts for the two selected symmetries of the small gap and two different values of the \( \alpha \) angle. It is clearly seen that, independently of the anisotropic symmetry of the small OP—provided it has zeros in some directions—and of the injection angle with respect to these directions, the \( ab \)-plane curves present a more or less pronounced zero-bias peak due to the small gap \( \Delta_1 \) and broader shoulders originated by the isotropic gap \( \Delta_2 \). This result is somewhat expected if one considers the curves shown in figure 2 for small \( Z \) values and \( \Gamma \neq 0 \). Quite different is the situation of the \( c \)-axis contacts. As shown in figure 4(b) the normalized conductance in this case presents no zero-bias peaks, independently of the symmetry of the small OP. On the whole, the curves appear very similar to what is expected in s-wave symmetry but for enhanced \( Z \) values (of the order of 0.2–0.4). Also the structures due to the small OP have an s-like appearance in both the symmetries and even for \( Z = 0 \), always resulting in more or less pronounced shoulders or peaks at about 4 meV in the total conductance. This result is only partially expected. In fact, now the HLQs and the ELQs feel the same phase independently of \( \theta \) and, thus, interference effects due to phase differences cannot occur. Nevertheless, the full integration in \( 0 < \theta < 2\pi \) gives rise to an average of conductance curves representative of the different gap values that are seen at different directions in the \( ab \)-plane. As it happens in the \( ab \)-plane contacts of panel (a), the contribution of arbitrary small OPs close to the nodes or zeros should yield zero-bias maxima in the total conductance.
and discussed in detail in the text. As a consequence, the resulting normalized conductance is zero as expected from equation (11) and already pointed out in [9].

But this is not the case. The reason is an additional and pure geometric effect.

When the current is injected along a direction mainly parallel to the FS (as in this case, when the current is injected along the c-axis) the normal transparency $\tau_{NC}(\theta, \phi)$ is markedly reduced in amplitude at any angle and its overall shape is modified accordingly. It can be easily shown that both these effects can be roughly simulated by inserting a properly enhanced Z value into the $\tau_{NC}(\theta, \phi) = \cos^2 \phi/(\cos^2 \phi + Z^2)$ valid for a spherical FS. For the FS geometries here discussed this Z-enhancing effect occurs also in the ab-plane contacts but to a quite minor extent since, in this case, most of the FS is almost perpendicular to the direction of current injection. In other words we can roughly say that, the larger is the projection of the FS along the tunneling direction, the smaller is the Z-enhancing effect. Of course, as extreme limits we have the spherical FS (where the Z enhancement is null for every tunneling direction) and the perfectly cylindrical FS (along whose axis the enhanced Z tends to infinity and, thus, $\tau_{NC}(\theta, \phi)$ tends to zero). In the latter case, however, the resulting normalized conductance is zero as expected from equation (11) and already pointed out in [9]. As a consequence of this Z-enhancing effect related to the FS geometry, of the strong Z dependence of the zero-bias peaks shown in figure 2 and of the absence of phase-difference interference effects, it turns out that the c-axis contacts on superconductors with warped cylindrical FSs cannot show ZBCPs or maxima even in the presence of d-wave or fully anisotropic s-wave symmetry of the OPs. In this case only zero-bias peaks or maxima in the ab-plane contacts can give information on the anisotropic symmetry of one or more of the OPs but, as shown in figure 4(a), without allowing the complete determination of this symmetry. In section 3 we will provide a couple of examples in which zero-bias maxima have been observed experimentally in single crystals and polycrystals of Fe-based compounds of different families.

These results are also interesting from another point of view. By reversing the previous reasoning one can say that if the OP on an FS sheet has a d-wave or fully anisotropic s-wave symmetry and AR experiments in the c-axis direction do show zero-bias peaks or maxima, it means that the Z-enhancing effect is very small, the relevant FS sheet has a closed surface (i.e. it is 3D) and the OP is zero along $k_c$. This situation can be easily simulated by substituting one of the two FSs of figure 3 with a suitable spheroid and introducing the proper $\phi$ dependence in the expression of the OP but a detailed discussion of these results is beyond the scope of this paper.

The only important message we would like to leave here is that in some particular situations, e.g. in the presence of anisotropic pair potentials, directional PCAR spectroscopy can provide information not only on the symmetry of the OPs but also on the geometry of FS sheets where the superconducting gaps open. Less univocal and drastic, but still interesting information on the FS geometry comes in any case from the observation that in the framework of this full 3D BTK model the weight factor of every band in the total normalized conductance comes directly from the FS topology and the directionality of the contact and is not a fit parameter as in the standard two-band fitting approach. It means that once the geometry of FS sheets is fixed (e.g. by first-principle band-structure calculations) it is then possible to compare the experimental PCAR results with the theoretical 3D BTK predictions getting information on the

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**Figure 4.** (a) Normalized AR conductance calculated using the full 3D BTK model described in the text for the FS shapes and the two OP symmetries shown in figure 3, for two different values of $\alpha$ angle and for current injection along the ab-plane. (b) The same as in panel (a) but for current injection along the c-axis and for two different values of Z. The other parameters of the calculations are shown in the labels and discussed in detail in the text.
true FS topology as compared with the theoretical one. Just as an example, we report here the weight factors of bands 1 and 2 coming from the results shown in figure 4 and, thus, for the geometries shown in figure 3. They are \( w_1^{ab} = 0.48 \), \( w_2^{ab} = 0.52 \), \( w_1^c = 0.33 \), and \( w_2^c = 0.67 \). These numbers are not far from the actual values obtained in PCAR experiments on Fe-based superconductors, particularly as far as \( w_1^{ab} \) is concerned [21–23].

In principle, one should always use this full 3D model in fitting the experimental data. However, (i) the 3D model is rather complicated to handle as a fitting tool; (ii) it requires knowledge of the FS geometry, which is not always available; (iii) most of the Fe-based superconductors have quasi-2D FSs so that the 2D model can be safely used as a first approximation. Indeed, the difference between the 3D and the 2D models is dramatic only along the \( c \)-axis, and in the case of d-wave or anisotropic s-wave symmetry as shown in figure 4. In the case of s-wave symmetry it is possible to show that the results obtained with the 2D model are totally compatible with those of the full 3D one. For example, we calculated the normalized conductances for injection along the \( ab \)-plane and along the \( c \)-axis using the full 3D model, using a 3D FS made of two moderately-warped one-sheeted hyperboloids of revolution.

The two s-wave gaps and the other parameters used in the calculation are the same as in figure 4, except the barrier heights that here are \( Z_1 = Z_2 = 0.2 \). When the theoretical 3D conductance curves are fitted by the 2D BTK model the resulting parameters are perfectly coincident with the starting ones (including the weights of band 1 and 2) with only the expected exception of the parameter \( Z \) that results about 20\% larger along the \( ab \)-plane and 2.8–3.6 times larger than the actual one in the fit of the \( c \)-axis conductance, due to the mentioned \( Z \)-enhancing effect. As a consequence, in s-wave symmetry, the use of the fully 3D model is mandatory only if a precise determination of the \( Z \) parameters is required.

In this rather long subsection we have discussed in detail the effects of FS geometry and directionality of the contact on the results of PCAR spectroscopy in multiband multi-gap superconductors like the Fe-based ones. In the next subsection we will focus instead on the effect in PCAR curves of the presence of a strong electron–boson interaction and on the role played by the shape of the electron–boson spectral function, by appropriately solving a three-band \( s \pm \) Eliashberg model for the determination of the \( \Delta_i(E) \) functions to be inserted in the above reported expressions for the normalized conductance.

2.4. Electron–boson interaction and shape of the spectral function

It is well known that, in BCS theory, the OP does not depend on energy. This is not the case when the Eliashberg theory of superconductivity is adopted. By starting from the electron–boson spectral function \( \alpha^2 F(\Omega) \) it is indeed possible, within the Eliashberg approach, to account for the full energy dependence of the OP which is now described by a complex function of energy, \( \Delta(E) = \text{Re}\Delta(E) + i\text{Im}\Delta(E) \). In particular, as the strength of the coupling increases, the imaginary part also increases and small deviations from the BCS density of states can be observed at the typical boson energies. In the moderate/strong-coupling regime these deviations can be experimentally detected by tunnelling and PCAR spectroscopy.

From the theoretical point of view, a precise knowledge of the shape of the spectral function is not really necessary, at least to a first approximation, to calculate \( T_c \), the gaps, etc., within the Eliashberg theory, since these quantities mostly depend on the representative frequency of \( \alpha^2 F(\Omega) \) [24–26]. However, we will show in the following that the shape of the spectral function and the maximum boson energy affect the possibility to observe electron–boson interaction features in the AR spectra. In this regard, we will compare different shapes of the spectral function, namely a Lorentzian function [27] (see the inset to figure 5(a) and the typical antiferromagnetic spin fluctuations (AFSF) spectral function [28] (inset to figure 5(c)).

The effect of the shape of the spectral function on the electron–boson features will be discussed within a three-band, \( s \pm \) Eliashberg model which revealed useful in describing several Fe-based superconductors [23, 27, 29]. Within this model, the electronic structure of Fe-based superconductors is described by two hole bands and one equivalent electron band in the case of hole doping, and by two electronic bands and one equivalent hole band in the case of electron doping. The other main assumptions of the model are that (i) the total electron–phonon coupling constant is small [30, 31]; (ii) phonons mainly provide intraband coupling; (iii) spin fluctuations mainly provide interband coupling. We will choose, as a representative example, the compound Ba(Fe\(_{0.9}\)Co\(_{0.1})_2\)As\(_2\) [23]. The parameters (\( \Delta \), \( Z \), \( w \), etc) will be indexed according to the bands, i.e. 1 for the hole FS, 2 and 3 for the electron FS sheets. Further details on the model and on the parameters of the calculations can be found in [23].

Figure 5(a) shows several AR conductance curves calculated using a three-band 2D BTK model (equation (4)) in which, however, the OPs are not constant but energy dependent. The functions \( \Delta_i(E) \) were previously calculated within the aforementioned three-band Eliashberg model using coupling constants able to give \( T_c \) and gaps similar to the experimental ones. The \( \alpha^2 F(\Omega) \) was chosen to have a Lorentzian shape, with representative boson frequency \( \Omega_0 = 12 \) meV, similar to the spin-resonance energy obtained from neutron scattering experiments in Ba(Fe\(_{1+x}\)Co\(_{1-x})_2\)As\(_2\) [32]. The curves in figure 5(a) refer to different values of the \( Z \) parameters (\( Z_1 = Z_2 = Z_3 = Z \)) from 0 (ideal AR contact with no barrier) to 20 (tunnel regime). Each conductance curve is the sum of three contributions (one for each band of the model) whose relative weight have been here chosen to be equal, \( w_1 = w_2 = w_3 = 1/3 \). The other parameters of the BTK model have been chosen so as to compare with real experimental situations, i.e. \( T = 2 \) K and \( \Gamma_i/\Gamma_i = 1/4 \). The calculated conductance curves in figure 5(a) feature structures at energies higher than the gap values, at about \( \Delta_{\text{max}} + \Omega_0 = 21 \) meV, which become more pronounced as \( Z \) increases. The features can be seen much more clearly by looking at the sign-changed derivative of the conductance, \( -dG/dV = -d^2I/dV^2 \), shown in figure 5(b). A peak is present above 20 meV and an additional feature can be
also seen around 40 meV (vertical dashed lines). When $Z$ decreases, the structures slightly reduce in amplitude but their position in energy hardly changes, showing that important information concerning electron–boson interaction can be obtained in the AR regime as well.

Figure 5(c) shows the same cases as in (a) but now calculated by adopting a normal AFSF spectral function, with maximum at $\Omega_0 = 12$ meV and maximum boson energy ($\Omega_{\text{max}} = 4\Omega_0 = 48$ meV). Here the total coupling constant $\lambda$ is fixed so as to give (approximately) the same $T_c$ and the same gaps as in panel (a). The additional structures are no longer visible in the conductance curves at any value of the $Z$ parameter. Only tiny deviations from the BCS case can be seen in the sign-changed derivative (not shown) but these features would be hardly observable in a real experiment. Figure 5(d) shows what happens if the value of $\Omega_{\text{max}}$ is reduced, though scaling $\Omega_{\text{tot}}$ so as to give the same $T_c$ and gaps (see the inset). If $\Omega_{\text{max}} = 3\Omega_0$ small additional structures start to become visible and they grow consistently in amplitude when $\Omega_{\text{max}} = 2\Omega_0$, but now they are at $\Delta_{\text{max}} + \Omega_{\text{max}}$ and not at $\Delta_{\text{max}} + \Omega_0$. Summarizing, in this case the electron–boson interaction structures are detectable only if the spectral function is abruptly cut off resulting in a shape no more physically plausible (see the inset to figure 5(d)) and are located at energies that have nothing to do with the representative boson energy $\Omega_0$. The conclusion is that reasonable parameters for the normal AFSF spectral function do not allow reproducing features that are actually observed in the experiment (see section 4). Hence, we suggest that this particular shape of the $\alpha^2 F(\Omega)$ is not suitable to catch finer details of the PCAR spectra measured in these compounds. This fact, however, may not be surprising since the AFSF function used here was calculated for a uniform electron gas in the normal state [28] which looks too rough an approximation in this case. Very recently, the AFSF electron–boson spectral function in the superconducting state has been calculated [33] and is indeed rather similar to the Lorentzian $\alpha^2 F(\Omega)$ used above, which is thus a reasonable and easy-to-handle approximation.

Figure 6(a) shows an AR spectrum (solid line) calculated at $T = 2$ K, $Z = 0.3$ and $\Gamma_c/\Delta_c = 1/4$ using a Lorentzian spectral function, together with the partial contributions from the three bands present in the model (dashed–dotted lines). The inset shows the corresponding sign-changed derivatives. Each of the three partial conductance curves shows strong-coupling structures at energies higher than the gap. However, while in a single-band case one could expect these features to appear at $\Delta + \Omega_0$ (and potentially at higher harmonics), in a three-band case with a dominant interband pairing the situation is not so straightforward. For instance, the derivative of the contribution of band 2 features a peak at $\Delta_2 + \Omega_0 \approx 22$ meV and not at $\Delta_2 + \Omega_0$. This fact, which is most probably due to the strong interband character of the coupling, has to be investigated further and suggests that quantitative calculations are recommended in order to reliably interpret electron–boson features in Fe-based superconductors.

Figure 6(b) shows what happens when the total conductance of panel (a), here represented by circles, is fitted to the two-band 2D BTK model which adopts constant BCS energy gaps (solid line). The agreement between the two curves is remarkable in the gap region, despite the fact that the BTK model contains only two gaps (a three-band model would contain too many parameters for the fit to be reliable). The fit allows determining very well the small gap (4.0 meV against 4.02 meV, see the parameters in the labels). The large gap obtained by the fit is similar to $\Delta_3$ given by the Eliashberg theory, with a slight overestimation (9.9 meV against 9.02 meV); the effect of the intermediate gap is a hardly visible excess of signal with respect to the fitting curve between the extremal gaps, which is indeed sometimes observed experimentally. At higher energies a considerable
deviation from the fit is observed: the calculated conductance shows additional features together with a higher conductance up to about 60 meV. Such an excess of conductance at intermediate energy has been observed rather often by PCAR in Fe-based superconductors (see figures 2(d) and (e) from [34] or figure 13(a)). Furthermore, a higher-energy excess conductance that some calculated curves show for particular bands can cause an increase in the amplitude of the tails even up to 80–100 meV, as shown in figure 13(a) and in the inset to figure 11(a). This effect can be further evidence of the strong-coupling character of these compounds. However, since the height of the tails at high energy in the experimental curves depends on the normalization procedure, one must be confident that the actual normal state is adopted, i.e. the curve at low temperature and $H > H_c$. Since the upper critical field in these compounds is usually not experimentally accessible, one could try using the normal state at $T > T_c$, provided that no heating effects are present in the point-contact which could cause a downward shift of the conductance curves with increasing temperature. Therefore, a systematic study of this effect is desirable, both from the experimental and theoretical point of view, as it could greatly help acquiring more information concerning the strength of the coupling and the energy of the mediating boson in Fe-based superconductors.

The fact that in the above discussion we have compared the results of a two-band BTK model with constant (energy-independent) OPs to those of a three-band BTK model with energy-dependent OPs might look a little confusing. Let us just explain this point.

On the one hand, if one starts from an experimental PCAR spectrum, as will be shown in section 3, the minimal BTK model able to fit the data—at least in the small-to-intermediate energy range—is the two-band BTK one. In some spectra, a discrepancy between the data and the fitting curve is observed at energies between the small and the large gap, which might be due to the presence of a third gap, which is, however, experimentally difficult to discern. Moreover, this discrepancy is too small to justify the use of a three-band BTK model that would contain 11 free parameters and, thus, would not be reliable. In this sense, the large uncertainty on the large gap $\Delta_2$ (especially in the case of Sm-1111) might partly arise from the oversimplification of the fitting model. Even if this fact has not prevented obtaining interesting information by PCAR measurements, this consideration has to be kept well in mind when studying these complex multiband systems.

On the other hand, the minimal Eliashberg $\pm$ model that allows the experimental gaps and $T_c$ to be obtained is a three-band, three-gap one as explained in [27]. If one wants to take into account the effects of the energy dependence of the OPs and of the strong electron–boson coupling on the shape of the PCAR spectrum, one is thus forced to generate the AR curve using a three-band BTK model with the three OPs coming from Eliashberg calculations. Note that, in the latter case, the OPs are not fitting parameters and only $\Gamma_i$, $Z$, and the weights can be adjusted to ‘fit’ the experimental spectrum.

3. Symmetry of the order parameters in Fe-based superconductors

3.1. ‘1111’ compounds

In most of the 1111 compounds, the model for spin-fluctuation mediated superconductivity predicts a $\pm$ gap symmetry with a sign change between hole-like and electron-like FS sheets. This is indeed compatible with what has been found by point-contact measurements, despite initial contradicting claims.
OP with nodes on the electron FS has been predicted in 1111 compounds with low $T_c$ [4] which have not been studied yet by PCAR.

The first PCAR measurements in 1111 materials such as LaFeAs(O, F) and SmFeAs(O, F) showed zero-bias peaks that were initially interpreted as being due to a nodal gap symmetry, namely the d-wave one. However, the appearance of these zero-bias features and their height were later discovered to depend on the pressure applied to the sample by the tip (in the needle-anvil configuration) [35]; in some samples, they were frequently found in some regions of the sample surface and never in others; moreover, their temperature dependence was odd and completely inconsistent with that expected for the zero-bias peak associated with Andreev bound states in nodal superconductors [36, 37]. At the same time and most importantly, increasing pieces of evidence were collected that, under suitable conditions (better sample quality, or zero pressure applied to the sample as in the ‘soft’ technique described in [9]) the zero-bias peak did not show up [21, 22, 34]. In the end, the majority of the scientific community got convinced that the zero-bias peaks early observed in 1111 compounds were not a signature of d-wave symmetry of the OP. We will thus not discuss these results any longer; a short review on this subject can be found in [9].

The absence of zero-energy bound states (particularly in the $ab$-plane contacts) certainly excludes those symmetries where nodal lines lie on the FS. However, the predicted symmetry of the OP in pnictides does involve a change of sign in the OP, but this should occur between hole-like and electron-like FS sheets [3]. According to some models, this sign change should give rise to observable effects in the PCAR spectra through interband interference effects. Here we will not deal with this aspect and show instead how the most reliable PCAR spectra in 1111 can be successfully fitted by simpler models that disregard interference effects. Indeed, the predicted features associated with interband interference (i.e. surface bound states, both at zero and nonzero energies [11]) may be often made indiscernible by various sources of broadening or overwhelmed by stronger effects.

It is however worth mentioning that, in contacts with vanishing barrier at the interface (let us say, $Z = 0$ in the BTK language), a strong reduction in the Andreev signal is predicted [11] as a result of destructive interference. In Fe-based superconductors a smaller amplitude of the Andreev signal than in more conventional systems (even multiband, such as MgB$_2$) is indeed often (but not always) observed experimentally. However, a similar reduction in the amplitude of the superconducting signal is also expected if the normal bank of the contact is a diffusive metal [38, 39], if a large inelastic scattering occurs at the interface [40], or if a fraction of the probe current is injected in normal regions (as it can happen if the dopant distribution is inhomogeneous), or even if some FS sheets are gapless. For the sake of completeness, it must be said that a small Andreev signal is also predicted if the gap is anisotropic (see figure 2). At this stage of the research it is impossible to say which of these effects is really taking place. This is particularly true for 1111, since the growth of large single crystals is still very difficult and most of the experiments have been carried out on polycrystalline samples which necessarily do not allow ruling out extrinsic effects due to grain boundaries, surface degradation, inhomogeneous doping and so on.

3.1.1. LaFeAs($O_{1-x}F_x$). LaFeAs($O_{1-x}F_x$) is chronologically the first Fe-based superconductor studied by point-contact spectroscopy, and also the first on which we performed ‘soft’ PCAR measurement (where the contact is made by placing a small drop of Ag paste on the sample surface instead of pressing a sharp metallic tip against it) to avoid pressure effects that could possibly give rise to spurious zero-bias peaks, as shown in some early measurements reported in the literature.

We studied polycrystalline samples with nominal F content $x = 0.1$ and thus at optimal doping. However, the local F concentration in the crystallites was found to show deviations $\delta x = 0.02$ around this value. Indeed, point contacts on different regions gave critical temperatures $T_{c}^A$ (defined as the temperature where the AR features disappear and the normal-state spectrum is recovered) ranging from 27.3 to 31.0 K. These temperatures lie in the upper part of the resistive transition (see figure 7(e)).

In most of the contacts we observed clear conductance maxima, symmetric about zero bias and related to a small gap $\Delta_1$, together with additional structures that we interpreted as being due to a larger order parameter $\Delta_2$ (although we acknowledged the possibility that they could be features of the normal state, which is also changing with temperature [21, 41]). In some contacts, these additional features were extremely clear and sharp (see figure 2 in [21]); in others (see figure 7(a)) they showed up as broad shoulders progressively decreasing in height and width on increasing temperature. Other peculiar features of the spectra are the right-left asymmetry, and the residual upward curvature in the normal-state conductance that looks like a ‘pseudogap’ feature and is progressively reduced on increasing the temperature. Curiously enough, the temperature at which it disappears, leaving a flat but asymmetric conductance, is close to the temperature of magnetic ordering in the parent compound. The origin of this behavior is still not clear and will be possibly clarified only when single crystals are available (see also section 3.1.2 for further discussion).

The complete absence of zero-bias peaks or maxima such as those shown in figure 4 in the conductance, together with the random orientation of the grains, made us conclude that none of the OPs shows line nodes or zeros on the FS. The further conclusion in favor of an isotropic gap symmetry came instead from the fit of the conductance curves, which was indeed always possible using two isotropic OPs.

The fit requires of course a normalization of the conductance curves, which is particularly crucial in these materials (as already mentioned in section 2.4) because the gap or boson structures can extend to very high energy. In some spectra, these structures become clearly visible only if a proper normalization is chosen. In principle, the normalization should be obtained by dividing the superconducting conductance curve measured at a given $T < T_{c}^A$ by the normal-state one at the same temperature. The latter is experimentally inaccessible
due to the large critical fields of these materials [42]. Some authors then choose to divide the raw conductance curve at a given temperature by a straight line [34] that connects its high-energy ‘tails’. This procedure generally allows a good estimation of the small gap alone. As a matter of fact, the pseudogap-like curvature of the normal-state conductance curves observed at \( T > T_c^\Lambda \) is presently present also below \( T_c^\Lambda \) (and likely to become more and more pronounced when the temperature is lowered). This curvature is completely disregarded by the aforementioned normalization procedure. To partially correct for this, a possibility is to divide all the raw conductance curves in the superconducting state by the normal-state curve measured just above \( T_c^\Lambda \), or (as we also did in La-1111) to try to mimic the temperature dependence of the (presumed) normal state [21]. We showed that choosing one or another of these two procedures changes very little the value of \( \Delta_1 \) extracted from the fit (less than 2%), while the value of \( \Delta_2 \) can change by about 10%, though preserving its trend as a function of temperature, magnetic field and critical temperature.

Figure 7(c) shows the low-temperature experimental curve of panel (a) after normalization (i.e. division by the normal state at \( T_c^\Lambda \)), together with its best-fitting curve calculated within the two-gap 2D BTK model discussed in section 2.1. Let us just recall here that this model is really suited to describe a 3D superconductor only if the gap is isotropic and the FS is spherical, which is clearly not the case in these materials [17,43]. More sophisticated models accounting for the real shape of the FS (see section 2.3) should thus be used, but calculations may become too heavy for a fitting procedure to converge. In practice, using an approximated 2D model often simply results in an overestimation of the barrier parameter \( Z \), as already mentioned in section 2.3. The values of the OPs extracted from the fit of the low-temperature conductance curve are \( \Delta_1 = 3.8 \pm 0.1 \) meV and \( \Delta_2 = 10.0 \pm 0.2 \) meV. The fit of another set of curves measured in a point contact with \( T_c^\Lambda = 28.6 \) K, but featuring clearer structures related to the second gap, gives instead \( \Delta_1 = 2.75 \pm 0.1 \) meV and \( \Delta_2 = 7.9 \pm 0.2 \) meV. How can these result be reconciled with the ± picture? As already mentioned above (section 2.4) we have shown [27] that the ± picture is compatible with the opening of gaps of different amplitude on the two hole-like FS sheets and on the electron-like sheet of hole-doped 1111 compounds. Eliashberg calculations assuming a mainly interband coupling due to spin fluctuations give, for the case of LaFeAs(O, F) analyzed here, three isotropic OPs of different signs: a small positive OP \( \Delta_a = 2.82 \) meV (presumably on the outer hole FS cylinder around \( \Gamma \)), a large positive OP \( \Delta_b = 8.01 \) meV (on the inner hole FS cylinder), and a large negative OP \( \Delta_c = -7.71 \) meV (on the electron FS sheets around M) [29]. In the absence of interband interference effects, AR is only sensitive to the amplitude (i.e. the absolute value) of the OPs (which is the actual energy gap). This, together with the similarity between the absolute values of the two large OPs, reconciles the findings of PCAR with the theoretical expectations in the ±± model.

The gaps (or, better, the relevant \( 2\Delta/k_BT_c^\Lambda \) ratios) extracted from the fit of the conductance curves in figure 7(a) are shown as solid squares in panel (f). Their temperature dependence is anomalous: both \( \Delta_1 \) and \( \Delta_2 \) follow a BCS-like trend up to \( T^* \approx 18 \) K, but above this temperature \( \Delta_2 \) is no longer detectable and \( \Delta_1 \) shows a ‘tail’ ending up at the real critical temperature of the contact, \( T_c^\Lambda = 27.3 \) K. The same result was found in other contacts with different critical temperature [21]. The data shown by open squares in 7(f) refer to a contact with \( T_c^\Lambda = 28.6 \) K on the same sample; also in this case the large gap tends to zero at \( T^* \approx 21 \) K, and above this temperature the small gap shows a ‘tail’ up to the real \( T_c^\Lambda \).

Very similar results have been recently obtained by Naidyuk et al [44] who performed PCAR spectroscopy with a
Figure 8. PCAR spectra obtained in SmFeAsO$_{1-x}$F$_x$ polycrystals [22, 45] (a) and films [44] (b). The bottom curve in (b) is an estimation of the normal state conductance. (c), (d) The low-temperature conductance curves from (a) and (b) normalized to the normal-state conductance at $T_c^A$ and the relevant two-gap 2D BTK fit. In (c) the left and right side have been fitted separately; in (d) the curve has been symmetrized. (e) Normalized gap values $(2\Delta /k_BT_c^A)$ as a function of $T/T_c^A$ as obtained in different samples: optimally doped polycrystals ($\triangle$, $\triangledown$ from [22]); underdoped polycrystals ($\circ$ from [22], $\star$ from [34]); single crystals ($\Box$, $\Diamond$ from [52]); films ($\bullet$ from [44]). The green stars indicate the results of the fit shown in panel (d). Lines are BCS-like curves. The dashed line fits the trend of the gap taken from [44], which closes at the ‘apparent’ critical temperature $T^* < T_c^A$. Colored regions approximately indicate the region where the values of $\Delta_1$ and $\Delta_2$ are spread.

Cu tip in LaFeAsO$_{1-x}$F$_x$ films with $T_c = 28$ K (defined as the temperature where the resistance drops to 90% of its normal-state value, see figure 7(e)) and a transition width $\Delta T_c \approx 6$ K. The conductance curves $dI/dV$ obtained from their data are shown in figure 7(b), and show two clear maxima related to a small gap $\Delta_1$. The authors normalized the curves to a parabolic curve that fits the data for $|V| \geq 10$ mV. This necessarily makes all the features at $|V| \geq 10$ mV become small oscillations around 1 in the normalized curve. As a matter of fact, the curves normalized in this way can be fitted by a single-band, s-wave BTK model including a broadening term and the fit thus gives only a small gap, shown in panel (f) as circles. The gap follows a BCS-like curve that, once extrapolated, would give again a critical temperature $T^* \approx 18$ K. Structures in the raw conductance curves, although impossible to fit with the same model, persisted well above that temperature and at least up to 25 K, as shown in panel (b). As a matter of fact, the temperature dependence of the raw conductance curves is not dissimilar from that observed by us in polycrystals (panel (a)). Let us show what happens instead if one normalizes the same curves by the normal state at $T_c^A$. Although the corresponding curve is not reported in [44], based on the similarity with panel (a) one can guess that it should look like the dashed curve in panel (b). If this is used to normalize the low-temperature spectrum, one obtains the curve depicted in panel (d), which shows a rather high Andreev signal and shows clear shoulders in addition to the structures related to $\Delta_1$. The two-band 2D model allows one to fit this curve very well, giving $\Delta_1 \approx 2.9$ meV and $\Delta_2 \approx 9.5$ meV (triangles in panel (f)). The agreement between the data sets measured by us in polycrystals and by Naidyuk et al in films is incredibly good if the raw conductance curves are treated in the same way. This proves that (i) the different sets of data are really compatible with each other; (ii) even if in the raw data by Naidyuk et al the large-gap features are not as clear as in ours, a suitable normalization makes them show up clearly enough to be fitted by the 2D model; (iii) the gap values are rather robust against the sample form and synthesis technique, provided that the critical temperature is similar, as in this case. The two data sets, however, also pose some questions on whether the observed anomalous tendency of the gaps to close around $T^*$ is an artifact or is intrinsic to this material. The simplest possibility, of course, is that the behavior of the gap is the result of the shortening of the mean free path on increasing temperature, so that the junction ceases to be ballistic at a voltage that decreases with temperature [9].

3.1.2. SmFeAs(O$_{1-x}$F$_x$). Also in Sm-1111 the PCAR results reported in the literature apparently give contradicting results, especially as far as the observability of multiple gaps is concerned. Here we will show that, however, raw data measured in different kinds of samples by different groups can give surprisingly consistent results if they are treated in the same way. Figure 8(a) shows the raw conductance curves measured using the ‘soft’ PCAR technique in an optimally doped SmFeAsO$_{0.5}$F$_{0.5}$ polycrystal with $T_c = 52$ K. We can notice that (i) the low-temperature curve shows maxima at about $\pm 5$ mV, plus additional structures (here in the form of shoulders) at about $\pm 15$ mV; (ii) the normal-state conductance (thick line, corresponding to $T = 52.1$ K) is not flat but shows a residual, asymmetric ‘hump’ around zero bias, which is progressively smoothed on increasing temperature. In all the soft point contacts we made in these polycrystals, this hump disappears—leaving a flat, though still asymmetric conductance—at about 140–150 K (which is the temperature of magnetic ordering in the parent compound) [22, 45]. The origin of this ‘crossover’ is unclear. One could doubt that it might be related to some residual magnetic order, but no trace of a secondary magnetic phase with $T_N \approx 140$ K has been observed in our samples at optimal doping (see e.g. [46]). A structural transition has been claimed to occur between 175
and 125 K along the whole phase diagram of Sm-1111 [47], but we do not have evidence of this effect in the samples studied here. A small anomalous kink in the resistivity at similar temperatures, common to 1111 compounds (see e.g. [48]), has instead been observed, but its origin is not well understood yet. Transport measurements [49] and angle-resolved photoemission spectroscopy (ARPES) [50] in detwinned BaFe$_2$As$_2$ crystals showed that in-plane electronic anisotropy occurs at temperatures above the structural transition, thus indicating the presence of fluctuation effects [49] which have been interpreted as spin anisotropy in the paramagnetic phase [51]. It might also be that similar effects are playing a role in the 1111 systems and are possibly connected to the kink in the resistivity and to the shape of the point-contact conductance. However, detailed studies have to be performed as soon as bigger crystals are available to clarify these points. Generally speaking, we can say that the proximity of superconductivity to the antiferromagnetic spin density wave state of the parent compound suggests the persistence, in the doped compound, of spin fluctuations which could possibly give rise to the observed behavior of the normal state at high temperatures. However, since there are no clear predictions concerning the expected shape of the PCAR conductance spectra and of their evolution with temperature in the situations reported above, further experimental and theoretical investigation should be performed in order to clarify this issue. Then, it could also be possible to better understand whether the different shape of the normal-state conductance in La-1111 and Sm-1111 polycrystals is due to different causes or it is only a different manifestation of the same phenomenon.

Anyway, the anomalous shape of the normal-state conductance again makes the normalization a problem. Dividing by the curve at $T_c^A$ is here a rougher approximation than in La-1111 because the critical temperature is higher and one could reasonably suspect that the normal state at $T_c^A$ can differ very much from that at low temperature. The result of such a normalization is shown in panel (c) for the curve at the lowest temperature. The normalized curve still presents a strong right–left asymmetry, which some authors remove by a symmetrization procedure. We chose instead to separately fit the left and right side of the curves with the two-band 2D BTK model, as shown by the lines superimposed onto the symbols in panel (c). The values of the small gap $\Delta_1$ extracted from the two fits (5.7 meV) coincide, but the values of $\Delta_2$ are rather different: 17.0 meV and 19.0 meV, respectively.

For the sake of completeness, if the conductance curve of figure 8(c) is symmetrized, the 2D BTK fit gives $\Delta_1 = 5.7$ meV and $\Delta_2 = 18$ meV. While the small gap remains the same the large gap is actually an average of those obtained from the separate fit of the right and left side of the unsymmetrized one. The symmetrization is thus an acceptable practice when the asymmetry of the conductance curve is not too large. This is what happened for example in the case of Co-doped Ba-122 (see [23]). Since in our results on Sm-1111 the curves show a rather large asymmetry we consider more reliable, in that specific situation, a separate fit.

The temperature dependence of the resulting OPs (normalized to $T_c^A$ as in figure 7(f)) is shown in panel (e) by up (left side) and down (right side) triangles. Unlike in La-1111, the gaps follow a BCS-like trend up to $T_c^A$, which coincides with the bulk $T_c$ [22]. The same panel also shows the gaps obtained by fitting the negative-bias side of conductance curves obtained in a different polycrystal, with a different doping content ($x = 0.09$) and thus a smaller $T_c^A = 39$ K (open circles). Despite these differences, once the temperature and energy scales are normalized as in panel (e), the values of the gaps agree very well with those obtained for $x = 0.20$ [22]. A few measurements of soft PCAR spectroscopy were also performed in very small Sm-1111 single crystals (about $200 \times 200 \mu$m$^2$) with the current (mainly) injected along the $ab$-planes [52]. As usual, we fitted the negative-bias and the positive-bias side separately to account for the observed strong asymmetry of the spectra. At low temperature, the gaps turned out to be $\Delta_1 = 6.45 \pm 0.25$ meV and $\Delta_2 = 16.6 \pm 1.6$ meV, while $T_c^A = 50.1$ K. The normalized values of the gaps (actually, the values of the gap ratio $2\Delta/k_B T_c^A$) are shown as a function of $T/T_c^A$ in figure 8(e) as squares and diamonds. The agreement of the data with those obtained in polycrystals is remarkable. In general, when all the data sets obtained in various polycrystals and crystals are considered together, the values of the $2\Delta_1/k_B T_c^A$ agree very well with one another, varying only between 2.5 and 3 (i.e. within the thinner colored region in panel (e)). As for $2\Delta_2/k_B T_c^A$, it is more scattered and varies at low temperature between 7 and 9 (i.e. within the wider colored region). This larger spread arises both from the asymmetry of the curves and from the greater uncertainty in the determination of the large gap, also related to the uncertainty introduced by the normalization or to the possible presence of two large gaps of similar amplitude.

PCAR measurements in the needle-anvil configuration were performed by Chen et al in polycrystals with a reduced $T_c = 43$ K with respect to the optimal-doping one [34, 53]. Most of the low-temperature curves shown in [34] resemble rather closely those measured by us; they present clear peaks related to a small gap plus additional shoulders and structures. Unlike in our measurements, the normal-state conductance above $T_c^A$ presents a pseudogap-like upward curvature similar to that reported above for La-1111. Prior to fitting their curves, the authors use a normalization procedure that is equivalent to supposing that the normal state is a straight line fitting the tails of the unnormalized curve. The problem is that the higher the temperature, the smaller is the voltage range where this approximation holds (see the supplementary information in [34]). Moreover, this obviously implies disregarding possible structures at energies much higher than that of the small gap. Traces of the (presumable) large gap remain in the curves, but become so small to be confused with minor features, possibly related to the electron–boson coupling (see sections 2.4 and 4). Instead, if the curves are divided by the normal-state conductance, the features connected to the large gap are enhanced with respect to other features at even higher energy. The fit of the conductance curves performed by Chen et al indeed gives a single gap, which follows an almost perfect BCS temperature dependence shown in figure 8(e) as solid stars (note that, because of the difference in critical temperature between different data sets, the axes are normalized). In [53]
the same authors notice that the energy of some extra features (which at $T = 4.5$ K occur at about 20, 40 and 55 meV) evolve in a BCS-like way on increasing temperature. On the basis of what was discussed in section 2.4, it is tempting to interpret these features as the hallmarks of the strong electron–boson coupling.

More recently, PCAR measurements in the needle-anvil configuration have been performed in Sm-1111 films by Naidyuk et al [44]. Figure 8(b) shows the temperature dependence of one of their curves, which shows very clear structures related to the small gap and a pseudogap-like normal state. The peculiar evolution of the tails of the curves as a function of temperature seems to indicate a large excess conductance at high energy, possibly due to electron–boson structures, as discussed in section 2.4. Features connected to the superconductivity are clearly present up to $T_c^\Lambda \simeq 30$ K. This is the temperature where the resistance has dropped to about 80% of the normal-state value, although the transition starts at about 34 K. As in La-1111, the authors’ normalization makes the Andreev signal decay to 1 already at $\pm 12$ meV, thus flattening all the structures at higher energy. This, again, allows a fit of the small-gap features alone, and only to about 18 K; above this temperature the normalization produces structures that cannot be fitted by a BTK model. The gap values follow a BCS-like trend that, if extrapolated, would give a critical temperature $T^* \simeq 21.6$ K. This, together with the low-temperature value $\Delta = 3.35$ meV, gives an almost perfect BCS ratio $2\Delta/k_BT^* = 3.6$. However, the ‘true’ critical temperature of the contact is $T_c^\Lambda \simeq 30$ K that gives instead a gap ratio of only 2.6, which is exactly the same we obtained for the small gap (see figure 8(e)). Based on this similarity, we tried to normalize the low-temperature curve in [44] following our method, i.e. we divided the saw curve by the presumable normal state at $T_c^\Lambda$ (dashed curve in panel b). The result of this normalization (and of a subsequent symmetrization) is shown by symbols in panel (d). The curve has then been fitted to a single-band 2D BTK model (dashed line) and to a two-band 2D model (solid red line). It is clear that the two-gap model allows a better fit of the small-gap feature’s width but also catches the position of the abrupt change of curvature, which turns out to be related to the second large gap. The values of the gaps given by this tentative fit are $\Delta_1 = 3.5$ meV and $\Delta_2 = 11$ meV. Their values, properly referred to the relevant $T_c^\Lambda$, are shown in panel (e) as green stars and again turn out to be in very good agreement with ours. The failure of the 2D BTK model to fit the tails of the curve in (d) is not too worrying; the shape of these tails is indeed suggestive of strong electron–boson structures in the conductance that could only be taken into account by inserting the energy-dependent OPs into the 2D BTK model (see section 2.4).

3.2. ‘122’ compounds

In 122 compounds, the model for spin-fluctuation-mediated superconductivity predicts a nodeless OP which, according to some authors, can however evolve in a peculiar nodal symmetry, with 3D nodes on one hole-like FS, when the latter acquires a more 3D character [5]. In a recent paper, a relationship is claimed between $2\Delta_0/k_BT_c$ (being $\Delta_0$ the gap on the hole FS) and the occurrence of nodes in the electron FS [54]. According to these authors, both the hole-doped system (Ba,K)Fe$_2$As$_2$ and the electron-doped system Ba(Fe,Co)$_2$As$_2$ present nodeless gaps around optimal doping, while a nodal OP is very likely in the isovalent-doped compound BaFe$_2$(As,P)$_2$ [5, 54].

122 compounds are more suited to PCAR measurements than 1111 compounds, since they can be grown in the form of large single crystals that can be cleaved more or less easily. This allows directional measurements with the probe current injected either in the basal plane or along the c-axis. Moreover, in some of these compounds, ARPES measurements have provided valuable information on the amplitude and symmetry of the gap on the various sheets of the FS. This information generally confirms or supports the finding of PCAR in these materials.

3.2.1. (Ba, K)Fe$_2$As$_2$. ARPES experiments in the hole-doped system (Ba, K)Fe$_2$As$_2$ at $x = 0.4$ (T$_c = 37$ K) [55, 56] showed the presence of four isotropic gaps: three of similar amplitude (between 11 and 13 meV) on the inner hole-like FS cylinder and on the two electron FS sheets around M, plus a small one ($\simeq 5.8$ meV) on the outer hole FS sheet. Within the uncertainty of the measurement, which is rather large, the gap amplitudes were shown to be compatible with a symmetry $\Delta(k) = \Delta_0 \cos(k_x) \cos(k_y)$ which is indeed the functional form of the $\pm$ symmetry in the reciprocal space. The gaps seemed not to follow a BCS-like curve as a function of temperature.

The first direct PCAR measurements in the same system were carried out by Samuely et al [57, 58] who used single crystals of B$_{0.35}$K$_{0.65}$Fe$_2$As$_2$ with superconducting transition between $T_c^{\text{on}} = 30$ K and $T_c^{\text{zero}} = 27$ K. By injecting the current along the $ab$-planes, they obtained spectra with very clear two-gap structures and no trace of zero-bias peaks or maxima, thus ruling out the possibility of any symmetry of the OP involving a change of sign or zeros on a single FS sheet. The conductance curves were systematically normalized to the conductance curve at $T_c^\Lambda$, which sometimes shows a hump-like structure (similar to that observed by us in Sm-1111 polycrystals) and sometimes a pseudogap-like, V-shaped feature. For current injection along the c-axis, a similar pseudogap-like feature and no Andreev signal were observed. The zero-bias conductance minimum was shown to be progressively filled on increasing temperature, up to the temperature (about 85 K in these samples) where weak signs of the onset of a magnetic order are found in resistivity and specific heat [57]. The most reasonable interpretation of these findings is that magnetic order and superconductivity coexist and are probed sometimes together, sometimes exclusively, by PCAR [57]. This possibility is confirmed by direct evidence of such a phase separation on a scale of about 50 nm [59], and also by successive PCAR measurements in B$_{0.60}$K$_{0.40}$Fe$_2$As$_2$ crystals with $T_c \simeq 37$ K carried out by Lu et al [60]. These authors indeed observed a typical V-shaped conductance valley with a universal functional form $G(V) = G(0) + c|V|^n$ being $n \simeq 2/3$ in a fraction of their c-axis contacts on
This compound, but also in the nonsuperconducting parent compound BaFe$_2$As$_2$, as well as in (Sr$_{0.6}$Na$_{0.4}$)Fe$_2$As$_2$ ($T_c = 36$ K) and Sr(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ ($T_c \approx 22$ K).

Let us go back to the $ab$-plane measurements in (Ba, K)Fe$_2$As$_2$ by Samuely et al. After the normalization, the conductance curves were fitted to a two-band 2D BTK model with two isotropic gaps. In different contacts, the small gap $\Delta_1$ was found to vary between 2 and 5 meV, and the large gap $\Delta_2$ between 9 and 10 meV. The temperature dependence of the gaps was found to agree very well with BCS-like curves.

The beautiful spectrum shown in figure 9(a) gives $2\Delta_1/k_BT_c^A \approx 2.7$ and $2\Delta_2/k_BT_c^A \approx 9$, in very good agreement with the findings in Lu-1111 and Sm-1111 shown in figures 7(f) and 8(e). In some cases, small-amplitude curves with a single broad maximum were observed, which can be fitted by the same model with very large values of the broadening parameters $\Gamma_1$ and $\Gamma_2$. Let us note that these latter spectra could be mistaken for evidence of nodal or anisotropic OPs if there were not clearer spectra ruling out this possibility. This indicates how the cleanliness of the surface is essential for the observation of clear gap structures (and thus a correct interpretation of the data) as also pointed out by Lu et al [60], who performed $c$-axis PCAR measurements in Ba$_{0.68}$K$_{0.4}$Fe$_2$As$_2$ crystals either cleaved or uncleaved. In uncleaved crystals, they observed spectra with a single, ill-defined maximum at zero bias and shallow structures at about $15$ meV. Instead, in freshly cleaved samples two clear conductance maxima were observed in the spectra. Once normalized to the normal-state conductance (showing a hump like structure) these spectra were fitted to a single-gap BTK model giving $\Delta_1 = 3.0-4.0$ meV, corresponding again to $2\Delta_1/k_BT_c^A \approx 2.6$ and thus in good agreement with Samuely’s measurements along the $ab$-plane. In addition to the clear small-gap features, the raw spectra also presented smaller structures that, in the normalized curve, show up as shoulders of very small amplitude. These structures were interpreted by Lu et al as being ‘dips’ due to the non-perfectly ballistic conduction regime through the contact, in turn due to the very small electron mean free path in these compounds [60]. They thus argued that $c$-axis PCAR measurements do not allow us to detect the large gap because it pertains to cylindrical FS sheets (the inner hole-like at $\Gamma$ and the two electron-like at $M$), while the small gap opens up on a more 3D FS sheet [61].

In figure 9 we compare two representative spectra taken along the $ab$-plane [57, 58] and along the $c$-axis [60], by plotting them as a function of the normalized energy $eV/k_BT_c$ (this is necessary because of the different $T_c$s of the samples). The similarity between the spectra is striking; not only the small-gap features, but also the additional structures now lie in the same position. This suggests that the shallow structures at $15$ meV observed in the $c$-axis spectrum might not be an artifact (as a matter of fact, they always occur at the same voltage irrespective of the junction resistance [60]) but might instead be related to the large gap. If this is the case, their small amplitude may be explained by the much smaller ‘weight’ of the relevant bands than in the $ab$-plane (see section 2.3). The normalized curves are reported (again as a function of $eV/k_BT_c$) in figure 9(b) as open symbols. The upper curve is compared with the two-band fit by Szabó et al [58], and the relevant gap amplitude and weight are reported. The lower curve is instead compared with a two-band 2D BTK fit that gives the same small gap obtained by Lu et al ($\Delta_1 = 4.1$ meV) but also a large gap $\Delta_2 \approx 16$ meV.

Note that the weight of the bands featuring the large gap is now only 0.1. Although this value of $\Delta_2$ seems huge, the ratio $2\Delta_2/k_BT_c^A$ is the same as for the $ab$-plane curve. If our interpretation is correct, the available PCAR experiments in (Ba, K)Fe$_2$As$_2$ thus concur to a picture of multiple nodeless gaps, in agreement with the findings of ARPES. They also seem to indicate that these gaps are isotropic (at least, this is what one

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**Figure 9.** (a) PCAR spectra obtained in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ single crystals by injecting the current along the $ab$-plane [57, 58] and along the $c$-axis [60]. The curves are plotted as a function of $eV/k_BT_c^A$ because the contacts had different $T_c$s. Dashed lines represent the normal-state conductance at $T_c$. (b) The same curves after normalization (symbols) and the relevant fit with a two-gap 2D BTK model (lines). The values of the gaps and of the weight $w_1$ are reported in labels. Vertical lines indicate the position of the gap structures. Inset: temperature dependence of the gaps measured along the $ab$-plane [57, 58]. (c) Low-temperature curves measured in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals, with current along $c$ (curves 1–4) and $ab$ (curves 5 and 6). From [57] (curves 1–2) and [23] (curves 3–6). Thick (thin) lines represent the one-gap (two-gap) 2D BTK fit. Arrows indicate bosonic structures. (d) Experimental conductance curves of a $c$-axis contact as a function of temperature, with the relevant two-gap fit. The gap values are reported in the inset.
would infer from the directional invariance of the gap ratios $2 \Delta_{1,2}/k_B T^{\Delta}_c$.

3.2.2. $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$. The first results of PCAR measurements in $\text{Ba(Fe}_{0.95}\text{Co}_{0.05})_2\text{As}_2$ single crystals with $T_c = 23 \text{K}$ are reported by Samuely et al [57]. The $c$-axis spectra show clear Andreev signals, and in one case a double-peak structure, but no evidence of multiple gaps. They were thus fitted to a single-gap, s-wave BTK model giving $\Delta = 5–6 \text{meV}$ which corresponds to $2\Delta/k_B T^{\Delta}_c = 5.3–6.3$ since $T^{\Delta}_c = 22 \text{K}$. A large broadening parameter ($\Gamma > 0.5\Delta$) was necessary to fit the curves. An example of these curves is shown in figure 9(c) (curves 1 and 2). In [60], also Lu et al reported on $c$-axis PCAR measurements on $\text{Ba(Fe}_{0.9}\text{Co}_{0.1})_2\text{As}_2$ crystals. They observed V-shaped conductance curves with no Andreev signal when the tip was gently put in contact with the cleaved sample surface, and a zero-bias conductance enhancement when the pressure was increased sufficiently. This feature is clearly related to superconductivity since it disappears at $T_c$, but its shape cannot be reconciled with an isotropic gap. One could think that this feature is rather suggestive of a d-wave OP, and try to fit it with a suitable generalized model. However, the current is here injected along the $c$-axis. In this configuration, no interference effects are expected for the d-wave symmetry (with nodes on the hole FS), for the so-called ‘nodal s’ symmetry (with nodes on the electron FS) [4] and even for the particular 3D nodal symmetry specifically predicted for 122 compounds [5]. More exotic symmetries (if any) should be imagined to make HLQ and ELQ experience a sign change of the pairing potential in this configuration. Alternatively, one could imagine the zero-bias maximum to simply arise from the anisotropy of the OP but in this case, as shown in 2.3, a closed 3D FS has to be invoked, which is not predicted by band-structure calculations.

We recently performed PCAR measurements with the ‘soft’ technique in single crystals of $\text{Ba(Fe}_{0.9}\text{Co}_{0.1})_2\text{As}_2$ (bulk $T^{\text{on}} = 24.5 \text{K}, \delta T_c = 1 \text{K}$). We obtained various series of spectra by injecting the current along the basal plane or along the $c$-axis [23]. The normal-state conductance at $T^{\Delta}_c$ presented a shallow V-shape and progressively flattened on increasing temperature. Figure 9(c) reports some examples of normalized (i.e. divided by the conductance at $T^{\Delta}_c$) and symmetrized curves for the $c$-axis (curves 3 and 4) and $ab$-plane contacts (curves 5 and 6). They all feature maxima related to a small gap, plus additional shoulders that can be related to a second, larger gap. The position of these features does not depend on the direction of current injection and this speaks in favor of isotropic gaps. In this regard, it is worth mentioning that also the relative weight of the two terms in the conductance (let us say, $w_1$ and $(1 – w_1)$) is the same irrespective of the direction of the current. This seems to indicate that all the FS sheets have a similar degree of three-dimensionality, as also shown by ARPES [62] and x-ray Compton scattering [63]. Thick lines in figure 9(c) represent the two-gap 2D BTK fit of the curves, while thin lines indicate the single-gap 2D BTK fit. It is clear that the latter model is unapt to reproduce the shape of the curves. The two-gap model works better in

the gap region but leaves out additional structures (indicated by arrows) which are very clear only in curves with a large amplitude and that can be related to the strong electron–boson coupling (see sections 2.4 and 4). Incidentally, note that in curve 5 these structures are probably masked by small dips, which however do not affect the clear double-gap structures. The absence of zero-bias peaks certainly rules out, also in this case, the presence of nodes or line zeros on the FS, and this is consistent with theoretical predictions [5]. Instead, these findings are not incompatible with the presence of gap minima or even zeros (but not line zeros) in some regions of the FS, as recently proposed to explain the Raman scattering data in this compound [64].

The gaps obtained by PCAR can now be compared with the results of ARPES measurements in the superconducting state. Terashima et al [65] measured a large isotropic gap $\Delta_2 \simeq 7 \pm 1 \text{meV}$ on the hole-like FS sheet around $\Gamma$ and a smaller isotropic gap $\Delta_2 \simeq 5 \pm 1 \text{meV}$ on the hybridized electron-like FS sheets around M. The values of the gaps as a function of temperature are shown as open circles in the inset to figure 9(d). As for the values of $\Delta_1$, ARPES and PCAR agree rather well, while the value of $\Delta_2$ is rather different, although the error bars overlap. A possible explanation of this difference can be found in [23]. Also note that the ARPES gaps show a weaker temperature dependence and go to zero abruptly; the same result has been found in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [55].

3.2.3. $\text{Ca(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$. Very recently, we have performed PCAR measurements on $\text{Ca(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$ single crystals, with a bulk critical temperature $T_c = 18 \text{K}$ as determined from dc susceptibility measurements. The ‘soft’ point contacts were made on the freshly exposed side surface of a single crystal. Figure 10(a) shows the temperature dependence, from 2.21 K up to 16.16 K, of the conductance curves of an $ab$-plane point contact ($R_S \simeq 3 \Omega$) normalized to the normal-state conductance at $T^{\Delta}_c = 18 \text{K}$. The conductance curves are very different from those observed in the other compounds presented so far. First of all, they have very small amplitude; second, they systematically present (in 100% of the cases) a zero-bias enhancement of the conductance, similar to that occasionally observed for example in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [60] and in Nd-1111 [35]; third, they have a rather broad, almost triangular shape. These characteristics do not change sensibly when a magnetic field up to 6 T is applied parallel to the $ab$-plane, as shown in panel (b). This rules out magnetic scattering and intrinsic Josephson junctions as the origin of the peak and indicates that the upper critical field is much higher than the maximum applied field. Furthermore, the systematic occurrence of the ZBCP, the similarity between different series of curves obtained in contacts with different resistance and the absence of effects normally observed in non-ballistic contacts point towards an intrinsic origin of the ZBCP.

As shown in section 2.3 a zero-bias peak or maximum in the $ab$-plane contacts can be a sign of a nodal OP. Let us assume that this is the case. This could be in agreement with the predictions by Suzuki et al [5] that, in 122, nodes appear on the quasi-3D hole-like FS around the $\Gamma$ point (called $\alpha_l$ in [5])
Figure 10. (a) PCAR spectra obtained in Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals by injecting the current along the $ab$-plane, normalized to their normal state at $T_A = 18$ K. (b) Magnetic-field dependence of the same spectra, at $T = 2.2$ K. The inset shows some raw conductance curves at different temperatures. (c) Some of the spectra of panel (a) with the relevant two-band 2D BTK fit with a large isotropic gap $\Delta_1$ and a small d-wave gap $\Delta_2$. (d) Temperature dependence of the gaps as obtained from the fit of panel (c). Lines are BCS-like curves.

when the height of the pnictogen on the Fe layer is small. In the similar compound Ba(Fe, Co)$_2$As$_2$ [66] band-structure calculations indeed show that one of the hole-like cylinders is strongly warped and that its diameter grows considerably going from $\Gamma$ to $Z$, which is the situation envisaged in [5]. However, in the absence of specific data about the FS of Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and of detailed information on the fine structural details, we must rely on the PCAR spectra alone. In the absence of a specific way to express the peculiar nodal symmetry predicted for 122 compounds, we just tried to see whether a simple nodal symmetry (i.e. the d-wave one) can account for the observed PCAR results. Note that quite similar results can be however obtained by fitting with a fully anisotropic s-wave OP as the one discussed in section 2.3. To reproduce the ZBCP a misorientation angle $\alpha$ between the lobes of the d-wave gap and the normal to the interface has to be included in the 2D BTK model (which is the simplest approximation, justified by the roughness of the fit). We were able to fit the conductance curves at any temperature up to $T_A = 18$ K using a small d-wave gap and a larger s-wave gap (presumably associated with the electron FS sheets). As usual, we kept the barrier parameters $Z_1 = 0.5$ and $Z_2 = 0.285$ as well as the weight $w_1 = 0.55$ and the angle $\alpha = \pi/9$ independent of temperature. The fit of a subset of the curves in figure 10(a) is shown in figure 10(c), and the relevant gaps are shown as a function of temperature in panel (d). Although the statistics is still to be completed, these results may suggest the Co-doped Ca-122 system as a possible good candidate for the study of nodal (or fully anisotropic) superconductivity in 122 compounds.

3.3. ‘22426’ compounds

Proofs of nodal OP have also been reported for another class of compounds, the highly layered ‘22426’ family. Yates et al [67] performed PCAR experiments, either with the conventional ‘needle-anvil’ technique or the ‘soft’ technique in Sr$_2$ScFePO$_3$ polycrystals with $T_c = 17$ K. This material is particularly interesting, though less known than other Fe-based compounds, for the study of OP symmetry. As a matter of fact, in 1111 [4] and 122 [5] the height of the pnictogen (here P) above the Fe plane has been indicated as being responsible for the appearance of nodes in the OP (in 1111 compounds, this is accompanied by a decrease in $T_c$ which does not necessarily occur in 122). In Sr$_2$ScFePO$_3$ the angle of the Fe–P–Fe bond (118°) and the $a$-axis lattice parameter (4.016 Å) mean that the height of the P above the Fe plane is 1.20 Å, which lies
between that of LaFeAs(O,F) and that of LaFePO (in which some proofs of nodal superconductivity have been found).

The spectra obtained in [67] systematically show a zero-bias peak irrespective of the junction resistance (ranging from 30 to 100 Ω) and of the PCAR technique used. Figure 11(a) shows the temperature dependence of one of the spectra obtained with a tip pressed against the sample surface. The curves are not offset; the apparent shift is due to a large conductance excess that extends up to very high energies. The inset indeed shows that it is only at $eV > 100$ meV that the tails of all the curves are superimposed. It is also clearly seen that the normal state conductance at $T_A$ is approximately flat. If this curve is used to normalize the low-temperature conductances, the resulting curves will look very similar to the raw ones, apart from the vertical scale. It is clear that a fit of these curves in the whole voltage range is impossible with any version of the BTK model with energy-independent OPs.

Figure 11(b) shows the magnetic-field dependence of the conductance curves (unfortunately, of a different contact) at $T = 9$ K, normalized at 20 mV [67]. The ZBCP is progressively depressed by the field, as well as the overall Andreev signal. A relatively small field of 7 T is sufficient to completely suppress superconductivity. Sr$_2$ScFePO$_3$ is thus peculiar since the normal state conductance at $T < T_c^A$ is experimentally accessible and can in principle be used to normalize the data. The inset indeed reports the raw conductance curve at 9 K in zero field (top) and at the upper critical field (bottom). The latter is different from the normal state at $T_c^A$ shown in the inset to panel (a) but unfortunately the two sets of curves refer to different contacts and it is not possible to draw conclusions in this regard.

A detailed analysis of the field-dependence [67] shows that the ZBCP is likely to have an intrinsic origin, apart from a small contribution from intergrain weak links which is suppressed already at 1 T. However, the attempts to fit the conductance curves with a single d-wave gap were not completely satisfactory due to the residual excess conductance at high bias (that persists even if one uses the normal-state conductance at $H_{c2}$ to normalize the curves). Even a two-gap model fails unless abnormally high values of the large gap are used to simulate the excess conductance. Only when choosing a normalization that removes this excess, the authors obtained a fairly good fit of the central peak that gave $\Delta = 4.34 \pm 0.04$ meV, corresponding to a gap ratio $2\Delta/k_BT_c \simeq 6.7$.

4. Electron–boson interaction in Fe-based superconductors

As explained in detail in section 2.4, in moderate- or strong-coupling superconductors the PCAR conductance curves can show signatures of the energy dependence of the superconducting gap. These structures are more easily observable if the amplitude of the Andreev signal is large; their signature in the second derivative of the $I$–$V$ curve can be related to the electron–boson spectral function. In the following, we will show some results obtained in Ba-122 single crystals and Sm-1111 polycrystals that provide examples of such strong-coupling effects and of their analysis. Especially for the case of Ba-122 compounds, when compared with inelastic neutron scattering measurements, these results strongly support a spin-fluctuation-mediated origin of superconductivity.

4.1. ‘122’ compounds

Figure 12(a) shows an experimental conductance curve (circles) obtained on a Co-doped Ba-122 single crystal close to optimal doping. It can be clearly seen that the curve features additional structures at energies higher than the large gap, around 20 mV and (less clearly) at about 40 mV. The solid line represents a theoretical conductance curve obtained by introducing in the two-band 2D BTK model the energy-dependent superconducting gaps calculated within a
Eliashberg calculations are theoretical one (line) obtained by introducing in the BTK model the energy-dependent superconducting gaps. The gaps as obtained by the guides to the eye. energy peak, line is obtained from the theoretical curve shown in (Figure 12. characteristic boson energy in [23]) by using a Lorentzian electron–boson spectrum with three-band Eliashberg model (further details can be found in [23]) by using a Lorentzian electron–boson spectrum with the temperature dependence of the characteristic energy of the boson spectrum, \( \Omega_b(T) = E_p(T) - \Delta_{\text{max}}(T) \) (see section 2.4).

Figure 12(d) shows the values of \( \Omega_b \) (open symbols) decrease on increasing temperature, and tend to zero when \( T \to T_c \). This indicates that \( \Omega_b \) cannot be the energy of a phonon mode (in that case it would not tend to zero!) and thus rules out a phononic origin of this feature. Instead, the trend of \( \Omega_b \) is very similar to that of the spin-resonance energy peak reported in [32] and thus strongly supports a spin-fluctuation-mediated pairing mechanism in these compounds.

In this regard it is worth noticing that the existence of a relationship between \( T_c \) and the spin-resonance energy observed by inelastic neutron scattering in Fe-based compounds does not necessarily prove the spin-fluctuation pairing. As Paglione and Greene point out, since such a relationship appears exclusively in nearly magnetic unconventional superconductors, it could be considered an independent remnant of nearby magnetic order rather than a strong signature of magnetically mediated pairing [68].

What PCAR spectroscopy provides is something more than that. Indeed, (i) it detects features related to the interaction of electrons with elementary excitations in the material (and not only to the excitation itself); (ii) it shows that these excitations enter the imaginary part of the energy-dependent OP; (iii) it allows the extraction of the characteristic energy of the interaction spectrum \( \alpha^2 F(Q) \), which turns out to coincide with that associated with spin fluctuations and observed by neutron scattering experiments.

4.2. ‘1111’ compounds

Figure 13(a) shows a normalized experimental conductance curve obtained by us on an optimally doped Sm-1111...
Since to the best of our knowledge no spin-resonance energy value is available for this compound, the characteristic energy has been chosen accordingly to [68] by extrapolating the relationship $\Omega_0 \sim 4.65k_BT_c \sim 20$ meV. Although the theoretical curve shows no structures at 27 mV (which by the way corresponds approximately to $\Delta_{\text{min}} + \Omega_0$), the feature at 40 mV is remarkably well reproduced as can be observed in figures 13(a) and (b) (dashed line). Similarly to the case of Co-doped Ba-122, only the structure present at approximately $\Omega_0 + \Delta_{\text{max}}$ is reproduced. This again indicates that the model has to be investigated further or that additional features of the spectral function are playing an important role. As expected, both structures shift in energy on increasing temperature, partly because the amplitude of the superconducting gaps is also decreasing. The inset to figure 13(a) reports the position of the energy peak in the second derivative, $E_p$ (full symbols) and the values of $\Omega_b = E_p - \Delta_{\text{max}}$ (open symbols) as a function of temperature. Similarly to the case of Co-doped Ba-122 reported in the previous section, $\Omega_b$ decreases in temperature indicating that the observed structure does not have a phononic origin and might instead be related to spin fluctuations. It is interesting to note that similar structures at about 20, 40 and 55 meV were directly observed in the PCAR spectra by Chen et al., who also observed their shift in energy, similar to that of the gap [53], but did not give them any special physical meaning.

5. The puzzle of $2\Delta_i/k_BT_c$ ratios

Figure 14 reports a collection of the values of the gap ratios $2\Delta_i/k_BT_c$ (where $\Delta_i$ is the $i$th band gap measured at low temperature) given by different PCAR measurements performed by us and other groups in various Fe-based systems. Only results referring to nodeless gaps have been reported essentially (i) because they represent the great majority the cases studied up to now and (ii) to allow a homogeneous comparison with the standard s-wave BCS ratio. The gap ratios are reported as a function of the $T_c$ of the sample or, when available, of the $T_c^A$ of the contact. Two representative sets of ARPES data are also shown for comparison. Let us start by analyzing the trend of $2\Delta_1/k_BT_c$ (open symbols) as a function of temperature. Similarly to the case of Co-doped Ba-122 reported in the previous section, the $T_c$ decreases down to approximately 30 K; then, it starts to increase continuously with further decreasing $T_c$. A qualitatively similar trend is also observed for $2\Delta_2/k_BT_c$, despite a larger spread of values which is not surprising since the larger gap is worst resolved than the small one, its absolute value could be affected by the choice of the normalization and moreover, as pointed out in section 4, could also be the average of two large gaps of similar value. We cannot, however, rule out that the spread is also due to specific features of each system such as nesting, vicinity to magnetism, etc, but also, and most probably, quality of the sample, homogeneity and disorder.
Although more data points are desirable in the low-$T_c$ region of the graph, figure 14 indicates that the increase in the $2\Delta_i/k_BT_c$ ratio below a certain $T_c$ (on the order of 30 K) appears to be a rather common trend for both gaps. But how can this trend be interpreted?

In order to make a reliable statement in this regard, the complexity of these systems has to be carefully taken into account. Because of the multiband nature of these compounds and their dominant interband pairing, a proper interpretation of the data would require a quantitative analysis (for example within a multiband Eliashberg model) taking into account the electronic structure of each compound. However, as a first approximation, we have done numerical simulations within the three-band $\pm$ Eliashberg theory (with feedback effect [29], i.e. by including in a self-consistent way the temperature dependence of the spin-fluctuation spectral function) to see in what conditions this trend can be reproduced. To simplify the problem, we fixed some parameters to the values that allowed us to reproduce the gaps in Sm-1111 compound with $T_c = 32$ K [29]. These parameters are $\lambda_{33}/\lambda_{13}$ (where $\lambda_{ij}$ is the coupling constant between bands $i$ and $j$), $n_{13}$ and $n_{12}$ ($n_{ij} = N_i/N_j$, where $N_i$ is the density of states of band $i$). According to [68], we assumed $\Omega_0$ to vary linearly with $T_c$, i.e. $\Omega_0 \approx 4.65k_BT_c$. For values of the critical temperature down to 30 K, the experimental values of $2\Delta_i/k_BT_c$ can be reproduced by keeping the total coupling constant, $\lambda_{tot}$, practically constant to a value of approximately 2.4. Below 30 K, to follow the experimental trend it is necessary to (i) increase $\lambda_{tot}$ and (ii) modify the temperature dependence of the peak energy. In standard energy, the latter evolves with temperature according to $\Omega_0(T) = \Omega_0 \tan\theta [1.76k_BT_c/(T_c - T)]$ [29] (i.e. in a BCS-like way) where $T_c^*$ is the critical temperature calculated without the correction due to the feedback effect ($T_c^* > T_c$). Here, we assume instead $\Omega_0(T) = \Omega_0 \tan\theta [1.76k_BT_c/(T_c - T)]$, where $k = 1$ for $T_c \geq 30$ K and decreases for $T_c < 30$ K. Roughly speaking, this is equivalent to a reduction of the representative frequency $\Omega_0$ at any $T$ between 0 and $T_c^*$, with respect to the above BCS-like curve. As a result, a larger $\lambda_{tot}$ is necessary to obtain the correct $T_c$; but this also gives larger gaps. This result, if confirmed by using detailed electronic calculations for each compound, might indicate that below $T_c = 30$ K the coupling increases and would also have interesting implications on the temperature dependence of the spin-fluctuation spectral function that, as shown in figure 12(d) and in the inset of figure 13, can be determined from high-quality PCAR spectroscopy experiments.

6. Summary and conclusions

In this report we have presented an overview of the (partly) solved and of the (still) debated points about superconductivity in Fe-based superconductors that have been (or can be) addressed by means of point-contact spectroscopy. To do so, we have also introduced generalizations of the usual models for the fit of the PCAR spectra, and presented some new results. Here, we would like to simply summarize the main conclusions of this long discussion, and outline the possible future challenges for PCAR spectroscopy in research on Fe-based superconductors.

In section 2 we have examined and discussed in detail the profound and often counterintuitive connections among the FS topology of multiband superconductors, the symmetry of the OPs present on the FS sheets, the directionality of the PCAR process, the strength and the spectrum of electron–boson interaction, and the resulting PCAR normalized conductance curves. Taking into account these connections greatly complicates the description of the AR process, but is unavoidable when dealing with Fe-based superconductors. The extension of the BTK model to its most general form, which we call the ‘full 3D BTK’ model (sections 2.3 and 2.4), allows direct comparison of the PCAR experimental results with the predictions of the theory for a specific shape of the FS, a specific symmetry of the OP in every band and a specific spectrum of electron–boson interaction (via the preliminary solution of the Eliashberg equations). The comparison of the results with those of the simplified BTK models provides some indications and warnings for the analysis of PCAR data in Fe-based compounds that can be summarized as follows:

1. The analysis of the $ab$-plane PCAR spectra on Fe-based superconductors requires at least the 2D version of the BTK model, because of the quasi-2D shape of their FS and the possible presence of non-isotropic OPs. Even in the case of pure $s$-wave symmetry of all the OPs, this model gives results slightly different from the full 3D one (in particular, an apparent enhancement of the $Z$ values is observed, due to FS-shape-related geometric effects).

2. In principle, the $c$-axis PCAR spectra in pnictides should be analyzed only by means of the 3D BTK model (simplified version of [15] or full version of equation (11)) because of the non-spherical shape of the FSs. However if the $ab$-plane contacts on the same material do not
show any sign of line nodes or zeros in the OP, and the precise determination of the \( Z \) values is not vital, the 2D BTK model can return correct information about the isotropic gap values and their temperature dependence. In this case, as shown for the large gap in figure 4(b), the \( Z \)-enhancement effect is remarkable especially when the FS is only slightly warped, but the gap-related peaks remain at the same energy positions.

(3) The application of the full 3D BTK model to the case of fully anisotropic s OPs (with line zeros) or d-wave OPs (with line nodes) that open on warped cylindrical surfaces leads to interesting conclusions. As expected, the normalized conductance of the \( ab \)-plane contacts in the AR regime (\( Z < 0.2–0.4 \)) shows characteristic zero-bias maxima or peaks, respectively. Unfortunately, in the presence of a small lifetime broadening the smoothed spectra become very similar, preventing the possibility to discriminate between the two symmetries. Under the same conditions, the \( c \)-axis contacts unexpectedly show no signs of zero-bias peaks or maxima even for \( Z = 0 \) because of the geometric \( Z \)-enhancement effect, as shown in figure 4. This prediction could be verified by means of directional PCAR experiments on high-quality single crystals. In other words, the observation of zero-bias peaks or maxima in the \( c \)-axis contacts can be reconciled with the previous two OP symmetries only if the corresponding FS sheet is 3D, thus giving to directional PCAR spectroscopy the capability to attain indirect information on the shape of the FS.

(4) The introduction of energy-dependent gap functions \( \Delta_i(E) \) (determined by the proper solution of multiband Eliashberg equations) into the BTK expressions leads to the conclusion that structures due to the electron–boson interaction (EBI) are certainly visible in the AR conductance at energies higher than the large gap (and for coupling constants compatible with the \( T_c \) and the gap values) provided that the spectral function of this interaction is sufficiently peaked (e.g. has a Lorentzian shape). The use of the spectral function typical of AFSF results in curves with no EBI structures unless unphysical, very low cutoff energies are chosen. Serious questions thus arise on the true shape of the bosonic spectrum since (as shown in two particular cases in section 4) EBI structures have actually been observed in the PCAR data of various compounds.

As for the OP symmetry in Fe-based superconductors, the analysis and comparison of various PCAR results reported in section 3 show that, despite the rather common opinion that PCAR results are contradictory, the most recent and reliable experiments are in fairly good agreement with one another. In particular:

(1) When data from various groups are available for a given compound, they generally give similar results if analyzed in a homogeneous way. The apparent conflicts are mostly due to a different normalization of the raw data or to a different interpretation of the common structures present in the conductance.

(2) In optimally doped and slightly underdoped \( 1111 \) compounds, if the PCAR curves are normalized to the relevant normal-state spectrum and the high-energy structures are not artificially reduced, all the data point to the presence of (at least) two isotropic gaps (with no nodes and no line zeros) with ratios \( 2\Delta_i/k_B T_c \) lower and sensibly higher than the BCS value, respectively.

(3) Similar observations apply to the 122 compounds where data of various groups concur in supporting a multi-gap \( \pm \) picture (though at most two gaps can be resolved by PCAR spectroscopy). Since in this case most of the experiments are made on single crystals, a dependence of the ‘weight’ of every band on the direction of current injection is also observed, in agreement with the predictions of section 2.3.

(4) In compounds of the 22426 family and in Co-doped \( Ca-122 \) (as shown here for the first time) PCAR spectroscopy gives some evidence of a d-wave or a fully anisotropic s-wave OP. In these cases, experiments along different crystallographic directions can be used as a ‘test’ of the predictions of section 2.3 or of the presence of a 3D FS sheet.

In section 4 we have given evidence of EBI structures in the PCAR spectra of Co-doped \( Ba-122 \) and \( Sm-1111 \). By properly combining the direct solution of the three-band \( \pm \) Eliashberg equations and the BTK models we were able to reproduce these structures in amplitude and position, thus obtaining important information on the characteristic energy of the bosonic spectrum and its temperature dependence. This energy turns out to coincide with the characteristic energy of the spectrum of spin fluctuations measured by inelastic neutron scattering thus giving a strong support to the spin fluctuation origin of the coupling in these compounds. In addition these EBI-related structures (not only small peaks or shoulders at the proper energy but also a general increase in the conductance at high bias) can nicely explain some frequently observed anomalies of PCAR spectra that cannot be reproduced by the BTK models using constant gaps. This is another example that too simplified models cannot explain the rather complex physics of AR in Fe-based superconductors.

Finally, in section 5 we have shown—by comparing the results of various experiments of different groups—that at the decrease in the \( T_c \) of the sample the ratios \( 2\Delta_i/k_B T_c \) for the small and the large gap have an anomalous behavior. Instead of merging at a value close to the BCS one at the lowering of \( T_c \), as in \( MgB_2 \) they both increase at \( T_c \sim 30 \text{ K} \) reaching values greater than 5 and 10, respectively. A preliminary analysis of this ‘strange’ behavior in the framework of the Eliashberg theory including the feedback effect [29] shows that it can be explained only supposing that below \( \sim 30 \text{ K} \) the temperature dependence of the characteristic boson energy is no more BCS-like but becomes more linear and, at the same time, the total coupling strength increases. Both these conclusions could be further investigated by directional PCAR experiments in low-\( T_c \) high-quality single crystals.

In conclusion, we have shown that PCAR spectroscopy can provide information on some debated properties of the Fe-based superconductors if the PCAR spectra are analyzed within suitably generalized models. In particular, a tighter
relationship between the electronic properties (and thus the geometry of the FS) and the PCAR results can be established. This could help in either verifying the plausibility of calculated FSs, or providing some experimental hints about what the FS should look like to explain the measured spectra. A systematic PCAR study of some selected systems as a function of doping, coupled to band-structure and FS calculations as well as with the determination of fine lattice details, could help in testing the proposed connection between these aspects and the symmetry of the OP, and to verify to what extent the scaling law of the gap ratios $2\Delta_i/k_B T_c$ as a function of $T_c$ is universal in these compounds (and, if so, what are its physical reasons and implications). As for the origin of the coupling mechanism, important hints can be obtained by extracting the typical boson energy from PCAR spectra and comparing it with the energy of spin resonance as measured, for instance, by neutron scattering experiments. In general, thus, the future developments of research on Fe-based compounds pose a challenge to PCAR spectroscopy, and might strongly benefit from the results of this experimental technique.

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